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Chromium Coating of Wollastonite Filled Polyamide 6 and Evaluation of Thermal Cycle Strength

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Abstract: The chromium coating of plastic/polymer materials through electrolysis method has attracted attention for improving material properties. The most common material used to be coated is the Acrylonitrile Butadiene Styrene (ABS), but has disadvantages compared to polyamides (PA), such as low thermal resistance. PA's high water retention disadvantage can be substituted by using fillers such as clay, etc; so in this study, 40% Wollastonite filled PA has been used for chromium plating to increase the thermal resistance of the PA. The plates used were produced by injection molding method. The research is focused on the effect of time and concentration on coating performance in etching, activation (by palladium) and accelerator processes. SEM and EDX were used to characterize samples for surface morphologies and the microstructures of etching, activation and accelerator in the PA sub-plates. Additionally, cross-cut adhesion test has been applied to analyze the adhesion power of the interfaces. It was found that the thermal resistance of the metal plate on the polymer surface decreased as the time increased, in relation with the increasing wearing time of the metal plate mentioned above. The thermal resistance decreased as the polymer deformed in relation with the increase in etching solution's concentration. It is also seen that the thermal resistance improved as the activation time increased. The adhesion and the thermal resistance did not improve as the time in accelerator process increased. Furthermore, the cross – cut adhesion tests on the same samples concluded that the results are in agreement with the other thermal resistance results.

Keywords: Adhesion, electrolysis, chrome plating, plating on plastics, thermal cycle resistance.

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1. INTRODUCTION

The use of plastics has increased greatly due to their important advantages such as lightness, durability, flexibility, lower unit cost compared to metal alternatives, easy reproducibility, resistance to abrasion, etc. They are the increasing industrial demands that have led to the replacement of metals with plastics as building materials in a wide range of applications. To respond to the increasing demands for metal replacement with plastics in fields such as automotive, aircraft, textiles, plumbing and household appliances, the use of metal coatings on plastics has a high potential. Such composite materials can outperform plastic or metal materials alone. In the industry, this process is known as POP-Plating On Plastics. In the literature, it is seen that the number of plastic coating studies carried out to increase the impact strength and thermal cycle resistance of plastics is very few. Probably, this is due to difficulties in coating the plastic. It should be remembered that not all plastics can be coated. Among the plastics with coating properties, there are a group of plastics such as Acrylonitrile Butadiene Styrene (ABS), Polyetherimide, Teflon, Poly-arylether, Polycarbonate, Polyphenylene oxide, Polypropylene, Polysulfone, Polyethersulfone, Polyacetal, mineral reinforced nylon, and platable phenolics. Although these plastics can be coated, the market has always been dominated by ABS. Currently, it is estimated that over 90%, ABS is used as the material in electroplating-related applications. Another material that has the potential to replace ABS is Nylon 6 (N6). However, the major challenge with N6 is that it readily absorbs water, which results in swelling and changes in physical and mechanical properties in wet conditions. This disadvantage of N6 makes the electrolysis process difficult, but if this problem can be overcome; N6 is a suitable and cheap material with good physical and mechanical properties. It can be partially coated in conventional industrial chrome plating lines. Although it can be coated, its thermal cycle resistance is very low. Plastics can be reinforced/filled with other materials to improve their properties such as tensile strength, impact strength, thermal strength, dimensional stability etc. Reinforcement materials can be in the form of fiber (fiber) and filler (elephant). Although there is no sharp difference between these two material groups, the fiber reinforcement system is generally preferred to improve the properties (Eksi O., 2007).

Wollastonite used as a filling material in this study is a naturally occurring calcium metasilicate ($Ca\text{-}SiO_3$). It is a non-metallic, acicular (needle-tipped) crystal structure, alkaline (pH 9.8), and a white mineral. The main reason for the commercial use of wollastonite is its crystal structure and special chemistry (Ciullo P.A., 1996; Kogel, 2006). Many unique properties of wollastonite have led to its use in many applications that are increasing day-by-day basis. Thanks to these properties, it is used as a filling material for ceramics, plastics and paints, in thermal and electrical insulators, as a melting and wetting agent for glazes, and as a metal melter (Springer, 1994)

Electroplating is an application in which electric current is used to form a metal coating on an electrode to improve the surface properties of objects such as providing lubricity, electrical conductivity or decorative appearance, as well as providing resistance to wear and corrosion in both industrial applications and decorative arts. The electrolyte used in the electroplating process acts as a conductive medium for the passage of electricity between the anode and the cathode. The sample to be coated is the cathode connected to the negative pole. The anode (positive) is the metal that dissolves and deposits on the cathode. When electric current starts to flow through the circuit, negatively charged ions begin to move towards the anode and positively charged ions move towards the cathode. The electric current flow in the circuit is completed by the transmission of ions from one electrode to the other through the electrolyte. The positively charged metallic ions in the electrolyte are attracted by the cathode and the surface at the cathode begins to be coated. Figure 1 below shows the various steps of electroplating of plastics.

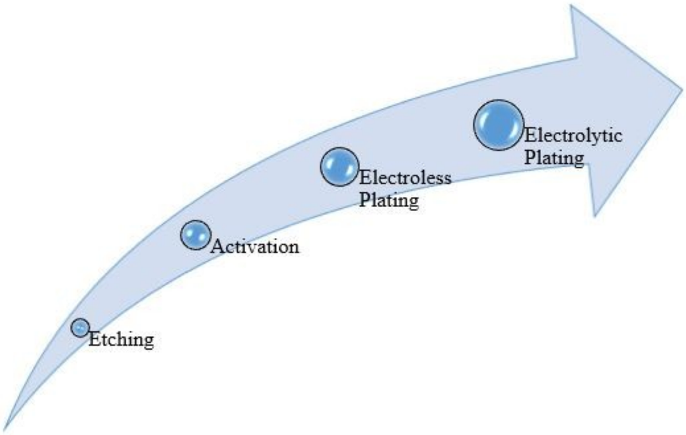


Figure 1: Steps related with the electroplating of plastics .

Among these steps, the most important steps are the etching and the activation for a successful plating. For the etching process, the mineral filler can be removed from the resin surface by contacting it with a suitable organic or mineral acid that will dissolve and be removed from the filler surface. Acids normally having a normality of less than 4.0 and preferably between about 1.0-3.0 are generally preferred. Preferably, the parts to be etched are immersed in a suitable acid bath at an operating temperature of about 15-45 ℃. Many different acids (acetic, chromic, formic, hydrochloric, sulfuric, etc.) can be used in the etching process, their concentrations vary greatly, dipping times are generally between 3-10 minutes (Stevenson, M. R., 1985).

In the patent study of Shigemitsu, H. (1986), inorganic filler, wollastonite, talc, glass fiber, carbon fiber, etc., which can be used alone or as a mixture, were used. In carrying out the invention, a desired molded article obtained by molding any of the above-mentioned polyamide resins by a conventional molding method was first subjected to initial etching with an aqueous solution of stannic chloride. After this initial etching, the molded product was washed with water. It was then subjected to a second etching with an aqueous acid solution. The concentration of the aqueous stannic chloride solution was 5 to 50% by weight, preferably 5 to 40% by weight. The acid used for the second etching was preferably inorganic acids such as hydrochloric acid, phosphonic acid, boric acid, and the like, and organic acids such as acetic acid, formic acid, oxalic acid, and the like, and especially hydrochloric acid and acetic acid. The concentration of the aqueous solution of the acid is 50 wt% or less, preferably 3-40 wt%. Although the temperatures of etching processes are determined by considering the concentration of etching solutions, they are usually 20 – 70 °C. It was preferred in terms of controlling the process to adjust the temperatures of etching processes and their concentrations. The contact times of the etching solutions were between 5 and 30 minutes (Shigemitsu H., 1986).

