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Ni Electroless Plating of ABS Polymer by Palladium and Tin-free Process

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Abstract

A palladium and tin-free process for the Ni electroless plating of acrylonitrile-butadiene-styrene (ABS) polymer has been developed**.** The ABS was first etched then activated with Ni (or Co) ions. Ni or Co adsorbed was quantified by atomic absorption spectroscopy. Sodium borohydride solution was found to be effective in reduction of Ni (or Co) ions. By immersing in a Ni plating bath the Co (or Ni) can then auto-catalytically deposit a Ni film on the ABS. The amount and thickness of Ni film determined by SEM-EDX were the highest when using 3 g/L of nickel acetate solution, 0.5 M sodium borohydride solution at 60 s of the reduction time. Adhesion of Ni films was evaluated by the Scotch\tape test according to ASTM D3359, which indicated good adhesion between Ni film and ABS substrate. The adhesion strength of the Ni layer deposited was successfully compared with the adhesion of similar films deposited by the usual palladium-based seed process.

Key Words: Electroless plating, Acrylonitrile butadiene styrene (ABS), Nickel, Cobalt

Introduction

Metallization of polymer substrates is an important technique in the automobile and electronics industries. It is used for various purposes, such as electromagnetic shielding, weight reduction, electrical conductivity, formability enhancements, high impact resistance and weatherproofing. Chemical(1) and physical vapor deposition,(2) metal-powder coating(3) and electroless plating are the techniques available for the metallization of polymer substrates. Electroless plating is the most commonly used technique for metal deposition on polymers due to its advantages, such as low cost, easy formation of continuous and uniform coating on the surface of substrate with complex shape, and capability of depositing on either conductive or nonconductive parts.(4,5) The electroless plating consists of many steps; (1) degreasing, (2) etching, (3) surface seeding with a catalyst, (4) electroless plating and (5) electroplating. The degreasing process uses alkaline or acid solutions containing surfactants to remove oils and other organic chemicals and cleans the surface of the polymer. Chemical etching requires a strong oxidative acid such as chromic acid and/or sulfuric acid(6,7) or sulfuric acid/hydrogen peroxide to roughen the substrate for adhesion enhancement.(8,9) This creates surface topography to provide mechanical adhesion of the plating to the polymer. In surface seeding step, the polymer substrate is dipped into a stannous chloride-palladium chloride ($SnCl_2$-$PdCl_2$ colloidal) bath to employ the catalyst palladium cluster.(10) This one-step procedure is preferred to the two-step process (sensitization by $SnCl_2$ solution, then activation by $PdCl_2$ solution) due to simplicity and shorter reaction time.(11) The reduction of Pd^{2+} ions to Pd metallic state has occurred via the reaction in equation (1). Pd^0 atoms are then going to act as nucleation sites for subsequent Ni or other metal deposition.

$$Pd^{2+} + Sn^{2+} \longrightarrow Pd^0 + Sn^{4+} \quad (1)$$

The sensitizing-activation method using $SnCl_2$-$PdCl_2$ bath involves numerous problems, such as the use of highly toxic Sn, waste of noble metal and failure in adhesion of plating player, which are still major problems in commercialization. Thus, it is very important to develop a cost effective activation, Pd-free technique.(12,13) $SnCl_2$ is needed as a sensitizer due to surface inertness of most polymers. It was reported that this can be bypassed if the polymer surfaces are subjected to plasma treatment.(14) A method on the substrate surface treatment was also reported which involved

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the spin-coating of metal-organic precursor on substrate, then irradiated by excimer to decompose the precursor to metal clusters.(15) The polymer films can be modified by plasma treatment and graft copolymerisation with aniline.(16) In a recent method the substrate surface was coated with a liquid containing chitosan or a chitosan derivative before catalyst fixation.(17) Alternatively the direct electroless metallization was performed without Pd^0 catalytic clusters by sulfonation of the surface, adsorption of the Cu^{2+} species from a cupric aqueous solution and reduction to Cu with sodium borohydride.(18) ABS polymer can also be electroless plating through grafting with poly(acrylic acid).(19)

