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CORROSION PROTECTION OF CARBON STEEL BY COATING WITH EPOXY

POLYESTER POWDER CONTAINING ZINC AND POLYANILINE

Miss Sureerat Tipoo

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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Thesis Title	CORROSION PROTECTION OF CARBON STEEL BY COATING WITH EPOXY POLYESTER POWDER CONTAINING ZINC AND POLYANILINE
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Field of Study	Petrochemistry and Polymer Science
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พอลิเอสเทอร์ที่มีสังกะสีและพอลิแอนิลีน (CORROSION PROTECTION OF CARBON STEEL BY
COATING WITH EPOXY POLYESTER POWDER CONTAINING ZINC AND POLYANILINE)
อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ศุภวรรณ ตันตยานนท์, 73 หน้า.

โดยทั่วไปนิยมใช้อิพ็อกซีเรซินในการเคลือบเหล็กกล้าคาร์บอนสำหรับป้องกันการกัดกร่อน   งานวิจัย
นี้ศึกษาการเคลือบเหล็กกล้าคาร์บอนด้วยผงอิพ็อกซีพอลิเอสเทอร์การที่มีสังกะสีและพอลิแอนิลีน   โดยทำการ
สังเคราะห์พอลิแอนิลีนโดยใช้การเกิดพอลิเมอร์ด้วยปฏิกิริยาออกซิเดชัน ใช้แอมโมเนียมเพอร์ออกซีไดซัลเฟต
เป็นตัวออกซิเดชัน ทำการพิสูจน์เอกลักษณ์ของพอลิเมอร์ที่เตรียมได้โดยใช้เทคนิคอินฟราเรดสเปคโตรสโคปี และ
วัดค่าการนำไฟฟ้าโดยใช้เครื่องโฟร์พอยท์โพรบ พบว่ามีค่าการนำไฟฟ้าในช่วง 3-4 x 10^{-2} ซีเมนต์ต่อเซ็นติเมตร
อนุภาคสังกะสีที่ใช้ในสูตรมีสองชนิดได้แก่ผงสังกะสีและเกล็ดสังกะสี โดยปริมาณของสังกะสีแตกต่างกันใน
ขณะที่ปริมาณของพอลิแอนิลีนคงที่ที่ 5 ส่วนในเรซินหนึ่งร้อยส่วน ทำการเตรียม   ผงอิพ็อกซีพอลิเอสเทอร์ที่มี
สังกะสีและพอลิแอนิลีนทั้งหมด 17 สูตรทำการเคลือบผิวเหล็กด้วยโดยการพ่นด้วยปืนพ่นไฟฟ้าสถิต จากนั้นทำ
การทดสอบการกัดกร่อนโดยใช้มาตรฐานการทดสอบด้วยหมอกเกลือตาม ASTM B-117 และประเมินการกัด
กร่อนตามมาตรฐาน ASTM D-1654 พบว่าเมื่อปริมาณของสังกะสีเพิ่มขึ้นขนาดและความถี่ของการพองของฟิล์ม
สารเคลือบจะลดลง และ พบว่าสารเคลือบที่มีเกล็ดสังกะสีเกล็ด 50 ส่วน แสดงความต้านทานการกัดกร่อนสูงกว่า
สูตรอื่น ๆ   ชี้ให้เห็นว่าปริมาณของสังกะสีเป็นสิ่งจำเป็น โดย สังกะสีจะเกิดการกัดกร่อนกลายเป็นออกไซด์ของ
สังกะสีและปิดกั้นรูพรุนของชั้นเคลือบเพื่อป้องกันการกัดกร่อนต่อไป   ทำการวัดความต้านทานการกัดกร่อนใน
สารละลายโซเดียมคลอไรด์เข้มข้น 3.5 เปอร์เซ็น ต์โดยน้ำหนัก ด้วยเทคนิคอิเลคโตรเคมิคัลอิมพีเดนซ์สเปคโตรส
โคปี เพื่อศึกษาสมบัติการกัดกร่อนที่ระยะเวลาต่างๆ   นอกจากนี้ยังทำการทดสอบสมบัติเชิงกลและสมบัติทาง
กายภาพของสารเคลือบได้แก่ การยึดติด การทนทานต่อแรงกระแทกและความเงา

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KEYWORDS: POWDER COATING / POLYANILINE / ZINC / CORROSION

SUREERAT TIPOO: CORROSION PROTECTION OF CARBON STEEL BY COATING WITH EPOXY POLYESTER POWDER CONTAINING ZINC AND POLYANILINE. THESIS ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 73 pp.

Normally the epoxy resins are used to coat the carbon steel for corrosion protection. In this research, the epoxy polyester powder was work, with the addition of zinc and polyaniline (PANI) for carbon steel coating. PANI was synthesized by chemical oxidative polymerization method using ammonium peroxydisulfate as oxidant. The resulting polymer was characterized by FT-IR spectroscopy and had conductivity in the range of 3 to 4 x 10^{-2} S/cm, measured by a four-point probe meter. PANI 5 phr was added. Two types of zinc particles, zinc dust and zinc flake were employed. The content of zinc dust and zinc flake was varied. These were 17 formulations of epoxy polyester powder. After depositing on carbon steel by electrostatic spray coating, they were subjected to the anti-corrosion test using the salt spray technique according to ASTM B-117 and then evaluating with ASTM D-1654. When the amount of zinc increased, size and frequency of blistering appeared to be smaller. It was also observed that the formulation with zinc flake 50 phr showed better anti-corrosion than the others. The results indicated that the presence of zinc was necessary as the zinc corroded and blocked further corrosion attack and zinc flake particles enable to secure the electrical conductive connection in the coating and create an impermeable barrier through their particles. Electrochemical impedance spectroscopy measurements in 3.5 wt. % NaCl were performed to study corrosion properties with the exposure time. The physical and mechanical properties of all the coated steel, such as adhesion to substrate, impact resistance and gloss had also been evaluated.

Field of Study: ...Petrochemistry and Polymer Science... Student's Signature ……………

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LIST OF ABBREVIATIONS

PANI	:	Polyaniline
°C	:	Degree Celsius
FT-IR	:	Fourier-Transform Infrared Spectrometer
SEM	:	Scanning Electron Microscope
min	:	Minute
EIS	:	Electrochemical impedance spectroscopy
Tg	:	Glass transition temperature
phr	:	Part per hundred resins
μm	:	Micro metes
DSC	:	Differential scanning calorimeter
VOC	:	Volatile organic compound
TGIC	:	Triglycidyl isocyanurate
ZRP	:	Zinc-rich primer
OCP	:	Open circuit potential

CHAPTER I

INTRODUCTION

1.1 Introduction

Steel is widely used as it has favorable mechanical properties. However, steel has got damaged by corrosion sooner or later. Corrosion is caused by the thermodynamically unstable of iron after it has been extracted from its ores. Reduction of iron from its state as an oxide in ore requires energy in the reduction process. The oxidized state in the case of steel is usually present as rust. Fortunately, Protection of steel against corrosion by using coatings is one of the most favorable methods for corrosion protection of steel by preventing them from the contact with environment. The new coatings based development attempts to improve the corrosion protection for steel [1-9]. Recently strict environmental regulations within the coating industry have led to the development of technologies that should meet the requirement of both the environmental allowance and high performance. Powder coatings are solvent free and prefer several advantages including little or no volatilization of solvent during application and baking, low or elimination of hazardous waste and high utilization [10].

Figure 1.1 Examples of products that coated with powder coating.

Normally the anti-corrosion powder coatings are often formulated from epoxy. Epoxies provided excellent for corrosion protection but have other limitations, importantly their suffered from sunlight or other ultraviolet light degradation with resultant loss of gloss and subsequent chalking. Epoxy polyester can be classified as an epoxy blended with high percentage of polyester, these coatings are more similarly to epoxies than polyester. A major advantage of having polyester in an epoxy would increase the resistance to yellowing due to over-bake during curing in the oven. Zinc, one of the most effective anti-corrosion pigments was also used for corrosion protection of steel, well performed by high loadings that must maintain zinc particle to zinc particle contact within its continue and contact between zinc and substrate to ensure electrical conductivity within the coating layer and across the interface [11-19]. The concentration of zinc above 70% by weight in formulations caused the powder coatings manufacturers meet problems of homogeneity in production process. This means that binder, zinc and other additives are not well dispersion in extrusion process and not well distributed in powder particles before application. When the coating is cured to film, this provides zinc-rich and zinc-poor areas inside the coating. Therefore zinc flake is mixed with spherical zinc dust for solve these problem [12-14]. Conducting polymers have been studied like a new type of materials for the anti-corrosion of metals such as steel [20-40]. The most favorite of conducting polymers for corrosion protection is polyaniline (PANI) due to its ease to synthesis and good stability together with a high electrical conductivity. In this study, we studied the influence of polyaniline and zinc content on the anti-corrosion of epoxy polyester powder.

1.2 Objectives of research

1. To develop epoxy polyester powder for anti-corrosion.
2. To investigate the effect of zinc on corrosion performance of epoxy polyester powder containing zinc and polyaniline.

1.3 Scope of research

1. To evaluate the corrosion protection on carbon steel.
2. To develop epoxy polyester powder for anti-corrosion by PANI, zinc dust and zinc flake.
3. To investigate on coated layer in film thickness range 40-60 micron.
4. To evaluate the corrosion protection by salt spray test and electrochemical impedance spectroscopy.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Corrosion [11]

Corrosion is known to be one of the damage mechanisms of the metal, which is caused by electrochemical process of an anodic reaction when a considerable amount of energy was applied to an ore. The ordinary aqueous environments offer possibilities for metals to form compound with other elements and return to their lower energy level. The anodic and cathodic reactions for the corrosion of iron can be written as follows:

At the anode where the metal goes into solution

$$Fe \text{ (solid)} \longrightarrow Fe^{2+} \text{ (ion)} + 2e^- \text{ (electrons)}$$

At the cathode –

$$2H^+ \text{ (hydrogen ions)} + 2e^- \longrightarrow H_2 \text{ (gas)}$$

or $2H^+ + \frac{1}{2}O_2 \text{ (air)} + 2e^- \longrightarrow H_2O$

or $O_2 + 2 H_2O + 4e^- \longrightarrow 4 OH^- \text{ (hydroxyl ion)}$
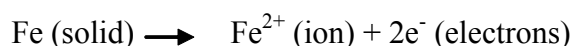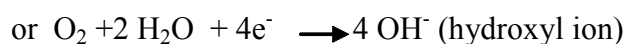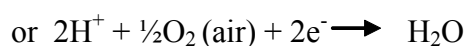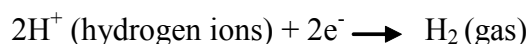
Iron ions (Fe^{2+}) and electrons generated by the anodic reaction. The electrons flow through the metal to a neighboring cathodic area where hydroxyl (OH^-) ions are liberated due to the presence of moisture and oxygen. Coupling the anode and cathode must be an electrolyte such as saltwater, or sulphates in industrial and domestic wastes. As a consequence of the above reactions, a two stage conversion to reaching the precipitated finally rust Fe_2O_3.

