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METALLIZATION OF ENGINEERING PLASTICS

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CERTIFICATION OF ORIGINALITY

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ABSTRACT

A material which has metallic like surface but in light weight is selected for different industrials, such as headlamp, crumple zone as well as hood in motor industry and rear mirror in optical application. Plastics are common materials for those applications because of their advantages, including light weight, low cost, ease of forming and corrosion resistance. Plastics are metallized as the presence of a functionalized surface (with carboxylate, $-COO^-$, group) and a certain degree of roughness. Different approaches, such as chemical and physical, have been studied to obtain these features. For industrial production, chemical approaches have been preferable used without limitation of size and shape. Chromium trioxide/sulphuric acid, $H_2Cr_2O_7$, is traditionally used as etching bath for acrylonitrile butadiene styrene (ABS). Due to the environmental concern and the increase demand of plastics other than ABS, other chemical approaches (e.g. alkali etching) instead of $H_2Cr_2O_7$ etching bath have been studied to modify a variety of engineering plastics, including polypropylene (PP), polycarbonate (PC) and 38% mineral filled poly(butylene) terephthalate-poly(ethylene) terephthalate (38% mineral filled PBT/PET) blend instead of ABS.

Surface modification of the plastics was carried out by using varies solvents, such as sodium hydroxide, chloroform and polyethylene glycol. The surface modified plastics were activated by using Pd/Sn^{2+} colloidal activating bath and subsequent electroless Ni plating, and then followed by Cu-deposition through electroplating technique. By alkali etching, rough surfaces with carboxylate functional group were obtained. The correlation between the etching rate and the surface morphologies was investigated. Surface composition after etching, Ni coating and Cu coating were analyzed by Fourier transform infrared spectroscopy and X-ray diffraction. The roughness and the cross-section morphologies of the samples before as well as after etching, Ni coating and Cu coating were characterized by surface profile analysis, atomic force microscopy and scanning electron microscopy respectively. Using contact angle measurements, the effects of the etching time on the hydrophilic character of the plastics surface were assessed. Adhesion of the Cu layer, evaluated by the Scotch tape test, was found to be depended on the surface roughness and the palladium concentration of the activating bath.

On the basis of our experimental results, we demonstrated that engineering plastics with ester functional groups can be etched by using alkali. As a result, carboxylate groups are procured to facilitate the formation of complex with Pd/Sn^{2+} colloidal in the activating bath. Besides a functional surface, a rough surface (10-20 µm) is also obtained by filling some insoluble salts into the plastics blends, so that the insoluble salts can react with alkali to produce pitting sites. It is important to control the surface roughness, because it directly affects the appearance of finished product and the adhesion between Cu coatings and the substrates. Generally, a plastic surface with optimal roughness and carboxylate groups promotes metallization.

LIST OF PUBLICATIONS

Journal Paper

1. **Ng, C. S.**, Mak, C. L., Wong, Y. W. (2008). Wet pre-treatment of poly(butylene) terephthalate-poly(ethylene) terephthalate blend and subsequent metallization by electroplating. *Physica Status Solidi (c)* **5**: 3535-3540

Conference Paper

1. **Ng, C. S.**, Mak, C. L., Wong, Y. W. (2008). Wet pre-treatment of poly(butylene) terephthalate-poly(ethylene) terephthalate blend and subsequent metallization by electroplating. *Proceeding of European Materials Research Society (E-MRS) 2007 Fall Meeting*, pp. 80

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Chapter 1 Introduction

1.1 General introduction

In the past forty years, the demand of metallized engineering plastics has been increased. Plated plastics have been replaced metals in many applications, such as motor industry, household fittings and anti-inference shielding in electronics (Muller, Baudrand et al. 1970). The major reason for this trend is high cost of metals (Simpson 1993; Garbassi, Morra et al. 1998; Ehrenstein 2001). Other reasons are that plastics are lighter in weight, better resistance to corrosion, easy formability and low cost. However, metals have their specific characteristics, which are superior to plastics. For instance, many metals have characteristic bright and reflective surfaces that may be enhanced by polishing or surface treatments such as electroplating. Although the original appearance of plastics is quite acceptable for many applications, sometimes it is required to make components with reflective surfaces similar to those appeared in metal (e.g. optical mirror). Therefore, metallized engineering plastics can combine the properties of the constituents to broaden their use of range. For example, it is easy to make a more successfully and less expensively decorative product from plastics and then electroplated with coatings of nickel, chromium, brass, copper, silver or even gold. Besides decorative interest, the plated plastics are favored to be applied in quite large components of motor cars. Interior and exterior trim, even bumpers and radiator grilles are being made in plastics for convenience and/or economy. The nickel-chromium plated surface gives them both the appearance and the feel of metal.

Furthermore, the mechanical properties and the natural effects of aging of plastics (e.g. ABS) can be improved by electroplating with metal coatings. The heat resistance of plastics can also be enhanced through electroplating. It demonstrates that the plated plastics can frequently be employed at temperatures which the unplated materials could be stand. In addition, plastics which tend to contract or distort under the influence of heat are rendered more stable dimensionally by electroplating.

Although the electroplating of plastics has been developed for commercial uses since 1960s, the techniques have been limited for metallizing ABS polymer. For other plastics, an ABS interface layer must be required. As a result, a chromic acid bath has been involved in etching step. This provokes serious water pollution problem. Therefore, it is necessary to develop other methods to ease these problems.

1.2 Development of ABS and other engineering plastics

In 1960s, ABS was the first engineering plastic which was ready to undergo metallization. Metallized ABS plastic products were widely used in different industries, such as household fittings and toys (Goldie 1969; Simpson 1993; Suchentrunk 1993; Garbassi, Morra et al. 1998). The demand of metallized engineering plastics has been increasing with various purposes, such as headlamp, crumple zone as well as hood in motor industry and rear mirror in optical application. Traditional metallized ABS plastic was not sufficient to suit the customers' needs because of its characteristics. In fact, ABS is a copolymer that is made of butadiene, acrylonitrile and styrene. This copolymer combines the strength and rigidity of the acrylonitrile and styrene polymers with the toughness of the polybutadiene rubber. However, the operation temperature of ABS is between -25 and 60°C. This restricts the application of ABS. Thus, ABS plastic has been modified. Different types of ABS blend polymers have then been developed, such as ABS/PC blend, ABS/PBT blend, ABS/PMMA blend, ABS/nylon 6 blend and ABS/vinyl-ester blend (Hale, Keskkula et al. 1999; Hou and Siow 2000; Pressly, Keskkula et al. 2001; Stevanovic, Lowe et al. 2002).

Meanwhile, other engineering plastics have been developed, in order to diversify the application of metallized engineering plastics (Goldie 1969; Margolis 2006). Besides ABS, polycarbonates (PC), poly(butylene) terephthalate (PBT) and poly(ethylene) terephthalate (PET) plastics are several most common engineering plastics. The use of these engineering plastics has been increasing recently. More researchers are interested in studying PET and PC because of their advantages, including good mechanical and electrical properties, together with reasonable thermal characteristics (heat-resistant up to 150°C), so that they are applicable to engineering parts of car (Charbonnier, Alami et al. 1997; Bruyn, Stappen et al. 2003; Domenech, Jr. et al. 2003; Charbonnier, Romand et al. 2007). As a result, PP, PC, PET and its blend were selected to be studied in this project.

1.3 Surface modification of plastics

Before metallization, plastics have to undergo surface treatment to produce functional groups (carboxylate groups) and pitting sites. In general, these functional groups and pitting sites are obtained either by chemical approach or physical approach. Many researches have been conducted in these areas. However, most of the researches have focused on modifying the plastics surfaces using physical means, such as plasma, laser and UV treatment (Frerichs, Stricker et al. 1995; Beil, Horn et al. 1999; Lin, Liu et al. 2006). These methods are not limited by the plastics compositions, but they are only suitable for flatten surface and small plastics size. Therefore, these physical approaches are not flexible and applicable for industrial production.

In fact, plastics surface can be also modified by chemical reactions (oxidation and hydrolysis). Chromium trioxide in concentrated sulphuric acid, $H_2Cr_2O_7$, is a well known acid etching bath for modifying ABS surface. Oxidation occurs in the reaction bath. Although this type of bath performs well in surface etching, the presence of Cr^{6+} ions causes serious pollution problem and hazes to human (Suchentrunk 1993; Teixeira and Santini 2005). Cr^{6+} ions are recognized as a human carcinogen via inhalation.

Traditional acid etching bath not only causes serious environmental problems, but also is limited to ABS polymer. Besides oxidation, plastics surfaces can be modified by hydrolysis, where electron-deficient carbon atoms in plastics surface are attacked by a nucleophilic agent, such as base. Hydrolysis always occurs at ester and amide group of the plastics. Both PC and PET have ester group in their plastics structure, so their surfaces were modified by hydrolysis (alkali etching) in this project.

1.4 Metallization of plastics

After surface modification, the treated plastics are still not ready for metallization. Thus, a continuous conductive layer must be deposited on the treated plastics surface before metallization. Electroless Cu and/or Ni platings are normally applied for this purpose. In this project, the latter plating bath was selected because of its stability and ease pollution problems (Domenech, Jr. et al. 2003; Charbonnier, Romand et al. 2006; Charbonnier, Romand et al. 2007). A series of metal layers are chosen for electroplating once the conductive Ni layer is formed. Cu layer is coated on top of the Ni layer here. This is because the expansion coefficient of Cu is similar to that of plastics. Cu acts as a buffer layer between the plastics substrate and the top metal layer. In addition, Cu is a ductile metal with excellent electrical conductivity, so adhesion test is easily executed on it. Details will be shown in Chapter 2.3.4 and Chapter 3.

1.5 Purpose of the research

The objective of this thesis is to better understand the mechanism of metallization of engineering plastics using chemical method. In metallization process, the most important step is etching that modifies the plastics surface with formation of functional group and optimum degree of roughness. Over twenty years of research, a rich literature has been developed in the area of modifying plastics surfaces. However, these technologies have not been widely applied in industrial production. This may be attributed to the limitation of plastics' shape and size, and the continuous development of plastics.

Due to the wide range of uses of metallized plastics products, metallic surface is not only for decorative purpose, but also acts as protective layer or severs as other particular functions (Goldie 1969; Muller, Baudrand et al. 1970; Jacobasch 1997; Garbassi, Morra et al. 1998; Ehrenstein 2001). Although there are many exiting studies on this area, most of them focus on the small scale applications and physical aspect. Therefore, this thesis addresses gaps in the existing literature in two areas:

It studies the mechanism for surface modification of various engineering plastics.

It studies the techniques for metallization of various engineering plastics other than acrylonitrile butadiene styrene, ABS plastics.

1.6 Contribution of the research

This project is to gain new knowledge to metallize plastics other than ABS. This can expand the usefulness of the products and allow us to develop new niche applications. The potential value of this project may attribute to new and efficient metallizing technique that applies to other engineering plastics. The technique will be compatible with the existing technique, so that it can be easily implemented in the production line in the related industry.

Chapter 2 Literature review

2.1 Introduction

Metallization of engineering plastics has been one of the most widely studied technologies in industrial production, with many academic articles have been published since the 1960s (Goldie 1969; Simpson 1993; Suchentrunk 1993; Jacobasch 1997; Ehrenstein 2001). The important step of metallization is etching. This step directly affects the properties of metal coated plastics that are determined by the characteristics of the adhesion between the components. The formation of an adherent metal layer on plastics depends on the boundary interaction (formation of bond) between the two components (Garbassi, Morra et al. 1998).

This thesis mainly focuses on the modification of plastics surfaces. This chapter presents a review of research and literature on metal deposition of plastics surfaces. There are two major sections in this chapter. The first provides the basic knowledge of plastics, including basic definitions of plastics, classification of plastics and introduction of engineering plastics. The second reviews the process of metallization of plastics, covering physical and chemical etching and sequences process of metallization.

2.2 Plastics

2.2.1 Basic definitions of plastic

A plastic (polymer) is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by usually covalent bonds. Polymers built up from small molecules called monomers through chemical reaction, the process by which this is achieved being known as polymerization. For example, polymerization of ethylene yields polyethylene, a typical sample of which may contain molecules with 50,000 carbon atoms linked together in a chain. This long chain nature sets polymers apart from other materials and gives rise to their characteristic properties.

2.2.2 Classification of plastics

Commonly, plastics can be classified into 3 groups, namely, thermoplastics, thermosetting plastics and elastomers. Thermoplastics are further separated into crystalline and amorphous (Young and Lovell 1991; Ehrenstein 2001). Figure 2.1 summarizes the classification of polymers.

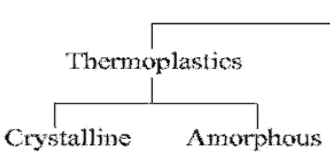
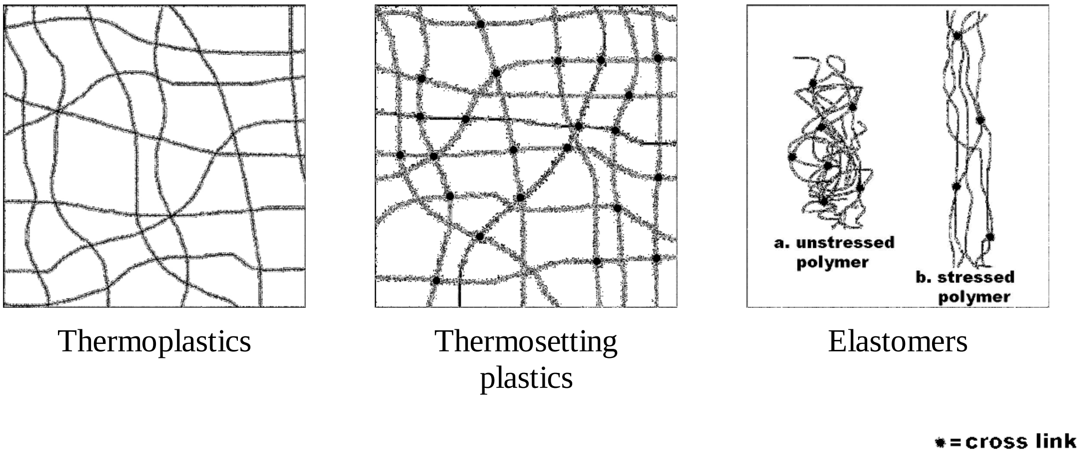


Fig. 2.1: Classification of plastics (Young and Lovell 1991).

Thermoplastics are made up of long chain polymers not chemically bonded but attracted together by weak intermolecular forces. They will be softened on heating and hardened to take up a fixed shape on cooling. The softening and hardening of thermoplastics can be done repeatedly. However, this type of plastics does not crystallize easily upon cooling to the solid state. This is because considerable high molecular weight molecules present in the liquid state. It is difficult for them to form a polymer in high order. Therefore, crystalline polymers do not invariably form perfect crystalline materials but instead are semi-crystalline with both crystalline and amorphous regions.

Thermosetting plastics (thermosets) are made up of long chain polymers with chemical bonds (cross links) between chains. Due to a high degree of crosslinking, thermosets are normally rigid materials and are network polymers in which chain motion is greatly restricted. Thermosets are different from thermoplastics. They will not be softened on heating and take up a definite shape forever. Thermosetting plastics will decompose when they are heated strongly.

Elastomers (rubbery polymers) are formed from long chain polymers with some cross links (i.e. rubbery networks). Unlike thermosets having high crosslink density, the network of elastomers is in low crosslink density. Thus, elastomers can be easily stretched in high extension and rapidly recovered their original dimensions when the applied stress is released. The rubbery networks make elastomers intractable once formed and degrade rather than melt upon applying heat. Figure 2.2 shows the structure of thermoplastics, thermosetting plastics and elastomers.



Thermoplastics

Thermosetting plastics

Elastomers

Fig. 2.2: The structures of thermoplastics, thermosetting plastics and elastomers.

2.2.3 Engineering plastics

Engineering plastics (thermoplastics) are defined as the group of plastic materials exhibit superior mechanical and thermal properties in a wide range of conditions over and above more commonly used commodity plastics. Both engineering plastics and commodity plastics refer to thermoplastics (Margolis 2006).

Polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP) and polyethylene (PE) are examples of commodity plastics. They are commonly used in convenient and disposal products, such as ‘polythene’ bags (made from polyethylene), vacuum-formed food packaging (low density polyethylene), disposable drinking cups (high-impact polystyrene) and window frames/wire insulation (PVC).

Nowadays, the demand of engineering plastics has been increased due to their range of enhanced physical properties, including high heat resistance, mechanical strength, rigidity, chemical stability and flame retardancy. For example, polycarbonate is highly impact resistant and polyamides are highly resistant to abrasion. In addition, engineering thermoplastics are ready for manufacture. Although engineering thermoplastics are expensive per unit weight, they are widely used in daily products.

For instance, ABS is used to manufacture car bumpers, dashboard trim and Lego bricks, polycarbonate is used in motorcycle helmets and polyamides (nylons) are used for skis and ski boots.

2.3 Metallization of plastics

2.3.1 Introduction

The demand of metallized engineering plastics has been increased in the past forty years. They have been replaced metals in many applications, such as household fittings, anti-inference shielding in electronics, decorative coating in general manufacturing etc. Many researches have been worked in this area (Mittal 1993; Niece and Craddock 1993; Simpson 1993; Jacobasch 1997; Garbassi, Morra et al. 1998; Mittal 1998; Ehrenstein 2001). For such applications, plastics substrates are commonly metallized by electroless deposition process which involves surface treatment to improve adhesion (etching), surface seeding with an electroless catalyst (generally a palladium containing compound), and immersion in an electroless bath (generally a Ni or Cu solution) (Goldie 1969; Garbassi, Morra et al. 1998; Charbonnier and Romand 2003).

However, this traditional electroless plating method is only suitable for etching of ABS plastics. Due to the development and the demand of engineering plastics, physical etching approach (direct metallization) has been developed, such as plasma treatments and laser treatments (Charbonnier, Alami et al. 1997; Garbassi, Morra et al. 1998; Guzman, Miotello et al. 2000; Wang, Eberhardt et al. 2006). Although physical method is applicable to a wide range of plastics, it is limited by plastics' size and shape. In addition, these techniques involve a large amount of installation cost and running cost.

Etching can be carried out by either physical approach or chemical approach. The main objective of these two approaches is to obtain a functional surface with carbonyl and/or hydroxyl group on plastics surface. For polyester plastics, carbonyl group is preferable.

2.3.2 Physical etching

Plastics surfaces which are modified by physically means can be divided into two main categories. One aims at chemically altering the surface layer. Another one deposits an extraneous layer on top of the existing material, thereby generating a sharp interface.

For the non-reactive character of plastics surfaces, it is difficult to carry out any reaction on the plastics surfaces under room temperature. The former reaction undergoes at the presence of high energy species, e.g. radicals, ions, molecules in excited states, etc. These energetic species can be produced by high temperature as well as high voltage. A number of methods, including flame, corona, plasma, laser, evaporation treatments, can be used to provide such desirable species (Frerichs, Stricker et al. 1995; Charbonnier, Alami et al. 1997; Bruyn, Stappen et al. 2003; Lin, Liu et al. 2006; Wang, Eberhardt et al. 2006). Etching occurs on the plastics surface at the same time during the physical approach.