In the electroless plating, the catalyst-impregnated polymer substrate is immersed in a solution containing a metal salt, a reducer, a stabilizer and a buffer system. A redox reaction occurs between metallic ions (Ni^{2+} or Cu^{2+}) and a strong reducer without the aid of an external electric potential. Metal forms around the catalyst in the polymer and grows in the polymer nearby surface as well as on the surface via an autocatalytic electroless reaction.(8,9) Almost all the metals of the Group IB and VIII of the periodic table (Au, Pt, Ni, Cu, Co, Fe, etc.) can be plated and exhibit autocatalytic behavior. Electroless deposited film has two functions: (1) it provides an electrically conductive substrate that allows further coating by electroplating and (2) provides a secure bond between the polymer substrate and the electroplated layer. Electrolytic plating is the final step in producing a finished part. This step will build a Cu or Ni thickness to about 12.7-25.4 or 5.1-10.2 µm., respectively and give a bright surface suitable for exterior automotive part.

ABS (Acrylonitrile-butadiene styrene) polymer is an important engineering material because of its excellent toughness, good dimensional stability, good processability, chemical resistance, and low cost.(20) However, its application is limited because it is non-conducting. It was reported that the ABS polymer can be surface activated by etching using H_2O_2/H_2SO_4 and a chitosan film was employed to fix Pd catalyst on the substrate, followed by Ni deposition in electroless plating bath.(21)

In this work Ni film was electrolessly deposited on the acrylonitrile butadiene styrene (ABS) surface without using the conventional $SnCl_2$-$PdCl_2$ catalyst to initiate the redox reaction leading to metallization. A simple method using Ni or Co catalyst is reported. Seeding the surface to be metallized with Ni^0 clusters should be able to initiate the electroless plating in the same way as Pd^0 clusters.(22-24) The parameters affecting the surface activation: types and concentrations of catalyst, types and concentrations of reducer ($NaBH_4$) and reduction time were studied. Adhesion of the Ni films was evaluated and compared to the film using $SnCl_2$-$PdCl_2$ catalyst to initiate the metallization.

Materials and Experimental Procedures

Materials

The ABS (22% acrylonitrile, 15% butadiene, 63% styrene) samples were fabricated by injection molding under injection condition: melting temperature 230°C, mold temperature 45°C, injection pressure 85 kg/cm^2 and injection time 4 s. For cleaning or degreasing, sodium carbonate (Na_2CO_3), disodium metasilicate (Na_2SiO_3), sodium dodecylbenzene sulfonate ($C_{18}H_{29}NaO_3S$) from United excel chemical were used. Chemicals used for etching were chromic acid (CrO_3) and sulfuric acid (H_2SO_4), from the East Asiatic (Thailand) and sodium bisulfite ($NaHSO_3$) from RCI Labscan. Nickel(II) acetate ($(CH_3CO_2)_2Ni{\bullet}4H_2O$), cobalt chloride ($CoCl_2$), sodium borohydride ($NaBH_4$), stannous chloride ($SnCl_2$), from Ajax Finechem were used for surface activation and reduction. For electroless Ni plating bath, nickel sulphate ($NiSO_4{\bullet}7H_2O$) sodium acetate (CH_3CO_2Na), sodium hypophosphite (H_2PO_2Na), sodium citrate ($C_6H_5O_7Na_3$) and ammonium hydroxide (NH_4OH) were used. Palladium chloride ($PdCl_2$) from Carlo Erba and hydrochloric acid (HCl) from RCI Labscan were used in $PdCl_2$-$SnCl_2$ process.

Characterization

Atomic absorption spectroscopy was carried out on a GBC 932/933 AA. The appearances of the activated surface on ABS and film thickness were characterized by Scanning Electron Microscopy (SEM, JSM-6380) equipped with a field-emission gun (FEG-SEM) and coupled with an energy dispersive X-ray spectrometer (EDX). The average content of Ni and its distribution on the surface was measured by EDX analysis.

Procedures

The process is divided into 4 steps.

1. **Degreasing:** The specimens were cleaned and degreased in a mixed solution containing sodium

carbonate 50 g/L, disodium metasilicate 35 g/L, sodium dodecylbenzene sulfonate 3 g/L at 40°C for 3 min. then rinsed in deionized water.

