

STUDY ON MOISTURE-CURED POLYURETHANE AS UNDERCOATING LAYER FOR METALLIZATION

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ABSTRACT

In this work a technique of metallizing substrate via electroless plating using moisture-cured polyurethane (MCPU) system as the undercoat is presented. MCPU prepolymer was prepared by mixing polyethylene glycol divinyl ether and diphenylmethane-4, 4'-diisocyanate in 1:1 ratio. The effects of etching time as well as curing period on the surface characteristic of MCPU undercoating were investigated. Contact angle measurements, FTIR and SEM were employed to study the changes on the surface of the treated MCPU undercoats prior to electroless nickel plating. Electroless plating was performed using nickel bath and visual inspection was performed after completing the electroless plating cycles. Relative increase in wettability of the treated MCPU was observed. The surface became hydrophilic after subjecting to mild etching for 1 minute. SEM analysis revealed different pitted structures on the treated MCPU that were cured at different periods. FTIR analysis of the treated MCPU showed some chemical changes marked by the presence of free hydroxyl group and decrease of CH (methylene), urethane C=O, urethane amide and ether peaks. FTIR also showed the sign of further NCO reaction, which indicates by the decrease of NCO peak and increase of NH and urea C=O peaks. The standard pull-off testing method (ASTM D 4541) was employed to evaluate the adhesion strength of nickel deposits coated on MCPU undercoating layer. The test results revealed that curing period and etching time influence the adhesion performance. The results also show that at a selected curing period, prolong etching time will decrease the adhesion strength. Meanwhile prolong curing period will improve the adhesion strength.

Keywords: Moisture-cured polyurethane, undercoating layer, electroless plating, nickel

1. INTRODUCTION

Electroless plating is the ideal for applications in automotive and non-automotive decoratives, electronics, sporting goods, appliances and plumbing [1]. Decorative application accounts for about 80% of the nickel consumed in plating [2]. However, this number does not reflect the genuine utilization of plating application for decorative structures. This was due to plating for decorative it is usually limited to platable substrates, whereas artworks such as relics and many crafts are fabricated from variety of non-platable materials. Many techniques are available nowadays for plating substrates other than the platable grades such as paints and vacuum

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metallization. Nonetheless, painted products cannot be finished to feel and look like a polish metal, while the vacuum metallization is not suitable for forming metallic layer on structures with intricate shape. An alternative technique is the use of adhesive coatings as undercoating layer before metallic plating. The process was introduced in the late 70s, which is according to Gaehde *et al.*, a thin metallic layer can be electrodeposited on various non-conductive substrates using polyurethane undercoat [3]. While Shirahata and his co-workers use the same concept to metallize objects via electroless plating by using polyvinylidene chloride undercoat [4]. However, too many additives such as plasticizers and/or solvent, heat stabilizers, copolymer additives and adhesion improving agent render the undercoating preparation relatively complicated. The practicality of undercoating technique is still feasible in many plating industries. However it is a prerequisite requirement for modern industries to come out with a relatively simpler process but effective for obtaining thin metallic coatings as per intended use.

One of the best polymer coatings candidates that is can offer simpler coating system is moisture-cured polyurethane (MCPU). One advantage of MCPU is it has room temperature curing ability. MCPUs are widely use for maintenance and repair because of the ease of application and their excellent mechanical performance⁵. Besides, MCPU has the potential to be exploited in electroless plating since it consists of functional groups such as carbonyl and ether, which are vital for surface modifications via chemical treatment method. The functional groups can be oxidized to yield the so-called reaction byproducts that exist in the form of extractable moieties. The reaction byproducts later can be washed away to leave micro size holes on its surface. The holes will act as a nucleus forming site for conductive materials such as palladium, gold or platinum catalyst to give catalytic activity for chemical plating [4, 5, 6].

The present work is to describe a technique for metallizing objects using moisture-cured polyurethane as the undercoat. The focus is given to the surface modification of MCPU, which was characterized through contact angle measurements, FTIR and SEM. The metallization performance was evaluated through SEM (surface and cross-sectional morphologies) and adhesion strength.

2. EXPERIMENTAL

2.1 Preparation of prepolymer solution

Poly(ethylene) glycol divinyl ether 200 (polyol) and diphenylmethane-4,4'-diisocyanate (MDI) were obtained from Merck-Schuchardt, Germany and were used without further purification. Prepolymer solution was prepared by mixing the polyol and MDI in 1:1 ratio in an amber bottle at room temperature. The MDI was added to the polyol and gently stirred with clean glass rod until the mixture becomes homogeneous. The final product was a clear yellowish liquid. The bottle was then properly sealed to avoid contact with air moisture. It was allowed to stable at room temperature for at least 12 hours before being used.