The relative rates at which the above reactions occur are directly related to the localized environment and specifically, the abundance and nature of the electrolytes component. It is for this reason that in areas of low humidity, such as deserts (hot or cold), corrosive action is generally negligible when compared to regions of high salt and humidity

2.2 Corrosion protection [11]

2.2.1 Environmental modification

Metal corrosion can be immediately reduced by changing the environment or removing the metal from these environments. The simple methods by limitations of metal to contact with seawater or rain by storing indoors or reducing the oxygen, chloride or sulfur content in the environment. It can be decrease the corrosion speed of metal.

2.2.2 Metal selection and surface conditions

Changing the metal type for used can also reduces the rate of corrosion. Corrosion resistance data of metal can be used in combination with the conditions of environmental to make decisions respecting of the suitability for each metal and for protecting against corrosion the surface condition is also important.

2.2.3 Cathodic protection

When two different metals are situated together in a corrosive electrolyte, galvanic corrosion was occurs. That known as a sacrificial system, uses metal acts as a sacrificial anode in order to protect the cathode. Sacrificial anodes are typically made of aluminum, zinc or magnesium due to that has the most negative electro potential. As a result of the zinc sacrificial corroding, these form insoluble zinc salt to fill in the pore of coating for reduced permeability of the coating.

2.2.4 Corrosion inhibitors

Corrosion inhibitors can work by adsorbing themselves on the metal's surface and forming a protective film. The corrosion inhibitors can be applied to metals as a corrective action for prevents corrosion.

2.2.5 Plating

Plating is metallic coatings that can be applied to inhibit corrosion and provide decorative finishes. The types of metallic coatings as electroplating, mechanical plating, electroless plating or hot dipping to coat a thin film layer of metallic adhered to the substrate.

2.2.6 Anodic protection

It used anodic current on the structure to be protected. This method related on the formation and maintain of an oxide film by anodic polarization. It is necessary for metals that exhibit passivity and can be achieved when the solution and steel has potential differences. It is applied in aggressive environments.

2.2.7 Coating

Coatings is common methods for provide corrosion protection by forming a barrier impermeable to moisture and electrolytes for separated the metals from environment. For optimum corrosion protection, the barrier should be as thick, continuous and impermeable.

2.3 Advantages of powder coatings [10]

The increasing use of powder coatings has been related to the need to reduce air and water pollution, combined with the rising costs of basic raw materials (particularly petroleum based) and labor. Powder coating is commercial alternative to conventional industrial liquid (wet) coating. Some of the most significant advantages of the powder coating technology are outlined below:

2.3.1 Ready to use:

Powders are supplied for immediate use. There is no additional pre-mixing, stirring, thinning or viscosity adjustment before use. This saves a considerable amount of time and labor, and also reduces a variable or erroneous step, vital to the control of liquid paint and their subsequent film performance.

2.3.2 Reduction of fire risks:

Since powder coatings are not a solvent based product, there is a sizable reduction in the risk or fire. This coupled with the fact that they are not subject to the class of Highly Flammable Liquids, can give further cost saving in relation to flame proof plants, safety measures and reduce of insurance premiums. It eliminates the need for special protected the application booths and storage area.

2.3.3 No solvent waste problems:

Due to no solvent present in powder coatings, no need solvents for thinning, spraying or cleaning thus reducing waste disposal problems. Thus there is no costly wastage through the volatilization of solvent, during application and baking. This is apart from the legislation in many countries which now limits the level of atmospheric discharge, such that after-burners have to be installed to eliminate emissions.

2.3.4 Health hazards reduced:

The omission of solvents in powder coatings, there is a marked decrease the amount of hazardous substance in inhalation and oral (particularly throat) irritations suffered by the operators especially during hot weather. There is also a dramatic reduction in dermal complaints as powders can simply be washed off the skin with warm water. Not initial removal via solvent or industrial cleaner is necessary for clean the skin. A face mask will prevent to inhale the powder dust. Very little smell is produced which reducing the ventilation system.

2.3.5 High utilization:

In solvent paints has very large losses incurred by over spraying and solvent wastage. With powder coatings a technology has arrived which when applied even by careful application and incorporating with a well maintained recovery and recycling system in the spray booth, utilization factors of over 95% are possible.

2.3.6 Wide range of finishes available:

Comparing with many conventional paints, improved performance can be achieved, including good corrosion protection and good adhesion to substrate. Furthermore, variety gloss; matt, semi gloss, high gloss and specialized effects, such as texture, antique, hammers, wrinkle finishes, metallic, leatherettes, clear or tinted lacquers, can be obtained in one single application.

2.3.7 Easier for re-works:

If the films are damaged on the powder application process before curing, it can easily to re-work by removed powder from damaged area with air or a vacuum and takes place by re-spraying. Moreover, the removed powder can be recycled and re- used.

2.3.8 Housekeeping:

Indeed with proper housekeeping powder application can be a very clean process. The spray booth walls and floors can be cleaned by use air or a vacuum. It is not necessary to use solvents for cleaning.

2.3.9 Economic advantages:

There is probably little difference to the small jobber with spray gun, spray booth and box oven. However the cost saving of a fully automatic spray unit, with conveyor and powder recycle facility against say two-coat electro-deposition wet paint system can be considerable. Simple automatic equipment enables easy application. Comparing to liquid coatings as a result of no solvents to flash off before curing, processing time is reduced. Storage space for powder coatings is required without special fire precautions. Therefore, a powder plant is simpler and cheaper to operate than a liquid paint application plant.

2.4 Powder coatings [10]

Powder coatings are free-flow dry grounded plastic material composing of resin, cross-linking agent in thermosetting, pigments or fillers and various additives for provide specific properties. Powder coatings were first developed in the United States in the late 1950's. These initial products were merely dry blends of a powdered resin, a small proportion of flow agent and a powdered curing agent, which were compounded in ball mills, mixing rollers and sigma blade mixers. It was not until 1961 that a West German company had the notion of compounding paints continuously by using an extruder. When they are applied and heated these powders was melting and flows to form a continuous film. Powder coatings are made a popular alternative in today due to an environmentally friendly that contain low Volatile Organic Compounds (VOC) and can achieved a wide range finishes.

Powder coatings can be separated in thermoplastic and thermosetting. Thermoplastic powders are not chemical react in curing process. Thermosetting powder coatings are chemical cross-linking will be caused by the cure process then changing the powder into a continuous film that will not re-melt.

Thermosetting powders are used in wide range for variety specific properties and usually applied in thinner films thickness.

A typical thermosetting powder will have a resin as the film forming component, pigments for color and hiding power, a curing agent and additive. The dry component are mixed in high speed mixture to create a homogenous mixture and then feed into an extruder for hot-melt compounding. The hot extrudate is cooled rapidly before flaking or granulating. The flakes are needed to be ground into a fine powder that suitable for application.

2.5 Type of Powder Coatings [10]

2.5.1 Thermoplastic

Vinyl, nylon and polyester are used as the primary resins in thermoplastic. These materials are used for various applications such as hospital shelving shopping carts, playground equipment, and other applications. Thermoplastic powders can offer high toughness and impact resistance. It requires high temperature to melt and flow these high molecular weight resins. The common application to apply these powders is fluidized bed.

2.5.2 Thermosetting

Thermosetting powders are widely used than thermoplastics. They are composed of relatively high molecular weight resins and cross-linking agents, which are applied in the coated process, then heated to the required temperature at certain time for cured. A cross-link network that provides excellent resistance is created by the chemical reaction in the cure cycle. Different cross-linkers can be applied to these primary resins to produce a variety of powder materials, including amine, anhydride, melamine and blocked or non-blocked isocyanate. The currently type of thermosetting powder available worldwide as below,

2.5.2.1. Epoxy

The first commercially thermosetting powder coating was epoxy. They provide good corrosion resistance, chemical resistance, toughness, and flexibility. The epoxies has primary disadvantage that they have poor over-baked resistance and leave stain when subjected to UV or other radiation. This reason they are poor decorative exterior durability.

2.5.2.2. Epoxy Polyester

Epoxy Polyester, is the blending of epoxy resins and higher percentage of polyester (often in excess of half of the resin). Combined epoxy resins with polyester resins to form epoxy polyester powder with most of the properties are more closely to epoxies than polyester. They show good flexibility in terms of impact and bend resistance but are slightly lower in hardness. Their corrosion resistance is comparable to epoxies, but less resistance to chemicals and solvents. A major advantage of this system, due to the influence of the high percentage of polyester component, it gives higher resistance to over-bake yellowing in curing on the oven. This also translates to improved weather resistance. These systems begin to chalk almost as fast as an epoxy, but the deterioration is slower and the discoloration less severe. Another advantage is competitively priced. Epoxy polyester is typically to be used in many applications as same as the epoxies with slightly to improvement of weathering resistance.

2.5.2.3. Urethane Polyesters

Urethane cured with polyester powders has excellent exterior durability, toughness and very good appearance. A smooth and thinner film can improve chemical resistance of the polyester. The urethane polyesters are one of the most popular finishes for high quality or premium products.

2.5.2.4. Polyester TGIC

Polyester TGIC coatings use Triglycidyl isocyanurate (TGIC) as the epoxy functional cross-linker to be cured with polyester. Polyester TGIC characteristic has a good exterior durability and very good adhesion with substrate. They can be cured at lower temperatures and/or shorter cure cycles. In the cure process, they have good over-baked characteristics and they are less

active to outgassing. The corrosion resistance is equal to urethane polyesters but the chemicals resistant are lower.

2.5.2.5. Acrylic

Acrylics give excellent exterior durability. They may show problems with outgassing at thicker films. They offer thin hard film, good chemical resistance, but poorer mechanical properties such as flexibility and impact resistance.

2.6 Application of Powder Coatings [10]

2.6.1 Fluidized bed application

The first commercial method of applying powder coatings to a substrate was by the fluidized bed dip process. All fluidized beds based on the principle of introducing compressed air into a plenum chamber at the base of the bed, which passes through a porous flow distributor tile into the main body of powder. Fluidized bed application is accomplished by immersion of a pre-heated substrate into the fluidized bed of powder. The powder will melt upon contact with the hot substrate, creating a thick continuous film on the surface and the part will be put through a short post-cure cycle to completely fuse the powder.

2.6.2 Electrostatic fluidized bed application

Electrostatic fluidized bed uses the development of powders suitable for electrostatic application, it becomes possible to use the fluidized bed system by passing the fluidizing air over a charging electrode prior to its passing through the porous flow distributor and into the powder. This effectively charges the powder and a substrate immersed into the bed will be coated. It is a simple and cost effective method since it does not require a complex recovery system as there is no loss in over spray. The main disadvantage with this type of system is the tendency for the powder sometimes to stratify in layers, leading to uneven charge distribution and subsequent difficulties in ensuring an even coating on the substrate. As with all dipping operations, care must be also taken over the speed and angle of immersion and withdrawal of the product.

2.6.3 Electrostatic spray application

Electrostatic spray application was established in the 1950s. It is based on the principle whereby paint particles transported by air pressure to the spray head of a dispensing gun, receive an electrostatic charge, and any grounded or earthed substrate in the path of the projected paint attracts and retains the particles by electrostatic adhesion. It is possible to apply thinner coatings with arious decorative and protective features. This principle applies of to powder coatings with the three most commonly used methods of charging being corona (ionization), tribo electric (friction charging) and a combination of both (sometimes known as air ionizing or tribo plus). However, of the three, by far most widely used is corona.