In the activation process, the sensitizing-activating method may involve adsorbing a relatively strong reducing agent, such as stannic chloride, hypophosphoric acid, hydrazine chloride, or the like, on the surface of the molded article, and then immersing the molded article in a catalyst solution. Gold, silver, palladium, or similar noble metal ions are deposited on the surface of the molded product as a catalyst. This catalyst-accelerator method involves immersing the molded material in a tin-palladium mixed catalyst solution and then activating the catalyst solution mentioned of with an acid such as hydrochloric acid, sulfuric acid, or the like to deposit palladium on the surface as a catalyst. Electroless coating process, electroless nickel plating, and electroless copper process are applicable. Electrolytic coating process, current copper plating process, double layer nickel (bright nickel, bright nickel) plating process, and chromium(VI) plating process are valid.

Electroless coating process are generally has a very similar electroless nickel plating and electroless copper processes described anywhere for ABS plastic coating. In the electrolytic coating process, the current copper plating process, double-layer nickel (bright nickel, bright nickel) plating process and chromium(VI) plating process described for ABS plastic plating are valid.

Metal atoms are deposited on a nonconductive surface via an electrochemical reaction in which a polymeric workpiece is immersed in a reducing agent to form a continuous metallic layer of nearly 1-μm thickness in electroless plating, (Melentiev et al., 2022). After electroless plating additional electroplating of a thicker metallic coating can be performed since the material surface is electrically conductive now. Kuzmik, J. J. (1974) proposed 14 foundational electroplating steps in the classic electroless plating process of nonconductive materials such as ABS, polyethylene, and polypropylene. The process proceeds in a series of stages: (i) pretreatment stage that involves cleaning or degreasing (Step 1) and chromic acid etching, followed by polymer surface modification via acid etching, neutralization, and water rinsing (Steps 2–5); (ii) catalytic stage that involves surface sensitization and activation by immersion in different chemical baths (Steps 6–10); (iii) electroless plating stage that involves chemical plating without an external current source (Steps 11–13); and (iv) final electroplating stage that involves the deposition of a thin metal layer on the electroless-plated substrate (Step 14). Kuzmik then combined two or more of the steps involving degreasing, chromic acid etching, sensitization, and activation to prepare a plastic substrate for the electroless plating of metals. More recently, Charbonnier (Charbonnier & Romand, 2003) confirmed a different route for the conventional method of Kuzmik with combined sensitization, activation, and acceleration steps. The first process involves sensitization (dipping in a $SnCl_2$ solution) and activation (dipping in a $PdCl_2$/HCl solution) steps. The second process, which is more practical today, involves activation (dipping in a $PdCl_2$/$SnCl_2$/HCl colloidal solution) and consequent acceleration (dipping in a HCl or NaOH solution) steps. In summary, polymer electroplating is a multistep procedure wherein a workpiece is placed in more than one dozen chemical baths to form conductive and then coated metallic layers. Only some of these electro-chemical plating routes have been discovered to date (Melentiev et al., 2022).

To understand the critical steps and mechanisms for the coating formation and adhesion strength the current understanding of the reactions in the electroless steps and their effects on the integrity of polymer surfaces should be described. These were summarized in the review of Melentiev (Melentiev et al., 2022) according to the recent studies and our electroplating experience: Cleaning or degreasing is performed to remove greasy substances from the polymer surface, during the cleaning step, the polymer plate is immersed in a bath containing an alkaline surfactant (NaOH). This step can increase the wettability of the surface by reducing the surface tension. Appropriate degreasing functions as a pre-etching process that preliminarily modifies the initial surface morphology and chemical properties (Mittal, 1990). The etching step is conducted to promote the formation of useful functional or chemical groups (chemical modification) and roughen the surface (morphological modification). Both modifications improve the chemical adhesion and mechanical interlocking at the polymer–metal interface. Etching is typically performed by immersing the polymeric substrate in a bath containing a mixed solution of chromium trioxide (CrO_3) and sulfuric acid (H_2SO_4) (called sulfochromic acid) at 65–75 °C. Taking ABS as an example since more than 90% of the polymers coated are ABS today, the hexavalent chromium ion in the sulfochromic etching solution removes or dissolves butadiene rubber particles via a redox reaction involving –CH double-bond opening to create a –COOH functional base and other polar groups, such as $–SO_3H$ or –CONH. The oxidation process consumes large amounts of acid and Cr(VI) and produces large quantities of Cr^{3+} and H_2O.

In the review of Melentiev (2022), it was also stated that excessive exposure of the polymer surface to acid—called overetching—can reduce the interlocking potential of the polymer topography and weaken the overall ABS. Over time, this causes the discoloration and severe degradation of the ABS surface. Overetching occurs when a high concentration of etching mixture is applied over a long duration. After performing experiments using various grades of ABS polymers, the optimal etching duration was found to vary between 3 and 10 min (Figure 4). At this etching duration, the level of interlocking guarantees the cohesive failure of the coated film during peeling. Exposure durations exceeding this range do not increase the peeling forces. We will soon present these findings in a separate report (Melentiev et al., 2022).

Kato et al. (Kato, 1968) investigated the effect of the sulfochromic etching duration on the morphology of two commercial grades of ABS along the thickness direction. According to his analysis, long etching durations severely damaged the polymeric material. The effects of different etching stages (underetching, optimum etching, and overetching) on an ABS surface were schematically presented by Bucknall (1977). The synergy between the etching effects on the surface porosity and functional groups transforms the nature of the polymer surface from hydrophobic to hydrophilic. Hydrophilicity ensures the pore penetration of the liquid solutions in the subsequent sensitization and activation steps and the deposition of a palladium seed layer for consequent chemical plating. After etching, the micropores and their interconnected cavities provide numerous sites for the mechanical interlocking (or anchoring) of the ABS surface.

2. MATERIALS AND METHODS

2.1. Materials

DuPont company's Minlon® material was used as the plastic raw material to be coated. This reinforced nylon material shows better dimensional stability and friction resistance than unreinforced nylons. The raw materials are originally in pellet form with a nominal granule size of 3 mm and a natural color. EKSAŞ AŞ for Cu and Ni electroplating. Two 5l polypropylene (PP) tanks produced by the company were used. In order to increase chemical resistance and acid resistance, the inside of the tank is covered with PVC. The tank is shown in Figure 2 below.

Figure 2: Polypropylene tank.

Electroplating bags: The anode bag (Figure 3) is basically a filter that prevents solid anode particles from entering the electroplating solution. It prevents these particles in the galvanic solution from causing roughness on the coating parts. Electroplating anode bags used in the research consist of PP material supplied by Coventya company.

Figure 3: Electroplating anode bag used in Cu and Ni coating.

The sides of the bags are double-stitched to prevent the bag from tearing by the rough movement created by the aerial agitation in the coating bath. PP material has excellent resistance to alkalis, mineral acids, organic acids, organic solvents, and oxidizing agents. Copper and Nickel anodes: Ni and Cu anodes were supplied from Ortam Metal and Luvata companies. Cu anodes are of two types, Electrolytic Copper (EC) and Phosphorus De - Oxidized (PDO). EC is a pure form of copper and is used in cyanide copper plating baths. PDO anodes have a low trace of phosphorus, on average 0.05% phosphorus. PDOs are important in acid Cu coating solutions using organic additives. Since organic additives are used in electroplating, the second type of anode (Ni anodes) were used in the study. These are the purest type of Ni anodes and generally cost less. It is usually available in strips or in small pieces ('F' - circles, 'R' - bullets). Flat type Ni anode was used in the study.