2.3.3 Chemical etching

Garbassi et al. (1998) stated that chemical etching is used to modify the chemical composition of plastics surfaces either by chemical reaction with a given solution (wet treatments) or by the covalent bonding of suitable macromolecular chains to the sample surface (grafting). Only wet treatments were employed in this thesis, because they can be scaled up for industrial production and are not restricted in products’ shape and size.

Wet treatments were a class of traditional surface modification techniques to improve surface properties of plastics. These treatments focus on modifying the structure of plastics. Plastics with functional groups (e.g. double bond, C=C and ester group, RCOOCR’) facilitate the surface modification (Bright, Malpass et al. 1969; Kreitz, Penache et al. 2000; Kisin, Scaltro et al. 2007). Generally, it undergoes either by oxidation at the presence of chromic acid ($H_2Cr_2O_7$) or by hydrolysis at the presence of sodium hydroxide (Simpson 1993; Garbassi, Morra et al. 1998; Domenech, Jr. et al. 2003).

In the electroplating industry, concentrated $H_2Cr_2O_7$ at ~80°C is the best condition for ABS etching. Generally, a good metal-to-plastics adhesion will be resulted. ABS is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15% to 35% of acrylonitrile, 5% to 30% of butadiene and 40% to 60% of styrene (Garbassi, Morra et al. 1998). The mechanism of ABS etching is carried by heating ABS plastics in $H_2Cr_2O_7$ solution. Oxidation mainly undergoes at 1,3-butadiene in ABS. 1,3-butadiene is oxidized to butan-1,4-diol (1° alcohol), and then further oxidized to butanedioic acid (Solomons and Fryhle 2000; Teixeira and Santini 2005). The proposed oxidation of ABS mechanism is shown in Fig.

2.3. Oxidation of ABS yields carboxylate group which facilitates the formation of seed. Meantime, the treated surface becomes very rough, containing a lot of cracks and crevices that work as mechanical anchoring sites.

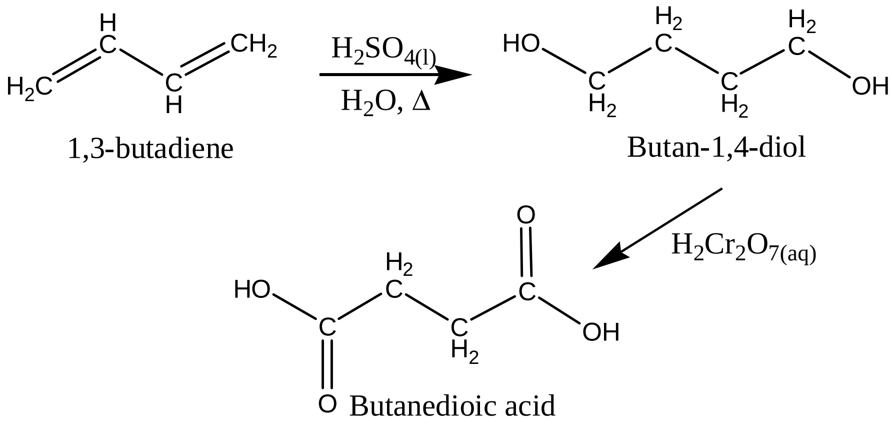


Fig. 2.3: Oxidation of ABS plastics in $H_2Cr_2O_7$ solution.

On the other hand, plastics surface can be modified via hydrolysis. For instance, PET has electron-deficient carbon atom which is easily attacked by a nucleophilic agent, such as base. Hydrolysis always occurs at the presence of ester and amide group in the plastics (Garbassi, Morra et al. 1998). Figure 2.4 shows that some of the plastics with special functional groups can undergo hydrolysis to improve their surface-related properties. Among them, hydrolysis of PET by hot sodium hydroxide attack is shown in Fig 2.5. This reaction significantly increases the number of hydrophilic (carboxylate) groups, which facilitate subsequent electroless deposition.

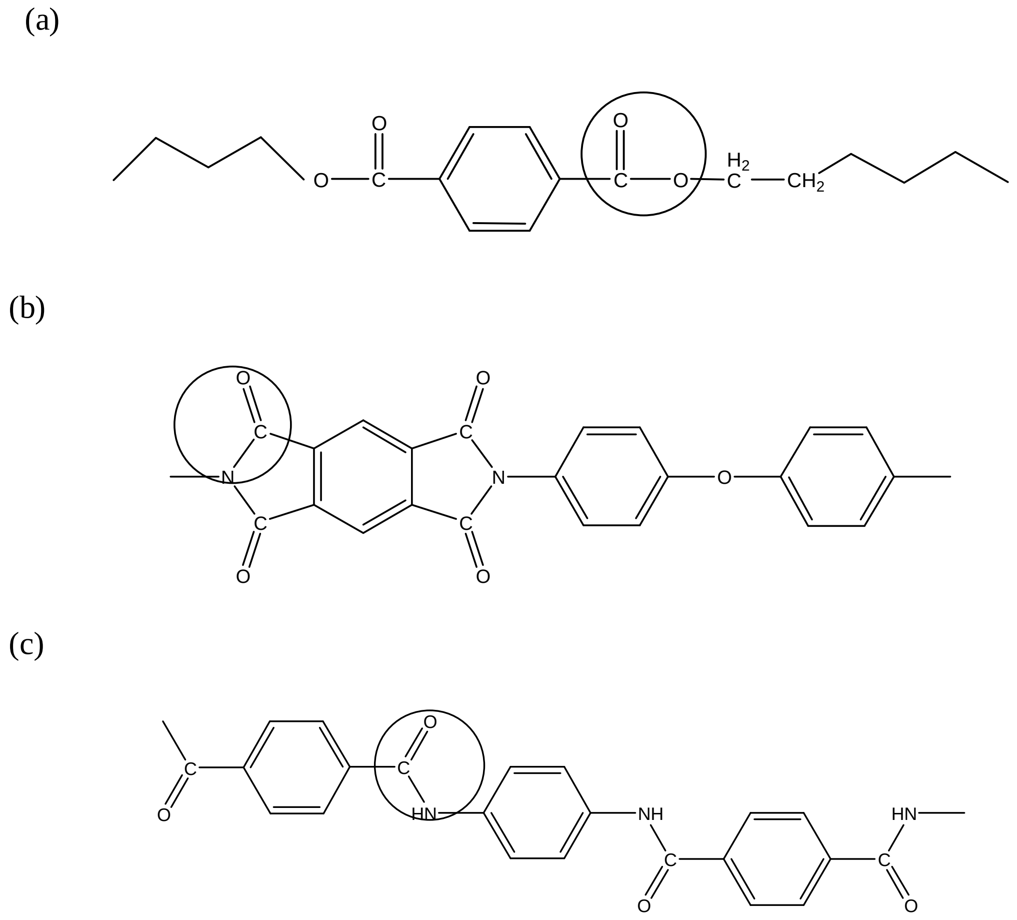


Fig. 2.4: Three different plastics surfaces modified by hydrolysis (Garbassi, Morra et al. 1998) Circles indicate the site of reaction: (a) PET, (b) polyimide, (c) Kevlar.

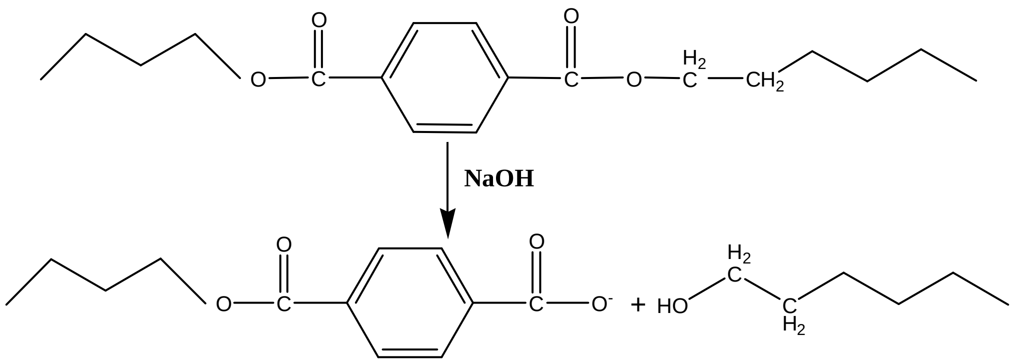


Fig. 2.5: NaOH attacks on PET (Garbassi, Morra et al. 1998).

2.3.4 Process of metallization of plastics

The established process consists of the following four stages: etching (surface modification), activation, autocatalytic metal deposition and building up deposition. The schematic diagram of the plastics metallization process is shown in Fig. 2.6.

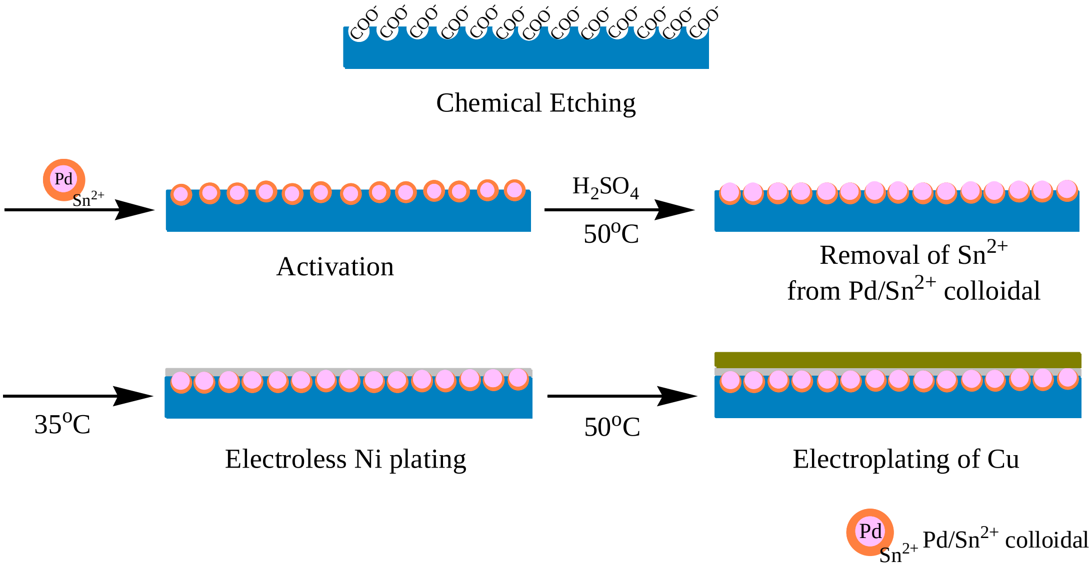


Fig. 2.6: Schematic diagram of the plastics metallization process using chemical etching pretreatment, activation procedures leading to the surface attachment of the catalyst and subsequent electroless Ni plating for forming a conductive layer.

Surface modification is a pre-treatment step to create functional groups (active sties) for carrying out reaction and mechanical anchoring sites on the substrate surfaces for enhancing the adhesion between the substrate surfaces and the deposited layer (Suchentrunk 1993; Garbassi, Morra et al. 1998). Plastic surfaces can directly be etched by immersing in an etching bath, and a metallic layer can be deposited by a plating bath. After that, the coating would be produced by connecting to a d.c. supply (Simpson 1993). However, it is difficult to undergo electroplating on plastics. This is due to the non-conductive electricity properties of plastics. In this situation, a conductive film should be provided on the surface as a basis for electro-deposition. Obviously, this conductive film must have good adhesion to the substrate, because this directly affects the quality of the finished work.

In order to obtain a conductive film, various methods, including physical and chemical means have been mentioned in Chapter 2.3.2 and Chapter 2.3.3. Kisin et al. (2007) stated that the adhesion strength of plastics to metals is enhanced by creating oxygen containing moieties (hydroxyl or carbonyl) on plastics substrates surfaces, followed by activation.

2.3.4.1 Activation

Activation is used to sensitize plastics surface. Treated plastics substrates with active sites are introduced into activation bath containing palladium/tin (II), Pd/Sn^{2+}, colloidal (Simpson 1993; Suchentrunk 1993). Sn^{2+} ions in Pd/Sn^{2+} colloidal form complex bond with carboxylate salt at active sites. In fact, Pd is surrounded by Sn^{2+} ions. The part which exposes to the air is removed by diluted H_2SO_4 solution. The implanted Pd acts as a catalyst for the electroless plating. Pd has high metal ion adsorption ability, so that metal ions are easily adsorbed on the Pd surface and reduction will be undergone. As a result, Pd must be employed in the electroless plating process.

2.3.4.2 Electroless plating (autocatalytic metal deposition)

After activation, an initial conductive metallic film is accumulated by electroless plating (chemical or auto-catalytic plating). It is a non-galvanic type of plating method that involves several simultaneous reactions (oxidation and reduction) in an aqueous solution. No external electrical power is needed. In electroless plating process, the oxidation of a soluble reducing agent R occurs on some sites on the substrate surface

$$R \longrightarrow ne^- + O \qquad (1)$$

where reduction of metal ion M^{n+} occurs simultaneously.

$$M^{n+} + ne^- \longrightarrow M \qquad (2)$$

The overall process is:

$$M^{n+} + R \xrightarrow{\text{seed (Pd)}} M + O \qquad (3)$$

The deposition of metal is autocatalytic. Once nucleation has occurred, further deposition is a very favorable process which occurs at a fast rate on the growing deposit (Pletcher and Walsh 1990; Suchentrunk 1993).

Generally, electroless Ni plating and electroless Cu plating are used for forming a conductive layer on plastics substrate surface. Ni bath is selected for electroless because of its stability, excellent corrosion and wear resistance. Besides Ni bath, Cu bath has also preferable to industrial electroless plating process. It is because the expansion coefficient of Cu is similar to that of plastics. Cu layer acts as a buffer layer between the plastics substrate and the top metal layer. For the formation of a continuous metal layer, thick deposited layers are possible in a short time using electroless Ni. It is easy to obtain 0.25 µm of Ni layer in about 5 minutes inside an electroless Ni solution. Laboratory tests have also shown that for depositing layers of thickness of ~0.25-1.25µm, electroless Ni is more conductive than electroless copper of the same thickness (Muller, Baudrand et al. 1970).

Table 2.1: Composition and properties of electroless alkaline nickel bath.

	Formulation	Function
Alkaline nickel	Nickel chloride	
	Sodium hypophosphite	Reducing agent
	Ammonium citrate	Buffer
	Ammonium chloride	Complexing agent and brightener
	pH 8-10	
	Temperature: 35°C	

Table 2.2: Composition and properties of electroless copper bath.

	Formulation	Function
Copper bath	Copper sulphate	
	Formaldehyde	Reducing agent
	Sodium hydroxide	Buffer
	Rochelle salt	Complexing agents
	EDTA	
	pH 11	
	Temperature: 25°C	

In addition, Electroless Cu plating potentially raises environmental problems. In Cu bath, EDTA and formaldehyde are commonly used as a complexing agent and reducing agent respectively (shown in Table 2.2). EDTA is used to improve the throwing power of the bath, assists the dissolution of anode and prevents passivation. Unfortunately, it has a serious environmental issue and affects the growth of the marine organisms. It has a high stability and thus is difficult to be removed from wastewater using traditional treatment. Besides EDTA, formaldehyde is carcinogenic. For industrial interest, electroless Ni plating is more preferable than Cu plating. This is because the electroless Ni plating bath is more stable and creates less environmental problems. However, nickel is an important cause of contact allergy. The amount of nickel which is allowed in products that come into contact with human skin is regulated by the European Union.

Reduction of Ni^{2+} ions (shown in equation (4)) and oxidation of sodium hypophosphite, NaH_2PO_2, (shown in equation (5)) carry out at the presence of Pd in the basic solution. Equation (6) shows the overall equation between the reaction of Ni^{2+} ions and NaH_2PO_2 (Suchentrunk 1993; Charbonnier, Romand et al. 2006).

$$\text{Cathode:} \quad Ni^{2+} + 2e^- \longrightarrow Ni \tag{4}$$

$$\text{Anode:} \quad H_2PO_2^- + 2OH^- \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} HPO_3^- + H_2O + 2e^- \tag{5}$$

$$\text{Overall:} \quad Ni^{2+} + H_2PO_2^- + 2OH^- \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} Ni + HPO_3^- + H_2O \tag{6}$$

Similarly, reduction of Cu^{2+} ions (shown in equation (7)) and oxidation of formaldehyde, HCHO, (shown in equation (8)) take place on the catalyst (Pd) in the basic solution and Equation (9) shows the overall equation between the reaction of

Cu^{2+} ions and HCHO (Suchentrunk 1993; Charbonnier, Romand et al. 2006).

Cathode: $$Cu^{2+} + 2e^- \longrightarrow Cu \quad (7)$$

Anode: $$HCHO + 3OH^- \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} HCOO^- + 2H_2O + 2e^- \quad (8)$$

Overall: $$Cu^{2+} + HCHO + 3OH^- \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} Cu + HCOO^- + 2H_2O \quad (9)$$

2.3.4.3 Electroplating

Once the initial conductive metallic film is prepared, the plastics substrate is ready for electroplating. For metallization of plastics, electroplating of Cu is preferential carried out. Cu layer acts as an expansion buffer layer between the plastics substrate and the top metal layer. Afterwards, other desirable metal layer is further deposited on this Cu layer by electroplating. Different plating baths are chosen according to the application purposes. Table 2.3 is a summary of the most common types of plating and their functions.

Table 2.3: The summary of the most common types of plating and their functions (Maroney 1991).

The most common types of plating	Functions
Copper	For conductivity and rust-proofing; often copper is “flashed” onto a part for a minimum time period to form a conductive plate and additional rust-proofing prior to the next plate, which may be nickel, sliver, or gold.
Nickel	For strength, corrosion resistance, decoration; often alloyed with another metal for both strength and hardness.
Chrome	For corrosion resistance, wear, decoration.
Hard chrome	For hardness and wear resistance of such items as crankshafts, drill bits, and dies.
Brass	Primarily for decoration.
Gold	Conductivity, decoration; used on electronic parts, electric contacts, solid-state circuits, jewelry, decorative items.
Cadmium	Corrosion resistance.
Tin	As a rust-proofing on steel, as an alloy, and for decoration.
Rhodium	On industrial machinery and automobiles, for corrosion resistance, and for decoration.
Platinum	On industrial machinery and automobiles, for corrosion resistance, and for decoration.

Chapter 3 Preparation and Characterization methods

3.1 Sample preparation

The present study focuses on three types of plastics, namely, PP, PC and PBT/PET blend (38% mineral filled PBT/PET, Model 7062, GE plastics). Before any treatments, the samples were cleaned in an ultrasonic bath of ethanol. The metallization process of the plastics consisted of the following steps: (1) surface treatment; (2) surface activation; (3) electroless Ni plating; and (4) electrodeposition of Cu.

For different kinds of plastics, different surface treatments were employed in this thesis. The details will be introduced in the following chapters. Then, the samples were dipped into 1% HCl for 30 s to get rid of dirty, grease and water. The chemisorption of the Pd on the functionalized surfaces was performed by dipping the samples in a MACuPlex activator D-34C concentrate bath, consisting of D.I. H_2O, 32% HCl, sensitizer 78 and MACuPlex activator D-34C concentrate, for 3 min. The bath must be free from air, light and water which accelerate oxidation as well as hydrolysis of Sn^{2+} into Sn^{4+} in the bath.

The samples were then dipped in 50 g/L H_2SO_4 at 50°C for 1 min to remove Sn^{2+} from Pd/Sn^{2+} colloidal, so that Pd in Pd/Sn^{2+} exploded to the electroless Ni plating bath. Oxidation of reducing agent and reduction of Ni^{2+} were taken place on the Pd seeds simultaneously.