In a corona charging system, the corona discharge is obtained by applying a voltage source generates current to a sharp needlepoint electrode at the end of the spray gun. The high voltage electric field can cause "breaks down" of the air in the immediate vicinity of the electrode, creating ions (normally negative), which are then free to attach themselves to the nearest object or surface. Powder particles passing through this field therefore become charged and in turn are attracted to and earthed substrate. An electrostatic spray application system comprises a powder feed system and a charging system. The basic set-up equipment for a single application unit is:
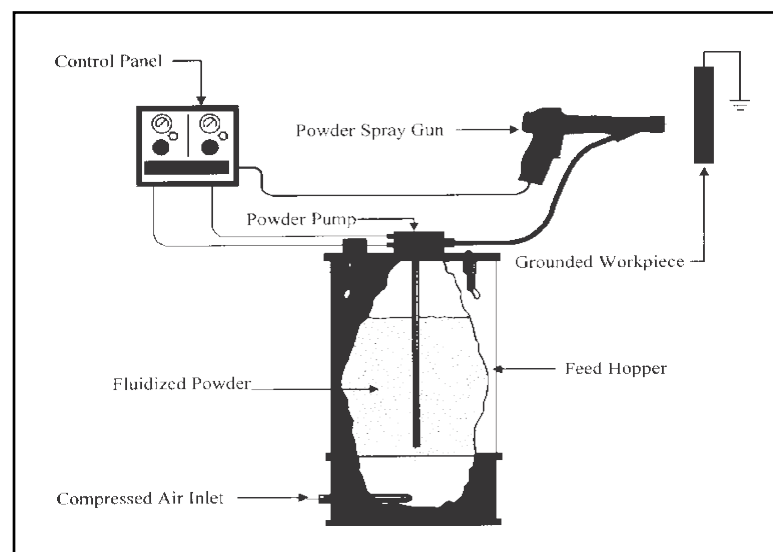

Figure 2.1 Single unit of electrostatic spray application system

These components are connected by all regulators and fittings, hoses and cables. With the fluidizing air on, the air/powder mixture will flow quite evenly through a hose system. The air pressure to the gun is controlled to give specified powder quality and powder output requirements, and the stability of the powder feed system can be controlled through an air flow meter. As to the corona gun, ionization charging, work through charge carriers which are produced by the spraying electrode, through impact ionization to give electrostatic charging of the powder by attaching to the surface of its particles. In the controller, a high frequency low voltage is generated from the principal voltage supply. Within the gun convert this to a high voltage. The electrical current is very low and compliance with regulatory standards is followed rigidly to ensure operator safety.

2.9 Literature Reviews

Improve corrosion protection with zinc [12-19]

In 2004, Marchebois et al. [12] studied the corrosion protection improvement of epoxy zinc-rich powder for coated steel in artificial sea water with conductive pigments such as carbon blacks. Characterize the cathodic protection ability and duration by open circuit potential measurements. Micro-Raman spectroscopy was used to identify the corrosion products and to measure the solution penetration of electrolytes inside the coatings. Two different effects were pointed out: the carbon addition was induced to increase the porosity and a galvanic action between zinc and carbon pigments. If the carbon amount is sufficient, the performance of the powder coatings was strongly improved.

In 2007, Meroufel et al. [14] studied the epoxy zinc-rich primer (ZRP) powder onto steel substrates with the effect of hydrochloride polyaniline (PANI-Cl) powder as a conductive pigment into formulations. The corrosion protection properties of coatings were studied by monitoring the free corrosion potential versus time and by using EIS on immersed in a 3% NaCl solution at ambient temperature. The results showed that the constant and cathodic corrosion potential was found for a long time up to 100 days of immersion. From EIS results, that higher impedance values of the coatings were found compared to those with liquid or other zinc-rich powder formulations containing carbon black.

Improve corrosion protection with polyaniline [20-40]

In 2005, José et al. [20] studied the corrosion protection of carbon steel coated with conventional thermoplastic polymers as a blend of poly (methyl methacrylate) with poly (butylmethacrlylate), phenoxy resin and a poly (vinyl chloride-co-vinyl acetate) 90/10 copolymer and compared with an alkyd resin containing 0.2, 0.4 and 0.6% (w/w) of polyaniline. The ability to protect metals against aqueous corrosion was investigated by laboratory accelerated tests. Field-tests in urban and marine environments were compared with respect to field tests was also evaluated in order to validate the accelerated cyclic tests. For both field and

laboratory conditions, it could be summarized that the alkyd resin with conductive polymer has higher protection against corrosion of the metal, degradation resistance of the coating. And the overall performances of the coated steel were also improved.

In 2008, Radhakrishan et al. [21] studied corrosion protection behaviors of epoxy type powder coatings by using specific grade of PANI with low doping. The corrosion resistance was tested by exposure to hot saline conditions followed by salt spray testing and also investigated by electrochemical impedance spectroscopy. The coatings that incorporated with PANI showed no degradation even after 1400 hours of hot saline condition. After the scratch of coatings, it exhibited self-healing property without rusting formation even after exposure to hot saline conditions. These results indicated that PANI could increase cross-linking density of coatings, which could be confirmed by DSC results. DSC showed a rise of barrier property and self-healing by PANI which could prevent corrosion of the underlying substrate.

In 2008, Kalendova et al. [23] studied the corrosion protection properties of epoxy enamel coatings containing PANI and PANI in combination with other anti-corrosive pigments such as zinc dust, $Zn_3(PO_4)_2 \cdot 2H_2O$, $Ca_3(BO_3)_2$ and $SrCrO_4$ have been tested. The adhesion, barrier, and anti- corrosion properties of the coatings containing PANI and selected chemically active pigments were investigated including the combination of PANI. The corrosion test was completely performed in the atmosphere of SO_2 and of NaCl. The study of the total anticorrosion efficiency of coatings with the PANI combination with zinc dust indicated that the PANI combined with a volume concentration (PVC) of 5% and zinc dust could result in high anticorrosion efficiency, which was higher than the coatings that modified with only zinc or PANI.

In 2009, Armelin et al. [25] studied the corrosion protection of solvent borne epoxy prepared by different conducting polymers when these materials were used as anticorrosive additives in the formulation such as polyaniline emeraldine salt, polyaniline emeraldine base, polyaniline emeraldine salt composite with carbon black, polypyrrole composite with carbon black and poly(3,4 ethylenedioxythiophene) doped with poly(styrene sulphonate). The corrosion protection was investigated by accelerated corrosion test using aggressive saline condition. Results showed that the corrosion protection of modified with addition of conducting polymers was higher than that of the unmodified coating. In contrast, the use of conducting polymer composite with carbon black reduced the efficacy of the coating and reveal that reduces the adherence of the paint to the steel. Results indicated that some conducting polymer compositions could be a suitable alternative choice to replace inorganic anticorrosive pigments in formulations.

In 2009, Akbarinezhad et al. [26] studied synthesized PANI as a corrosion inhibitive pigment in a solvent borne epoxy coating. An undoped polyaniline (PANI) was obtained by chemical oxidative polymerization. The corrosion protection performance of steel coated panels was evaluated by determination of open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) in 3.5% sodium chloride solution. Result showed that passivation effect of PANI could shift OCP to the noble region. Results also showed that undoped PANI paint coating was able to provide corrosion protection to carbon steel which was exposed in 3.5% sodium chloride solution.

In 2009, Radhakrishnan et al. [29] studied corrosion protection of moisture curable epoxy resin and ketimine coating systems on wet surface. Micaceous iron oxide (MIO) was used as pigment. Polyaniline and silica and talc were used as extender pigments. The pigment volume concentration (PVC) of the prepared paint was varied as 20, 25 and 30%. Result showed that, the coating with 20% PVC had higher corrosion protection than that of coating with 25 and 30% PVC. Polyaniline in the coating was found to offer protection in the scribed areas.

Synthesis of polyaniline [41-43]

In 2009, Blinova et al. [42] studied the preparation of polyaniline and polypyrrole in aqueous solutions at the same concentrations of hydrochloric acid. Aniline and pyrrole were oxidized with ammonium peroxydisulfate, which led to polyaniline and polypyrrole. The pyrrole was oxidizing faster than aniline. The yield increased when the proportion of oxidant-to-monomer molar concentration increased up to 1.5. The optimum stoichiometry of the oxidant-to-monomer molar ratio is 1.25. The conductivities of the polymers were a bit dependent on the oxidant-to-monomer ratio in the range 0.3–1.5. Outside this interval, the conductivity of both polymers was reduced.

In 2011, Bhadra et al. [43] studied the synthesis, processing and applications of polyaniline (PANI). PANI can be prepared by various methods. The obtained product could be varied from coarse to fine powder, fiber to nanofiber, thin film, etc. The properties of the obtained polymer also depended on the method of preparation. The conductivity of PANI depends on molecular weight, oxidant level, molecular arrangement, percentage of crystallinity, inter-chain separation and degree of doping. Therefore, various types of dopants could be used to improve the conductivity and processability of PANI.

CHAPTER III

EXPERIMENTAL

3.1. Material

1. Polyester resin, Synthese (Thailand)
2. Epoxy resin, Aditya Birla Chemicals (Thailand)
3. Levelling agent, Cytec industries (USA)
4. Degassing agent, Jingjiang hongtai (China)
5. Zinc dust, mean diameter 4 μm, Umicore (Malaysia)
6. Zinc flake, mean length 20 μm, Eckart (Germany)

3.2 Chemicals

1. Hydrochloride aniline, (Sigma-Aldrich Inc, USA)
2. Ammonium peroxydisulfate, (Sigma-Aldrich Inc, USA)
3. Hydrochloric acid, (Merck KGaA, Germany)
4. Acetone, (Merck KGaA, Germany)

3.3 Apparatus

1. High speed mixer ("Mixaco" Model mixer Lab CM 3)
2. Single screw extruder ("BUSS" Model PCS30-7D)
3. Ultra centrifugal mill ("Retsch" Model ZM-200)
4. Electrostatic spray gun ("ITWGema" Model OptiTronic)
5. Oven ("WTB Binder" Model FD-115)
6. DSC ("Perkin Elmer" Model Dimond DSC)
7. FTIR spectrometer ("SHIMADZU" Model IR Prestige-21)
8. Scanning electron microscope ("JEOL" Model JSM-6480LV)
9. Raman spectrophotometer ("Renishaw" Model Via Raman Microscope)
10. Gloss meter ("BYK-Gardner" Model micro-TRI-gloss)
11. Thickness gauge ("Fischer" Model Dualscope MPOR)

12. Impact tester ("Sheen" Model 1.8kg weight, 40" Tube)

13. Salt fog chamber ("Q-FOG", Model SSP 1100)

3.4 Experimental procedures

3.4.1 Synthesis of polyaniline

- Preparation of 1 M hydrochloric acid.

500 mL of DI water was added into a 1,000 mL volumetric flask, followed by 83 mL of 37% w/w hydrochloric acid and DI water was added to make up 1,000 mL solution.

- Preparation of 0.2 M aniline.