The chemicals used in the preparation of electrolytic baths are shown in Figure 4 and respectively; Hydrochloric acid (a), Sulfuric acid (b) were supplied from Ortam Metal Kimya. Cubrac 440 Base (c), Cubrac 440 Brightener (d), Cubrac 440 Leveller (e), Crystal Surfact 47G (f), Criterion Sb100 Brightener (g), Criterion Sb 100 Additive (h), Criterion Sb100 Base (i) Coventya Supplied from. Copper sulfate salt (m), Nickel sulfate salt (l), Nickel chloride salt (k), Boric acid (j) were supplied from Ortam Metal Kimya.

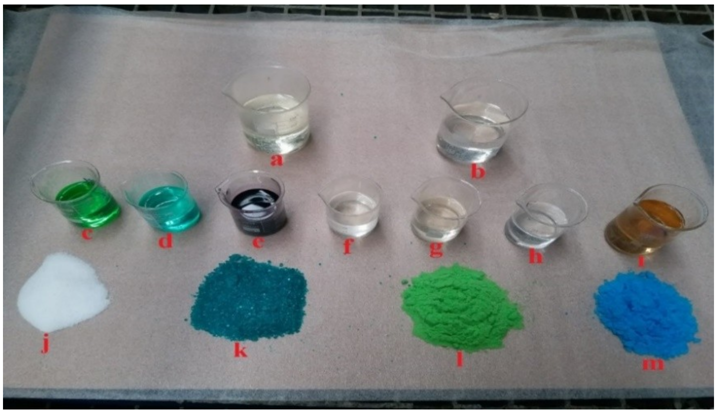


Figure 4: Chemicals used in electroplating.

2.2. Methods

PA6 M40 (40% mineral filled) polymer pellets are produced by injection molding to form standard test specimens by drying at 80 oC for 4 hours. The molded PA samples are then subjected to electroplating. In this study, the effects of time and concentration values in the etching, activation, and accelerator processes on the morphology of the material and thermal cycle resistance were investigated for PA samples. For this purpose, SEM images, EDX analysis characterization studies and thermal cycle resistance tests of the coated PA samples were carried out. The research flow chart of the study is given in Figure 5.

Preparation of PA samples by injection molding method: A HAITIAN 1200KN branded injection machine was used in the preparation of PA samples. The injection molding process is carried out by feeding the pellet thermoplastic (PA6) into the chamber of the injection machine. The injection molding machine consists of a hollow steel sleeve in which heaters are provided for the liquefaction of pellets; The barrel also includes a rotating screw to advance the molten plastic through the entire sleeve and into the die. Barrel temperature varies between 220-280 °C. The temperatures of the four zones of the injection molding machine are; the feeding zone is 220 °C, the compression zone is 240 °C, the measuring area is 260 °C and the nozzle tip is 280 °C. Once enough plastic has been collected in the barrel, a hydraulic pusher is used to push the screw forward to inject the plastic through a casting hole into the mold cavity. Care is also taken to see that the mold heats up before the mold is injected into the plastic. This process allows rapid injection into the mold before it hardens. The molding then takes the shape of the mold cavity. The samples are stored in an oven at 80 °C for 24 hours before being taken to the coating process. Figure 6 (A,B,C) shows the sample produced and the width, length, depth and wall thickness measurements of the sample.

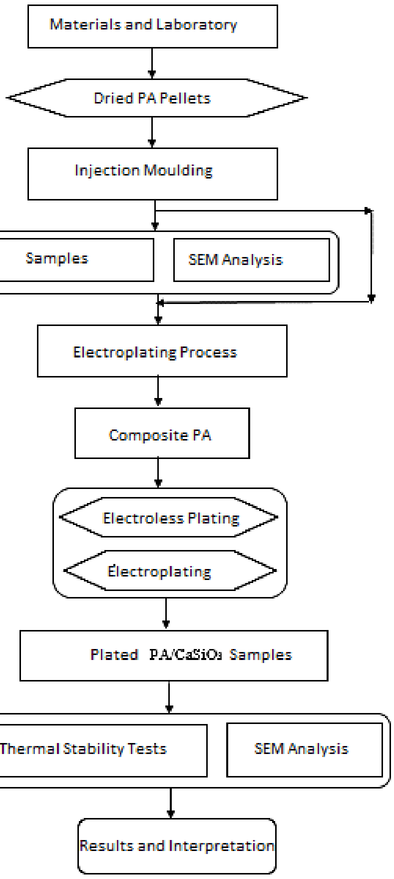


Figure 5: Research flow-chart.

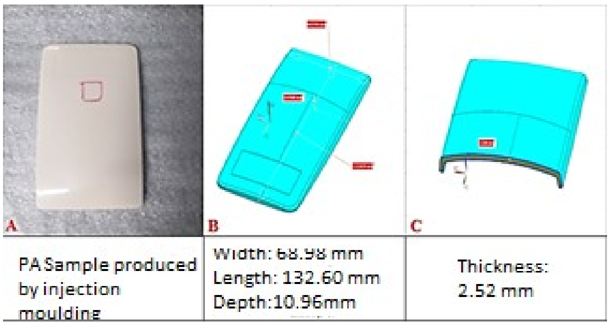


Figure 6: Produced sample and its width, length, depth, and wall thickness measurements.

Metallization of PA samples: Detailed information on the various steps followed during the electroplating of ABS plastics is covered in the following sections.

Etching Process: In this process, samples are immersed in a tank containing ethylene glycol and hydrochloric acid. The etching solution creates tiny microscopic holes on the surface of the samples. These holes act as places to hold the metallic particles. The prepared etching bath chemicals and their compositions are as shown in Table 1. Ethylene glycol up to 75% of the bath is added to the bath. Then, the required amount of Silken Etch PA 310 is added and the bath temperature is kept constant at 45 ℃ and mixed until a homogeneous mixture is obtained. The samples to be etched are dipped into the etching solution. After the etching process is finished, it is rinsed with 33% HCl acid solution and then rinsed in demineralized water.

Table 1: Etching bath chemicals and their compositions.

Samples	**Chemicals and Concentrations**	
	Silken Etch PA 310 (HCL)	Ethylene Glycol
1,2,3,7,8,9,10	245 mL/L	75%
4	300 mL/L	75%
5	350 mL/L	75%
6	400 mL/L	75%

Activation Process: The activation process, also called the catalysis process, is a process in which a catalytic film on the surface is deposited to prepare the substrate for electrolytic metal plating. Activation bath chemicals and their compositions are given in Table 2.

Table 2: Activation bath chemicals and their compositions.

Sample	**Chemical**	**Concentration**
1,2,3,4,5,6,7,8,9,10	Silken Catalyst PA 510	500 ppm
	Silken Etch PA 310	138mL/L

Micro and macroporous samples from the previous step are immersed in the bath for the times given in Table 3 and then removed.

Table 3: The immersion times of the samples in the activation bath.

Sample	**Duration (min)**
1,2,3,4,5,6,9,10	5
7	10
8	15

Samples subjected to the activation process at different durations are as in Figure 7. They are then rinsed in de-mineralized water.

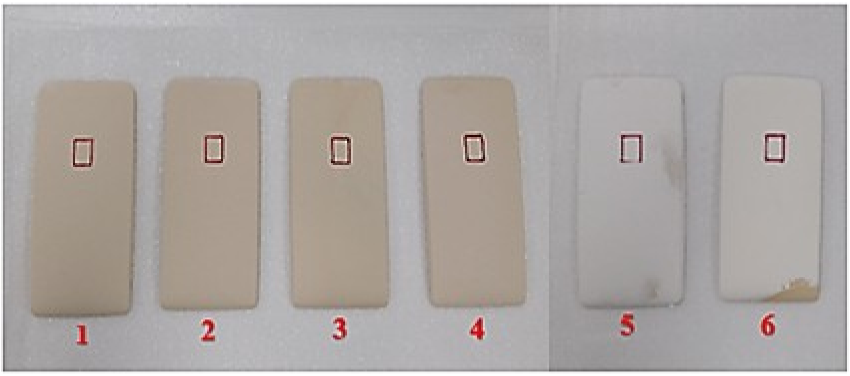


Figure 7: Etched PA specimens.