2.2 Sample preparation

A platable grade acrylonitrile-butadiene-styrene (ABS) plastic plate with dimension of 25 mm X 55 mm and thickness of 2 mm was used as substrate. The ABS substrates were degreased with commercial detergent, rinsed thoroughly with distilled water and subsequently dried in an oven at 70°C for a minimum of 1 hour. A thin polymer coating was achieved by dipping an ABS plate into prepolymer solution for approximately 30 s and gently withdrew. Due to gravitational force, polymer flowed to the bottom tips of the substrates. The excess prepolymer was then

carefully removed using a soft brush. The sample was allowed to cure at room temperature for one day. The coating obtained was uniform and did not peel off. Three sets of samples were aged (post-cured) in an oven at 70°C at three different curing times, i.e. 2, 4 and 7 days respectively. The samples were characterized by contact angle measurements and SEM analysis.

Meanwhile for transmittance FTIR analysis, a separate MCPU film was prepared for the analysis. MCPU adheres very strongly on ABS substrate, removal of MCPU coating from ABS substrate will cause damage, fracture and non-uniform of the removed parts. Therefore, a thin moisture cured polyurethane film with average thickness between 5 – 6 µm (measured using Mitutoyo Digital Thickness Gauge) was prepared on a clean microscope glass slide. The microscope slide was dipped in the prepolymer solution and cured using the same process as applied on the ABS substrates. The film was gently and carefully detached from the microscope slides by slashing the edge of the polymer film using an alcohol cleaned razor blade.

2.3 Mild etching treatment

Surface treatment was carried out by immersing the specimens in a solution containing 0.17 mol L⁻¹ of KMnO₄, 1.24 mol L⁻¹ of HNO₃ and Enplate Wetter 62 aqueous solution (a commercial wetting agent supplied by Enthone (M) Sdn. Bhd.) at 60 – 63°C. Each sample was treated for 1, 2, 3, 4, 5, 7, 10 and 15 minutes etching duration respectively. Samples were then neutralized with a neutralizing solution containing 70 g L⁻¹ Na₂C₄O₆.2H₂O, 25 g L⁻¹ NaOH and 25 ml L⁻¹ N₂H₄.H₂ at room temperature for 45 seconds. Finally, samples were rinsed with distilled water.

2.4 Static contact angle measurements

Wettabilities of the substrates were evaluated as static contact angle using Kyowa Kaimenkagaku Face Contact Angle Meter Type CA-P. Distilled water was used in contact angle measurements as an indication of the degree of surface polarity (i.e. activation) [7]. Contact angle measurements were also used to characterize the time dependence of a pre-treatment effect. The treated polyurethane coating samples were placed on the cell (sample holder) and 15 µL distilled water was plunged on the specimen using a preset syringe. Due to the tendency of water to evaporate, the measurement was taken after 60 seconds. Five readings (n = 5) were made on different parts of the polymer surfaces and were presented as a mean with a standard deviation. Results were presented as a mean of five readings conducted on different parts of the polymer surface.

2.5 FTIR analysis

The change of functionality of polyurethanes after mild etching was measured by using a conventional FTIR (Fourier Transform Infrared) transmission spectroscopy technique. The pretreated polymer films were placed on a PVC Cardboard Window.

The cardboard window was mounted on a cell holder in the FTIR chamber of a Perkin Elmer Spectrometer System 2000. The samples were scanned in the range of 4000 to 900 cm⁻¹ with 4 cm⁻¹ resolution. The samples were then mildly etched according to the parameters as described in Section 2.2 (curing time) and Section 2.3 (etching time). Samples were carefully dried in air for 10 minutes and subsequently scanned for FTIR measurement. In order to investigate the peaks of modification and intensity change, a positive subtraction was made by subtracting the background spectrum with the post-treated spectrum using Perkin Elmer software V3.02. Spectral assignments of untreated moisture-cured PU are listed in Table 1.

Table 1: FTIR spectral assignment of untreated MCPU [18]

Wave number (cm ⁻¹)	Functional groups	Wave number (cm ⁻¹)	Functional groups
3488	O-H (H-bonded)	1598	C=C (aromatic ring)
3333	N-H (H-bonded)	1541	C-N stretch with N-H bending (Amide)
3124, 3028	C-H (aromatic)	1509	N-H bending
2908	C-H (methylene), vs	1412	C-C (aromatic ring)
2870	C-H (methylene), vs	1309	C-N & N-H
2278	N=C=O	1234	C-N
1707	C=O (urethane, H-bonded)	1106	C-O-C
1659	C=O (urea, H-bonded)		

2.6 SEM analysis

Leica Cambridge S360 Scanning Electron Microscopy (SEM) was used to examine the topography of the treated PU as well as the metallized samples (Section 2.7). The strength of electron beam was set at 10 kV.