25.9 g of solid aniline hydrochloride was weighed and then dissolve into enough 1 M hydrochloric acid that it dissolves completely. Transfer this to a volumetric flask and 1 M hydrochloric acid was added to make up 500 mL solution. Solution was kept for 1 h at room temperature before use.

- Preparation of 0.25 M ammonium peroxydisulfate.

57.1 g of solid ammonium peroxydisulfate was weighed and then dissolve into enough 1 M hydrochloric acid that it dissolves completely. Transfer this to a volumetric flask and 1 M hydrochloric acid was added to make up 500 mL solution. Solution was kept for 1 h at room temperature before use.

- Preparation of polyaniline

A 250 ml of 0.20 M aniline was stirred by magnetic stirrer and then a 250 mL of 0.25M ammonium peroxydisulfate was added to the solution which was magnetically stirred for 60 min and left to polymerize for one day. Each resulting green suspension product was filtrated in a Buchner funnel and washed with 0.2 M hydrochloric acid and acetone until the filtrate became colorless. The resulting dark green product was dried in air and characterized by Infrared Spectroscopy (IR) and conductivity was measure by four point probe meter.

3.4.2 Preparation of epoxy polyester powder containing zinc and PANI

All formulations are given in parts-per-hundred resin (phr), where the mass of resins totals 100 and all other ingredients are given as a fraction of this mass. The following compositions have been used: epoxy resin (30% by weight), polyester resin (70% by weight), leveling agent (1 phr), degassing agent (0.3 phr), PANI (5 phr) and content of zinc dust and zinc flake was varied in formulations are shown in Table 3.1.

Table 3.1 Zinc and PANI content in epoxy polyester powder

Material	Contents (phr)				
Formulation no.	**1**	**2**	**3**	**4**	**5**
Zinc dust		50			40
Zinc flake			50		10
PANI				5	

Table 3.1 (cont.) Zinc and PANI content in epoxy polyester powder

Material	Contents (phr)				
Formulation no.	**6**	**7**	**8**	**9**	**10**
Zinc dust	40	35	30	25	20
Zinc flake	10	8.75	7.5	6.25	5
PANI	5	5	5	5	5

Table 3.1 (cont.) Zinc and PANI content in epoxy polyester powder

Material	Contents (phr)						
Formulation no.	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Zinc dust						40	
Zinc flake	50	40	30	20	10		30
PANI	5	5	5	5	5	5	

All ingredients were prepared to powder coatings as followed stage.

3.4.2.1 Weighing and premixing of raw materials

Each component is weighed and placed in a mixer. The purpose of premixing is thorough mechanical agitation to homogenize the distribution of all raw material and suitable for feeding to an extruder.

3.4.2.2 Extrusion of the premix

The premix is fed as a powder at room temperature into the single screw extruder which the extruder barrel is kept at temperature 70 ºC. The heat in the form of mechanical energy and direct heating is supplied to melt the carrier resin, which is then, along with all ingredients subject to shear to facilitate distributive mixing and produce a completely homogenous melt. The molten product discharge from extruder must be cooled rapidly for prevent premature reaction. After solidifying, the cooled strip need to broken up into suitable chips for feeding to a grinding atomizer.

3.4.2.3 Grinding of the chip

The chips are ground in an atomizer. The chips are fed into an enclosed grinding wheel with stainless steel pins, which cuts the chips down creating a fine powder and then sieve with 140 mesh size sieving.

3.4.3 Thermal properties of epoxy polyester powder

Differential scanning calorimetry (DSC) was used to evaluate the thermal behavior of powder coating. A few milligram samples of powder sample were placed in aluminium DSC pans and then recorded from room temperature to 280 ˚C at heating rates 10 ˚C/min. The samples were then cooled to at least 30 ˚C and heating route was repeated at a rate of 10˚C/min, and recorded the heating curve until all transitions have been completed. Glass transitions temperature (Tg) of cured powder was determined.

3.4.4 Preparation of coated carbon steel sheet

Carbon steel sheet (7 cm x 15 cm x 0.8 mm) were polished with fine emery paper and then cleaned with xylene. Coating the carbon steel with electrostatic spray gun used for deposition of powder coating which was held at 80 kV potential with respect to the steel sheet that was grounded. After that the coated steel sheets were placed in oven for curing at 180 ˚C for 15 minutes and then cooled in air.

3.4.5 Coating thickness measurements

The Dualscope MPOR from Fischer is used to measure the thickness of coated layer with magnetic inductive method based on ASTM B 499. Place gauge probe in a vertical and level position on top of the surface. Report the thickness reading indicated on the thickness gauge in micron.

3.4.6 Gloss measurements

The micro-TRI-gloss from BYK-Gardner is used to evaluate of specific light reflected from a surface at given angle. Put the gloss meter in a vertical and level position on top of the surface and all reported values are the average of three reading. Use the 60 angle as the default mode. The specimen shall have substantially plane-parallel surfaces free of blemishes, cratches, grease s and dust. The procedure used to measure the gloss was based on the ASTM D 523.

3.4.7 Adhesion test

Measuring adhesion by Tape Test was based on the ASTM D 3359. It is typically used method for checking the adhesion of a coating system on a substrate. Create a grid structure of 6 parallel cuts, through the cured film to the substrate surface. The cross hatch spacing has fixed of 2 mm. Adhesive tape is applied over area of cuts by pressing down tightly against coating to eliminate voids and air pockets. Pull off the tape sharply at a right angle to the plane of the surface in an attempt to detach the squares of the grid.

3.4.8 Impact resistance

The impact resistance of a powder coating applied to a carbon steel sheet follow ASTM D 2794 could be determined by using a 15.9 mm (5/8 inch) diameter semi-cycle head impact tester, 1.8 Kg-m range, such as a Sheen impact tester. In order to check direct impact, the coated sheet should be placed on the table with the coated surface up. Then the cylinder weights were raised to top and allow dropping freely. Continue to drop cylinder weights at lesser heights until an impact is made that does not crack the coating. Report result in kilogram-metes (height in meters multiplied by cylinder weight in kilogram equals kilogram-metes).

3.4.9 Salt spray test

The coated sample was scored the coated layer deeply enough in order to expose the base metal using a sharp knife to create a cross mark. The scratch lines (scribe) were made through on the corner of the sample to the opposite corner of the sample. The adhesive tape was used to seal the edges and rear side of the steel sheet. The sample was exposed for 240 hours in   5 wt% salt solution according to ASTM B 117. Then, the sample is removed and wiped. The evaluation of corrosion process was based on ASTM D 1654.

Select the formulation that had good corrosion resistance from result of salt spray test to evaluate corrosion resistance by electrochemical impedance spectroscopy (EIS), the microstructure and surface morphology of the coated sample were determined by Scanning electron microscope (SEM) and corrosion product by Raman spectroscopy.

3.4.10 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to determine the corrosion behavior of the samples during immersion in 3.5% NaCl at room temperature. A three-electrode set-up was used with impedance spectra to record the results. A saturated calomel electrode (SCE) was used as the reference electrode and a stainless steel was used as a counter electrode. EIS was performed between 0.01Hz - 65 kHz frequency range using a frequency response analyzer (Autolab PGSTAT 30,

Eco-Chemie, Netherlands). The amplitude of 10 mV was used as the sinusoidal voltage signal.

3.4.11 Scanning electron microscopy

SEM was used to study the surface morphology of different samples before and after exposure to salt spray. A variety of signals at the surface of solid specimens was generated by a focused beam of high-energy electrons. The obtained electron signals revealed information about the sample including external morphology and orientation of materials.

3.4.12 Raman spectroscopy

Zinc corrosion product was analyzed by Raman spectroscopy. This is a spectroscopic technique obtained by a variation of light-scattering technique. Visible light will pass into the sample before scattering according to wavelength. An inelastic component will present the same scattered wavelength. Normally, the light exchanges energy with the molecule. This inelastic scattering causes light of slightly longer or shorter wavelengths to be scattered. As above, there is an increase or decrease in a specific molecular motion.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The characteristic of PANI

The PANI was synthesized by the oxidative polymerization of hydrochloride aniline by ammonium peroxydisulfate in hydrochloric acid as in equation 1.

$$4\,n \left(\bigcirc\right)-NH_2.HCl \; + \; 5\,n\,(NH_4)_2S_2O_8 \longrightarrow \left[-NH-\bigcirc-\underset{Cl^\ominus}{\overset{\oplus\cdot}{NH}}-\bigcirc-NH-\bigcirc-\underset{Cl^\ominus}{\overset{\oplus\cdot}{NH}}-\bigcirc\right]_n \quad (1)$$
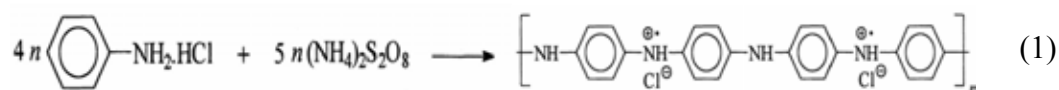
The synthesized PANI was characterized by Fourier transform infrared techniques (FT-IR). The FT-IR spectrum of the compound is shown in Figure 4.1.
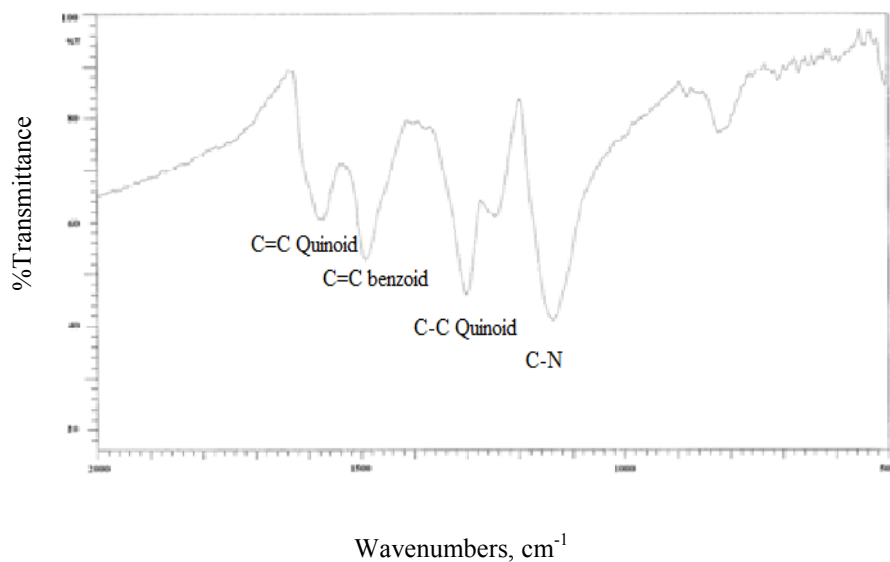
Figure 4.1 FTIR spectrum of PANI

The IR spectrum (Fig. 4.1) of the synthesized PANI is in a good agreement with previously reported results [44-47]. The main peaks at 1570 cm^{-1} and 1490 cm^{-1} in the spectrum correspond to quinoid ring and benzenoid ring stretching deformation. The band at 1300 cm^{-1} corresponds to C-N stretching of primary aromatic amine. The band at 1246 cm^{-1} is characteristic of the conducting protonated form and interpreted as a C-N stretching in the polaron structure. The 1136 cm^{-1} band is assigned to a vibration mode of the –NH$^{+=}$ structure, which is formed during protonation.