2. **Etching:** The etching step was carried out using chromic/sulfuric acid (1:1 by weight), 400 g/L each, at 60°C for 3 min. (following current industrial practice). The residual amount of Cr^{6+} that remains in the ABS surface was removed by putting into a reducing agent (sodium bisulfite) for 1 min, this can prevent Cr^{6+} inhibition of the catalyst in the subsequent step.
3. **Surface Activation and Reduction Step:** In surface activation the etched specimens were dipped into an aqueous solution containing nickel acetate, $(CH_3CO_2)_2Ni$ or cobalt chloride, $CoCl_2$ in different concentrations (1, 3 and 5 g/L) at 60°C for 3 min.(25) The specimens were then rinsed in deionized water. After activation the quantity of Ni (or Co) was determined by AAS. In reduction the specimens were then immersed in a reducing agent, sodium borohydride ($NaBH_4$) in different concentrations (0.1, 0.5 and 1 M) for different time (5-300 s).
4. **Metallization or Plating Step:** The surface-activated ABS specimens were finally placed in the electroless Ni plating bath. The composition of electroless bath and the operating conditions were shown in Table 1. Sodium citrate was used as the complexing agent to control the rate of release of free metal ions for the reduction reaction. Plating time and temperature were fixed at 10 min. and 38°C. After plating, the specimens were carefully rinsed with deionized water and dried.

Table 1. Composition of electroless plating bath

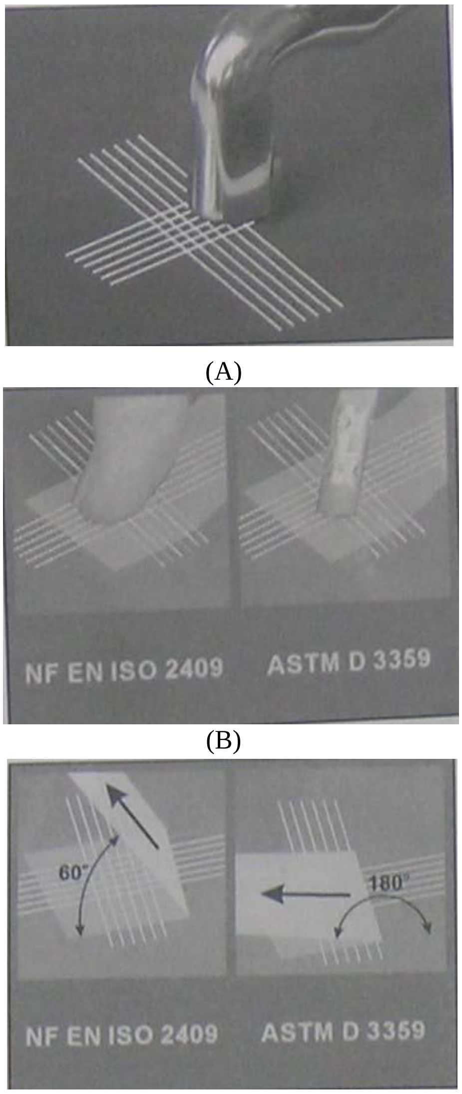
Chemicals	Concentration (g/L)
nickel(II)sulfate heptahydrate	26
sodium acetate trihydrate	16
sodium hypophosphite monohydrate	38
sodium citrate	46
ammonium hydroxide	To adjust pH = 9

$PdCl_2$-$SnCl_2$ Process

The commercial Pd-based process was also used for comparison. The above steps (1) and (2) were performed. In step (3) the specimens were dipped in the mixed $PdCl_2$-$SnCl_2$ solution (1.06 g/L $PdCl_2$, 4.25 g/L $SnCl_2$, 40 mL/L 38% HCl) at 30°C for 3 min. In step (4) the activated samples were electroless plated using the same condition as in the above process.

Mechanical Adhesion Test

The mechanical adhesion between the Ni layer and the ABS substrate was studied by a qualitative Scotch tape test by the standard ASTM D3359 Scotch tape test (cross-cut tape test performed with a 3 M 250 3710 Scotch\tape). This method (shown in Figure 1) consists of applying and removing pressure-sensitive adhesive tape suddenly over 16 cross-hatched squares of 1x1 mm^2. This standard test allows a direct comparison of the adhesion of films obtained under various conditions on similar substrates. The adhesion scale ranges are shown in Table 2.



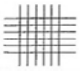
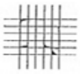
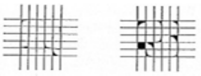
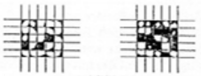
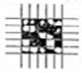
(A)

(B)

(C)

Figure 1. Adhesion strength measurement (A) cut (B) apply tape and (C) remove tape at 60° and 180°.