2.7 Electroless Metallization Process

The prepared substrate (as per Section 2.2 and Section 2.3) were activated in an activator solution (1.8 g L⁻¹ PdCl₂, 106 g L⁻¹ SnCl₂, 12.4 g L⁻¹ Na₂SnO₃·3H₂O and 530 ml L⁻¹ HCl (32% %/)) for 3 minutes at room temperature. The samples were then accelerated immediately in HCl solution (pH < 1) for 2 minutes at room temperature before being thoroughly rinsed with distilled water. The samples were then metallized in a commercial electroless nickel bath supplied by Enthone (M) Sdn. Bhd. for 10 minutes at 60°C with pH value of 6.5 – 7.5. Finally, samples were rinsed with distilled water and dried in an oven at 70°C for 4 day.

2.8 Adhesion Measurement

The pull-off adhesion test method was performed according to ASTM D 4541. For each of selected parameters (combination of different curing time and etching period), five replicate samples were measured and the average value was quoted.

3. RESULTS AND DISCUSSION

3.1 Functional group derivatives

The IR spectra of the MCPU product (before mild etching treatment) are presented in Fig. 1(a) and its spectral assignments are tabulated in Table 1.

There is no indication of prolong curing time changes the functional group characteristics.

The peak appeared at ~2278 cm⁻¹ is indicative of the presence of NCO groups that remained unreacted in the MCPU product. The formation of absorption bands at ~3334 and ~1659 cm⁻¹ that attributed to NH and urea C=O groups respectively showed the characteristic of moisture-

cured reaction. It is also interesting to highlight that the absorption bands at ~ 1708 and ~ 1108 cm^{-1} attributed to the urethane C=O and C-O-C stretch respectively also exist. This outcome suggested that the isocyanate also reacted with the polyether polyol. The reaction between isocyanate and moisture and between isocyanate and alcohol had been explained elsewhere [5, 6, 7, 8]. A preliminary study on the formation of the functional groups is essential in order to monitor changes in the surface functionality and polarity before and after the surface modification via chemical etching treatment.

3.2 Contact angle measurement

Table 2 lists the results of contact angle measurements of MCPU films coated on ABS substrates after mild etching treatment. Results show a significant decrease in contact angle after etching for 1 minute for all post-cured samples at 2, 4 and 7 days. This highly suggested that the surfaces were modified from hydrophobic character to hydrophilic type. Furthermore within the limit of experimental error, there is no indication that the increase in etching time reduces the contact angle.

Table 2: Result of contact angle measurements after mild etching treatment

Etching time (minutes)	Post-curing period		
	2 days (°)	4 days (°)	7 days (°)
0	83 ± 4	74 ± 3	72 ± 2
1	52 ± 4	44 ± 4	44 ± 3
2	48 ± 3	46 ± 3	44 ± 3
3	50 ± 4	47 ± 3	42 ± 4
4	51 ± 3	47 ± 3	41 ± 3
5	50 ± 4	45 ± 4	44 ± 3
7	47 ± 3	47 ± 3	39 ± 4
10	48 ± 5	46 ± 4	42 ± 4
15	54 ± 6	52 ± 5	49 ± 6

3.3 FTIR analysis of treated PU coated specimens

Fig. 1(b) shows the FTIR spectra of treated PU specimens. The spectra exhibit similar absorption pattern. However, comparing the untreated and the treated PU, the later shows broad peak at 3620 cm^{-1} attributed to OH (free) group. This suggested that the treated sample contained more polar group as a consequence of surface treatment. This finding supports the observation from the contact angle measurements that after the mild etching, the contact angle reduced at higher extent to give a hydrophilic surface due to the formation of OH group. Another important observation from the FTIR spectra of the treated PU is the disappearance of peak at 1707 cm^{-1} , which was assigned to the urethane carbonyl functional group (Fig. 1(b)). The reason for the disappearance will be explained in Section 3.4.

In order to perceive the overall effect of surface modification of moisture-cured PU, the subtraction technique was implemented in this study. Several researchers used this method to obtain the intensity difference as a consequence of surface treatment [9, 10, 11]. In this study, the positive subtraction that refers to the unmodified spectrum subtracted from the modified

spectrum was applied. The subtraction spectra of PU2, PU4 and PU7 were overlaid in Fig. 2. Since the prominent feature in the subtraction spectra is the intensity difference, the smaller change in PU7 spectrum might suggest that PU7 underwent less modification compared to PU2 and PU4. Despite some differences in the subtraction values, all spectra show similar spectral patterns. It is clear that from Fig. 2, the CH (methylene), NCO, urethane C=O, urethane amide and C-O-C peaks depreciated after etching treatment.

The decrease of $\sim 1110\text{ cm}^{-1}$ and $\sim 1707\text{ cm}^{-1}$ peaks intensity were due to the oxidation reaction of C-O-C and urethane C=O respectively. The oxidation reaction of the corresponding functional group is expected to yield esters and carboxylic acids respectively as its degradation byproducts [12]. Perhaps the increase of OH (bonded) peak at $\sim 3490\text{ cm}^{-1}$ of the treated PU (Fig. 1(b)) can be correlated to the formation of carboxylic acid side product. While the decrease of ~ 2907 and $\sim 2873\text{ cm}^{-1}$ peak intensity as attributed to the heterolytic C-H bond cleavage from methylene group [13].