The samples were immersed in the accelerator bath for rapid reduction of the catalysts. In Table 4, accelerator bath chemicals and their compositions; In Table 5, the immersion times in the accelerator bath were given.

Table 4: Accelerator bath chemicals and their compositions.

Sample	**Chemical**	**Concentration**
1,2,3,4,5,6,7,8,9,10	Silken Accelerator 610F	28 mL/L
	Demineralized water	97%

Table 5: The immersion times of the samples in the accelerator bath.

Sample	**Duration (min)**
1,2,3,4,5,6,7,8	3.5
9	7.5
10	11.5

Electroless Coating Process: The solution is prepared by mixing nickel sulfate, sodium hypophosphite, and demineralized water in the desired proportions, then adjusting the pH with ammonium hydroxide. After completion of the activation process, all PA samples are immersed in an alkaline bath partially complexed with ammonium hydroxide at a pH of about 9.0 for 12 minutes at 30 °C. It is then rinsed with demineralized water. The chemicals used and their compositions are listed in Table 6.

Table 6: Electroless Ni bath chemicals and their compositions.

Sample	**Chemical**	**Concentration**
1,2,3,4,5,6,7,8,9,10	Nickel sulfate hexahydrate, $NiSO_4.6H_2O$	2,5 g/L
	sodium hypophosphite hydrate, $NaPH_2O_2.H_2O$	15 g/L
	Ammonium hydroxide, NH_4OH (30%)	pH:9

Acid copper plating process: Acid copper plating is called “Copper electroplating”. Acid copper plating solution is prepared by mixing copper sulfate, sulfuric acid, and hydrochloric acid with demineralized water. The chemicals used and their compositions are listed in Table 7. The prepared solution is mixed with high-intensity air for 1 hour to achieve homogeneity. Cubrac 440 Base, Cubrac 440 Brightener, and Cubrac 440 Leveller are added to the prepared solution in organics and then transferred to the electroplating bath. The copper anode is placed in a titanium basket and placed in the bath. The current density is 2.5 A/dm^2 and the operating temperature is kept around 25 °C. The current efficiency is between 95-99%. PA samples are then immersed in the prepared solution for 45 minutes. Electroplated samples are then rinsed with 50% H_2SO_4 to clean and dull the copper shiny copper layer surface. The samples are then rinsed in demineralized water to remove surface acid.

Table 7: Acid copper bath chemicals and their compositions.

Sample	Chemical	Concentration
1,2,3,4,5,6,7,8,9,10	Copper sulfate, $CuSO_4{\cdot}5H_2O$	190 g/L
	Sulfuric acid, H_2SO_4	65 g/L
	Hydrochloric acid, HCl	90 mg/L
	*Cubrac 440 Base	8 mL/L
	*Cubrac 440 Brightener	**---**
	*Cubrac 440 Leveller	0.5 mL/L
*** Organic compounds**		

Nickel (Half bright Ni and bright Ni) plating process: Semi-bright nickel plating solution is prepared by mixing copper sulfate, sulfuric acid, and boric acid with demineralized water. The chemicals used and their compositions are listed in Table 8. The organics of Criterion Sb 100 Base, Criterion Sb 100 Brightener, Criterion Sb 100 Additive, Crystal Surfact 47 G are added to the prepared solution and transferred to the electroplating bath. The working temperature of the solution is kept constant at 55 °C, the nickel anode is placed in a titanium basket and placed in the bath containing the solution. Current density 2.2 A/dm^2 is applied. The current efficiency is about 95%. The copper plating samples are then immersed in the nickel plating bath solution for approximately 12-16 minutes. The coated samples are then rinsed with demineralized water. The same conditions, chemicals and concentrations are established in the bright nickel plating solution as in the semi-bright nickel solution.

Table 8: Nickel bath chemicals and their compositions.

Sample	Chemical	Concentration
1,2,3,4,5,6,7,8,9,10	Nickel sulfate, $NiSO_4 \cdot 6H_2O$	290 g/L
	Nickel chloride, $NiCl_2.6H_2O$	50 g/L
	Boric acid, H_3BO_3	50 g/L
	*Criterion SB 100 Base	15 mL/L
	*Criterion SB 100 Brightener	0.6 mL/L
	*Criterion SB 100 Additive	0.3 mL/L
	*Crystal Surfact 47 G	10 mL/L

Chromium (hexavalent) plating process: Chromium plating solution is prepared by mixing chromic acid and sulfuric acid with demineralized water. The chemicals used and their compositions are listed in Table 9. Chrome plating provides excellent hardness, gloss, and a bright appearance resistant to corrosive environments and can be easily applied at low cost. The working temperature of the solution is 40 ℃. Wear resistant lead anodes are used as anodes. The current density is 5 A/dm^2. PA samples coming out of the bright nickel bath are immersed in the +6 valence chrome bath solution for 4 minutes. The coated samples are then rinsed with demineralized water.

Table 9: Chromium bath chemicals and their compositions.

Sample	**Chemical**	**Concentration**
1,2,3,4,5,6,7,8,9,10	Chromic acid, CrO_3	280 g/L
	Chromic acid/sulfate	280:1

2.3. Characterization Methods

Thermal cycle endurance test: Coated samples are subjected to thermal cycle endurance test by using BİNDER ED 720 heating oven and Uğur UED 380 deep freezer. This test method is usually done to measure the adhesion of the coating on the plastic surface. The most important point to be considered in this test is to ensure that the temperature is not higher than the melting temperature of the plastic. The samples are first left in the heating furnace at 104 °C for 60 minutes. Then it is kept in the environment at 250 °C for 15 minutes. It is then left in the cooling cabinet at -30 °C for 60 minutes. This process is repeated 3 times, continuing with the same samples.

Cross – Section: Coated samples are prepared for cold mounting by precision cutting with the Metkon MİCRACUT 152 device. Cold mounting specimens are prepared for SEM with Metkon FORCIPOL 2V sanding and polishing device. The coated samples are first sanded with Metkon DEMPAX Ø200 Sandpaper, 800 Grit for 7 minutes, and Metkon DEMPAX Ø200 Sandpaper, 2500 Grit for 13 minutes. Then FEDO-3 Ø200mm is polished with 3 µm diamond suspension for 8 minutes, Metkon FEDO-1S Ø200mm with 1 µ diamond suspension for 2.5 minutes.

Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis: Plastic and metallized samples were coated for SEM with QUORUM Q150R ES model coater at 80%Au+20%Pd ratios. Microstructures and surface morphologies of the samples whose surfaces were coated with gold and palladium were visualized with the ZEISS SUPRA 40VP model scanning electron microscope and energy dispersive x-ray analyses were performed (Bilecik Şeyh Edebali University Central Research Laboratory).