The conductivity of PANI was checked by the four probe method using a Keithley current source and the room temperature. Electrical conductivity was in range of 3 to 4 x 10^{-2} S/cm. It suggested that moderately doped PANI was obtained in acidic media [21].

4.2 Formulation of epoxy polyester powder containing zinc and PANI

The epoxy polyester containing zinc and PANI is prepared at described in Chapter 3. Epoxy polyester powder coatings compose of both epoxy resins and carboxyl-terminated polyester resins. Totals 17 formulations prepared for studying the effect of zinc content which combined with PANI 5 phr followed Radhakrishnan et al [21] reported that the polyaniline generates an electrical field which restricts the flow of electrons from the metal to outside oxidising species in order to prevent the corrosion. In this study, hydrochloride polyaniline was chosen, because it is easy to synthesise [40-43] and had good performance for anti-corrosion in other research [20-40]. In previous study of Meroufel et al [7] reported epoxy-based ZRP containing 50 wt% of zinc in order to increase the electronic conduction paths between zinc particle inside the coating, the zinc mixture of spherical (mean diameter of 30 μm) and flake (mean length of 5 μm) in ratio 4:1 was used. It was found that the cathodic polarization duration of formulation with zinc mixture 50 wt% is higher than the formulation with zinc dust 70 wt% and tends to the cathodic polarization duration is longer if more zinc particle is involved in the conduction process with conductive pigment is devoted to improve electrical contacts between zinc particle. In this study, we chose zinc dust (mean diameter of 4 μm) due to the zinc dust particle size affects the anti-corrosion coating properties: the smaller zinc powder particles give the

higher anti-corrosion efficiency in the coating [19] as the result of clogging of pores between particles with the oxidation zinc products on the transition from electrochemical action mode to the barrier mechanism was considered. Free spaces between the particles of large particles are much larger than small particles. In other research, different average size of zinc flake can be found between 5 to 50 μm and we beside to used zinc flake with mean length of 20 μm, that a medium size for keep the large surface of zinc flake particles cause a better contact for secures electrical conductivity.

4.3 Thermal properties of epoxy polyester powder containing zinc and PANI

Thermal properties of epoxy polyester powder were performed using a "Perkin Elmer" Model Dimond DSC. The experiments were used to monitor the thermal behavior of powder coatings. Figure. 4.2 is a typical DSC spectrum of epoxy polyester powder formulation no.6 in first heating rout by dynamic experiment, heating from room temperature to 280°C at scanning rate 10 °C/min. The inflection point by a sudden increase of the specific heat that shown the beginning of the melt. The melting point can be considered a type of softening of system and thus can be related to the storage stability of the powder. The instability of powders storage is generally induced by physical softening and consequent sticking together of the powder particles. The result of the above melting temperature is a bad or unavailable of free-flow properties or starts caking or blocking that resulting in a difficulty or impossibility for application of the powder [49].
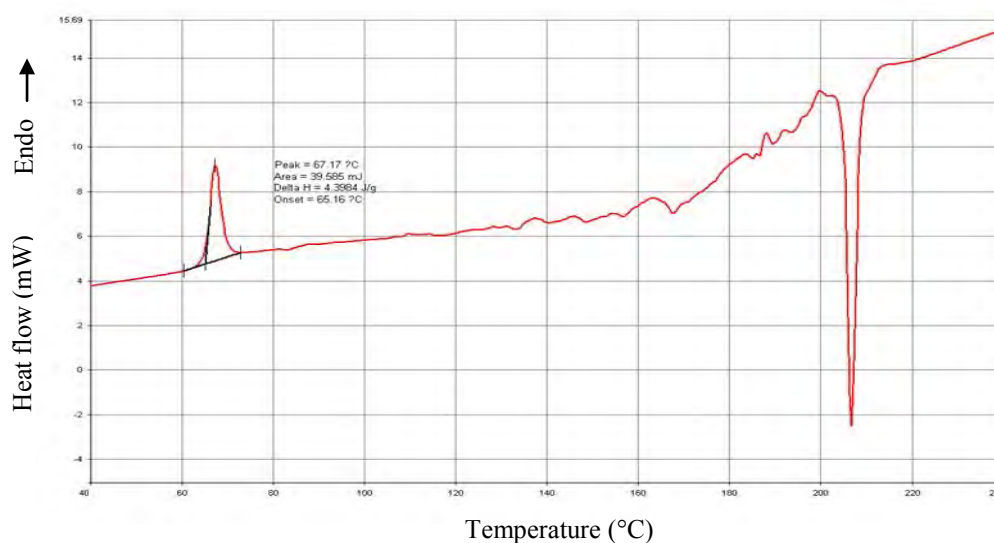
Figure 4.2 Typical non-isothermal DSC spectrum of epoxy polyester powder
containing zinc and PANI (Formulation no. 6)

Glass transition temperature is useful of assessing the degree of cure of a
powder. By cooling of the same sample under liquid nitrogen and then heating from
room temperature to 150°C at scanning rate 10 °C/min, the Tg of the cured film is
obtained. The Tg is definable as the temperature at which an amorphous material
changes from glassy to a solf or rubbery state [54].
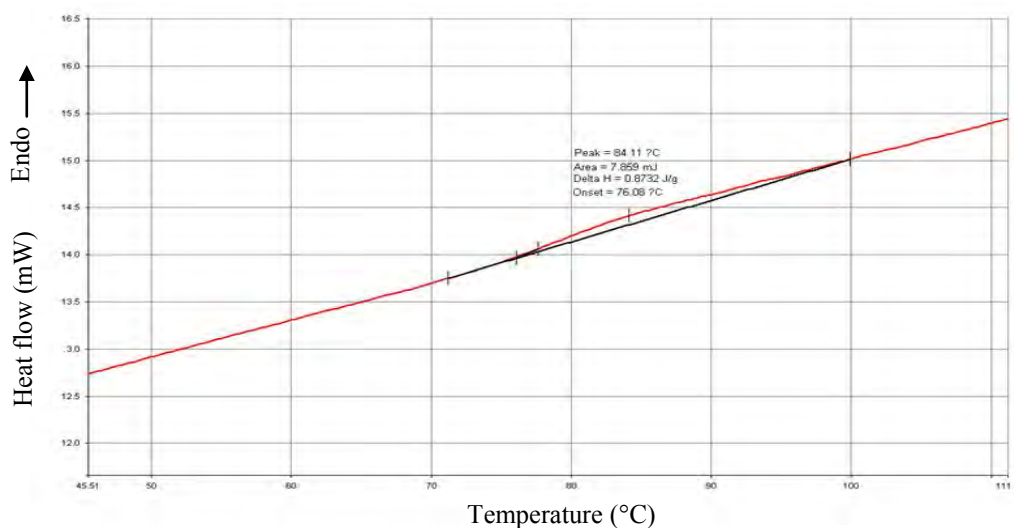
Figure 4.3 Typical DSC spectrum of cured epoxy polyester film containing zinc
and PANI coating no.6 for assignment of Tg.

From Table 4.1, the result showed that when compared to coating no. 1 that is pure epoxy polyester, melting point of all formulation was similarly in range 64-69 ˚C.

Table 4.1 Melting point and glass transition temperature of epoxy polyester containing zinc and polyaniline.

No.	Zinc dust (phr)	Zinc flake (phr)	PANI (phr)	Melting point (˚C)	Tg (˚C)
1	0	0	0	65.86	75.70
2	50	0	0	66.30	78.09
3	0	50	0	65.12	80.05
4	0	0	5	67.30	72.43
5	40	10	0	64.79	79.75
6	40	10	5	67.34	84.11
7	35	8.75	5	67.04	83.58
8	30	7.5	5	67.07	82.72
9	25	6.25	5	66.38	80.62
10	20	5	5	66.32	79.80
11	0	50	5	69.72	87.56
12	0	40	5	68.70	86.89
13	0	30	5	68.36	85.88
14	0	20	5	68.57	85.11
15	0	10	5	68.54	83.22
16	40	0	5	68.29	77.82
17	0	30	0	67.52	80.00

The Tg that obtained from DSC result. There is considered that the Tg of epoxy polyester containing zinc and PANI had effected from many factors, one from zinc content in formulations that resulted from coating formulations   no. 6 – 10 and coating formulations no. 11 – 15, the Tg was decreased with decreasing zinc content according to rigid characteristic of zinc.   Moreover, the Tg of coating no. 6

and coating no. 11 that containing zinc and PANI are higher than coating no. 5 and coating no. 3 that has containing only zinc in same concentration, which indicates higher cross-link density. The change in the glass transition temperature with increasing cross-link density through following equation [20]:

$$\Delta Tg = Tg\text{-}Tg(0) = \frac{5}{(M_c/M) \times N_{rot}}$$

Where Tg(0) is the glass transition for uncross-linked sample, M_c is the molecular weight between cross-links, M is molecular weight of the whole linear chain and N_{rot} is degree of freedom for rotation of the group between cross-link. PANI effected to Tg of due to higher cross-link density of epoxy with amino terminal group in PANI [21].

4.4 Coating thickness

An epoxy polyester powder was applied to the steel sheet using Gema electrostatic spray gun. The powder coated samples were place to cure in an oven for about 15 min at 180 ℃. These powder coatings in this studied was designed to perform their intended function when a tight thickness range as 40-60 μm that is thin film layer when compared to other commercial or other research which normally controlled film thickness in range minimum 80 μm . This ensures optimum product performance for minimize cost with low film thickness. Many physical and appearance properties of the finished coating are affected by the film thickness. Film thickness can affect the surface appearance, gloss, color, adhesion to substrate, impact resistance, flexibility, hardness, chip resistance, weathering resistance, edge coverage and resistance to corrosion of the coating. Powder sprayers attempt to apply an even coat meeting that range. Results of film thickness measurements enable the sprayer to adjust their process. The thickness of cured powder was measured using a Fischer Dualscope MPOR instrument. Measurements were carried out on a set of three different replicate samples and if the film thickness of coated sample had out of controlled range that was rejected. The film thickness of epoxy polyester containing zinc and poly aniline coated on of film thickness don't relate to the formulation due to

steel sheet that obtained as shown in table 4.3. Results of film thickness don't relate to the formulation due to we use manual spray process and adjust our process for obtaining the film thickness in controlled range.

Table 4.2 Film thickness of epoxy polyester containing zinc and PANI

No.	Zinc dust (phr)	Zinc flake (phr)	PANI (phr)	Thickness (µm)			
				Min.	Max.	Avg.	SD.
1	0	0	0	48	60	56.5	3.7
2	50	0	0	48	57	52.4	3.2
3	0	50	0	45	56	49.9	3.0
4	0	0	5	48	60	53.0	4.1
5	40	10	0	45	60	55.3	4.4
6	40	10	5	54	60	57.7	2.3
7	35	8.75	5	48	60	54.7	4.7
8	30	7.5	5	46	60	53.0	5.0
9	25	6.25	5	51	60	55.8	3.1
10	20	5	5	52	60	57.8	2.8
11	0	50	5	48	60	52.9	4.0
12	0	40	5	50	60	53.8	2.7
13	0	30	5	50	60	56.8	3.0
14	0	20	5	46	58	56.1	4.4
15	0	10	5	48	60	55.4	3.6
16	40	0	5	45	60	54.4	5.3
17	0	30	0	48	58	53.5	4.0

4.5 Evaluation of physical and mechanical of coated film

Mechanical properties of coated layer such as adhesion and toughness are importance characteristic of coatings. Adhesion is the ability of coating to resist removal from the surface to which it is applied. The toughness can be defined as the ability of a coating to resist an impact without cracking or destroying which is measured impact resistance with the falling weight test. The results of physical and mechanical test are given in Table 4.3.