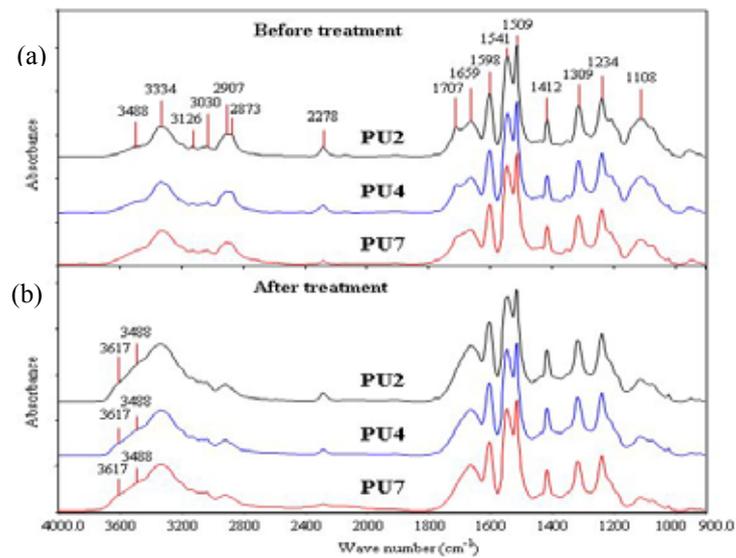


Fig. 1: (a) FTIR spectra of MCPU before mild etching treatment (b) FTIR spectra of MCPU after mild etching treatment

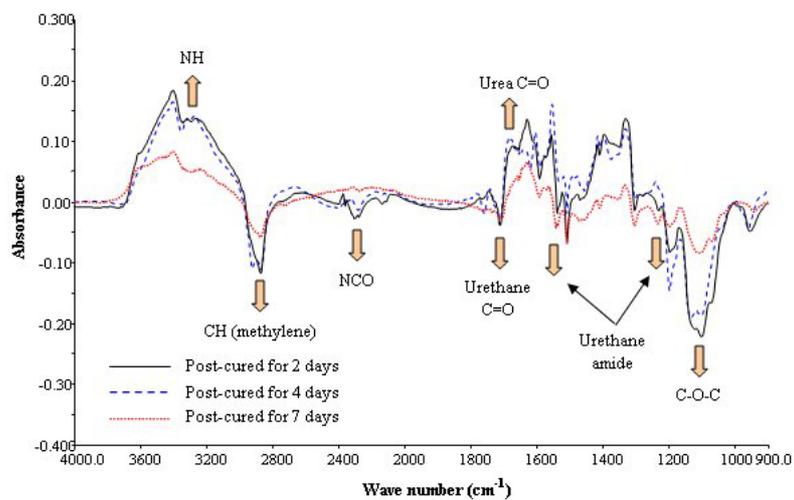


Fig. 2: The subtraction spectra of treated MCPU at different post-curing periods

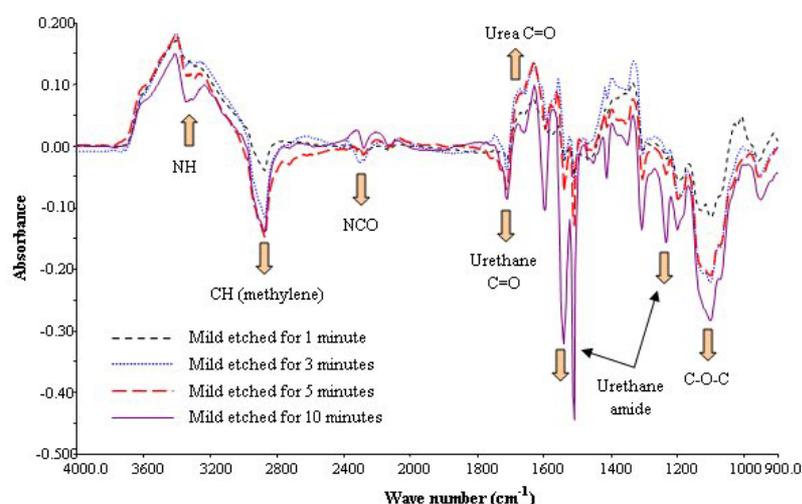


Fig. 3: The subtraction spectra of treated PU4 at different mild etching times

On the other hand, peaks at $\sim 3334\text{ cm}^{-1}$ and $\sim 1659\text{ cm}^{-1}$ that attributed to NH and urea C=O showed a significant increase. This finding offers evidence that mild etching treatment rendered further isocyanate reaction. The decrease of 2278 cm^{-1} peak intensity shows that NCO is further consumed for the reaction, while the increase of NH and urea C=O is correlated to the formation of polyurea linkages as a result of NCO reaction with water [8 – 14].