Table 2.Adhesion scale according to standard ASTM D3359

Classification	%Area removed	Surface of cross-cut area from which flaking occurred
5	**0 %**	
4	**<5 %**	
3	**5-15 %**	
2	**15-35 %**	
1	**35-65 %**	
0	**>65 %**	

Results and Discussion

Many steps were conducted in order to obtain a good adhesion of Ni film on the ABS substrate. The first step was to make the surface rough so that enough Ni or Co ions can be strongly adsorbed on the surface to initiate the autocatalytic reaction. NaBH$_4$ was used as a reducing agent to obtain Ni or Co metal seeds which then followed by Ni electroless plating. Figure 2 summarizes the succession of the different steps of the process studied.

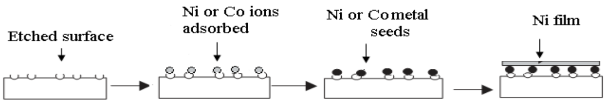
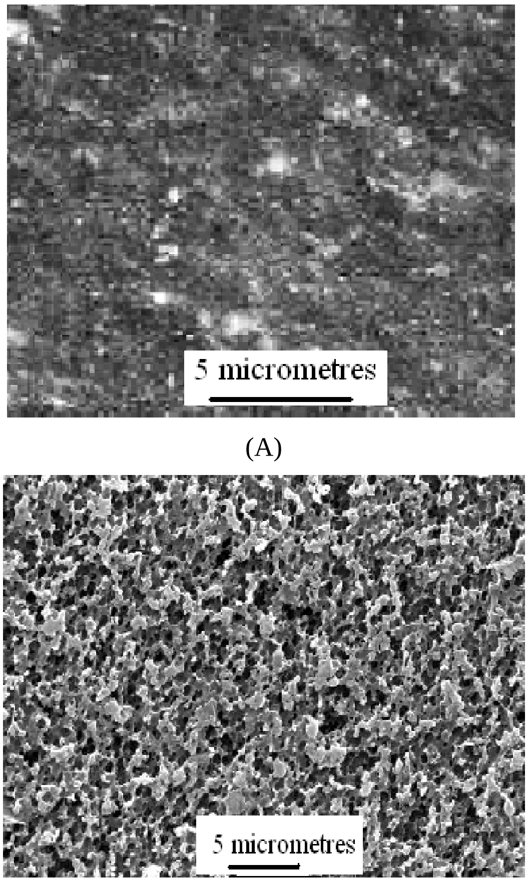


Figure 2. Step To obtain Ni film on the ABS surface

The characteristic of ABS surface after etching

As ABS does not possess any polar groups which can form a complex with metal ions so it was first etched with chromic/sulfuric acid. The surface characterized by scanning electron microscopy (SEM) is shown in Figure 3. By this treatment, the surface of the ABS is strongly oxidized and forms polar radical which has hydrophilicity. The butadiene oxidizes faster than the acrylonitrile-styrene copolymer, so the surface becomes porous because of the removal of butadiene spheres. Many possible polar groups were produced such as -COOH, -S0$_3$H or -CONH, on the surface of the substrate. It can be seen that the polymer surface is rough. The holes in the surface of the polymer provide the bonding sites for the deposited metal. These sites are needed for adhesion between the polymer and the metal.



(A)

(B)

Figure 3. SEM micrographs of the ABS surfaces (A) before and (B) after etching with chromic/ sulfuric acid.

Activation

The etched ABS specimens were dipped into different activators (catalysts): $(CH_3CO_2)_2Ni$ or $CoCl_2$ in different concentrations (1, 3 and 5 g/L) at 60°C for 3 min. The amount of Ni (or Co) species adsorbed on the ABS substrate determined by AAS was shown in Table 3. It can be seen that when using $(CH_3CO_2)_2Ni$ as catalyst, the amount of metal ions was higher than that using $CoCl_2$ at the same concentration. The amount of Ni (or Co) was increased with the increasing concentration of the catalyst solution.