Table 4.3 Physical and mechanical data of epoxy polyester film containing zinc and polyaniline.

No.	Adhesion	Impact resistance (Kg.m.)	Gloss (%)
1	5B	> 1.8	107.0
2	5B	0.6	89.6
3	5B	> 1.8	59.7
4	3B	0.1	95.0
5	5B	1.7	79.7
6	5B	> 1.8	73.2
7	5B	> 1.8	73.3
8	5B	> 1.8	73.9
9	5B	0.5	78.6
10	5B	0.3	79.3
11	5B	1.5	30.4
12	5B	> 1.8	46.1
13	5B	1.2	57.6
14	5B	0.8	65.5
15	5B	0.6	73.2
16	5B	0.6	77.3
17	5B	> 1.8	67.2

*Adhesion test by tap test result: (5B) None remove, (3B) 5-15% of area remove

The simple method of testing coating adhesion was test according to ASTM D 3359. The cut surface is observed the degree which the coating is removed which compared with standards. The results were shown in Table. 4.3. The coating no.4, which is epoxy polyester containing only PANI had poor properties in adhesion and impact resistance. This indicates that a curing of coatings had not been fully completed [10], but in other formulation did not have adhesion problem.

Impact resistance is used in an attempt to simulate the knocks and blows that can cause deformations or dents to a product during its lifespan. This technique involves dropping a weight of known mass and from a known height on to coated layer under assessment and reported values is the highest level of impact at which the coatings showed no cracking or other failure. Result showed that the coating formulation that containing zinc flake (coating no. 3) had impact resistance higher than formulation containing zinc dust (coating no. 2) or zinc dust combined with zinc flake (coating no. 5). Specially, in formulations that containing zinc dust combined with zinc flake, the impact resistance was increased when add PANI into formulation. On the other hand, in formulation that containing only zinc flake, the impact resistance was decreased when PANI was added into formulation. This indicates that at the critical concentration of zinc and PANI the dropping of impact resistance is especially steep.

Figure 4.5 showed the impact resistance of epoxy polyester containing zinc dust blended with zinc flake and PANI decreased with the decrease of zinc content. In Figure 4.6, the impact resistance of epoxy polyester containing zinc flake and PANI showed the same tendency. It indicated that amount of zinc was necessary for packing in the binder and not attempt to agglomerate for decreased the impact resistance.
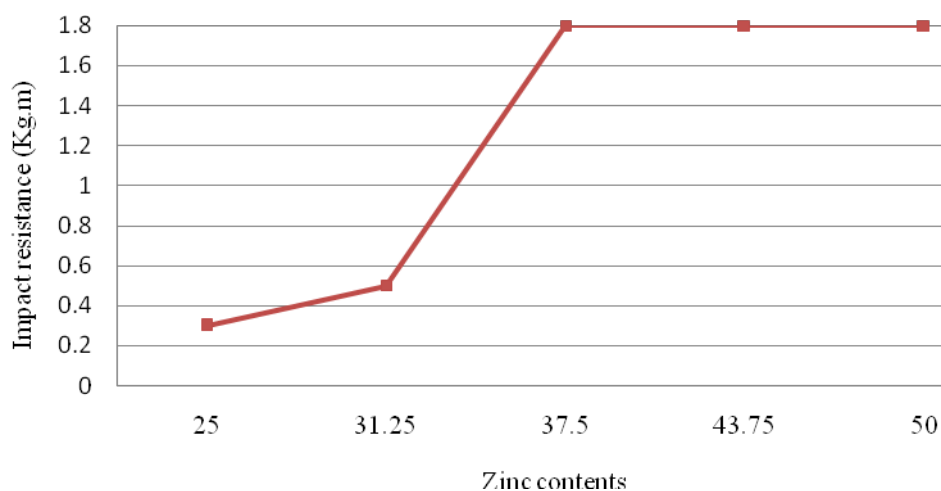
Figure 4.4 Effect of zinc content on the impact resistance of epoxy polyester containing zinc dust blended with zinc flake and PANI
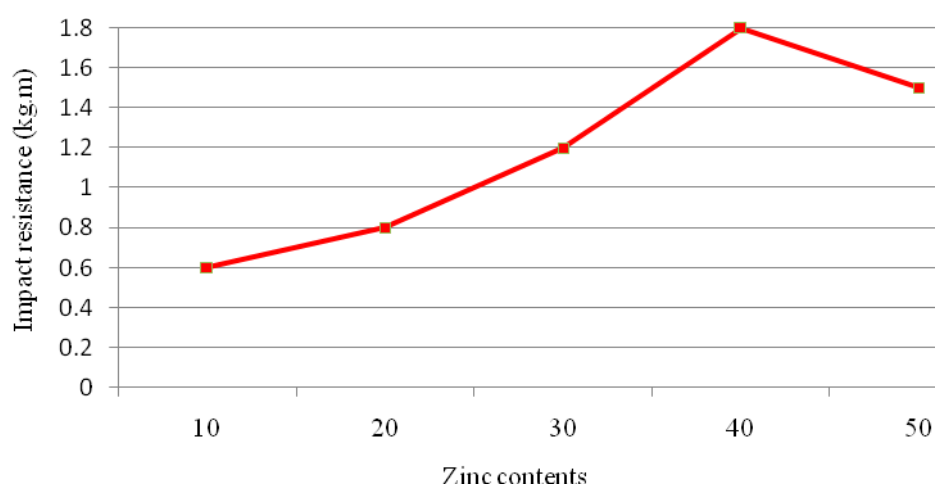
Figure 4.5 Effect of the zinc flake contents on the impact resistance of polyester containing PANI

The gloss of coated layer is not an important property from the anti-corrosion coating, but on the basis of differences between zinc content, optimum zinc particle packing in the coating can be evaluated. A rapid loss of coating film glosses is observed in zinc flake, however zinc dust and PANI are effect to the gloss of the coating too. The gloss of coating no. 11 is lowest with contain both of zinc flake 50 phr and PANI 5 phr. Measuring the gloss of coating have shown that decreasing the

zinc concentration entails increasing gloss as result of coatings no. 6-10 and coatings no. 11-14.

4.6 Evaluation of salt spray test

The performance of the coating was confirmed by using additional assays with the standardized salt spray test method (ASTM B117). Accordingly, steel sheets coated with the epoxy polyester powder containing zinc and PANI were submitted to a corroding environment in the salt spray cabinet for 240 hours, the corrosion on the coated sheets being determined after exposure periods.

According to ASTM standard method D 1654, the progress of rust indicates the loss of adherence near to the scribe mark. Figure 4.6 shows the coated steel sheets that were scrapped after 240 hours of corrosion assays. It is evident that the loss of adherence was significantly higher for the epoxy polyester coating without zinc and PANI, which indicate that PANI combination with zinc promote the adherence between the coating and the substrate and offer protection in the scribed areas. This is also reflected by the evolution of the area corroded under the coating layer.

    (a)   (b)   (c)   (d)   (e)
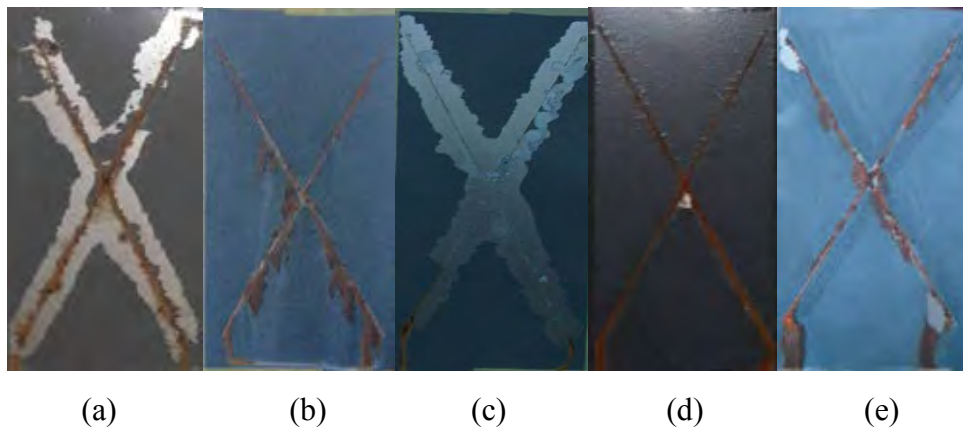
Figure 4.6 Scrapped coated carbon steel sheets after exposure to salt spray 240 hrs

(a) coating no.2 (b) coating no.3 (c) coating no.5

(d) coating no.6 (e) coating no.11

Table 4.4 Rating of failure at scribe mark according to ASTM D 1654

No.	Zinc dust (phr)	Zinc flake (phr)	PANI (phr)	Rating Number
1	0	0	0	2
2	50	0	0	4
3	0	50	0	9
4	0	0	5	2
5	40	10	0	4
6	40	10	5	8
7	35	8.75	5	4
8	30	7.5	5	4
9	25	6.25	5	3
10	20	5	5	2
11	0	50	5	8
12	0	40	5	6
13	0	30	5	5
14	0	20	5	5
15	0	10	5	4
16	40	0	5	3
17	0	30	0	3

*corrosion resistance increases from rating 0 to 10

The progress of rust indicates the loss of adherence near to the scribe mark. Table 4.4 represents the evolution of the corroded area under the film, which was evaluated according to the ASTM D 1654. The coated steel sheets that were scrapped after 240 hours of corrosion assays and gave the rating of failure at scribe mark. The rating of failure of steel sheets coated with the epoxy polyester containing with zinc and PANI formulations after 240 hours of salt spray test are evaluated. Visual inspection of the steel sheets submitted to corrosion test shows that the resistance against corrosion of the coating depends on the type and concentration of zinc. The

zinc flake particles exhibit worse result than the zinc dust at same concentration and when the amount of zinc decreased, rating of failure appeared to be lower (higher of failure). It suggested that the presence of zinc was necessary as the zinc corroded and blocked further corrosion attack. Formulation of zinc -pigmented coatings appears to be critical, because such a coating must be acted electrochemically and further will create an impermeable barrier for water, water vapor and on the occasion for other gases. The zinc flake particles can to secure the electrically conductive connections in the coating and at the same time, to create an impermeable barrier through their particle.

Specifically, the incorporation of PANI with zinc dust blended with zinc flake improves the protection imparted by the formulation that containing only zinc dust blended with zinc flake. It indicates that PANI combination with zinc promotes the adherence between the coating and the substrate and offer protection in the scribed areas. This is also reflected by the evolution of the area corroded under the coating layer. The corrosion protection of zinc-rich coatings relies on the electrical communication between this active zinc with the underlying metal, forming a galvanic pair, where the zinc acts as sacrificial anode (cathodic protection). Whereas in the conductive polymer containing coatings the main role played by a passivating oxide layer formed in the interface is one of the protection mechanism proposed and being usually accepted (anodic protection) [23].