Adhesion tape testing: The durability of coatings is fundamental in many applications, and one of the main factors governing this durability is adhesion. Adhesion refers to the bond (chemical or physical) between two adjacent materials and relates to the force required to achieve their complete separation (Davies & Whittaker, 1967). The adhesion of a coating to the surface is critical to its function. Mechanical, chemical and metallurgical factors may contribute to these adhesions. For a coating to maintain and function, its adhesion to the substrate must tolerate mechanical stresses and elastoplastic degradation, thermal stress, and environmental or process fluid displacement. The good adhesion performance of a coating depends on various properties of the interface region, including its atomic adhesion structure, elastic modulus and stress state, thickness, purity, and fracture toughness (Baglin, 1988). In the adhesion tape test, samples are drawn with a cross cutting tool on the coating in the directions indicated in Figure 8.

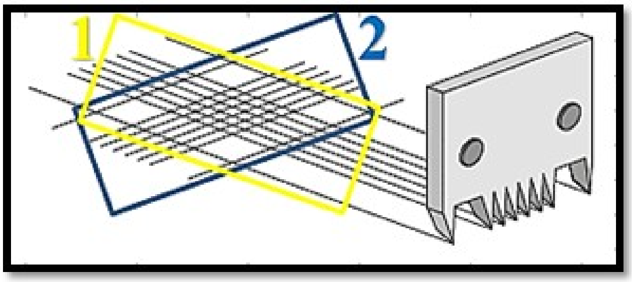


Figure 8: Drawing on the part with the cross cutter.

A special adhesive tape (Tesa 4657) is used in this procedure. The tape is pressed against the grid and then quickly pulled away in a smooth motion. The grid area is then examined using an illuminated magnifying glass (Figure 9).

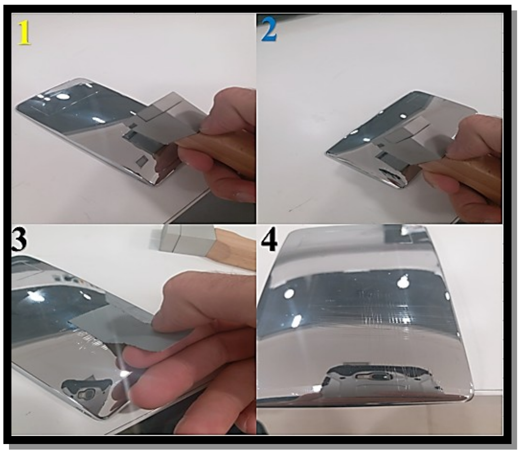
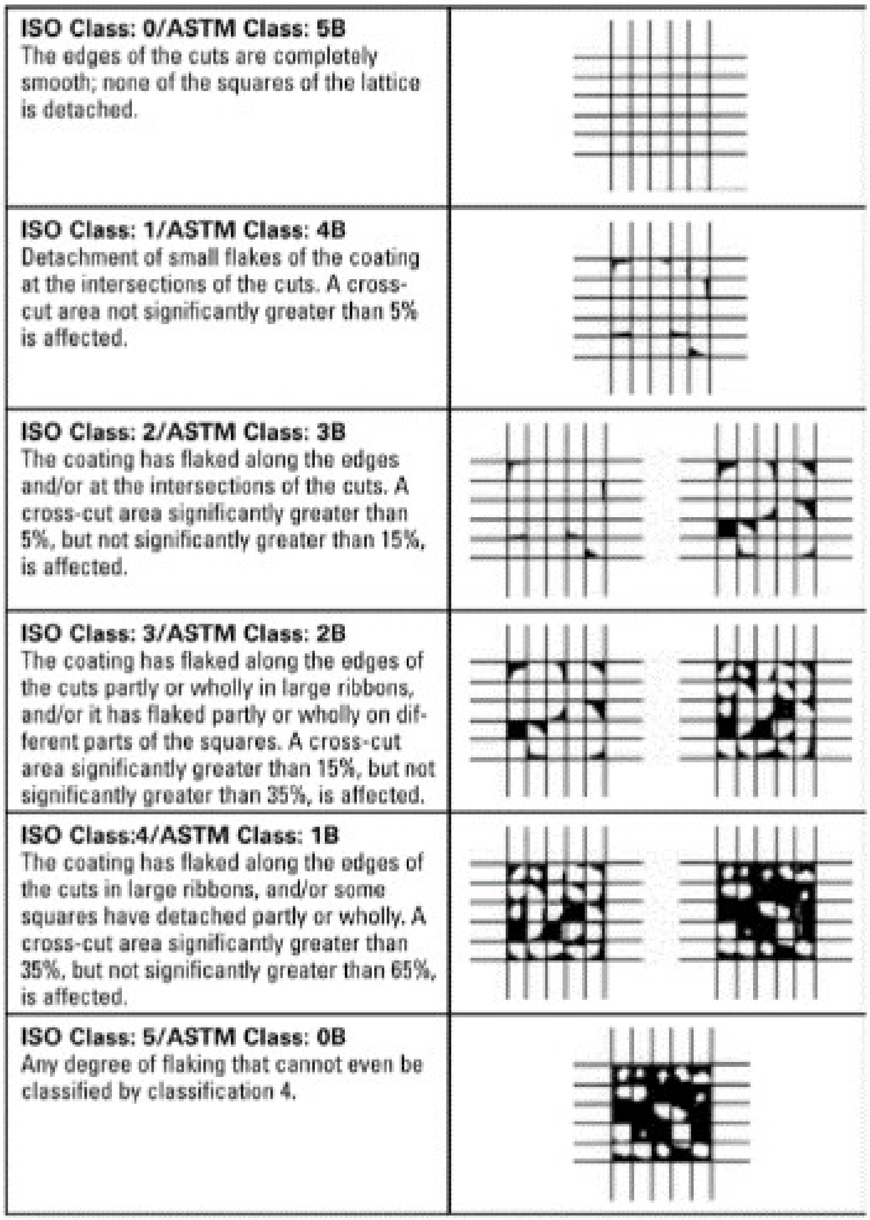


Figure 9: Adhesion tape test application.

Adhesion tests were carried out on the coated samples with the BYK - Gardner cross cut test device in accordance with DIN EN ISO 2409, ASTM D 3002, ASTM D 3359 International standards. The results obtained in this way are then classified by comparison with the standards given in Figure 10 (ASTM Adhesion Standards)).