Electroless Ni plating was carried out by slightly heating the samples in a MACuPlex J-64 Ni bath at 35°C for 6.5 min. The MACuPlex J-64 Ni bath comprised D.I. H_2O, 28% NH_4OH, MACuPlex J-60 and MACuPlex J-61. Finally, the Ni plated samples were electrodeposited with Cu. Before electrodeposition of Cu, the Ni plated samples were cleaned in an electrolytic cleaning bath for 1 min at 50°C using 3 ASD (ASD = Total surface area of sample x number of samples for plating), in order to remove any grease on the samples. The cleaned samples were deposited a thin Cu layer, which was a protective layer for further plating, via Cu strike plating for 5 min at 50°C using 2 ASD. (The purpose of strike is used to improve the adhesion and activation of passive substrates.) Eventually, Cu-plated samples were dipped in acid Cu bath for 25 min at 50°C using 2.5 ASD. The samples were thoroughly rinsed by D.I. H_2O for 30 s after each step to remove residues on the surfaces.

3.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was employed to determine the chemical bonding of the samples after surface treatment. Surfaces of samples were collected by using sand paper. The powder obtained from the surfaces of the samples were mixed with KBr and pressed into pellet. The IR spectra were collected by a FTIR spectrometer (Nicolet MAGNA-IR® 760 spectrometer E.S.P) using transmission mode.

3.3 Optical microscopy

Optical microscopy was used to observe the marco-feature of the samples before and after the NaOH etching. Optical micrographs were collected by using a polarizing optical microscopy (Nikon Microphot-FXA) equipped with a digital camera (Pixar).

3.4 Scanning electron microscopy (SEM) with Energy dispersive X-ray analysis (EDX)

Scanning electron microscope (SEM) was used to determine the surface and the cross section morphologies of the samples. Energy dispersive X-ray spectroscopy (EDX) was used to determine the surface chemistry of the samples. SEM data were collected by a Leica Stereoscan 440 and EDX data were colleted by an EDX detector.

3.5 Atomic force microscopy (AFM)

The root-mean-square surface roughnesses (R_q) of the samples after alkali etching and electroplating of Cu were investigated by using an atomic force microscope (AFM, Digital Instruments, Nano Scope IV). All AFM images were collected in a tapping mode.

3.6 Surface profile analysis

For macro-surface roughness, the root-mean-square surface roughnesses (R_q) of the samples after alkali etching and electroplating of Cu were investigated by using a surface profiler (KLA-TENCOR® P-10). All data were collected in a contact mode.

3.7 Contact angle measurements

The influence of the alkali etching on the surface hydrophilicity was investigated by a contact angle measurement (Ram´e-hart) based on the sessile drop experiment which was carrying out by dropping 5 μl of D.I H_2O on the plastics surfaces. The contact angle was measured until the probing liquid attained an equilibrium state.

3.8 Adhesion test

Adhesion of the electroplating Cu films on substrate was evaluated using the standard Scotch tape test (cross-cut tape test, ASTM D 3359-02) performed with 3M Scotch tape. A lattice pattern with eleven cuts in each direction was made in the film to the substrate, pressure-sensitive tape was applied over the lattice and then removed. The adhesion of the film was classified in the following scale ranges. The adhesion scale ranges from 5B (The edges of the cuts are completely smooth; none of the squares of the lattice is detached) to 0B (The coating has flaked along the edges of cuts in large ribbons and whole squares have detached; the area affected is more than 65% of the lattice). This test shows a comparison of the adhesion levels of films obtained under various preparation conditions.

Chapter 4 Surface modification of Polypropylene and subsequent metallization by electroplating

4.1 Introduction

Polypropylene (PP) is a thermoplastic. It is synthesized from the addition polymerization of propene. This plastic has long hydrogencarbon chain with methyl group. The structure of PP is shown in Fig. 4.1. From the figure, no active site can be found in the PP structure. This makes PP very inert to chemicals, including organic solvents, acids and bases. Besides excellent chemical resistivity, PP is cheap and is easy for production, including extrusion and molding (Domininghaus 1993). PP plastics is used in a wide variety of applications, including packaging, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers and automotive components (Karian 2003; Krupa, Boudenne et al. 2007; Krupa, Mikova´ et al. 2007). Surface modification of PP can promote it to become a metallizable material and diversify its application.

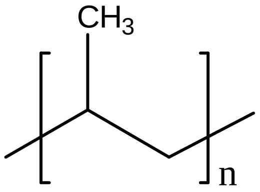


Fig. 4.1: The structure of polypropylene (PP).

Theoretically, PP surface can be modified by acid bath similar to ABS (Goldie 1969; Garbassi, Morra et al. 1998; Bruyn, Stappen et al. 2003). PP can be roughened by $H_2Cr_2O_7$ acid, but the effect is not significant. Physical means, such as laser treatment, ion beam treatment and plasma treatment, have been introduced to treat this type of plastics. They, not only roughen the PP surface, but also activate the PP surface by introducing active species (free radicals, ions). Among varies physical etching methods, sandblasting is the simplest method that mechanically creates pitting sites on the plastics surface without introducing any new functional groups to the plastics.

After roughening the plastics surface, a polyethylene glycol thin coating layer was introduced onto the surface. Poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) refer to an oligomer and polymer of ethylene oxide respectively. PEG refers to oligomers and polymers with a molecular mass below 20,000 g/mol, PEO refers to polymers with a molecular mass above 20,000 g/mol. One function of PEG is to couple with hydrophobic molecules to produce non-ionic surfactants. This increases the surface's wettability, two hydroxyl groups appear in the structure of PEG (shown in Fig. 4.2). These hydroxyl tails are water-loving, so that the hydrophilicity of the coated surface is enhanced. According to literatures, a polymer possessing certain roughness with functional groups (e.g. hydroxyl and carbonyl) promotes electroless plating process (Bright, Malpass et al. 1969; Goldie 1969; Garbassi, Morra et al. 1998; Kreitz, Penache et al. 2000; Kisin, Scaltro et al. 2007). Hence, the purpose of adding PEG is to functionalize the polymer surfaces.

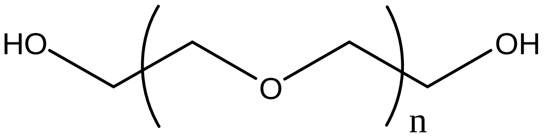


Fig. 4.2: The structure of polyethylene glycol (PEG).

In this chapter, sandblasting was selected to modify the PP surface. The roughened surfaces were then coated with PEG layer. The relationship between the adhesion and the roughness of the functionalized surface was investigated.

4.2 Methodology

4.2.1 Sample preparation

Polypropylene from polystone® was employed in our studies. The dimension of the samples was 35x45 mm^2, and the thickness was fixed at 3 mm .Before any treatments, the samples were cleaned in an ultrasonic bath of ethanol. The cleaned samples were followed by surface treatments, surface activation for electroless Ni plating and electrodeposition of Cu.

For surface treatment, the cleaned samples were roughened by 80 grit SiC in either pulsed sandblasting mode or continuous sandblasting mode. In the pulsed mode, each pulse was held for 6 s, while for the continuous mode, the sandblasting times were adjusted between 15 s and 60 s. The etched samples were then rinsed by D. I. H_2O thoroughly, in order to wash away any sand remaining on the sample surface. The etched samples were rinsed by ethanol to get rid of grease and were dried in an oven at 70°C. Afterward, the etched samples were coated with PEG of different molecular number (M_n, n: 1100 – 8400). The as-coated PEG samples were dried in the oven at 50°C for 2 days.

After coating PEG, the treated samples were rinsed by 2% HCl for 2 min. Then, the treated samples were activated in a MACuPlex activator D-34C concentrate bath containing D.I. H_2O, 32% HCl, sensitizer 78 and MACuPlex activator D-34C concentrate (2.5 min and 5 min for coated PEG solution and without coated PEG solution respectively). Sequentially, the activated samples were carried out the electroless Ni plating and the Cu electrodeposition. The detailed procedures of electroless Ni plating and Cu plating were mentioned in Chapter 3.

4.2.2 Characterization

Fourier transform infrared spectroscopy (FTIR) was employed to determine the chemical bonding of the samples after sandblasting. The IR spectra were collected by a FTIR spectrometer (Nicolet MAGNA-IR® 760) using transmission mode.

Optical microscopy was used to observe the surface morphology of the samples before and after the roughening process. Optical micrographs were taken by a polarizing optical microscope (Nikon Microphot-FXA) equipped with a digital camera (Pixar). The root-mean-square surface roughnesses (R_q) of the samples after roughening and electroplating of Cu were investigated by using a surface profiler (KLA-TENCOR®

P-10). For each sample, 10 different locations of length 1000 µm were selected. The R_q of each sample was obtained by taking the average of the 10 scans. The influence of the roughening on the surface hydrophilicity was investigated by a contact angle measurement (Ram´e-hart, Model 200) based on the sessile drop experiment which was carrying out by dropping 5 µl of D.I H_2O on the plastics surfaces. The contact angle was measured until the probing liquid attained an equilibrium state.

Finally, adhesion of the electroplating Cu coatings on the plastics was evaluated using the standard Scotch tape test (cross-cut tape test, ASTM D 3359-02) performed with 3M Scotch tape.

4.3 Results and discussion

4.3.1 Characterization of plastics substrates

Figure 4.3 shows the FTIR spectra of PP before and after sandblasting. General speaking, saturated compounds have their characteristic CH stretching frequencies. For example, CH_3 groups have characteristic peaks at 2960 cm^{-1} and 2870 cm^{-1}, the CH_2 bands are at 2930 cm^{-1} and 2850 cm^{-1}. All of them are due to the CH asymmetric and symmetric stretching of CH_3 and CH_2 in aliphatic compounds. As the carbon chain becomes longer, the CH_2 group bands increase in intensity relative to the CH_3 group absorptions. The doublet at 2960 cm^{-1} is due to the asymmetric CH_3 stretching mode. Asymmetric deformation of the HCH angles of a CH_3 group gives rise to very strong IR absorption in the 1470-1440 cm^{-1} region. The symmetric CH_3 deformation gives a strong, sharp IR band between 1380 cm^{-1} and 1360 cm^{-1}.

As compared Fig. 4.3b to Fig. 4.3a, no new characteristic peaks were discovered after sandblasting. This implies that the surface composition was not changed under sandblasting. It only changed the surface roughness of the samples. The details will be shown in contact angle measurements and surface profile analysis.

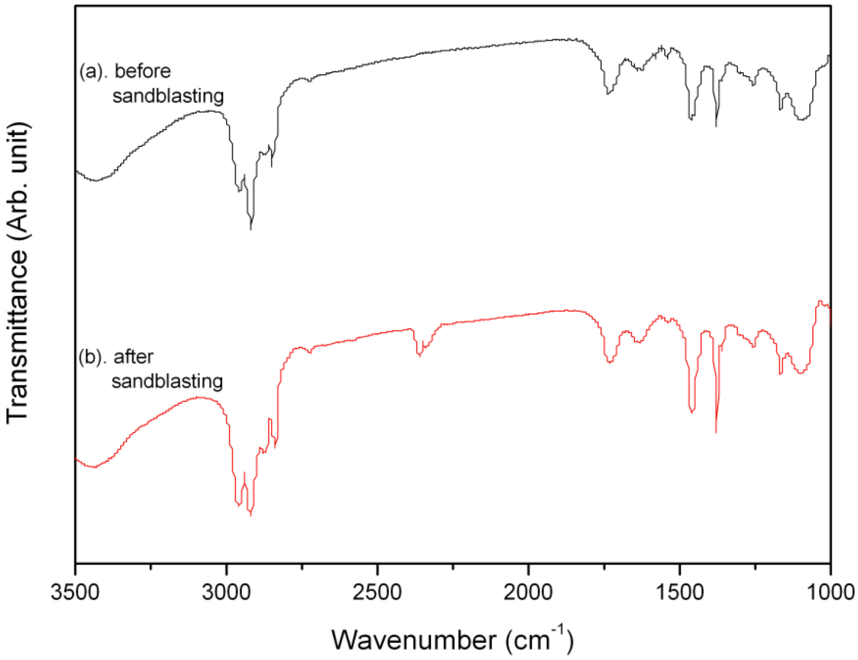


Fig. 4.3: FTIR spectra of PP samples (a) before and (b) after sandblasting.

Figure 4.4 shows the optical micrographs of PP before and after sandblasting. Before sandblasting, the sample surface was featureless showing the sample surfaces, were very smooth, flat with no observable pitches. After sandblasting, a nest like surface was obtained. Even though different processing parameters of sandblasting (pulsed mode and continuous mode, different sandblasting times, etc.) had been applied, all the results display similar optical micrographs. The abrasion of sand was randomly applied on the surface. Some parts might be etched first, and then resulted some tracks. Shadow effect might occur. The tracks were continuously etched layer-by-layer, so the nest structure was obtained.

The nest feature was further enhanced after coating with the PEG solution, as shown in Fig. 4.5. From the figure, the holes of size 40-100 µm and 80-160 µm were obtained when pulsed sandblasting mode (5 pulses) and continuous sandblasting mode (15 s) were used respectively. In general, if the sandblasting time and the number of pulse increased, the size of hole would be further enlarged.

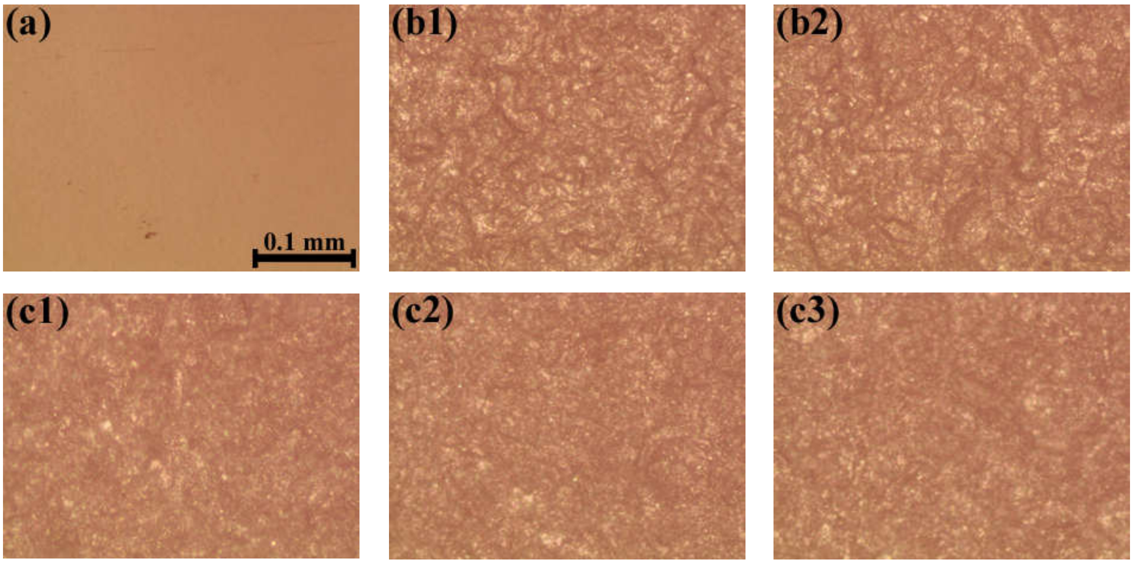


Fig. 4.4: Optical micrographs of PP samples (a) before and after (b) pulsed sandblasting (1: 5 pulses and 2: 10 pulses, each pulse lasted for 6 s) and (c) continuous sandblasting (1: 15 s; 2: 30 s and 3: 60 s).

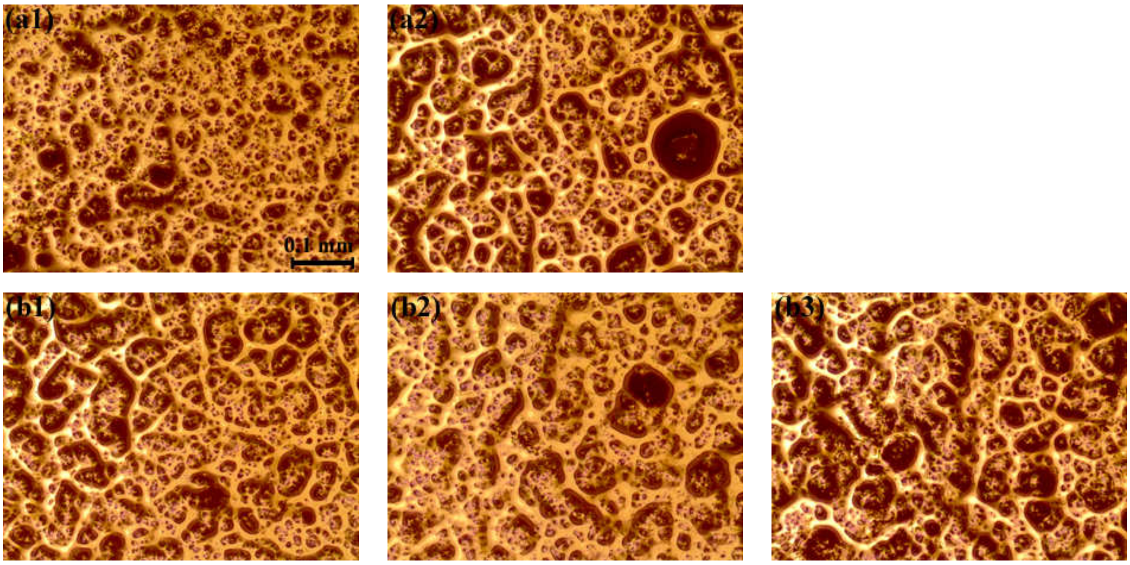


Fig. 4.5: Optical micrographs of PP samples after (a) pulsed sandblasting (1: 5 pulses and 2: 10 pulses) and (b) continuous sandblasting (1: 15 s; 2: 30 s and 3: 60 s) and then coated with 30% v/v PEG_{5800}.

Obviously, sandblasting increased the surface roughness of the samples. Before sandblasting, the sample surface was quite smooth and flat. Its R_q was ~10 nm (shown in Fig. 4.4a). After sandblasting, the value of R_q dramatically raised up to 1700-2300 nm. Our results also indicate that the R_q from the pulsed sandblasting mode was less than that from the continuously sandblasting mode. The R_q of samples after coating with PEG has not carried out surface profile analysis, as the PEG would contaminate the needle of surface profiler easily. We expect that the roughness was slightly improved by soaking the samples with PEG. Vas ko et al. (2004) reported that the surface roughness was leveled up after adding PEG.

Types of Sandblasting modes	R_q after roughening (nm)
0	13
5 pulses	1706
10 pulses	2071
15 s	1936
30 s	2070
60 s	2272

Table 4.1: Values of root mean square surface roughness (R_q) for PP samples after sandblasting.

The surface roughness affects the hydrophilicity of the samples, and thus changes the contact angle values. Indeed, a rough surface has higher hydrophobicity than a smooth surface because of the increase of the surface area. Air molecules can be trapped in the voids, so that water droplet partially sits on air. Therefore, the surface roughness increases with contact angle value.