4.7 Electrochemical impedance spectroscopy

The specimen (exposed area of 1 cm x 1 cm) immersed in 3.5% w/w NaCl solution equipped with a three-electrode arrangement. An Ag/AgCl electrode and a stainless steel counter electrode was used with the specimen. EIS plays an important role to monitor and predict degradation of organic coatings [19-25]. Fig.4.4 represents the typical Nyquist plots of powder coated sample in various immersion time in 3.5% NaCl electrolyte.
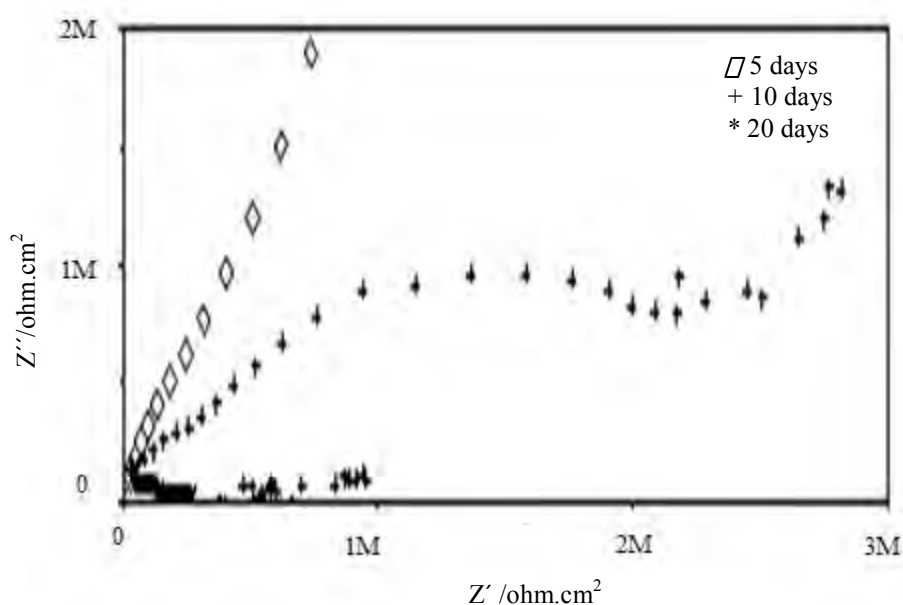
Figure 4.7 Typical impedance spectra of epoxy polyester powder coating no. 6 at difference immersion time in 3.5% NaCl electrolyte

From Fig. 4.7, when immersion time was increased (5 days), the radius of the semi-circle increased. The coating resistance increased during the first few days of immersion. This could be implied that the coating resistance was increased with the theory of electrochemical action of zinc particles such as zinc sacrificial corroding and form insoluble zinc salt. To support these results, the block of pores between particles on the transition from electrochemical action mode to the impermeability mechanisms was considered. When immersion time increased (20 days), the radius of the semi-circle also decreased. This is due to penetration of the electrolyte through the coating because of water uptake, of which the molecules of pure water diffused into the microspores of the coatings. It was suggested that decreasing of the coating

resistance value may be caused by the penetration of water and movement of ionic species among the coating layer, resulting in higher conductivity of the coating. At the beginning, the electrolytes penetrated through the coating layer, and created conducting paths at different depths within the coating [21] resulting in higher the corrosion rate, possibly through the presence of further pores in the coating or an increase in the area exposed at the base of the existing pores or flows [27].

Analyses of Nyquist plots suggest that different equivalent circuit models are necessary to fit the results, also shown in Fig. 4.8. These models reveal the electrolyte resistance, R_s, the coating capacitance, CPE, the coating resistance, R_p, and the Warburg resistance, Z_w. The EIS data were analyzed based on proposed equivalent electrical circuit using suitable fitting procedure elaborated by Frequency Response Analyser (FRA) software. The results of the analysis and calculation of the impedance data are shown in Table 4.5.

(a)

(b)
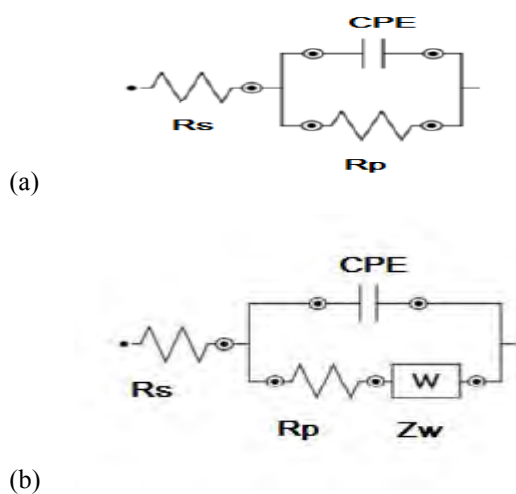
Figure 4.8 Purposed electrical equivalent circuits.

Table 4.5 Coating resistance of powder coated sample at different immersion time in 3.5% w/w NaCl solution

No.	Coating resistance (R_p)(Ωcm^2)			
	Immersion time (days)			
	0	5	10	20
2	9.12E + 01	-	5.78E + 02	1.36E + 06
3	-	-	2.69E + 06	1.08E + 06
5	2.60E + 06	1.85E + 06	9.41E + 04	7.37E + 04
6	8.09E + 02	3.47E + 02	2.54E + 06	1.83E + 05
11	-	2.77E + 06	1.94E + 06	5.32E + 02

*- (not applicable)

Table 4.6 Coating capacitance of powder coated sample at different immersion time in 3.5% w/w NaCl solution

No.	Coating capacitance (C_c)(F/cm^2)			
	Immersion time (days)			
	0	5	10	20
2	1.70E - 08	-	1.19E - 08	5.29E – 12
3	-	-	2.46E - 13	1.15E – 12
5	4.95E - 12	7.51E - 12	1.77E - 13	8.11E – 13
6	8.09E - 02	3.59E - 09	5.25E - 12	1.86E – 12
11	-	1.63E - 13	1.63E - 13	3.18E – 13

*- (not applicable)

From Table 4.5 that the coating resistance in 10 days immersion of coating no. 3 is higher than other coated system. This could be contributed to the large surface of zinc flake particle, which caused better contact and secured electrical conductivity than the zinc dust. By increasing immersion time (20 days), the coating resistance was decreased. The penetration of water and movement of ionic species through the coating layer, which increased the coating conductivity, could explain a decrease in the coating resistance. The conducting paths at different depths within the coating [6,26,27] were created by the penetration of the electrolyte through the coating layer.

The dielectric constants of organic coatings and water are about 4–8 and 80, respectively, at ambient temperatures [28]. Therefore, the permeation of a small amount of water through the coating could exhibit a relatively large change in the coating capacitance. Normally, the coating capacitance was affected by ingress of electrolyte and ions into coating pores. The improvement of coating characteristics such as ion resistance and crosslink density could highly decrease the coating capacitance [17, 29]. According to data mentioned in Table 4.6, the coating resistance decreased when coating capacitance was increased.

4.8 Scanning electron microscopy

Surfaces morphology was observed by SEM (JEO, Model JSM-6380). Figure 4.8 shows surface views obtained by scanning electron microscopy at before and after exposure to salt spray. These images show that zinc oxide was not observed before exposure to salt spray. The oxidation of zinc in the coating, create zinc corrosion, which is necessary to secure the barrier mechanism of the substrate [19]. The surface morphology of coating no.2, coating no.5 and coating no.6, before and after exposure to salt spray showed slightly difference but the surface morphology of coating no.3 had totally differences which cover the surface with zinc oxide. This phenomenon can be explained by the fact that the large surface of zinc flake particle causes a better contact and this secures electrical conductivity better than with zinc dust, which contacts each other by a rather small surface. For coating no. 3 (Fig. 4.9b) a corroded zinc layer was found into the outer part of coating body which reveal the pores in the coating takes place with zinc oxidation product form into the pores, which makes difficult to the electrolyte penetration. In coating no.11 that same concentration of zinc flake with coating no.3 which added PANI showed zinc oxide after exposure to salt spray was found on surface less than in coating no.3. This means that after zinc corroded, zinc corrosion products were not able to approach the coating/ electrolyte interface due to zinc salts can form coordination complexes with non-conductive PANI (emeraldine base) giving a zinc-PANI complex. These new products would be maintained within the coating at the neighborhood of the corroded zinc particles. Moreover, they could also contribute to the isolation of zinc particles as a protective barrier which reduces the corrosion rate of zinc [20].

Before exposure x 1,000   After exposure x 1,000   After exposure x 5,000

(a)

(b)

(c)
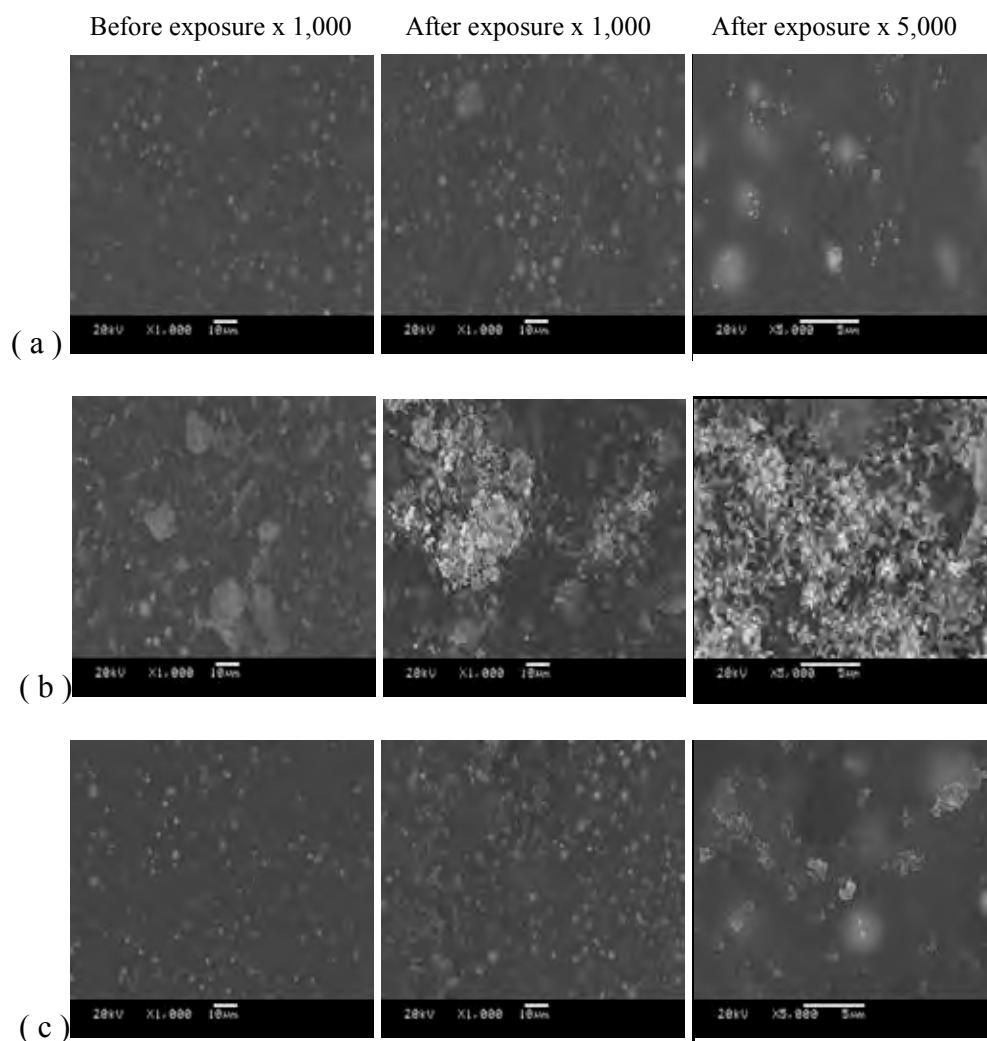
Figure 4.9 SEMs of the epoxy polyester powder before and after exposure to salt
spray 240 hours: (a) coating no.2 (b) coating no.3 (c) coating no.5 (d)
coating no.6 (e) coating no.11