3. RESULTS AND DISCUSSION

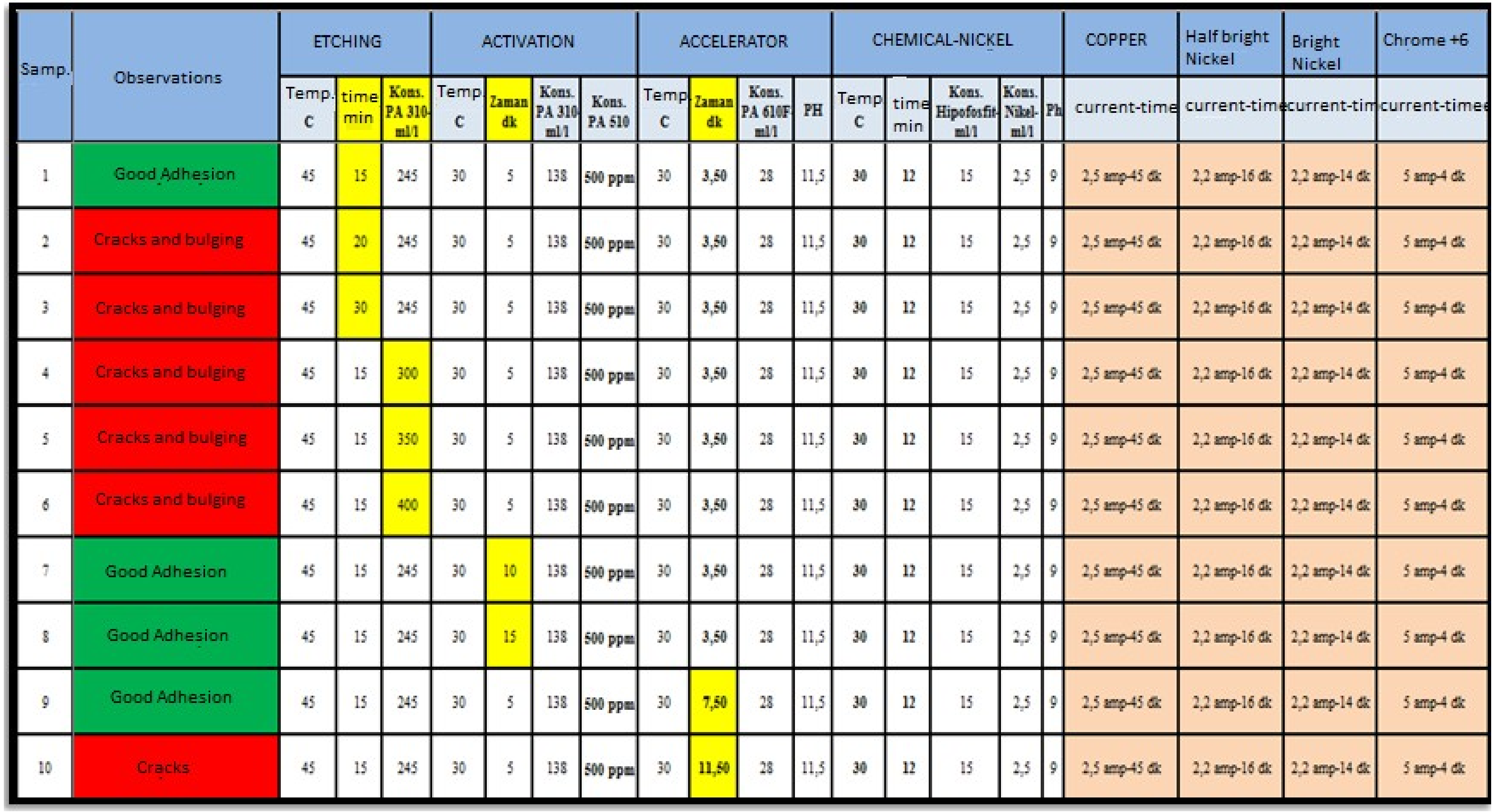
All process parameters of 10 samples prepared according to different etching time, etching concentration, and different accelerator times selected are summarized in Table 10. SEM images of these samples were taken and SEM/EDX analyzes, thermal cycle resistance tests and cross-cut adhesion tests of the coated samples were performed. Parameters indicated with yellow fill in Table 10 show the modified parameters.



ISO Class: 0/ASTM Class: 5B The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	
ISO Class: 1/ASTM Class: 4B Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not significantly greater than 5% is affected.	
ISO Class: 2/ASTM Class: 3B The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.	
ISO Class: 3/ASTM Class: 2B The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.	
ISO Class:4/ASTM Class: 1B The coating has flaked along the edges of the cuts in large ribbons, and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.	
ISO Class: 5/ASTM Class: 0B Any degree of flaking that cannot even be classified by classification 4.	

Figure 10: Adhesion tape test method classification standards (ASTM).

Table 10: Process parameters used for all samples.



Samp.	Observations	ETCHING			ACTIVATION				ACCELERATOR				CHEMICAL-NICKEL					COPPER	Half bright Nickel	Bright Nickel	Chrome +6
		Temp. C	time min	Kons. PA 310- ml/1	Temp. C	Zaman dk	Kons. PA 310 ml/1	Kons. PA 510	Temp C	Zaman dk	Kons. PA 610F ml/1	PH	Temp C	time min	Kons. Hipofosfit ml/1	Kons. Nikel- ml/1	Ph	current-time	current-time	current-tim	current-time
1	Good Adhesion	45	15	245	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
2	Cracks and bulging	45	20	245	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
3	Cracks and bulging	45	30	245	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
4	Cracks and bulging	45	15	300	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
5	Cracks and bulging	45	15	350	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
6	Cracks and bulging	45	15	400	30	5	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
7	Good Adhesion	45	15	245	30	10	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
8	Good Adhesion	45	15	245	30	15	138	500 ppm	30	3,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
9	Good Adhesion	45	15	245	30	5	138	500 ppm	30	7,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk
10	Cracks	45	15	245	30	5	138	500 ppm	30	11,50	28	11,5	30	12	15	2,5	9	2,5 amp-45 dk	2,2 amp-16 dk	2,2 amp-14 dk	5 amp-4 dk

The images of the samples after the thermal cycle resistance test are given in Figure 11.

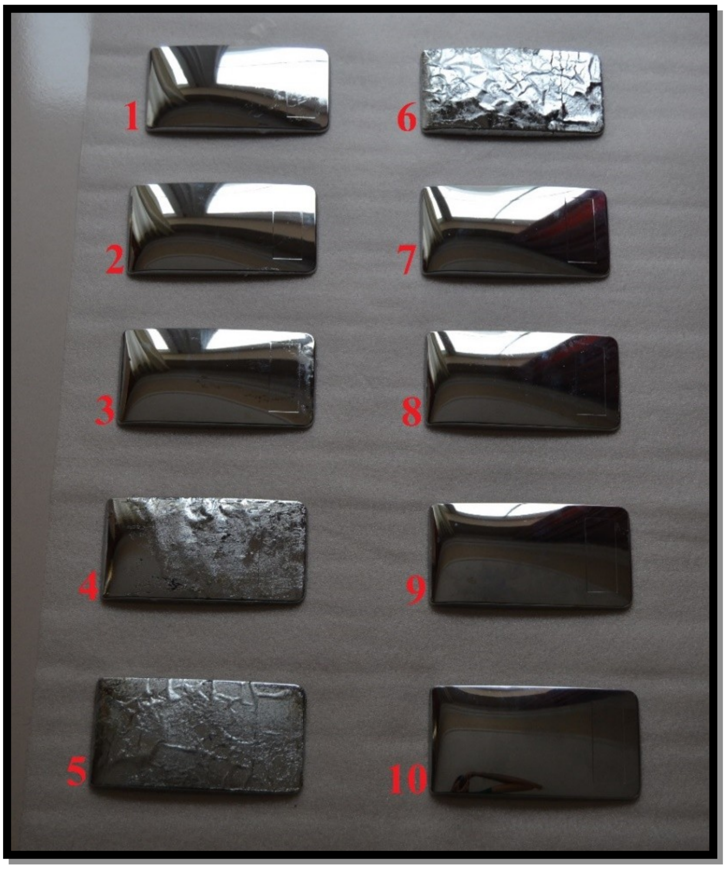


Figure 11: Samples after thermal cycle endurance test.

Figure 12 shows the SEM micrograph of the non-abraded PA material.

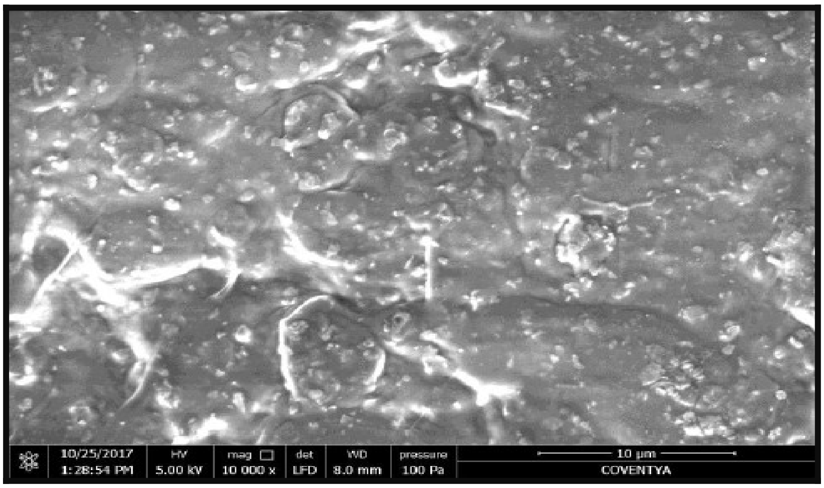


Figure 12: SEM micrograph of the PA specimen (no etching).