Hydrophobicity also relates to the surface free energy of the material, which is governed by the existence of functional groups. Shang et al. (2005) reported that the surface free energy increases in the order of $-CF_3 < -CF_2H < -CF_2- < -CH_3 < -CH_2-$. The lower surface free energy gives higher hydrophobicity. PP is a long hydrogencarbon chain polymer (Fig. 4.1). Except methyl group, there is no other functional group in PP. This makes PP to be a hydrophobic plastic. Without applying any treatments, its surface showed ~105˚ in contact angle measurements. After applying sandblasting on the PP surface, the contact angle values slightly increased to ~120˚ (shown in Table 4.2). Our results indicate that sandblasting enhanced the surface roughness as well as increase the hydrophobicity of PP. As expected, the contact angle values in continuous sandblasting mode were slightly greater than those in pulsed sandblasting mode. The extended roughness was due to the continuous impact on the samples.

When PP substrates were coated by different M_n of PEG, the contact angles dramatically dropped from ~120˚ to ~50˚. This implies that the surface of PP substrates became more hydrophilic after adding a PEG layer. According to the structure of PEG, hydroxyl group exits in its molecular structure. It increases the surface free energy of the material, thereby enhancing its hydrophilicity. Theoretically, PEG acts as a surfactant to hydrophobic species, so that reaction reagent can spread on the water-hating substance surface and undergo reaction (Tanaka, Doi et al. 2007). Normally, the increase of hydrophilicity of the surface facilitated the process of nucleation. Here, PEG effectively acted as a surfactant to improve the hydrophilicity of surface. In addition, it can be found from the table that the contact angles further decreased from ~50˚ to ~20˚ as the increase of the M_n of PEG. The hydrophilicity of the surface relates to the M_n of PEG. Higher M_n of PEG used can enhance the hydrophilicity of the surface.

M_n of PEG / sandblasting mode	w/o PEG	PEG_{1100}	PEG_{2000}	PEG_{5800}	PEG_{8400}
5 pulses	113°	58°	51°	46°	16°
10 pulses	119°	36°	30°	30°	33°
15 s	112°	37°	13°	33°	30°
30 s	124°	42°	20°	23°	20°
60 s	122°	58°	28°	19°	21°

The sample before sandblasting: 104˚

**concentration of PEG 30% v/v in chloroform*

Table 4.2: Measured values of contact angle for PP samples after applying different sandblasting modes with coating different M_n of PEG.

4.3.2 Characterization of plastics substrates

The treated samples were then carried out activation and electroless Ni plating. The results showed that a continuous Ni film was obtained when higher M_n of PEG (PEG_{5800} and PEG_{8400}) and longer sandblasting time were applied. For the samples coated with lower M_n of PEG (PEG_{1100} and PEG_{2000}) and shorter sandblasting time, the Ni randomly appeared on the samples' surface, indicating that the reduction of Ni did not occur uniformly on the plastics surface. Actually, PEG is water soluble. The solubility of PEG decreases as its molecular size increases, i.e. PEG of lower M_n dissolves easier than the high M_n one in the water. For samples coated with PEG of lower M_n, a large part of PEG coating dissolved in the activation bath. The dissolved PEG contaminated the activation bath and lowered the bath activity. The bath could not be used after carrying out several activations. Furthermore, the dissolved PEG might lead to the oxidation of Sn^{2+} forming Sn^{4+} in the Sn^{2+}/Pd colloidal. Once the oxidation has occurred, the oxidized Sn^{4+}/Pd colloidal preferable accumulated together and sunk down to the bottom of the container. Black precipitates were formed under such situation. Also, the presence of Sn^{4+}/Pd colloidal accelerated the oxidation of the remaining unoxidized species. Then, the concentration of activated ingredients dramatically fell and affected the activation process.

On the other hand, samples without PEG coating also obtained a continuous Ni film. All of them were treated with longer sandblasting time (60 s and 10 pulses). Furthermore, these samples also required longer time (5 min) for activation process.

The required time for uncoated PEG samples was about 2 times longer than that for the coated PEG samples. The results illustrate that PEG efficiently improves the surface energy of sample and facilitates the formation of seed with Sn^{2+}/Pd colloidal in the activation bath. These results are in good agreement with those obtained by the contact angle measurements.

Electroplating of Cu was carried out after the formation of the electroless Ni layers. The results were displayed in Fig. 4.6. If a continuous Ni layer formed, Cu could grow on it. The surface roughness was slightly decreased, although the surface was still roughness. According to Fig. 4.6, the Cu grew in nest structure. The growth of Cu followed the nest structure of the treated plastics. The R_q was 820-860 nm and 520-560 nm when the samples were only applied roughening and were further treated with PEG respectively. The surface was too rough under sandblasting. Even though a ~30 μm Cu layer was deposited, the roughness of surface would not be improved. This seriously affected the appearance of the samples.

Figure 4.7 shows the XRD pattern of the top Cu layer. Only Cu(111), Cu(200) and Cu(220) peaks are observed indicating that the Cu layer is in single phase only. The

XRD results indicate that continuous Cu layers were formed when longer roughening time (~60 s) was applied.

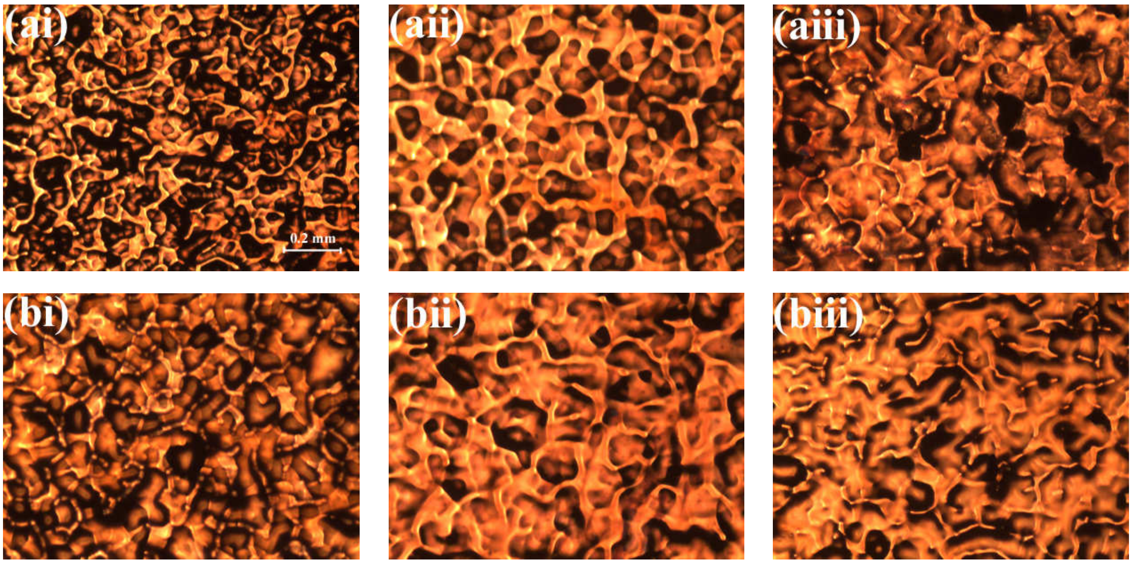


Fig. 4.6: Optical micrographs of PP samples after electroplating of Cu by applying (a) 10 pulses sandblasting and (b) 60 s sandblasting and coating with different M_n of PEG (i. without coating with PEG; ii. PEG_{5800}; iii. PEG_{8400}).

M_n of PEG / Sandblasting mode	w/o PEG	PEG_{5800}	PEG_{8400}
10 pulses	821 nm	522 nm	547 nm
60 s	861 nm	562 nm	563 nm

Table 4.3: Values of root mean square surface roughness (R_q) for PP samples after electroplating of Cu.

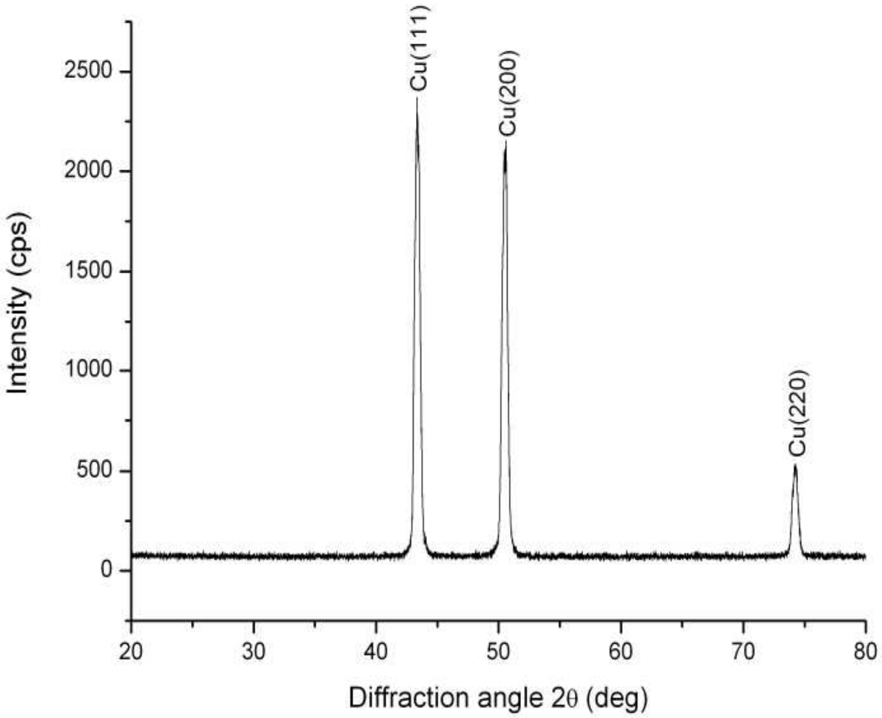


Fig. 4.7: XRD analysis of Cu film on the sample roughened for 60 s.

Adhesion test was carried out after electroplating of Cu layer in order to investigate the influence of PEG on the adhesion of the Cu layer to the samples. Although the surface roughness was improved and a continuous Cu film was formed, the adhesion between the Cu layer and the substrate was poor (shown in Table 4.4). For all succeeded Cu coating samples, the coating flaked along the edges of cuts in large ribbons and the Cu layer peeled off easily. Cu coating was only physically formed on the PP plastics. This mechanical surface modification of PP simply provided pitting sites for implantation of seed in the activation. Although the metal ions grew on the seed to form a continuous metal layer, chemical bond didn’t exist between the substrates and the metal coating. As a result, the metal coating flaked easily along the edges of cuts. To sum up, sandblasting was not an effective method to modify PP surface.

M_n of PEG / Sandblasting mode	w/o PEG	PEG_{5800}	PEG_{8400}
10 pulses	0B	0B	0B
60 s	0B	0B	0B

Table 4.4: Results of adhesion test of he Cu films to the PP samples.

4.4 Conclusion

According to the experimental results, sandblasting can be used to roughen the PP plastics surface. Pitting sites are obtained during the process. Hydroxyl group is introduced to the PP plastics by adding PEG. The existence of PEG is important in the electroless Ni plating. Hydroxyl group in PEG can increase the surface free energy of PP, so that its surface become more hydrophilic and facilitated the reaction with Sn^{2+}/Pd colloidal. PEG of higher M_n (PEG_{5800} and PEG_{8400}) should be used, because they are relatively difficult to be dissolved in the activation bath.

Electroplating is only taken place when the samples are treated with longer sandblasting time (10 pulses sandblasting and continuous 60 s sandblasting). However, for samples having too long sandblasting time, their surfaces become too rough. It is difficult to smooth out the roughness in the subsequent steps. The R_q ranges from 520 nm to 560 nm, after Cu coating.

Adhesion test was carried out to investigate the strength of the adhesive layer. Unfortunately, the test was failed in all the samples. The coating is easily detached along the cuts. Although PEG efficiently provides active sites for the formation of seeds, it just physically adsorbs on the plastics surface. Therefore, the adhesion of the metal layer is very poor. The results show that sandblasting is not an efficient method for the modification of plastics surface. Our results suggest that pitting sites with functionalized surface can produce a better adhesion film to substrate.

Chapter 5 Surface modification of polycarbonate and subsequent metallization by electroplating

5.1 Introduction

Polycarbonate (PC) is manufactured by transesterification of bisphenol A with diphenyl carbonate at elevated temperature or by dissolving bisphenol A in pyridine and reacting with phosgene. Here, bisphenol A is obtained from phenol and acetone (hence the A). The structure of PC is showed in Fig. 5.1.

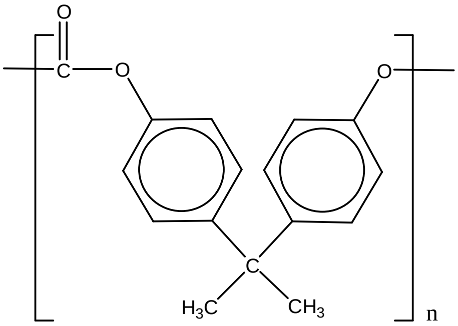


Fig. 5.1: The structure of polycarbonate.

PC is a thermoplastic plastic. It is easily molded and thermoformed. Because of its excellent properties, PC is a well-known engineering plastic in the market. It has high mechanical strength, stiffness, hardness and toughness over the range from -150°C to

+135°C when unreinforced and from -150°C to +145°C when reinforced. It possesses large resistance to high energy radiation and good electrical insulation properties which are not impaired by moisture (Goldie 1969; Domininghaus 1993). To suit the customers' need, PC can be colored in all important shades, including transparent, translucent or opaque with great depth of color. Therefore, PC has widely been used in various areas, such as moulding covers, housings for computers and other electronic equipment. This means that it is essential to develop satisfactory methods of plating this material (Tanaka, Doi et al. 2007). Traditionally, PC has been mixed into ABS to enhance the mechanical properties of ABS and to diversify its applications. For some applications, such as bumper and hood in car industry, in order to have high enough mechanical strength, the percentage of PC in the ABS/PC blend increases. However, the maximum percentage of PC is limited to 50%. This is because the traditional acid etching cannot properly function at high content of PC (Bruyn, Stappen et al. 2003). The adhesion between the metal layer and the substrate becomes poor as the PC content in the polymer blend increases. In fact, PC is more resistant to etching solution than ABS. Therefore, before etching, PC is preferable attacked by organic solvents, in order to create swelling and cracking at the surface. Afterwards, etching is applied on it (Simpson 1993).

General speaking, PC is resistance to many chemicals, such as alcohols (except methanol), oils, glycol, dilute acids and alkaline solutions. However, it reacts with some solvents, such as benzene, toluene, chlorinated hydrocarbons like chloroform ($CHCl_3$), strong acids and bases. In this chapter, $CHCl_3$ would be used to modify the PC surface. PC is dissolved in $CHCl_3$ and is being reformed as $CHCl_3$ vaporized. Once the PC starts to reform, a rough surface with some anchoring sites are obtained.

In addition, PC belongs to polyester. The chemical properties of PC can be deduced from its ester group. The electron-deficient carbon atoms on the plastics surface are attacked by nucleophilic species (sodium hydroxide, NaOH) which are present in the reaction solution (Tanaka, Doi et al. 2007). Hydrolysis of PC yields carboxylate salt (carboxylate group) and alcohol. Then, the plastics surface with carboxylate group is feasible to form metal complex with Pd/Sn^{2+} colloidal in activation bath. Since PC is a polar plastics, the hydrolysis process further increases the number of hydrophilic groups, which then facilitate the subsequent electroless deposition (Simpson 1993; Garbassi, Morra et al. 1998; Margolis 2006). The effects of different processing parameters, such as etching time and alkali concentration, on the morphology and hydrophilicity of the plastics surfaces were investigated in this project.

5.2 Methodology

5.2.1 Sample preparation

Polycarbonate (Calibre 1080DVD) was manufactured in a standard CD disc size (120 mm in diameter and 1.5 mm in thickness). The disc was cut evenly into 4 pieces for the experiments. Before any treatments, the samples were cleaned in an ultrasonic bath of ethanol. The cleaned samples were soaked into $CHCl_3$ (to create swelling and cracking at the surface), and then followed surface treatment (to introduce carbonyl group) and surface activation for electroless Ni plating and electrodeposition of Cu.

To create swelling and cracking at the surface, the samples were dipped in $CHCl_3$. The soaking time was varied from 5 to 15 s. This step was repeated 2-3 times, in order to compare the degree of cracking. The samples were then etched by NaOH solution at 80°C (aiming at functionalization and formation of pitting sites). The etching time was varied from 0.5 to 5 hr and the alkali concentration was adjusted from 2 to 10 M, in order to observe their influences on the surface hydrophilicity and surface roughness. The functionalized surfaces were then rinsed by 2% HCl for 2 min. The treated samples were then activated in a MACuPlex activator bath D-34C concentrate bath containing D.I. H_2O, 32% HCl, sensitizer 78 and MACuPlex activator D-34C concentrate, for 3 min. (Precaution: The bath must be free from air, light and water which would accelerate oxidation and hydrolysis of Pd/Sn^{2+} into Pd/Sn^{4+} in the bath.) Sequentially, the activated samples were carried out electroless Ni plating and electrodeposition of Cu. The procedures of electroless Ni plating and Cu plating have been mentioned in Chapter 3. The effects of $CHCl_3$ on the surface morphology were investigated. Part of samples were attacked by $CHCl_3$ and followed by alkali etching. Only alkali etching was carried out for another group of samples.

5.2.2 Characterization

Fourier transform infrared spectroscopy (FTIR) was employed to determine the chemical bonding of the samples after roughening. The IR spectra were collected by a FTIR spectrometer (Nicolet MAGNA-IR® 760) using transmission mode.

Optical microscopy was used to observe the surface morphology of the samples before and after all the surface treatments. Optical micrographs were collected by using a polarizing optical microscope (Nikon Microphot-FXA) equipped with a digital camera (Pixar). The root-mean-square surface roughnesses (R_q) of the samples after roughening and electroplating of Cu were investigated by using a surface profiler (KLA-TENCOR® P-10). For each sample, 10 different locations of length 1000 µm were selected. The R_q of each sample was obtained by taking average of 10 scans. The influence of the roughening on the surface hydrophilicity was investigated by a contact angle measurement (Ram´e-hart, Model 200) based on the sessile drop experiment which was carrying out by dropping 5 µl of D.I H_2O on the plastics surfaces. The contact angle was measured until the probing liquid attained an equilibrium state.

Finally, adhesion of the electroplating Cu coatings on the plastics was evaluated using the standard Scotch tape test (cross-cut tape test, ASTM D 3359-02) performed with 3M Scotch tape.

5.3 Results & Discussion

5.3.1 Alkali etching of PC without swelling in $CHCl_3$

For industrial production, ABS is etched by $H_2Cr_2O_7$ to obtain $–COO^-$ groups on its surface. The detailed mechanism of the reaction between ABS and acid has been mentioned in Chapter 2.3.3. It is noticed that the etchant reacts with the active site in the plastics to form new functional groups. For ABS, the active site is the –C=C– in the 1,3-butadiene. It is oxidized to butanedioic acid (i.e. $–COO^-$ group) using the acid etching bath.

Besides oxidation, the $–COO^-$ group can be obtained by hydrolysis of ester at the presence of alkali. In fact, PC is a polyester plastic containing ester groups in its chain. Thus, it is ready to undergo hydrolysis in the alkali bath. The mechanism of reaction between ester and NaOH is shown in Fig. 5.2.