Meanwhile, the subtraction spectra of PU4 as a function of etching time are presented in Fig. 3. Same spectral patterns were observed. The spectra reveal that the CH (methylene), urethane C=O, urethane amide and C-O-C peaks depreciate after etching treatment. The decrease of these peaks was previously correlated to the oxidation reactions of these groups. Other spectral changes such as the decrease of NCO peak concurrent with the increase of NH and urea C=O peaks were also observed. This type of spectral changes was previously correlated to the formation of post-polyurea linkages. It is also observed (Fig. 3) that the sample that was etched for 1 minute has the least intensity difference. The subtraction intensity becomes more pronounce with prolong etching time. Perhaps this would suggest that the longer etching time induces surface degradation.

3.4 SEM analysis

SEM images of the untreated and treated PU specimens are shown in Fig. 4. All treated specimens exhibit pitting on its surfaces confirming the occurrence of surface modification as a result of mild etching treatment. The formation of pitting on PU surfaces has been described by few authors as due to the extraction of low-molecular weight degradation products and reagents that employed in the chemical treatments [6, 15]. As shown earlier in Section 3.3, FTIR analysis confirmed the degradation of C=O and C-O-C groups. The yields produced by permanganate reaction as discussed by Miloš Hudicklý are carboxylic acids and esters respectively [12]. The yields of these reactions are also known as degradation byproducts, which exist in the form of extractable moiety. The reagent and degradation byproducts were removed through rinsing process, leaving micro size holes or pitting on its surfaces.

Despite pitting formation, SEM micrographs demonstrate differences on the morphology of treated specimens that cured at different post-curing period. PU4 has the largest pit sizes ranging from 0.1 to $1\text{ }\mu\text{m}$, while PU2 has relatively smaller pit sizes ranging from 0.1 to $0.6\text{ }\mu\text{m}$. PU7 has the smallest pit sizes ranging from 0.1 to $0.3\text{ }\mu\text{m}$ and scarcely distributed on the surface. The differences of pit sizes for different post-cured samples may be attributed to the level of cross-

linking portion or the oxidation rate in the sample. This postulation however cannot describe the slightly bigger pit size on PU4 compared to PU2.

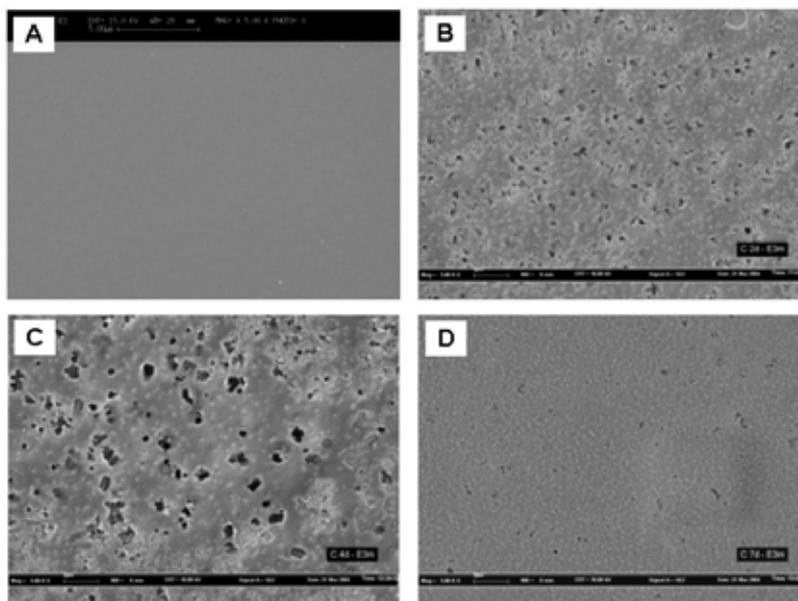


Fig. 4: *The morphology of the untreated MCPU (A) and treated MCPU at different post-curing period: (B) 2 days (C) 4 days and (D) 7 days*

A possible explanation for smaller pit formation on PU2 can be attributed to the availability of functional groups for oxidation is fewer compared to PU4.

This is due to PU2 possibly has lower cross-linking level compared to PU4.

The entanglement of the unreacted molecular chain may also cover the functional groups hence reduce its accessibility towards oxidation. It can be correlated that the induce cross-linking such as urea carbonyl linkages yields more C=O functional groups while ether linkages provide C-O-C groups, which both groups can participate in the oxidation reaction. For PU4, it possibly has higher cross-linking degree compared to PU2, therefore it will generate more oxidation sites. Due to the entanglement of molecular (polymer) chains, some functional groups might agglomerate in a domain. In a domain that consists of many functional groups, the oxidation may cause the formation of localized degradation byproducts resulting in bigger pit formation.