Table 3. The amount of metal ions on the ABS substrate

Activator or catalyst	$(CH_3CO_2)_2Ni$			$CoCl_2$		
	1 g/L	3 g/L	5 g/L	1 g/L	3 g/L	5 g/L
Metal ions (ppm)	1.30	2.50	3.90	0.55	1.50	2.40

The distribution of the metal ions chemisorbed on the ABS surface was also analyzed by SEM-EDX. A representative EDX mapping of Ni on the surface (the sample using 5 g/L $(CH_3CO_2)_2Ni$) was shown in Figure 4. At different points of the surface the Ni concentrations were found to be close. It could be conjectured that each Ni atom is homogeneously chemisorbed on the polymer surface, which would make the surface very reactive towards the autocatalytic reaction.(24)

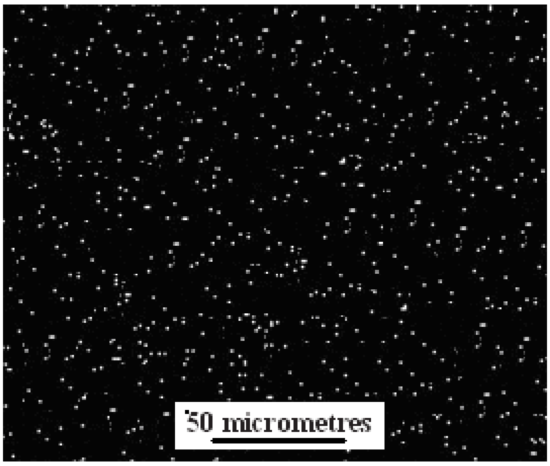


Figure 4. EDX mapping of Ni on the ABS surface.

Reduction

Using $NaBH_4$ as a reducing agent can reduce adsorbed Ni^{2+} (or Co^{2+}) on the ABS surface to Ni^0 (or Co^0). The decomposition of $NaBH_4$ in basic solution is shown in equation (2).(24)

$$BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4H_2O + 8e^- \quad (2)$$

The redox potential E_0 ($B(OH)_4^- / BH_4^-$) is equal to -1.24 V at pH = 14. Under these conditions, the overall redox reaction is as in equation (3):

$$4Ni^{2+} \text{ (or } Co^{2+}) + BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4Ni^0 \text{ (or } Co^0) + 4H_2O \quad (3)$$

This operation maintains enough Ni^0 (or Co^0) on the substrate surface to allow immediate Ni deposition in the next electroless plating step. It was reported that $NaBH_4$ was an efficient reducer in Ni plating bath(24) and it can also reduce Cu^{2+}.(18) Ni film thickness and Ni amount obtained from different concentrations of $NaBH_4$ and reduction time will be discussed after electroless plating step.

Electroless Plating

In electroless plating, metal ions are reduced to metal by the action of chemical reducing agents which are simply electron donors. In this work an electroless plating bath containing hypophosphite ions ($H_2PO_2^-$) as reducing agent (used in industry) was used. The reaction could be expressed as shown in equation (4). During electroless nickel deposition, byproducts of the reduction, orthophosphite and hydrogen ions accumulate in the solution. These can affect the performance of the plating bath. As the concentration of orthophosphite increases, there is usually a small decrease in the deposition rate and a small increase in the phosphorus content of the deposit. Phosphorus in the Ni deposit results from a secondary reaction due to hypophosphite disproportionation in acidic medium, as shown in equation (5).(26) As the electroless plating deposition rate is controlled by temperature, pH and metal ion/reducer concentration, these parameters were fixed using optimum values used in industry (see Table 1).

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni^0 + 2H_2PO_3^- + H_2 + 2H^+ \quad (4)$$

$$3H_2PO_2^- + 2H^+ \longrightarrow + H_2PO_3^- + 3H_2O \quad (5)$$

After plating the ABS surface was grayish which demonstrated the deposition of Ni on the surface. A representative SEM photograph of Ni plating layer on ABS surface (when using 1 g/L $(CH_3CO_2)_2Ni$ solution, 0.5 M. $NaBH_4$ for 300 s reduction time) was shown in Figure 5. The cross sectional image was shown in Figure 6. A very thin layer of Ni can be observed near the interface.The thickness of the Ni plating was measured. Ni amount from SEM-EDX of Ni plating layer on ABS surface was shown in Figure 7.