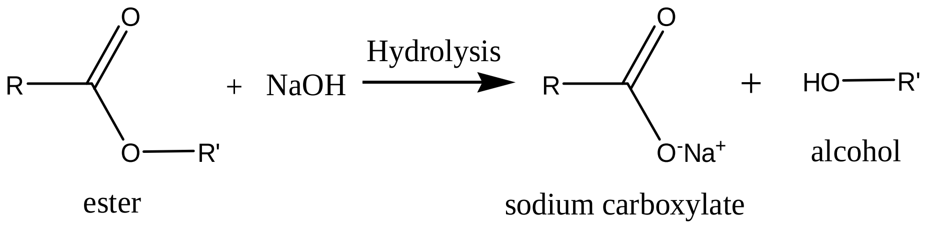


Fig. 5.2: Hydrolysis of ester in NaOH solution.

FTIR was used to identify the composition of PC plastics before and after etching. FTIR spectra of PC plastics before and after etching are shown in Fig. 5.3. According to the structure of PC, the FTIR spectrum shows the C=O stretching band at about 1770 cm^{-1}. The symmetric C-O-C stretch also gives a band at lower frequencies between 1160 cm^{-1} and 1000 cm^{-1} in aromaticity esters. Aromaticity is also confirmed in the FTIR spectrum by the sharp ring stretching bands near 1600 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1}.

For samples etched at high alkali concentration (> 5 M) and long etching period (> 5 hr), the intensities of the characteristic peaks at 1650-1550 cm^{-1} and 1440-1350 cm^{-1} are enhanced. These two broad bands are attributed to the asymmetric and symmetric stretching of –COO^{-} group in carboxylates salts. This enhancement of these two peaks' intensities indicates that large numbers of carboxylate salts are formed due to the hydrolysis of the substrate at the presence of base. Our results are consistent with Garbassi's (1998) and Margolis's (2006) results stating that the plastics with ester group (RCOOR') undergo hydrolysis at the presence of base.

Here, OH^{-} ions react with the C atom in the RCOOR' chain, and then yield alcohol and carboxylate salts. The formation of carboxylate salts was confirmed in the FTIR spectra. Indeed, these carboxylate ions facilitate the formation of complex with Sn^{2+} in Pd/Sn^{2+} colloidal solution (Garbassi, Morra et al. 1998; Kisin, Scaltro et al. 2007).

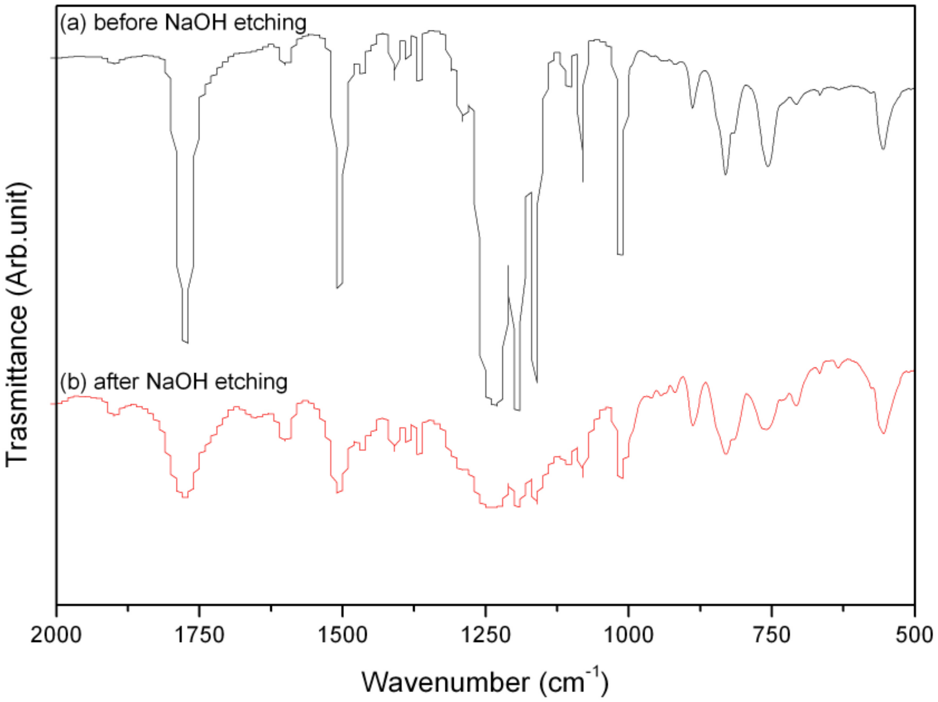


Fig. 5.3: FTIR spectra of PC samples (a) before alkali etching and after alkali etching for 5 hr at (b) 10 M NaOH.

Figure 5.4 displays the optical micrographs of PC samples before and after NaOH etching. Before alkali etching, the sample surface was quite smooth and flat with R_q ~10 nm (shown in Table 5.1). When the lowest NaOH concentration (4 M) was used, some scratches appeared on the samples. These might be due to the friction between the samples and the magnetic stirrer. By increasing the etching time, some small pitting sites of 10-20 µm were obtained. The R_q steadily raised to ~200 nm. If the concentration of etchant and reaction time were further increased to 5 M and 5 hr respectively, the top layer of the PC samples would start to detach from the surface.

Some large cavities (150-300μm) were formed. The remaining parts looked like islands on the sample surfaces (shown in Fig. 5.4c). This extremely affected the surface roughness. It dramatically jumped from ~160 nm to ~1200 nm (underlined in Table 5.1). If the etching concentration and time were further enhanced, some pores could be randomly observed on PC surface. By lasting longer in the etching bath, a uniform rough surface was formed. Figure 5.4d2 shows that the pore size is of 40-60 μm. The results imply that high R_q (> 1100 nm) represents the initiation of detachment of the top layer. R_q ranged 600-900 nm is suitable for the subsequent metallization process. From Table 5.1, the optimum roughness is obtained when the samples were etched by high NaOH bath (> 7 M) and were lasted longer time (> 3 hr) in the alkali bath.

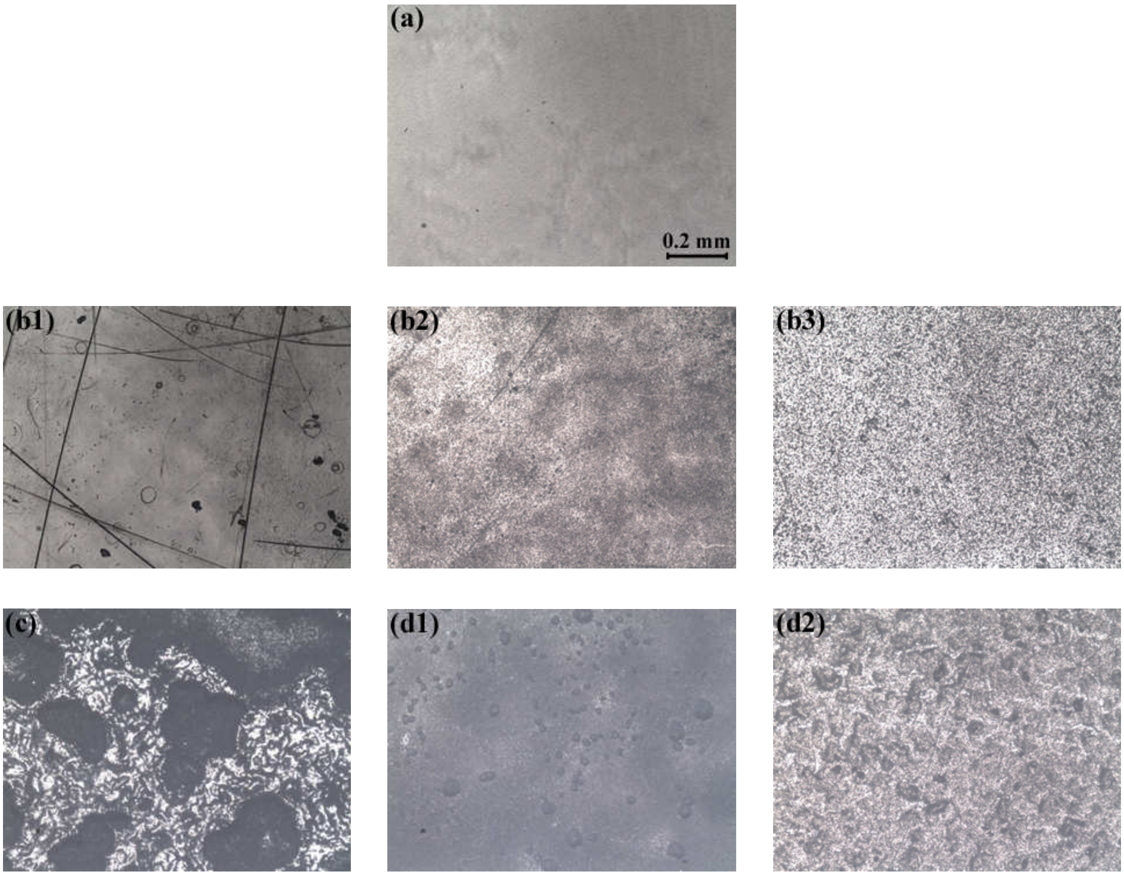


Fig. 5.4: Optical micrographs of PC samples before (a) and after etching in different NaOH concentrations and times (b) 4 M (1: 1 hr; 2: 3 hr and 3: 5 hr), (c) 5 M at 5 hr and (d) 7 M (1: 4 hr and 2: 5 hr).

etching time (hr) / conc. of NaOH (M)	1	2	3	4	5
4	38 nm	37 nm	120 nm	93 nm	198 nm
5	73 nm	126 nm	163 nm	133 nm	1146 nm
6	62 nm	161 nm	215 nm	1324 nm	2358 nm
7	45 nm	50 nm	582 nm	317 nm	835 nm
8	58 nm	577 nm	1344 nm	401 nm	451 nm
9	83 nm	1235 nm	424 nm	487 nm	648 nm
10	436 nm	1690 nm	568 nm	687 nm	646 nm

The roughness of PC before etching: 12 nm

Table 5.1: Values of root mean square surface roughness (R_q) for PC samples under different concentrations of alkali etching with different etching times.

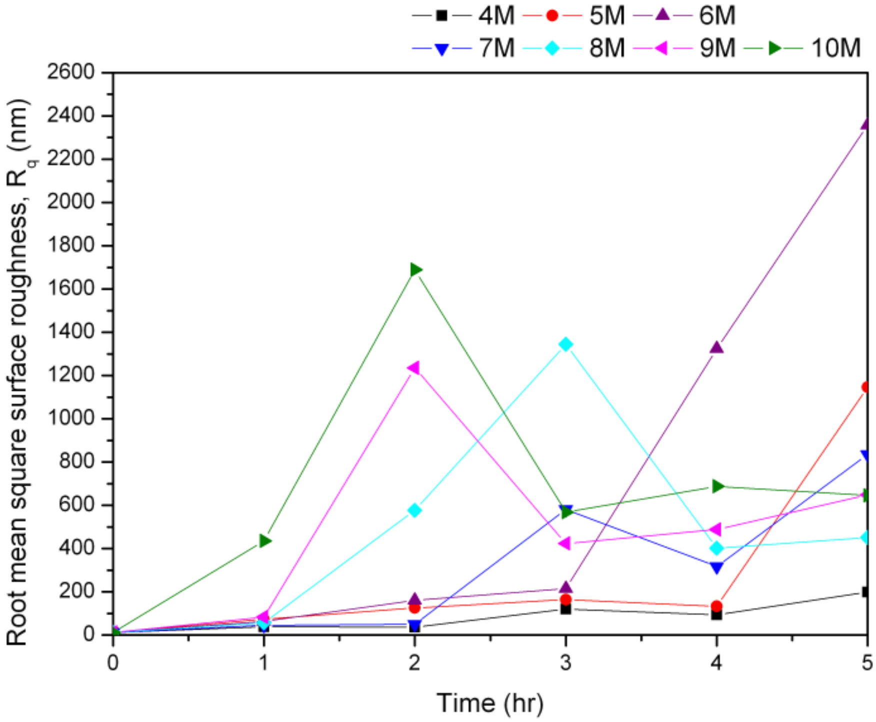


Fig. 5.5: The graphs of root mean square surface roughness (R_q) against time under different NaOH concentrations from 4 M to 10 M.

In Chapter 4, we have been mentioned that the hydrophilicity of the samples is governed by the existence of functional groups as well as the surface roughness. PC possesses ester group in its structure. This makes PC to be a hydrophilic plastic. Without applying any treatments, its surface displayed ~80° in our contact angle measurements (shown in Table 5.2). In general, the contact angle values significantly dropped to ~50° when 4-9 M NaOH was used. Carboxylate group (COO^-) was formed once the alkali etching had occurred. The existence of $–COO^-$ can effectively enhance the hydrophilicity of the samples. Thus, the values of contact angle measurement decreased in the beginning of alkali etching. Another determinant factor of hydrophilicity is surface roughness. When 10 M NaOH and longer etching time were applied, sample surfaces were full of crests, troughs and even cracks. All of them affected the surface roughness as well as the hydrophilicity of the samples. From Fig. 5.6, it is found that the values of contact angle were fluctuated.

etching time (hr) / conc. of NaOH (M)	1	2	3	4	5
4	66°	75°	79°	72°	52°
5	77°	67°	85°	70°	52°
6	70°	61°	88°	80°	85°
7	75°	69°	89°	88°	70°
8	61°	73°	86°	64°	54°
9	50°	81°	71°	82°	75°
10	94°	109°	113°	112°	90°

The sample before etching: 80˚

Table 5.2: Measured values of contact angle for PC samples after different concentrations of NaOH etching with different etching times.

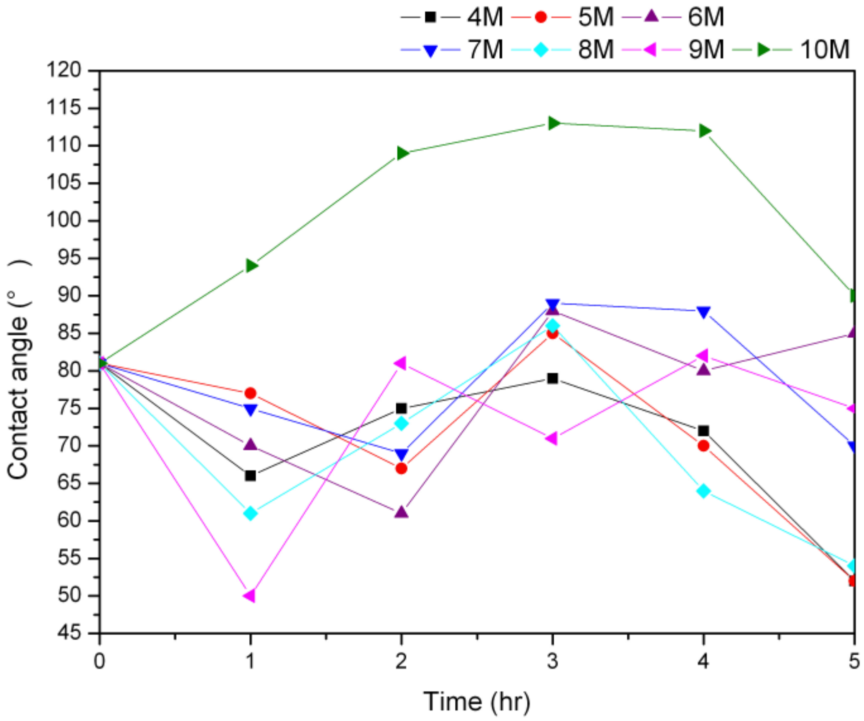


Fig. 5.6: The graphs of contact angle against time under different NaOH concentrations from 4 M to 10 M.

5.3.2 Alkali etching of PC with swelling in $CHCl_3$

In previous section 5.3.1, our results showed that an optimum roughness was obtained when high NaOH concentration (> 7 M) and long etching time (> 3 hr) were applied. This highly lowered the efficiency of etching process. Simpson (1993) suggested that the PC samples were attacked by $CHCl_3$ before NaOH etching. The function of $CHCl_3$ is to create swelling and cracking on the PC surface. After dipping in $CHCl_3$, the R_q significantly increased to 100-200 nm with respect to swelling time. It is clearly noticed in Fig. 5.7 that some pores of size 40-60 µm were formed on the sample surfaces. The values of contact angle also raised with the increase of surface roughness.

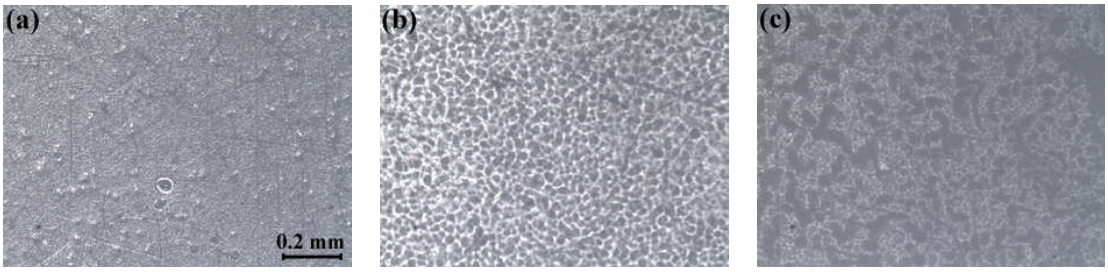


Fig. 5.7: Optical micrographs of PC samples after swelling in $CHCl_3$ for different dipping times of (a) 5 s, (b) 10 s and (c) 15 s.

Swelling time (s)	root mean square surface roughness, R_q (nm)
5	95
10	198
15	214

Table 5.3: Values of root mean square surface roughness (R_q) for PC samples dipped in $CHCl_3$ with different swelling times.

Swelling time (s)	Contact angle (°)
5	96
10	106
15	112

Table 5.4: Measured values of contact angle for PC samples dipped in $CHCl_3$ with different swelling times.

The swollen samples were then etched in 2-6 M NaOH bath and were collected at different times (0.5-2 hr). The number of cracks formed on the surface increased with respect to the concentration of etchant (shown in Fig. 5.8). By comparing the swelling time, cracks were early formed as the longest swelling time (15 s) was used. Generally, the R_q increased with respect to the etchant concentration and the etching time. The degree of increment also depended on the swelling time. Shortest swelling time (5 s) was used, the increment was relatively small. Finally, all of them reached the R_q at ~1300 nm at the end of etching. The details of R_q for each sample are shown in Table 5.5. For the contact angle measurements, the values of contact angle ranged 50º-70º were obtained after NaOH etching for all samples.

Fig. 5.8: Optical micrographs of swollen PC samples (dipping for 15 s) after etching in different NaOH concentrations and times (a) 2 M for 2 hr; (b) 4 M for 2 hr and (c) 6 M for 2 hr.

(a)

conc. of NaOH (M) \ etching time (hr)	0.5	1	2
2	208 nm	328 nm	689 nm
4	538 nm	681 nm	860 nm
6	752 nm	1078 nm	1232 nm

(b)

conc. of NaOH (M) \ etching time (hr)	0.5	1	2
2	430 nm	527 nm	806 nm
4	684 nm	775 nm	962 nm
6	804 nm	1025 nm	1280 nm

(c)

conc. of NaOH (M) \ etching time (hr)	0.5	1	2
2	606 nm	672 nm	898 nm
4	746 nm	862 nm	1046 nm
6	864 nm	1147 nm	1366 nm

Table 5.5: Values of root mean square surface roughness (R_q) for PC samples dipped in $CHCl_3$ with different swelling times (a) 5 s; (b) 10 s and (c) 15 s, followed by different concentrations of NaOH etching with different etching times.