PU7, which has the smallest average pit sizes, possibly has the highest cross-linking level compared to PU2 and PU4. Although it is expected that PU7 might has more functional groups available for oxidation, the SEM result (Fig. 4) shows it has the least surface modifications. Probably this can be correlated with the effect of induce cross-linking, which are normally increase in hardness and chemical resistance [5, 8]. As result PU7 became less accessible to oxidation.

Meanwhile the SEM images of the treated PU4 as a function of etching time are presented in Fig. 5. All specimens show appreciable surface modifications. The fractures and holes were correlated earlier due to the extraction of low-molecular weight degradation products and reagents that employed in the chemical treatments. Qualitatively, the sample that was etched for 1 minute shows less topographical modifications compared to the samples that were etched at longer etching times. This is in accord with the subtraction spectra, which indicate that 1 minute etching confers the least intensity difference.

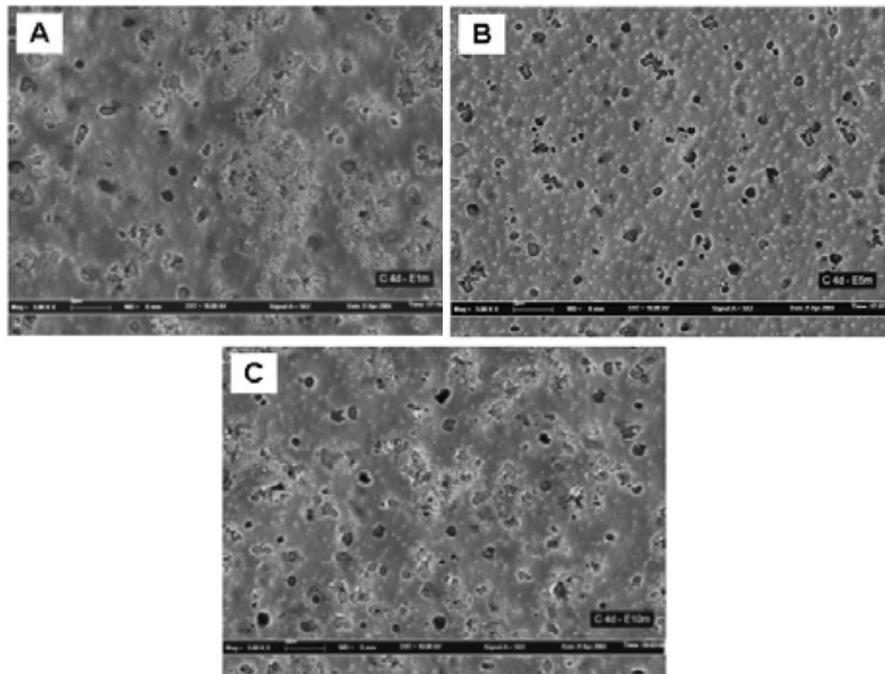


Fig. 5: The morphology of treated MCPU at different mild etching times: (A) 1 minute (B) 5 minutes and (C) 10 minutes

3.5 Metallization and adhesion test

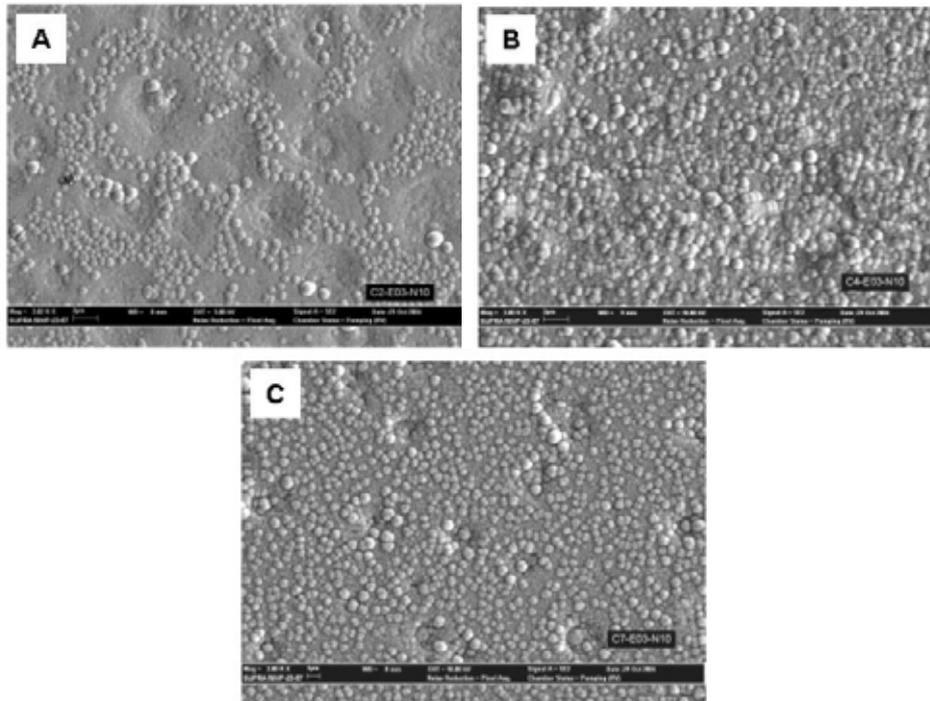


Fig. 6: The morphology of nickel alloy deposited on treated MCPU at different post-curing period (A) 2 days (B) 4 days and (C) 7 days