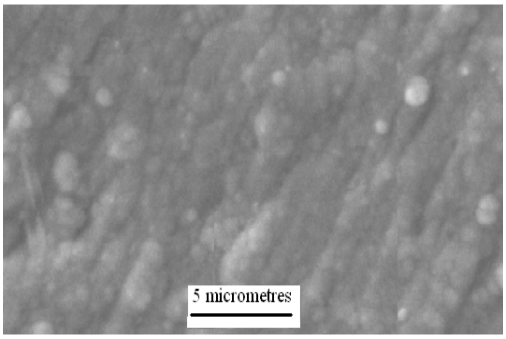


Figure 5. SEM photograph of Ni plating layer on ABS surface.

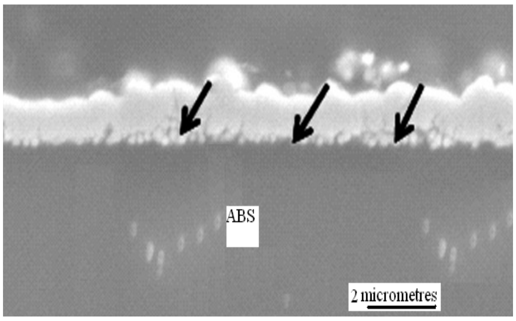


Figure 6. Cross sectional SEM image of Ni plating layer on ABS surface.

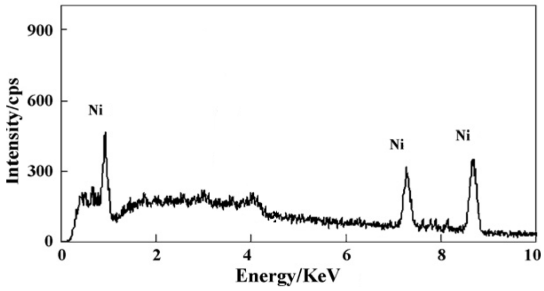


Figure 7. SEM-EDX of Ni plating layer on ABS surface.

The specimens which were performed activation (using different $(CH_3CO_2)_2Ni$ concentrations), reduction (using different $NaBH_4$ concentrations) for different periods of time (5-300 s) were then undergone electroless plating. Effects of these reaction parameters as well as reduction time on Ni film thickness and Ni amount were investigated. Results are given in Tables 4-6.

Table 4. Ni film thickness and Ni amount obtained from different concentrations of $NaBH_4$ and reduction time at 1 g/L $(CH_3CO_2)_2Ni$ solution.

$NaBH_4$ concentration	0.1 M		0.5 M		1 M	
reduction time (s)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)
5	*	20	*	24	*	25
30	*	28	1.6	39	1.5	39
60	1.6	37	2.0	42	2.0	42
180	1.4	35	1.8	41	1.7	40
300	1.3	34	1.4	39	1.4	39

*cannot be measured

Table 5. Ni film thickness and Ni amount obtained from different concentrations of $NaBH_4$ and reduction time at 3 g/L $(CH_3CO_2)_2Ni$ solution.

$NaBH_4$ concentration	0.1 M		0.5 M		1 M	
reduction time (s)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)
5	1.3	30	1.9	39	1.8	38
30	1.5	33	2.0	40	2.0	39
60	2.0	39	2.2	43	2.2	42
180	1.8	36	2.1	41	2.0	40
300	1.6	34	1.7	38	1.7	38

Table 6. Ni film thickness and Ni amount obtained from different concentrations of $NaBH_4$ and reduction time at 5 g/L $(CH_3CO_2)_2Ni$ solution.

$NaBH_4$ concentration	0.1 M		0.5 M		1 M	
reduction time (s)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)	Ni film thickness (μm)	Ni amount (mg/dm^2)
5	1.5	35	1.7	38	1.8	38
30	1.6	37	1.8	39	1.9	39
60	1.9	39	2.0	40	2.0	40
180	1.4	37	1.7	39	1.7	39
300	1.4	35	1.4	37	1.5	37