5.3.3 Characterization of the metallized plastics substrates

Adhesion test was carried out to study the effects of processing parameters (swollen time, concentration of NaOH and etching time) on the adhesion strength of the Cu layer to the PC plastics. The results of the adhesion tests are shown in Tables 5.6 and 5.7. The results indicate that Cu layer of poor adhesion would be obtained, if the PC plastics was etched only by NaOH without $CHCl_3$ pre-treatment. From Table 5.6, the best result in adhesion test was 2B only. This means that 15 to 35% of the lattice was detached along edges and at intersections of cuts. Also, a continuous Ni layer could only form on the samples treated in NaOH with concentration higher than 7 M.

As compared to samples treated with $CHCl_3$ before etching, they obtained better results in the adhesion test. Some of the samples could have 4B in the adhesion test. In the electroless plating, almost all the samples formed a continuous Ni layer. This fundamental conductive metal layer was important for Cu plating. For short etching time, longer swelling time and higher NaOH concentration (4-6 M) produced better adhesion results. However, longer swelling time also seriously affected the structure of the samples. The samples' thickness dropped from 1.5 mm to 0.5-0.8 mm after high NaOH (4-6 M) etching. The sharp decrease of thickness made the samples to be brittle and fatigue. This strongly destroyed the structure of samples. Generally, better adhesion results were obtained when the etching time was increase up to 1 hr. If the etching time was further increased, the adhesion results would be in bad performance.

NaOH was used to react with the surface of the plastics and create surface roughness. This means that NaOH deteriorates the plastics structure in some degree. Although Cu layer could be formed on the samples, it detaches easily due to the destruction of structure.

Our results illustrate that swelling in $CHCl_3$ is necessary to be carried out before alkali treatment for successful surface modification of PC plastics. Since long swelling and etching time deteriorated the structure of samples, the swelling time and etching time were suggested to be about 5-10 s and 0.5-1 hr respectively when 4-6 M NaOH was used.

etching time (hr) conc. of NaOH (M)	1	2	3	4	5
8	--	--	0B	0B	0B
9	0B	0B	0B	1B	2B
10	--	0B	1B	2B	2B

Table 5.6: Results of adhesion test of the Cu films to the PC samples after different concentrations of NaOH etching with different etching times.

(a)

etching time (hr) conc. of NaOH (M)	0.5	1	2
2	2B	3B	3B
4	2B	3B	1B
6	4B	1B	0B

(b)

etching time (hr) conc. of NaOH (M)	0.5	1	2
2	2B	3B	1B
4	3B	4B	1B
6	1B	1B	0B

(c)

etching time (hr) conc. of NaOH (M)	0.5	1	2
2	2B	3B	1B
4	4B	3B	1B
6	1B	0B	0B

Table 5.7: Results adhesion test of the Cu films to the PC samples dipped in $CHCl_3$ with different swelling times (a) 5 s; (b) 10 s and (c) 15 s, followed by different concentrations of NaOH etching with different etching times.

Figure 5.9 exhibits the optical micrographs of Cu layer grown on PC samples with the optimal processing results of the adhesion test. Figures 5.9a and 5.9b show that the ~40 µm of Cu layers were quite smooth with R_q ~70-80 nm. Compared with R_q obtained before the deposition of Cu layers, the values are ~700-800 nm. Even though the surface roughness improved around one order of magnitude by the deposition of Cu, the surface still had a few defects. This could be improved by adjusting the duration and the current of electroplating. If the sample was swollen in $CHCl_3$ for 15 s and was etched by 4 M NaOH for 0.5 hr, obvious cracks were observed on the Cu layer. This implies that a long swelling time was not suitable for producing a smooth Cu coating. In general, the PC sample should be lasted a few seconds (5-10 s) and followed by NaOH etching to obtain a successful Cu coating. Figure 5.10 shows the XRD pattern of the top Cu layer. Only Cu(111), Cu(200) and Cu(220) peaks are observed indicating that the Cu layer is in single phase only. The XRD results indicate that continuous Cu layers were formed under all conditions.

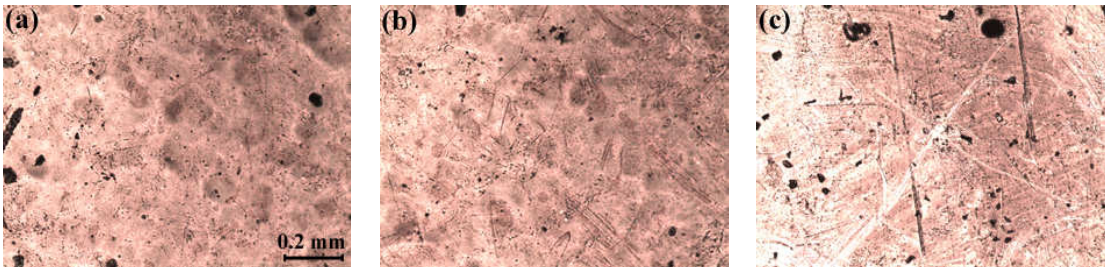


Fig. 5.9: Optical micrographs of Cu layer on the PC samples swollen in $CHCl_3$ for (a) 5 s and etched in 6 M NaOH bath for 0.5 hr; (b) swollen in $CHCl_3$ for 10 s and etched in 4 M NaOH bath for 1 hr and (c) swollen in $CHCl_3$ for 15 s and etched in 4 M NaOH bath for 0.5 hr.

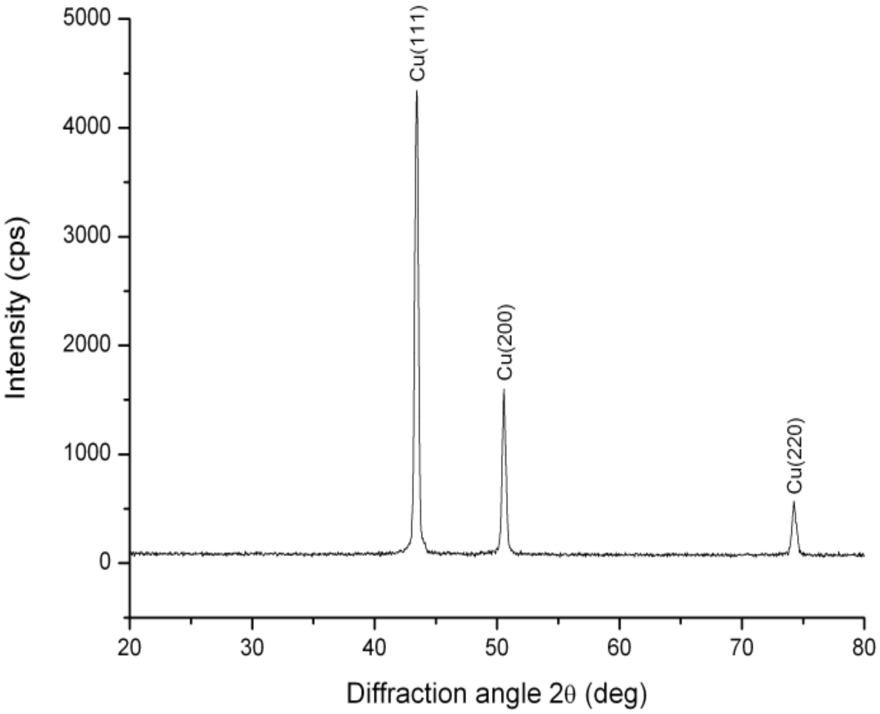


Fig. 5.10: XRD analysis of Cu film on the PC sample swollen in $CHCl_3$ for 15 s and then etched in 4 M of NaOH for 0.5 hr.

5.4 Conclusion

To sum up, PC plastics should be attacked by $CHCl_3$ before the alkali etching. It is an important step to create swelling and cracking on plastics surface, so that the plastics surface can be etched by NaOH easily. In compliance with the results, $CHCl_3$ is an efficient solvent to achieve the swelling and cracking purpose. Without $CHCl_3$ treatment, 8-10 M NaOH is required to be used for completing the etching process. With assistance of $CHCl_3$, the concentration of NaOH can be reduced to 4-6 M.

The swelling time should be governed carefully. A long swelling time (~15 s) and subsequent in alkali bath is etched too much to the samples. Their structure is seriously destroyed, so that the samples become brittle and fragile. This would directly affect the mechanical properties of the samples. Therefore, the swelling time should be controlled within 5 to 10 s.

Generally speaking, swelling in $CHCl_3$ and subsequent NaOH etching is an effective method in modifying the PC plastics surface. This modified plastics surface can successfully be carried out metallization process.

Chapter 6 Alkali pre-treatment of poly(butylene) terephthalate - poly(ethylene) terephthalate blend and subsequent metallization by electroplating

6.1 Introduction

Different kinds of engineering plastics and their blends have been rapidly developing to diversify their applications. Among them, poly(butylene) terephthalate-poly(ethylene) terephthalate blend, PBT/PET, is introduced for making lamp screen, optics mirror and etc. PBT and PET have high thermal performance (up to 180°C), good chemical resistance, good mechanical properties and high surface quality (Goldie 1969; Suchentrunk 1993; Margolis 2006). The plastics blend between PBT and PET further enhance thermal performance (up to 250°C), so that they can be used for high temperature applications. Indeed, PBT and PET have high melting point and low crystallization rate; they are not suitable for manufacturing process such as injection molding. These restrict the production of PBT/PET. Recently, many researches have been focused on studying the effect on physical properties of PET by the additional of polymeric nucleating agents such as thermotropic liquid crystalline plastics (Ou and Huang 2000; Ou, Li et al. 2002) and inorganic material (Ke, Long et al. 1999; Zhu and Ma 2000; Ke, Yang et al. 2002; Saujanya, Imai et al. 2002). They found that the crystallization rate of PET can be increased either by adding thermotropic liquid crystalline polymer or inorganic fillers (e.g. $CaCO_3$ and $BaSO_4$). The incorporation of inorganic materials results in plastics possessing high degree of stiffness, strength and gas barrier properties.

Therefore, 38% mineral filled PBT/PET blend (Model 7062, GE plastics) was suggested by Jing Mei Industrial Limited, a well-known company to produce metallized plastics for household uses to be the plastic material for our studies. The mineral reinforces the dimensional stability of the polymer blend.

Both PBT and PET plastics belong to polyester. The structures of PBT and PET are shown in Fig. 6.2. There are electron-deficient carbon atoms on the polymer blend surface, so they can be attacked by nucleophilic species which present in the reaction solution (Garbassi, Morra et al. 1998; Margolis 2006). Here, sodium hydroxide, NaOH, is a good nucleophilic agent carries out hydrolysis of PBT/PET blend and yields carboxylate salt (carboxylate group) and alcohol. The blend surface with carboxylate group is feasible to form metal complex with Pd/Sn^{2+} colloidal in activation bath. The hydrolysis process significantly increases the number of hydrophilic groups, which then facilitate the subsequent electroless deposition (Bright, Malpass et al. 1969; Kreitz, Penache et al. 2000; Kisin, Scaltro et al. 2007). The effects of different processing parameters, such as etching time and alkali concentration, on the morphology and hydrophilicity of the plastics surfaces were investigated.

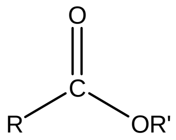


Fig. 6.1: The structure of ester group.

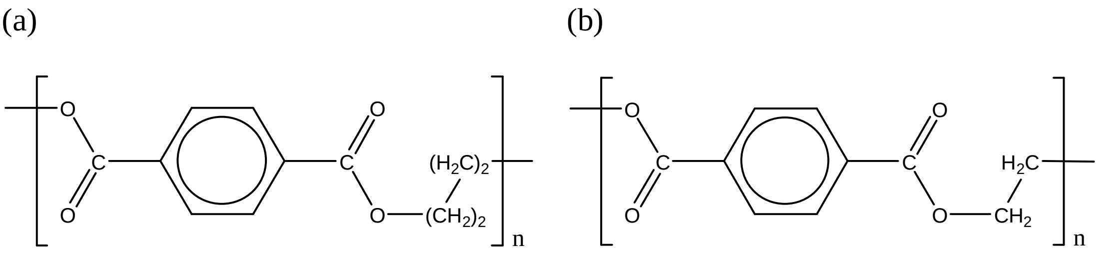


Fig. 6.2: The structures of (a) PBT and (b) PET.

In this chapter, this commercial engineering plastic was used as the plastics substrate for the metallization. Firstly, this commercial engineering plastic was etched by alkali.

The treated plastic was then carried out the standard electroless plating and electroplating.

6.2 Methodology

6.2.1 Sample preparation

Before any treatments, the samples were cut into 40x75 mm^2 area with thickness of about 2 mm. They were then cleaned in an ultrasonic bath of ethanol. Afterward, surface treatment and surface activation for electroless Ni plating and electrodeposition of Cu were performed.

For surface treatment, the cleaned samples were etched in NaOH solution at 80°C (aiming at functionalization and formation of pitting sites). The etching time was varied from 10 to 300 min and the concentration of the alkali was adjusted from 2.5 to 7 M, in order to observe their influences on the surface hydrophilicity and roughness. The functionalized surfaces were then rinsed by 2% HCl for 2 min. The treated samples were then activated in a MACuPlex activator bath D-34C concentrate bath containing D.I. H_2O, 32% HCl, sensitizer 78 and MACuPlex activator D-34C concentrate, for 3 min. The concentration of MACuPlex activator D-34C concentrate was adjusted from 28.5 ppm to 57 ppm. (Precaution: The bath must be free from air, light and water which accelerate oxidation and hydrolysis of Pd/Sn^{2+} into Pd/Sn^{4+} in the bath.) Sequentially, the activated samples were carried out electroless Ni plating and electrodeposition of Cu. The procedures of electroless Ni plating and Cu plating were mentioned in Chapter 3.

6.2.2 Characterization

Fourier transform infrared spectroscopy (FTIR) was employed to determine the chemical bonding of the samples after NaOH etching. The IR spectra were collected by a FTIR spectrometer (Nicolet MAGNA-IR® 760) using transmission mode.

Optical microscopy was used to observe the marco-feature of the samples before and after pre-treating in NaOH. Optical micrographs were collected by using a polarizing optical microscope (Nikon Microphot-FXA) equipped with a digital camera (Pixar). Scanning electron microscope (SEM, Leica Stereoscan 440) was used to determine the surface and the cross section morphologies of the samples. Energy dispersive X-ray spectroscopy (EDX) was used to determine the surface chemical composition of the samples. The root-mean-square surface roughnesses (R_q) of the samples after alkali etching and electroplating of Cu were investigated by using an atomic force microscope (AFM, Digital Instruments, NanoScope IV). All AFM images of 40x40 μm^2 scan area were collected in a tapping mode. The influence of the alkali etching on the surface hydrophilicity was investigated by a contact angle measurement (Ram´e-hart, Model 200) based on the sessile drop experiment which was carried out by dropping 5 µl of D.I H_2O on the plastics surfaces. The contact angle was measured until the probing liquid attained an equilibrium state.

Finally, adhesion of the electroplating Cu coatings on the plastics was evaluated using the standard Scotch tape test (cross-cut tape test, ASTM D 3359-02) performed with 3M Scotch tape.

6.3 Results and discussion

6.3.1 Characterization of plastics substrates

In Chapter 5, we have mentioned that carboxylate salt and alcohol were obtained by alkali etching the polyester (PC plastics). FTIR was used to identify the composition of

PBT/PET blend before and after etching. The corresponding spectra are shown in Fig. 6.3. In accord with the structures of PBT and PET, the FTIR spectrum shows a υC=O band at ~1725 cm^{-1}, and υC-O bands at ~1250 cm^{-1} and ~1100 cm^{-1} that are characteristic of an aromatic ester. Aromaticity is also confirmed in the FTIR spectra by the sharp ring stretching bands near 1600 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1}.

For samples etched at high alkali concentration (>5 M) and long etching period (>5 hr), the intensities of the characteristic peaks at 1650-1550 cm^{-1} and 1440-1350 cm^{-1} are enhanced. These two broad bands are attributed to asymmetric and symmetric stretching of the $–COO^-$ group of carboxylates salt. This enhancement indicates that $–COO^-$ group is obtained due to the hydrolysis of the substrate at the presence of base. Garbassi et al. (1998) and Margolis (2006) stated that the plastics with ester group (RCOOR’) undergo hydrolysis at the presence of base.

Here, OH^- ions acts as a nucleophile and attacks the C atom in the RCOOR’ chain. As a result, this reaction yields alcohol and carboxylate salt. The formation of carboxylate salt was confirmed in our FTIR spectra. These $–COO^-$ ions can facilitate the formation of complex with Sn^{2+} in the Pd/Sn^{2+} colloidal solution.

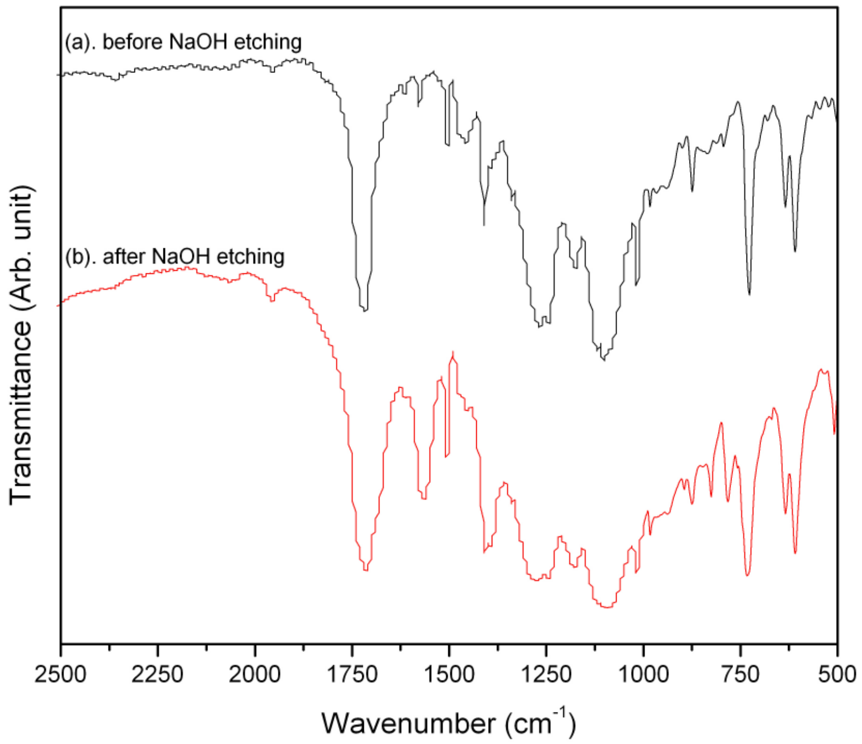


Fig. 6.3: FTIR spectra of PBT/PET samples (a) before alkali etching and after alkali etching for 5 hr at (b) 5 M NaOH.

Figure 6.4 displays the SEM micrograph and EDX spectrum on the surface of fractured PBT/PET blend before etching. According to our EDX spectrum, the major components in PBT/PET blend are Ba (~9%), S (~8%) and O (~37%). The filled mineral in the sample was suggested to be barium sulphate ($BaSO_4$), commonly known as barite. $BaSO_4$ has been widely used as a filler which is added to plastics to enhance its physical properties (Qi, Ma et al. 1996; Qu, Wang et al. 2005; Chen, Bao et al. 2008). From the SEM micrograph, the size of mineral filler is range from 5 µm to 20 µm.