Full coverage of nickel coatings is obtained after approximately 30 seconds of immersion in the nickel bath. Visual inspection was performed and all samples produced without any sign of visual defects. Fig. 6 shows the surface morphology of nickel coatings deposited on different post-cured samples. All samples exhibit spherical nodular structure and virtually uniform grain size. In addition, there is no sign of cracking and skip plating, which is an evident of fully metallized surface. Meanwhile, the performance of electroless nickel plating on PU undercoating samples that were subjected to different etching times are portrayed in Fig. 7. All samples are noticed to have virtually similar surface morphology of nickel deposits.

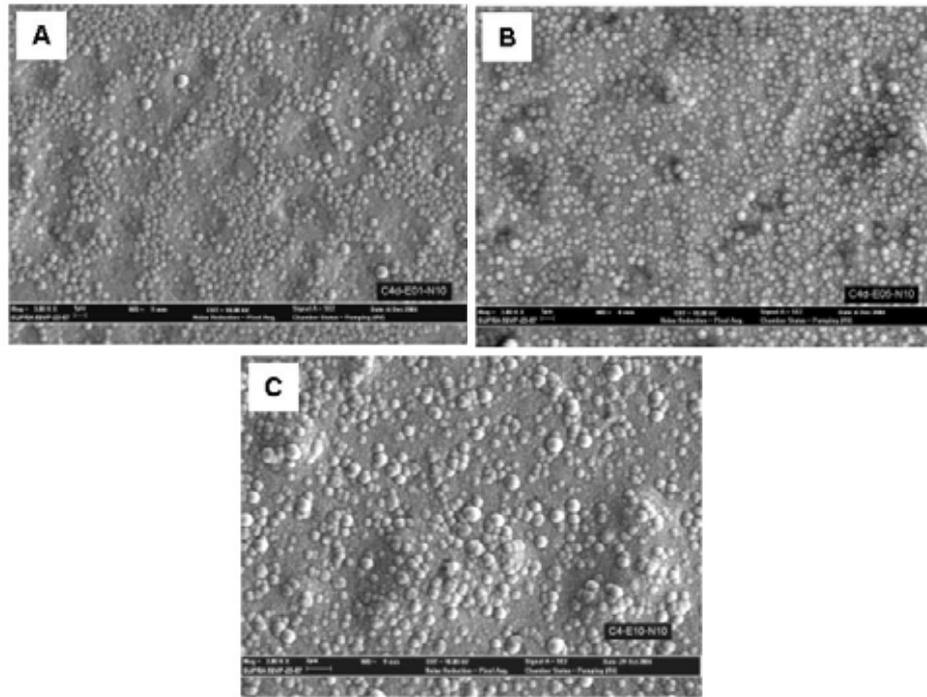


Fig. 7: The morphology of nickel alloy deposited on treated MCPU at different mild etching time (A) 1 minute (B) 5 minutes and (C) 10 minutes

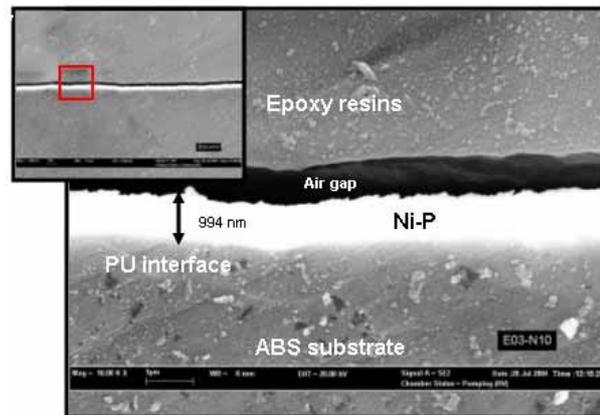


Fig. 8: The cross-sectional morphology of nickel alloy deposits plated on MCPU undercoat at 10,000 X magnification. The inset is the cross-sectional morphology of nickel alloy at 2,000 X magnification

The EDX analyses (Table 3 and 4) reveals that the phosphorus content for all samples resides between 1.7 and 2.9 percent, which falls under the category of low phosphorus content [16, 17]. It was reported that the deposits shall appear crystalline due to phosphorus atoms are not sufficient to distort the nickel lattice [16].