The results show that the Ni^0 surface seeding depends on the reduction time. When using 1 g/L $(CH_3CO_2)_2Ni$ solution, and 0.1 M $NaBH_4$ solution, at a very short reduction time of 5-30 s, the Ni film was not fully plated on over the surface. This also occurred for 0.5 and 1 M $NaBH_4$ solutions at 5 s. This observation demonstrated that adequate reduction time is necessary to obtain good entire film formation. The film thickness as well as the Ni amount in the plated ABS was found to increase with increasing reduction time in range of 5-60 s. The measured thickness of the film is in the range of 1.3-2.2 µm. The highest Ni amount (43 mg/dm^2) and thickness of the Ni film (2.2 µm) were obtained when 3 g/L $(CH_3CO_2)_2Ni$ solution was used. As for the concentration of the $NaBH_4$, the results show that both 0.5 M and 1 M gave similar film thickness. When the reduction time was prolonged beyond 60 s , it was found that the Ni amount and thickness of Ni film were decreased. This might be due to formation of Ni-B species from reaction of Ni ions and $NaBH_4$ which was reported to show higher resistant to Ni film formation than the Ni nuclei.(27) Therefore the optimum condition for good film formation is 3 g/L $(CH_3CO_2)_2Ni$ solution, 0.5 M $NaBH_4$ and 60 s reduction time. For comparison, the film thickness and Ni amount of the specimen prepared by the Pd-based process are 2.4 µm and 48 mg/dm^2, respectively.

To compare efficiency of different type of catalyst, $CoCl_2$ (1, 3 and 5 g/L solutions) was used. It was found that only in cases of using 3 and 5 g/L $CoCl_2$, 0.5 M $NaBH_4$ that the Ni film can be fully plated over the ABS surface Results are given in Table 7. Similar to the case using $(CH_3CO_2)_2Ni$ catalyst, the film thickness as well as the Ni amount in the plated ABS was found to increase with increasing reduction time. These were decreased at reduction time longer than 60 s due to a re-oxidation of metal. The $CoCl_2$ is a less efficient catalyst than the $(CH_3CO_2)_2Ni$ as the plated-Ni thickness was lower, due to lower metal catalyst formed on the ABS (see Table 3).

Table 7. Ni film thickness and Ni amount obtained from different concentrations of $CoCl_2$ and reduction time at 0.5 M $NaBH_4$ solution

$CoCl_2$ concentration	3 g/L		5 g/L	
reduction time (s)	Ni film thickness (µm)	Ni amount (mg/dm^2)	Ni film thickness (µm)	Ni amount (mg/dm^2)
30	1.4	35	1.6	37
60	1.8	39	2.0	40
180	1.7	37	1.8	39
300	1.4	34	1.6	36

Evaluation of the Adhesion of Ni Films on ABS

In this study, after the electroless nickel plating, the ABS surface was grayish, which indicated the adsorption of Ni film on the surface. The adhesion of the coated ABS was checked by the tape test according to ASTM D3359. Results from the evaluation of the adhesion strength show that none of the 16 cross-hatched squares was removed from the tested specimens (classified as no. 5 in the standard method), shown in Figure 8. This demonstrated well adherent Ni film similar to that produced by the conventional Pd-based process.

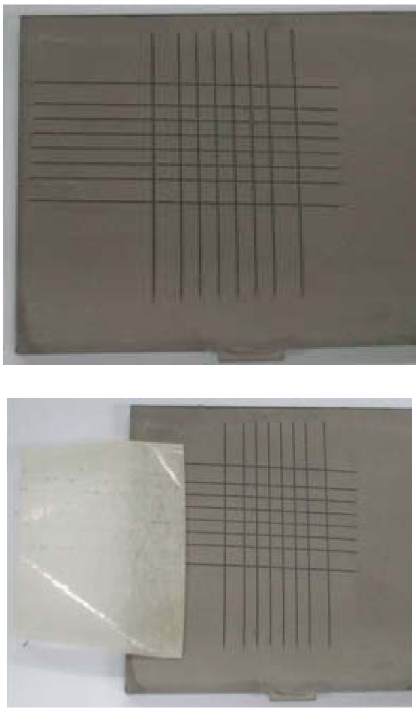


Figure 8. Surfaces of cross-cut area of the plated ABS.

Conclusion

This work has shown how to obtain an autocatalytic Ni film on an ABS surface without using the Pd conventional catalyst. Use of $(CH_3CO_2)_2Ni$ or $CoCl_2$ is more cost-effective. When increasing the concentration of the $NaBH_4$ reducing agent solution, the reduction of metal ion to metal was higher. These metal sites on the ABS surface act as the catalyst for electroless nickel plating. The ABS was metallized easily. At 60 s reduction time, the Ni amount and thickness were the highest. This process showed a good adhesion between the final Ni layer and the ABS substrates.

Acknowledgements

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