Figure 13 shows 10-micron SEM micrograph showing the etched PA surface. The micro- and macro-pores formed on the surface of the plastic represent the binding sites for the deposited metal.

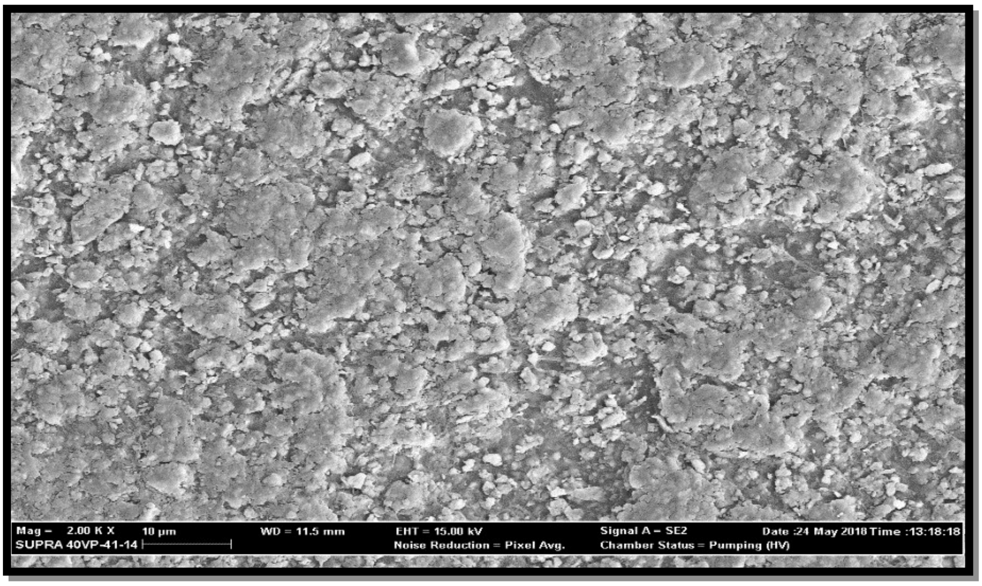


Figure 13: 15-min etching SEM micrograph of plastic PA sample 1.

Copper layer thickness and nickel layer thickness were measured in the SEM micrograph of PA sample 1 from the cross-section as 29.64 µm 13.27 µm respectively (Figure 14). After the thermal resistance test of Sample 1, it was observed that the plastic layer and the metal film layer adhered well to each other.

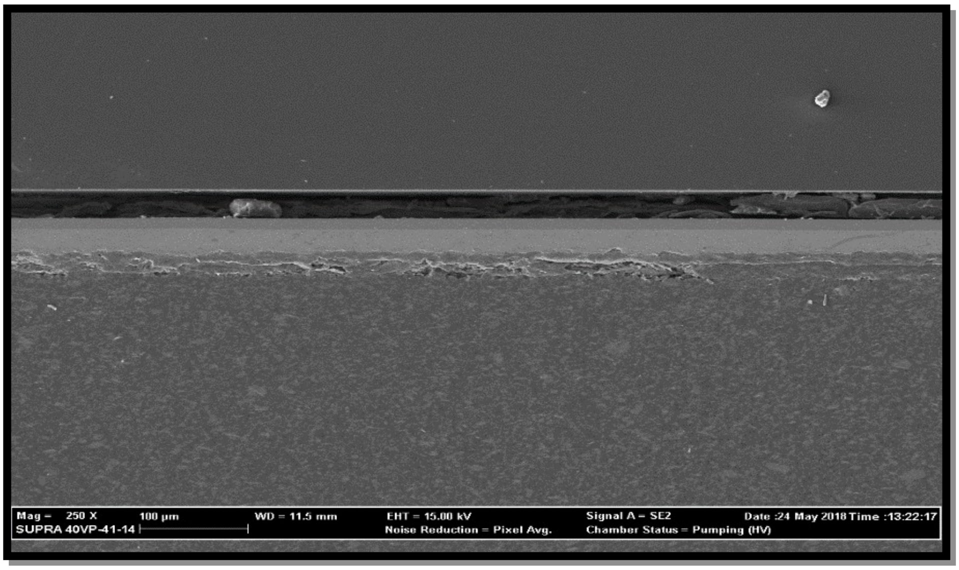
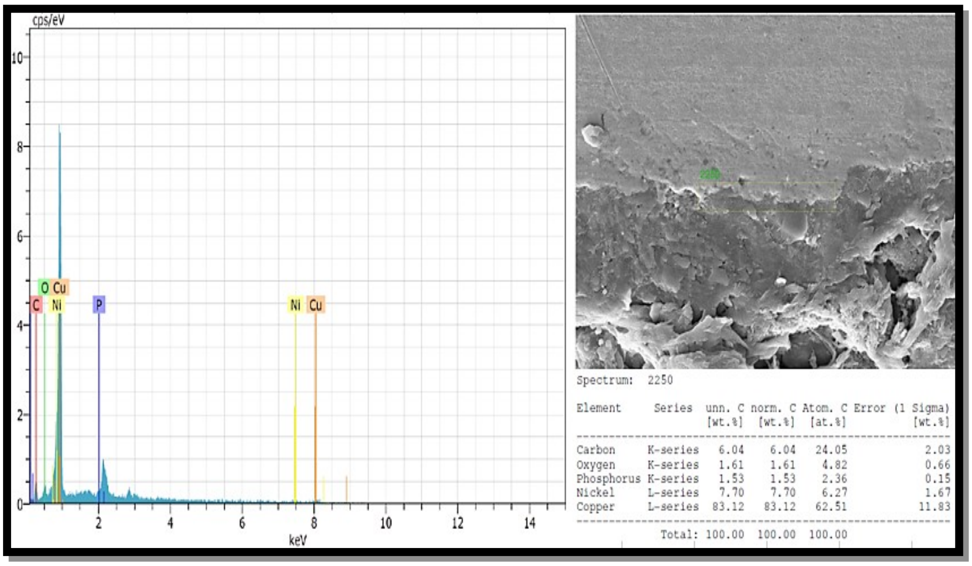


Figure 14: Cross-section SEM micrograph of metallized PA sample 1.

No impurities were observed in the elemental composition analysis between the plastic and copper layer of PA sample 1 in Figure 15. The copper element percentage is seen as 83.12.



```
Spectrum:  2250

Element     Series   unn. C norm. C Atom. C Error (1 Sigma)
                     [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------
Carbon     K-series   6.04    6.04   24.05            2.03
Oxygen     K-series   1.61    1.61    4.82            0.66
Phosphorus K-series   1.53    1.53    2.36            0.15
Nickel     L-series   7.70    7.70    6.27            1.67
Copper     L-series  83.12   83.12   62.51           11.83
-----------------------------------------------------------
              Total: 100.00  100.00  100.00
```

Figure 15: EDX analysis of PA Sample 1.

The thermal cycle endurance observation results are summarized in Table 11.