Table 3: EDX analysis for nickel alloy deposits plated on MCPU undercoating at different post-curing period

Sample	Etching time	Element contents (%wt)	
		Nickel	Phosphorus
PU2	3 minutes	98.0	2.0
PU4	3 minutes	98.3	1.7
PU7	3 minutes	98.2	1.8

Table 4: EDX analysis for nickel alloy deposits plated on PU4 undercoating at different etching time

Sample	Etching time	Element contents (% wt)	
		Nickel	Phosphorus
PU4	1 minutes	97.8	2.2
PU4	3 minutes	98.3	1.7
PU4	5 minutes	97.8	2.2
PU4	10 minutes	97.1	2.9

The cross-section view of a metallized ABS substrate using MCPU as the undercoat is presented in Fig. 8. The SEM image depicts a metallic film of approximately 1 μm thick was homogeneously deposited on the superficial of the PU undercoat.

After metal deposition, the main issue is the adhesion between MCPU and nickel deposits. The adhesion is compared with the control specimen, in which nickel was deposited directly on ABS substrates without MCPU intermediate using conventional process. The results of adhesion performance (pull-off test) are presented in Figs. 9 and 10. Data shows that the MCPU curing period and etching parameters have a direct influence on adhesion performance. Some samples have a far better adhesion compared with the control specimen. Data also shows that prolong curing period improve nickel adhesion to polymer (Fig. 9). PU7 has the strongest adhesion compared to PU2 and PU4 under similar treatment condition. Although the contact angle is known to be quite informative for adhesion studies, the results obtained by means of static contact angle alone may not be appreciable enough to reflect the adhesion performance. Despite having a slightly lower contact angle compared to PU2 and PU4, the experimental error shows that all samples have almost similar degree of wettability. There are many factors that can influence the adhesion performance such as surface roughness and the presence of weak boundary layer, which are not in the scope of this study. The degradation byproducts that exist as extractable moieties might not fully washed off after rinsing process and have the possibility to form weak boundary layer prior to metallization [9, 15]. As described in many literatures, weak boundary layer can impair the joint strength of two surfaces [9, 15]. Meanwhile, the nickel to polymer adhesion as a function of etching time is presented in Fig. 10. The result shows that a

prolong etching time decreases the adhesion strength. Without knowing other physical characteristics of MCPU such as surface roughness before metal deposition, pull-off testing can deduce the choice of curing time as well as etching time in order to obtain the best adhesion.

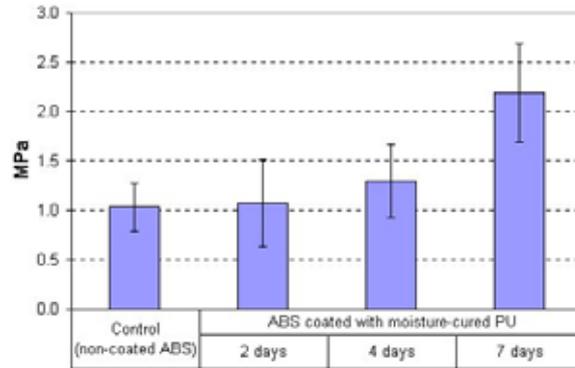


Fig. 9: Pull-off test result of nickel alloy plated on different post-curing period MCPU undercoating samples

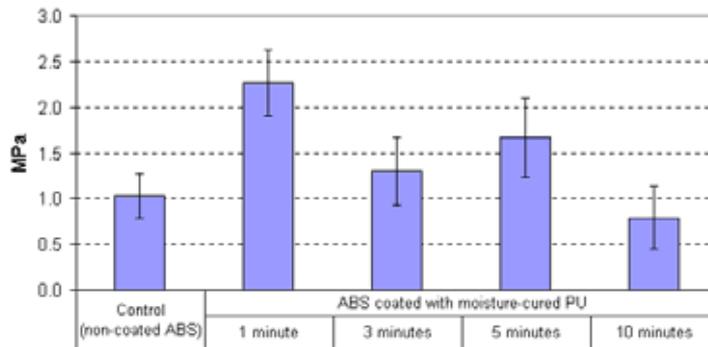


Fig. 10: Pull-off test result of nickel alloy plated on MCPU undercoating at different mild etching times

4. CONCLUSION

The surface of moisture-cured PU can be modified via mild etching process to give morphology that compatible for electroless metallization. This study showed that mild etching treatment is effective for improving the wettability of moisture-cured polyurethane undercoating. It is evident in this study that the surface morphology of treated MCPU is influenced by the ageing (post-curing) period of MCPU. Under a similar mild etching condition, longer curing period produces fewer pitting. FTIR reveals that the surface modification of MCPU was due to the degradation (oxidation) of mainly urethane C=O, urethane amide and ether groups. Besides oxidation, FTIR also confirmed further NCO reaction, which is indicated by the decrease of NCO peak and increase of NH and urea C=O peaks that was correlated to the formation of post-polyurea linkages. Regardless the morphology of treated MCPU, this technique can produce a fully metallized surface after electroless deposition with smooth metal-polymer interface. The pull-off testing reveals that a prolong curing time gives a better adhesion. While for a selected curing period (PU4), a prolong etching time decreases adhesion.

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