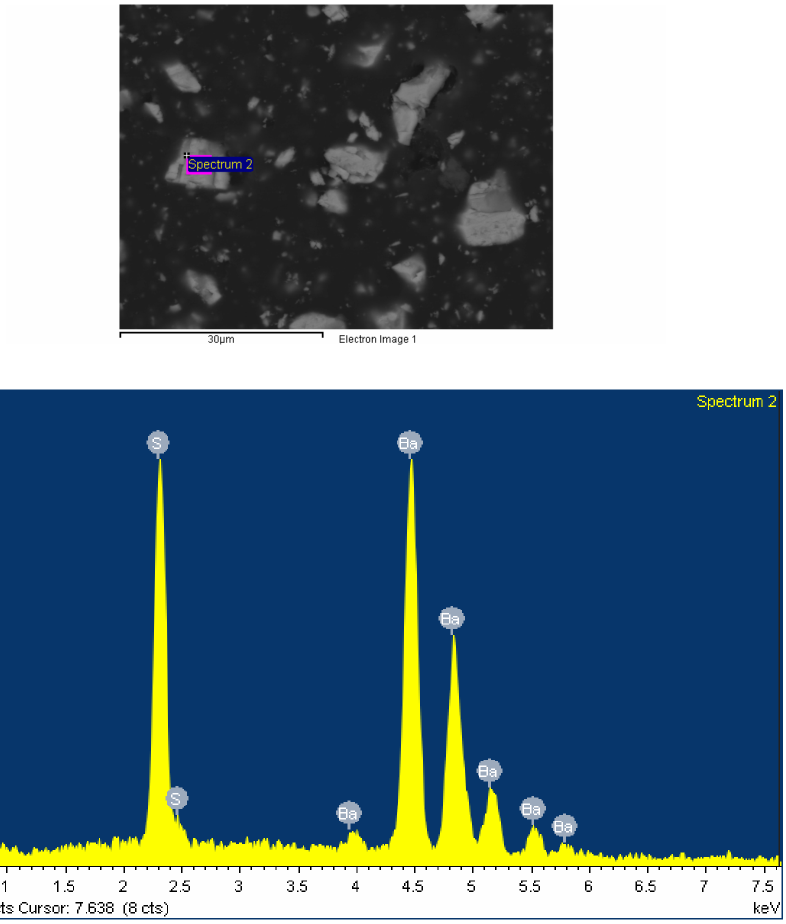


Fig. 6.4: The SEM micrograph and EDX spectrum on the surface of fractured PBT/PET sample before etching. (selected point, marked as a cross)

Pores were observed after NaOH etching. Figure 6.5 displays the SEM micrographs and EDX spectrum (in selected area, 30x25 μm^2) performed on the surface of fractured PBT/PET samples after 7 M NaOH etching for 30 min. According to our EDX spectrum, both Ba and S atoms were not found after etching. This indicates that $BaSO_4$ dissolved in NaOH during etching process. The pore’s size depended on the etching time and the concentration of alkali.

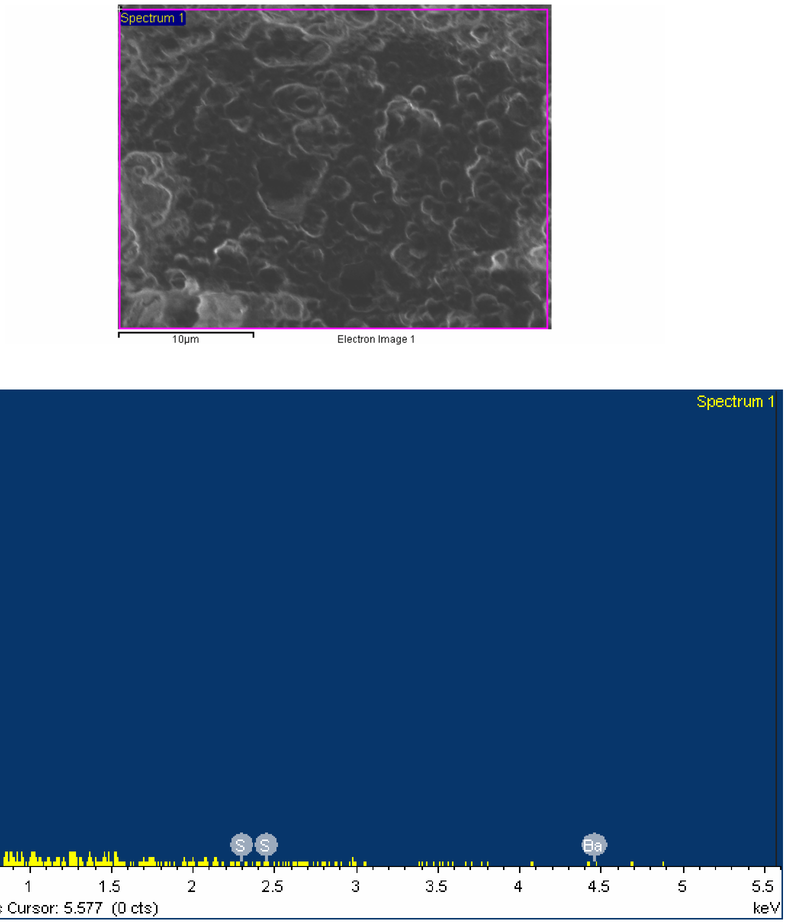


Fig. 6.5: The SEM micrograph and EDX spectrum on the surface (selected area, 30x25 µm^2) of fractured PBT/PET blend after 7 M NaOH etching for 30 min.

Besides forming carboxylate salt on plastics surface, another function of using NaOH is to create anchorage sites on the sample surfaces (shown in Fig. 6.5). In the PBT/PET blend, $BaSO_4$ particles were added in order to reinforce the dimensional stability of the polymer blend. As $BaSO_4$ dissolved in NaOH during etching, the occupied space of $BaSO_4$ in the polymer blend became pores, which acted as pitting sites and thus enhanced the anchoring effect between the sample surface and Pd/Sn^{2+} colloidal.

Optical micrographs of the plastics before and after etching for different time periods are shown in Fig. 6.6. From the figure, different degrees of roughness (depending on the size and density of the anchorage site) were obtained using different concentrations of alkali as well as different etching times. As for samples treated in 2.5 M NaOH solution, surface's pore size increased from ~10 μm to ~50 μm as the etching time increased from 1 hr to 5 hr. On the other hand, if 5 M NaOH solution was used instead of 2.5 M, the corresponding pore size would increase from ~20 μm to ~50 μm when the samples were etched for 3 hr. If the etching time was further increased to 4 or 5 hr, the pore size would also be remained at ~50 μm. This suggests that pore sizes with upper limit of ~50 μm are obtained, despite further increasing of NaOH concentration as well as etching time. This was because high concentration of NaOH and long etching time corroded the structure of sample and caused the upper layers of the samples peeling off layer-by-layer. Our results show that NaOH was an efficient etching agent to generate carboxylate salt and create pitting sites for the 38% mineral filled PBT/PET polymer blend.

As indicated by the pore size and density of pore, it is believed that plastics surfaces with more functionalized groups would be obtained by using higher NaOH concentration or longer etching period. However, under these extreme conditions, the structure of the plastics surface was seriously damaged. For example, the surface became brittle after etching the sample using 5 M NaOH for 5 hr. During electroless Ni plating, this plastics surface peeled off layer-by-layer easily. Hence, this would inhibit the electroless Ni plating and contaminate the Ni bath. It was noticed that for samples treated by high alkali concentration (> 5 M) and long etching time (> 5 hr), Ni did not continuously form on the plastics surfaces. As a result, the etching time was reduced to 10-30 min for further study. Under this condition, plastics surface with carboxylate group and certain degree of roughness could be obtained without destroying the plastics structure.

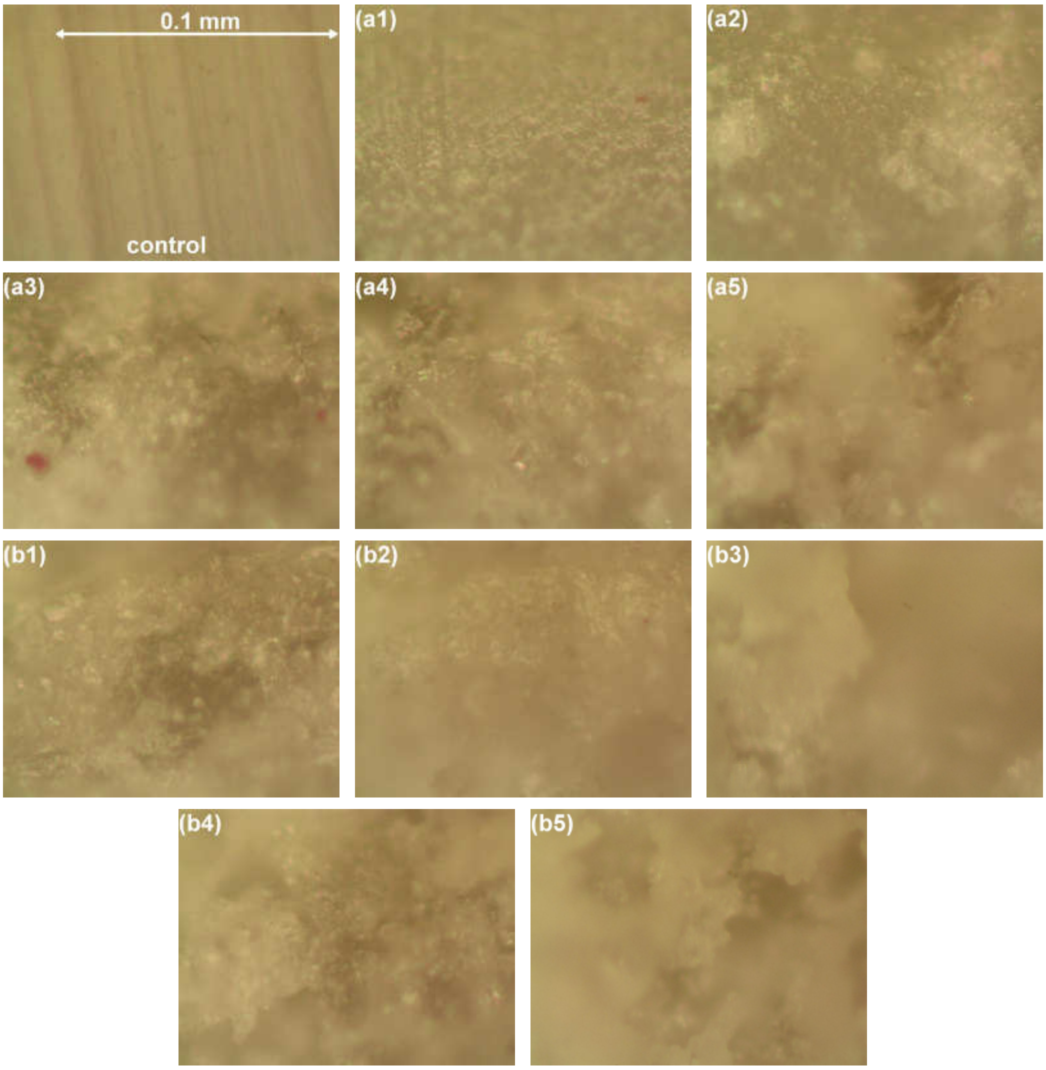


Fig. 6.6: The optical micrographs of PBT/PET samples before and after etching for different time periods using (a) 2.5 M NaOH and (b) 5 M NaOH ((1) 1 hr; (2) 2 hr; (3) 3 hr; (4) 4 hr; and (5) 5 hr.

Figure 6.7 shows the SEM micrographs of the plastics surface before and after etching using 5 M and different etching times. For short etching time (~10 min), pore size ~1-5 μm was observed on the sample surfaces. As expected, the amount of pores on the sample surfaces increased with etching time. Besides, the pore size slightly increased to

~6-12 μm at etching time of ~20 min. After 30 min of alkali etching, some micro-cracks appeared on the sample surfaces.

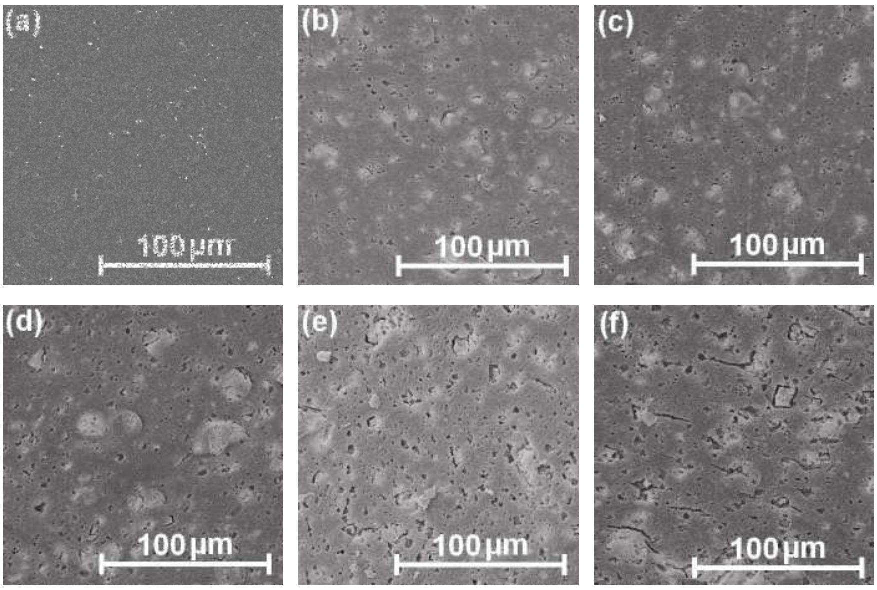


Fig. 6.7: Plane-view SEM micrographs of PBT/PET surfaces subjected to 5 M NaOH etching for: (a) 0 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 25 min; and (f) 30 min.

The surface roughness affected the samples' hydrophilicity. In additional, Garbassi et al. (1998) mentioned that a hydrophilic surface is benefit to the formation of nucleation. Thus during the activation process, with a hydrophilic surface, Pd/Sn^{2+} colloidal solution uniformly spread and adsorbed on the surface, so that it could undergo chemical reaction with the carboxylate group on the sample surface easily. In order to show that the use of NaOH increases the hydrophilic character as well as surface roughness of the samples and thus promotes anchorage of the Ni coating, contact angle measurements were performed to investigate the effects of etching time on the hydrophilicity of the plastics surfaces. The results are presented in Table 6.1.

etching time (min) conc. of NaOH (M)	10	15	20	25	30
3	72°	60°	54°	47°	52°
4	74°	58°	52°	47°	43°
5	62°	53°	62°	47°	39°
6	89°	71°	102°	96°	66°
7	95°	89°	87°	78°	62°

The sample before alkali etching: 74°

Table 6.1: Measured values of contact angle for PBT/PET samples after alkali etching.

The sample without etching had a contact angle at ~74°, i.e. preferentially hydrophobic. According to Table 6.1, contact angle significantly decreased from ~74° to ~40° after etching in alkali with concentration < 5 M for 30 min. The results show that alkali etching promoted the formation of active sites and anchorage points at the plastics surfaces. These modified surfaces increased the interaction between water molecules and plastics chains at the surface. As a result, the electroless Ni plating was readily carried out.

When higher alkali concentrations (6 M and 7 M) were applied, the contact angles increased to ~100° and then slightly decreased ~60°. This might be due to the decomposition of plastics, which affected the surface roughness and impaired the surface hydrophilicity. From these results, the best hydrophilic character of the plastics surface was obtained by using 5 M of NaOH with etching time of 30 min (shown in Fig. 6.8).

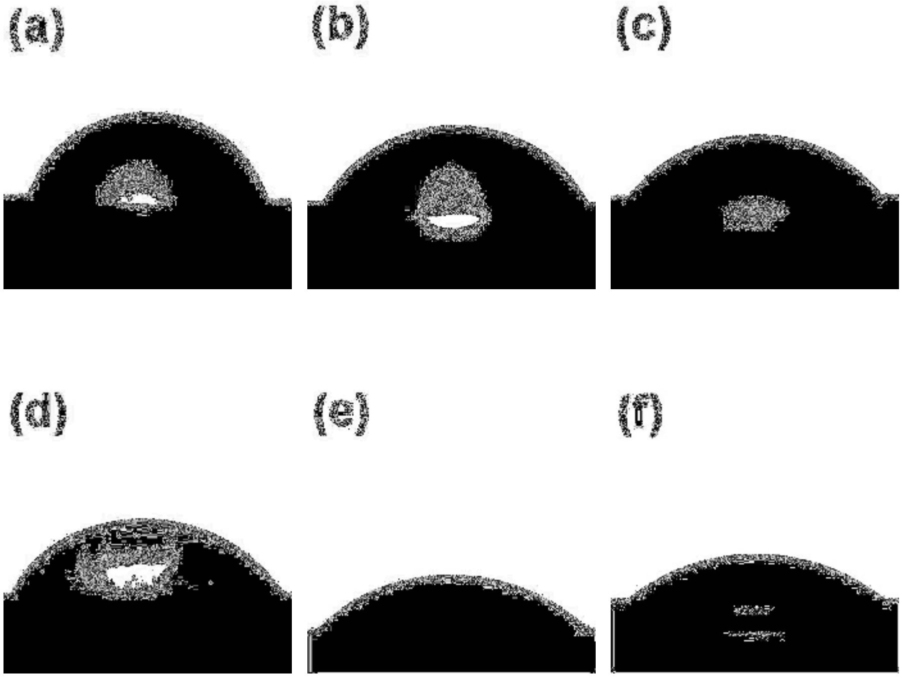


Fig. 6.8: Profiles of a water drop (5 μl) on the PBT/PET surfaces subjected to alkali etching for: (a) 0 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) 25 min; and (f) 30 min. The concentration of NaOH used was 5 M.

6.3.2 Characterization of the metallized plastics substrates

Figure 6.9 presents the cross-section and plane-view SEM micrographs of the plastics surfaces after electroplating of Cu corresponding to different etching times in 5 M NaOH. Compared the plane-view SEM micrographs in Fig. 6.9 to that in Fig. 6.7, the surface roughness apparently deceased after metallization. Figure 6.9 depicts a metallic film homogenously distributed onto the plastics substrate covering the superficial defects. This suggests a leveling action promoted by coating Cu layer on the plastics surfaces.

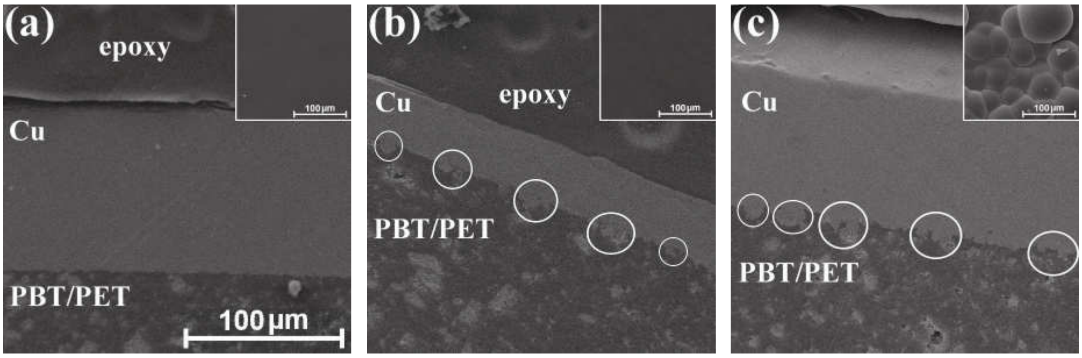


Fig. 6.9: Cross-section SEM micrographs of PBT/PET subjected to 5 M NaOH etching of etching time of (a) 10 min; (b) 20 min; and (c) 30 min followed by electroplating of Cu. Inserts are their corresponding plane-view SEM micrographs.