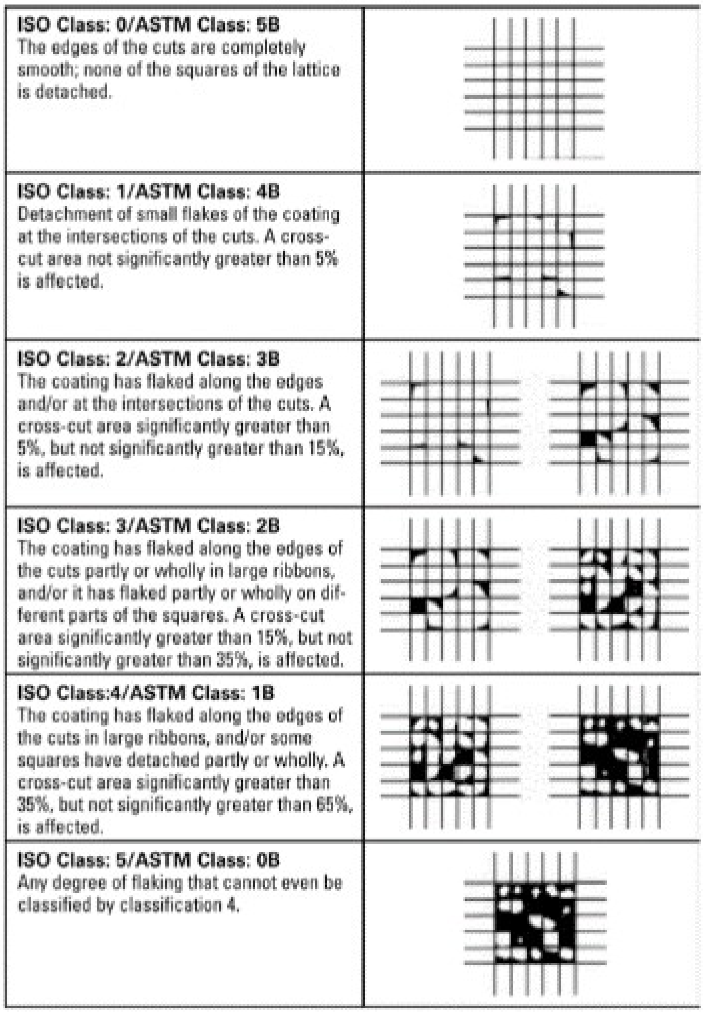
Table 11: Thermal cycle endurance test results.

Sample	Observation	Result
1	Crack, no bulging	Good adhesion
2	Crack, bulging	Bad adhesion
3	Crack, bulging	Bad adhesion
4	Crack, bulging	Bad adhesion
5	Crack, bulging	Bad adhesion
6	Crack, bulging	Bad adhesion
7	Crack, bulging	Good adhesion
8	Crack, bulging	Good adhesion
9	Crack, bulging	Good adhesion
10	Crack	Bad adhesion

Cross-Cut Adhesion Test Results of PA samples are given in Table 12.

For samples 1, 2, and 3: All parameters were kept constant and the metal plating process was carried out by keeping them in the etching bath for 15 minutes, 20 minutes, and 30 minutes, respectively. Considering the thermal cycle resistance test and cross-cut test results of Sample 1 (etching bath time 15 min), it was observed that the plastic and metal layers adhered to each other very well. It was observed that the plastic and metal layers did not stick to each other and were separated from each other in sample 2 (etching bath time 20 min) and sample 3 (etching bath time 30 min). The increase in the etching time adversely affects the adhesion of plastic and metal layers to one of them. In addition, in the SEM/EDX analyzes performed for the samples, it was observed that the metal layer could not adhere to the surface as a result of deformation as a result of deterioration in the polymer structures of sample 2 and sample 3. For sample 4 (etching bath concentration 300 mL/L), sample 5 (etching bath concentration 350 mL/L) and sample 6 (etching bath concentration 400 mL/L), the etching bath concentrations based on the parameters of sample 1 are 300 mL/L, respectively. Metal coating process was carried out by making 350 mL/L, 400 mL/L. Thermal cycle endurance test and adhesion tape test results are negative for all three samples. It was observed that the adhesion between the plastic and metal layers was very bad. The increase in the abrasive concentration adversely affected the adhesion between the plastic and metal layer. In the SEM/EDX analyzes performed for the samples, it was observed that the metal layer could not adhere to the surface as a result of deformation in the polymer structures of all three samples.

Table 12: Cross-cut adhesion test results of PA samples.



Samples	Standard and Explanation
1, 7 and 8	**ISO Class: 0/ASTM Class: 5B** The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
9	**ISO Class: 1/ASTM Class: 4B** Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not significantly greater than 5% is affected.
-	**ISO Class: 2/ASTM Class: 3B** The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.
2	**ISO Class: 3/ASTM Class: 2B** The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.
3	**ISO Class:4/ASTM Class: 1B** The coating has flaked along the edges of the cuts in large ribbons, and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.
4, 5, and 6	**ISO Class: 5/ASTM Class: 0B** Any degree of flaking that cannot even be classified by classification 4.

For sample 7 (activation process time 10 min) and sample 8 (activation bath time 15 min), metal plating process was carried out by keeping the times in the activation bath for 10 min and 15 min, respectively, based on sample 1 parameters. Thermal cycle resistance test and adhesion tape test results were positive for both samples. In SEM / EDX analyses, it was observed that the increase in the activation bath time increased the amount of Pd catalyst on the polymer surface and positively affected the adhesion between the polymer and the metal layer.

For sample 9 (accelerator bath time 7.5 min) and sample 10 (accelerator bath time 11.5 min), metal plating was carried out by keeping the accelerator bath for 7.5 min and 11.5 min, respectively, based on sample 1 parameters. It was observed that the thermal cycle strength test and adhesion tape test result of sample 9 were positive, but the results for sample 10 were negative. It was observed that as the waiting time in the accelerator bath increased, it negatively affected the adhesion between the polymer and the metal layer. In SEM / EDX analyses, the presence of Pd catalyst decreased with the increase in bath time, which negatively affected the good adhesion of the metal layer.

As a result of the study, it can be used together with Vollastonite ($CaSiO_3$), which helps form a conductive surface on PAs, to improve coatings on PAs. Increases in the etching time, etching concentration and acceleration process time in the coating process adversely affected the thermal cycling resistance of PAs. Since the coatingability of PAs is difficult, it is recommended that the etching process time be kept at 15 minutes and the etching process concentration should not exceed 245 mL/L, activation process time up to 15 minutes and acceleration process time not exceeding 7.5 minutes. In order to obtain better results, different chemicals, different etching concentrations and times, different activation and accelerator bath times can be tried. In addition, in order to reduce the cost in the industry, different filling materials are added to PAs, for example clay, talc, or silica can be added and their ability to be coated can be examined.

4. CONCLUSION

In this study, the trade name Minlon 73M40 NC010 40% Wollastonite Filled PA (Dupont) polymer was used to increase the thermal cycling resistance of PA. The plates used in the experiments were produced by injection molding method. The effects of time and concentration parameters on the coating performance were investigated in etching, activation (with palladium), and accelerator processes of the PA coating.

As a result of the study, it can be used together with Vollastonite ($CaSiO_3$), which helps to form a conductive surface on PAs, to improve coatings on PAs. Increases in the etching time, etching concentration and acceleration process time in the coating process adversely affected the thermal cycling resistance of PAs. Since the coating ability of PAs is difficult, it is recommended that the etching process time be kept at 15 minutes and the etching process concentration should not exceed 245 mL/L, activation process time up to 15 minutes and acceleration process time not exceeding 7.5 minutes. In order to obtain better results, different chemicals, different etching concentrations and times, different activation and accelerator bath times can be tried. In addition, in order to reduce the cost in the industry, different filling materials are added to PAs, for example; Clay, talc, silica can be added and their ability to be coated can be examined.

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