Figure 6.10 shows the XRD pattern of the top Cu layer. Only Cu(111), Cu(200) and Cu(220) peaks are observed indicating that the Cu layer is in single phase only. The XRD results confirm that continuous Cu layers were formed under all conditions.

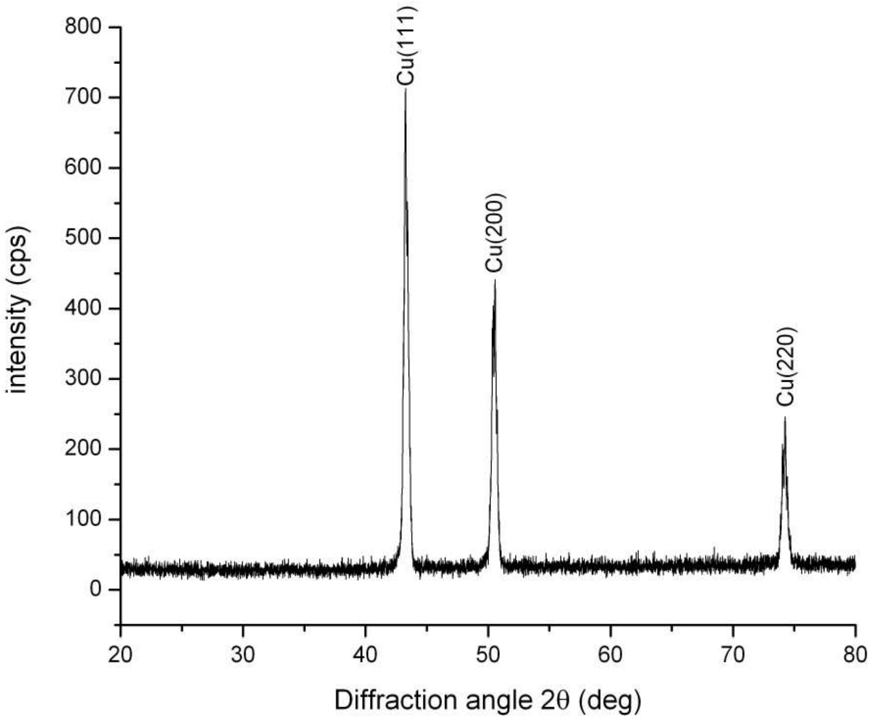


Fig. 6.10: XRD analysis of Cu film on the sample etched in 5 M of NaOH for 30 min.

AFM was used to investigate changes in the surface roughness before and after electrodeposition of Cu. According to Fig. 6.7, alkali pretreatment indeed induced the change of substrates' topography. After electroplating of Cu, the surface roughness was significantly impaired (shown in Fig. 6.9). In Table 6.2, the R_q of PBT/PET samples after alkali etching and electroplating of Cu are listed for composition. Obviously, the

R_q rapidly increased from ~80 nm to ~450 nm after alkali etching. The surface roughness was increased with the etching time. A sufficient rough surface was obtained from 5 M NaOH etching. The surface roughness also affected the appearance of the Cu layer and the adhesion between the Cu film and the substrates.

After electroplating of Cu layer, the surface roughness was significantly improved by an order of magnitude (~9-50 nm). Although the surface roughness was indeed improved, the surface was quite rough (shown in Fig. 6.9c) as 30 min etching time was applied. With this roughness, the inset of Cu surface looked a little bit rough. This implies that the appearance of the metal coating was straightly related to the etching time. In general, a smooth Cu coating can be obtained by using shorter etching time; however, this would affect the adhesive strength of the Cu films to the substrate.

Alkali etching time (min)	R_q after alkali etching (nm)	R_q after electroplating of Cu (nm)
0	87	---
10	106	9
20	235	14
30	449	53

Table 6.2: Values of root mean square surface roughness (R_q) for PBT/PET samples after alkali etching using 5 M NaOH and electroplating of Cu.

Adhesion test was carried out to study the correlation between the adhesive strength of the Cu layer to the PBT/PET blend and the concentration of alkali used as well as etching time. The results of adhesion test are shown in Table 6.3. It is found that the Cu films formed on plastics surfaces with etching time of 10 and 20 min present lower adhesive strength as compared to those of 30 min samples. In Figures 6.9b and 6.9c, more anchorage sites (marked in white circles) are found in samples of longer etching time. Therefore, the optimal conditions of surface treatment for obtaining adhesive metallic films should be treated with 4-5 M NaOH for ~30 min.

Besides etching time, the adhesive strength was also depended on the concentration of Pd/Sn^{2+} colloidal used in the activation process. Higher Pd/Sn^{2+} colloidal concentration (57 ppm) can obtain higher adhesive strength of the Cu films to the substrates. Pd/Sn^{2+} colloidal acted as a seed for initiating the formation of conductive Ni layer on the plastics blend. Higher Pd/Sn^{2+} colloidal concentration was used to ensure that the substrates were entirely covered with Pd/Sn^{2+} colloidal. Pd/Sn^{2+} colloidal not only physical embedded into the anchorage sites on the plastics surfaces, but also formed chemical bonds with the carbonyl group on the plastics surface (Kisin, Scaltro et al. 2007). Once the Pd/Sn^{2+} colloidal chemically bonded to carbonyl group on the plastics blend surface, electroless metallization that involved redox reaction between Ni^{2+} and a strong reducer started. Reduction of Ni^{2+} ions started in the presence of a catalyst, which is usually palladium (Pd). The overall reaction equation between Ni^{2+} and the reducing agent is shown in equation (3).

$$\text{Cathode:} \quad Ni^{2+} + 2e^{-} \longrightarrow Ni \qquad (1)$$

$$\text{Anode:} \quad H_2PO_2^{-} + 2OH^{-} \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} HPO_3^{-} + H_2O + 2e^{-} \qquad (2)$$

$$\text{Overall:} \quad Ni^{2+} + H_2PO_2^{-} + 2OH^{-} \xrightarrow[\text{Heat}]{\text{Catalyst (Pd)}} Ni + HPO_3^{-} + H_2O \qquad (3)$$

Palladium, in its zero oxidation state, is a universal catalyst used to initiate most electroless reactions (Touchais-Papet, Charbonnier et al. 1999; Charbonnier and Romand 2003). To metallize an insulating substrate by this technique, depositing Pd seeds on its surface was good enough to initiate the redox reaction in the electroless plating bath, and then followed by electroplating. According to the experimental results, a good adhesion between the Cu layer and the substrates was obtained when 57 ppm of Pd/Sn^{2+} colloidal was used.

Visual inspection of the Cu coatings showed that the samples activated in low Pd/Sn^{2+} colloidal concentration presented better metallic shine. Lower metallic shine was observed in samples activated in high Pd/Sn^{2+} colloidal concentration. This might be related to the formation of too much active sites on the plastics surface. It led to increase the reduction rate of Ni. Even though ~40 μm of Cu layer was deposited, the roughness of surface would not be improved as compared to the sample in shorter etching time (shown in Fig. 6.9c). The Pd/Sn^{2+} colloidal concentration was also determined by the sample's size. For sample's size with total surface area ~40-100 cm^2, coating with strong adhesive strength as well as good metallic shine can be obtained by etching the samples with 5 M NaOH for 30 min and using 28.5 ppm of Pd/Sn^{2+} colloidal in the activation bath. If the total surface area increased to ~150-350 cm^2 (size of industrial product), high Pd/Sn^{2+} colloidal concentration would be used to achieve a better metallic shine with excellent adhesion of the metal layer to the substrate. Figure 6.11 shows the photo of a Sn/Co coated 38% mineral filled PBT/PET blend. From Fig. 6.11, we observe that the metallized sample performs good metallic shine indicating by the fact that the surroundings are clearly reflected by the sample surface. The appearance and the results of adhesion test demonstrate that alkali etching is suitable for modifying this polymer blend to achieve an excellent metallized product.

Fig. 6.11: The photo of 38% mineral filled PBT/PET blend after Sn/Co plating.

conc. of NaOH(M) \ etching time (min)	10	20	30
3	0B (0B)	0B (0B)	2B (4B)
4	0B (0B)	0B (2B)	4B (5B)
5	0B (0B)	1B (5B)	5B (4B)

Table 6.3: Results of adhesion test of the Cu films to the PBT/PET samples as using 28.5 ppm of Pd/Sn^{2+} colloidal in the activation bath (ASTM D 3359-02). (Brackets representing the samples activated with 57 ppm of Pd/Sn^{2+} colloidal in the activation bath)

6.4 The enhancement of surface roughness of 38% mineral filled PBT/PET polymer blend by introducing PEG_{5800}

In Chapter 4, PEG was introduced onto the PP surface to make the surface become hydrophilic, so that activation could easily take place. Although metallization was not successfully performed on PP, the results demonstrated PEG was an effective surfactant to improve the hydrophilicity of the coated surface. Vas ko et al. (2004) stated that PEG is useful in leveling up roughness and improving surface hydrophilicity in the plastics metallization process.

In fact, activation could directly carry out on the 38% mineral filled PBT/PET blend surface. For industrial production, the process time should be as short as possible. Furthermore, the adhesion between the metal coating and the plastics structure can be improved by enhancing the wettability of the plastics surface (Li, Charters et al. 2004). Among different M_n of PEG, PEG_{5800} was chosen to be coated on the etched samples. PEG_{5800} did not easily dissolve in the activation bath. However, it is ready dissolved into the $CHCl_3$. By using PEG_{5800}, our results showed that the activation time could reduce from 3 min to 1.5 min. For the sample soaked in 5 M NaOH etching bath for 30 min, further with PEG_{5800} treatment, the surface roughness of the final Cu plating was

35 nm, compared to those without PEG$_{5800}$ treatment, the surface roughness of the final Cu plating was 53 nm. The metal layer was classified as 5B in the adhesion test. This means that the edges of the cuts were completely smooth and none of the squares of the lattice was detached under removing the tape. The result revealed that PEG enhanced the appearance of the metal coating. Also, PEG is a stable chemical. It can be decomposed by strong oxidizing agent. Generally, PEG can be introduced in the plastic metallization industry.

6.5 Conclusion

On the basis of our results, NaOH effectively modifies surfaces of 38% mineral filled PBT/PET blend to provide $–COO^-$ group and pitting sites. Higher alkali concentration and longer etching period result in a much functionalized surface. However, the alkali concentration should not be higher than 5 M and the etching time should not be lasted too long. Otherwise, the structure of the plastics surface would be damaged. Thus, the etching time and concentration of NaOH are maximized to 30 min and 5 M respectively, in order to achieve a surface with optimum degree of roughness and carbonyl groups.

Contact angle measurement is used to study the change of hydrophilicity of plastics surface by varying the alkali concentrations and the etching periods. A more hydrophilic surface facilitates the electroless plating process. The hydrophilicity of the plastics surface increases with etching time up to 30 min by using 5 M NaOH, and decreases with higher alkali concentration.

After alkali etching, the samples are introduced into the activation bath containing Pd/Sn^{2+} colloidal. The Pd/Sn^{2+} colloidal concentration is determined by the sample's size. 57 ppm of Pd/Sn^{2+} colloidal is suggested to be used. It is guaranteed to provide good adhesion strength. To sum up, the results demonstrate that NaOH is an effective etching chemical for the metallization of 38% mineral filled PBT/PET polymer blend.

For industrial production, PEG is suggested to use to shorten the activation time and enhance the appearance of the metal coating.

CHAPTER 7 CONCLUSION

7.1 Conclusion

The main objective of this study is to investigate the possibility of using other etching methods instead of the traditional chromic acid etching in the plastics metallization. After etching, surface of the engineering plastics are modified and metallized in feasible way and industrial production scale. The traditional chromic acid etching bath is only suitable for modification of the surface of ABS plastics which composes of acrylonitrile, 1.3-butadiene and styrene. In the acid etching process, the strong acid oxidizes the 1.3-butadiene into butanedioic acid. Thus, a functional group (carbonyl group) is formed. Pitting sites are created at the same time. These functional groups and pitting sites are essential in metallization of ABS plastics.

In this project, apart from ABS plastics, other engineering plastics, including PP, PC and PBT/PET blend were used. PP is a long hydrogencarbon chain plastic without any functional groups in its structure. The study of metallization of PP indicates that only the existence of pitting sites is not sufficient for obtaining metal coating with good adhesion. By cooperating with PEG, the activation process could run smoothly. However, no functional groups exist on the PP surface to form bonding with the coated PEG. Even though PEG could form complex with Pd/Sn^{2+} colloidal and metal could grow on it, the metal layer detaches easily from the PP surface.

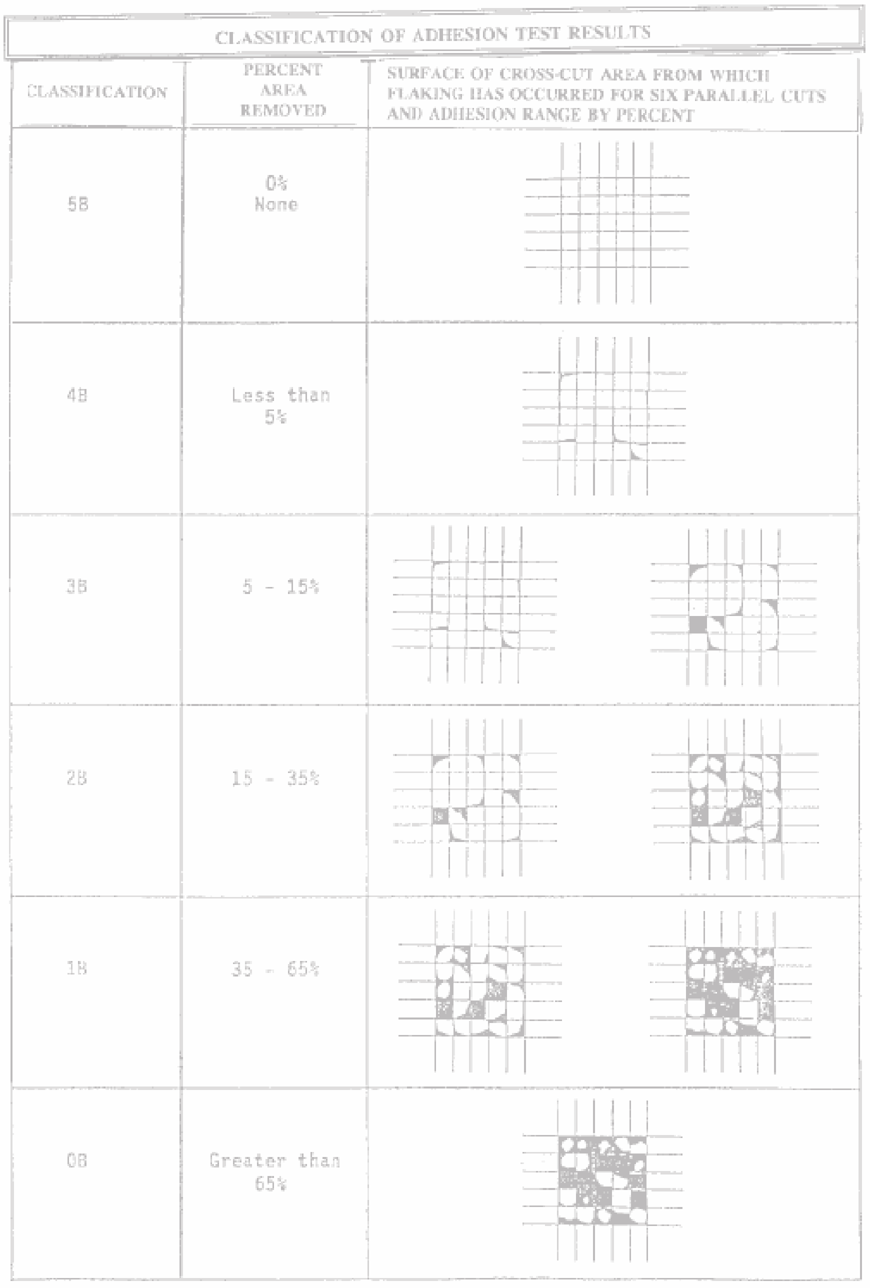
For the most common engineering plastic, PC, ester groups exist in its structure. This ester group allows PC to react with NaOH to yield carbonyl group and alcohol. The reaction rate is quite slow. We demonstrated that it is necessary for PC plastics to be attacked by $CHCl_3$ first, in order to create swelling and cracking (pitting sites). The increase of surface area can facilitate the alkali etching process, so 4-6 M NaOH bath can be used effectively to etch the PC samples. Ultimately, metallization can successfully apply on the PC surface.

The commercial plastics, 38% mineral filled PBT-PET polymer blend, was also studied. Similarly to PC, both PET and PBT are polyester. This means that they could also undergo hydrolysis at the presence of NaOH and thus similar products would be resulted. In this polymer blend, the filled mineral is $BaSO_4$, which dissolves in NaOH during the etching process. For this commercial plastic, alkali etching is used to produce both functional groups and pitting sites at the same time. By cooperating with PEG, the surface smoothness is further improved. The activation time is also shortened. These two improvements are preferable for the industrial production.

To summarize the results of Chapter 4 and Chapter 5, both functional group (either hydroxyl or carbonyl group) and pitting sites are vitally important in the metallization of plastics. Based on the studied plastics, our main objective is to generate carbonyl group on the plastics surface. Functional group provides place for undergoing reaction to facilitate the formation of chemical bonds between the plastics and the metal layer. For pitting sites, the metal grows on the plastics surface and strongly anchors to the plastics surface. From the results of Chapter 4 and Chapter 6, PEG is able to shorten the activation time and improve the appearance of the coated metal layer. Our results showed that the adhesion between PEG and PBT/PET is better than that between PEG and PP. This is because the polar molecular PEG is ready to have intermolecular force with polar polymer PBT/PET but not the non-polar polymer PP. As a result, a successful metal layer with good adhesion is formed on PBT/PET.

In conclusion, for chemical surface modification of plastics, both pitting sites and functional groups (either hydroxyl or carbonyl group) exist on the plastics surface. To sum up, alkali etching is effective on surface modification of polyester plastics. For environmental concern, although alkali is corrosive, it is more environmental friendly than the tradition acid etching bath, which consists of chromium trioxide in concentrated sulphuric acid. Both of them are strongly corrosive and induce serious environmental toxin, which may cause substantial and long-term damage to human.

APPENDIX



CLASSIFICATION OF ADHESION TEST RESULTS

CLASSIFICATION	PERCENT AREA REMOVED	SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT
5B	0% None	
4B	Less than 5%	
3B	5 - 15%	
2B	15 - 35%	
1B	35 - 65%	
0B	Greater than 65%	

FIG. 1 Classification of Adhesion Test Results

Standard Test Methods for Measuring Adhesion by Tape Test, Designation: D 3359-02, American Society for Testing and Materials, ASTM, West Conshoboken, PA, 19428-2959.

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