Before exposure x 1,000   After exposure x 1,000   After exposure x 5,000

(d)

(e)
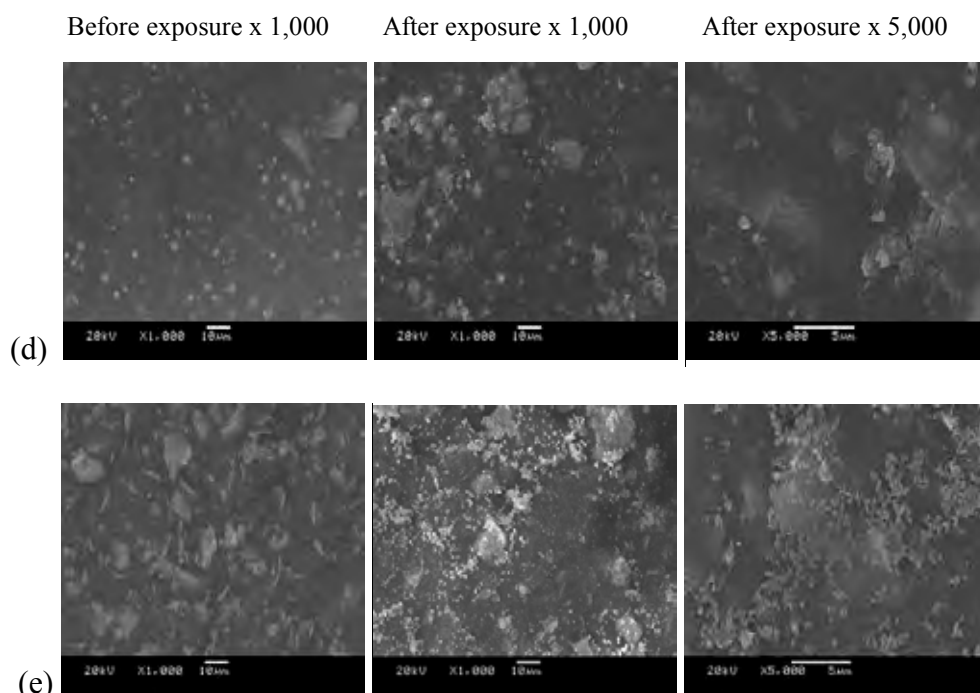
Figure 4.9 (cont.) SEMs of the epoxy polyester powders before and after exposure to salt spray 240 hours: (a) coating no.2 (b) coating no.3 (c) coating no.5 (d) coating no.6 (e) coating no.11

4.9 Raman spectroscopy

The coated sample before and after exposure to salt spray were analyzed by Raman spectroscopy. In the case of coating no.3, the characteristic peak was observed at 380 cm^{-1}. It indicated that the upper layer composition was identified to be a mixed zinc hydroxi-sulphate and zinc oxide [12].
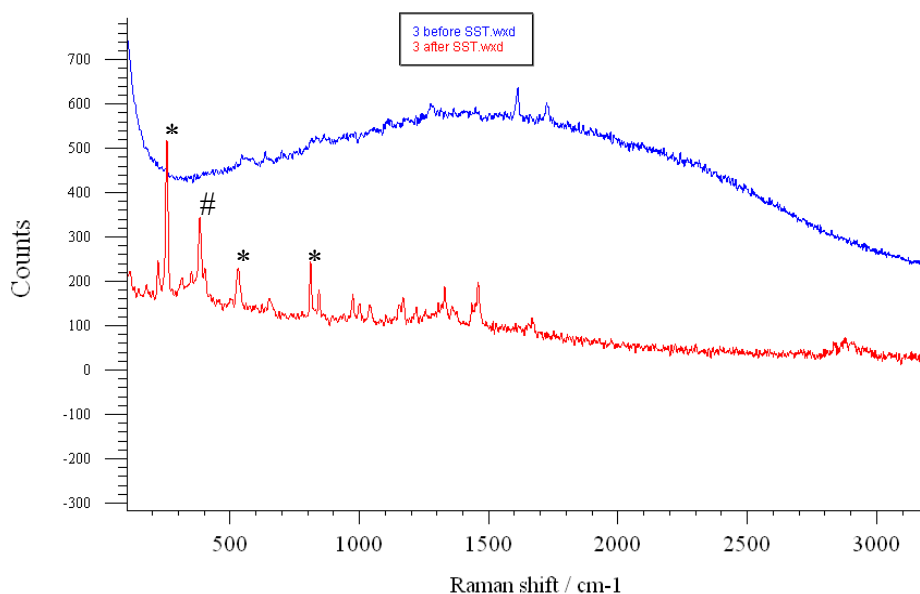
Figure 4.10 Raman spectra observed on coating no.3 before and after exposure to
salt spray 240 hours : (#) peak belonging to zinc oxide, (*) peak
belonging to zinc hydroxychlorode.

The band at 251, 528 and 727 are indicated to zinc corrosion product as zinc
hydroxychloride [56]. The zinc corrosion products are located in the outer part of the
coating near the coating/electrolyte interface which means that oxygen reduction is
located onto the zinc particle surface. Refer to Raman and SEM results, it can be
proposed that coating no.3 behaves like a zinc bare electrode just after immersion to
electrolytes and after that mainly like a barrier-type coating for anti-corrosion [19].

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

The conductive form of polyaniline (emeraldine salt) was synthesized and added to epoxy polyester powder containing zinc. The synergic effect of PANI and zinc was proved with various zinc contents to their anti-corrosion competency. The incorporation of PANI and zinc provided better anti-corrosion and mechanical properties when compared to epoxy polyester containing zinc or PANI alone.

The anti-corrosion of epoxy polyester containing zinc and polyaniline increased with the increase of zinc content. The ability of cathodic protection of steel with high content of zinc particles inside the film depends of the continuity of the electrical contact between the particles themselves and the steel substrate.

The coatings with zinc flake exhibit more appropriate anti-corrosion and mechanical properties compared to zinc dust in the same concentration. Zinc flake particles were able to provide the electrical conductive connection in the coating and create an impermeable barrier through their particles. Zinc flake can yield better results for almost every investigated property including the financial savings and a better anti-corrosion protection by barrier effect can be achieved.

5.2 Suggestion for the future work

Future work should be the study of the effect of zinc flake particle size in anticorrosive powder coating due to effect to the rate of filling the pore with the oxidation zinc products to create an impermeable barrier for anti-corrosion.

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APPENDICE

Appendix A

Adhesion test by tape test (ASTM D 3359)

    Procedure

Figure A-1 second cut

    1. Place the cutting tool on the sample. Gently press down and pull the tool towards yourself in one steady movement for 20 mm to create a series of parallel cuts. A sufficient pressure was required to ensure that the sample was cut right through the coating to the next layer of coating, or to the substrate. Then, place the cutting tool on the sample at 90° to the first cut and repeat the pulled-cutting to make a lattice pattern on the coating as presented in Figure A-1.

Figure A-2 Apply tape

    2. Brush the area to remove debris. And place the adhesive tape over the center of the lattice, using finger or a pencil eraser to smooth the tape to the sample, as shown in Figure A-2.
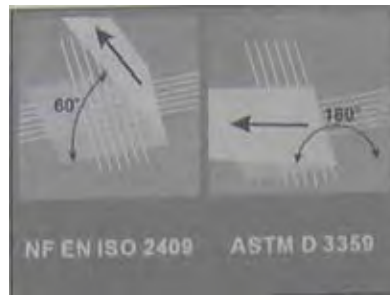
Figure A-3 Remove tape at 60^0 or 180^0

3. Remove the tape by pulling in a single smooth action at the angle of 60° or 180° as shown in Figure A-3

Table A-1 Standard ASTM D 3359
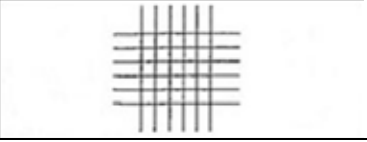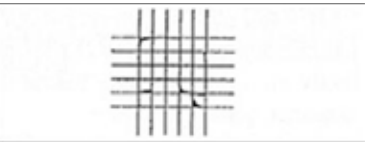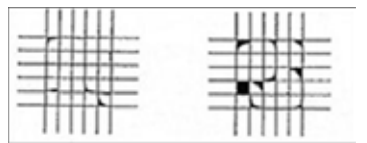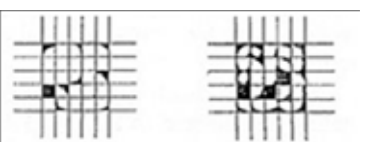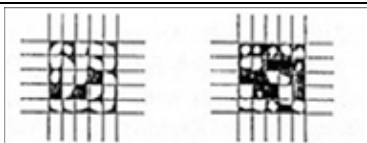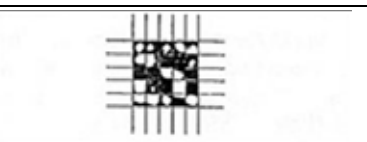
Classification	% of Area removed	Surface of Cross-cut area from which flaking has occurred for 6 parrallel cuts & adhesion range by %
5B	0 % None	
4B	Less than 5 %	
3B	5 - 15 %	
2B	15 - 35 %	
1B	35 - 65 %	
0B	Greater than 65 %	

Table A-2 Adhesive results of epoxy polyester containing zinc and polyaniline coated film
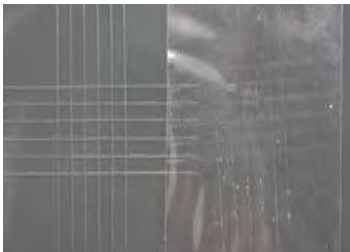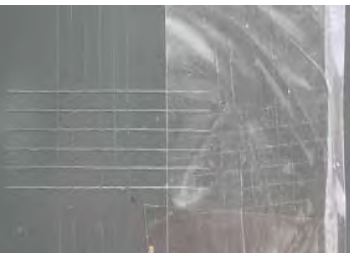
No.	Before	After	Classification
1			5B
2			5B
3			5B
4			3B
5			5B

Table A-2 (cont.) Adhesive results of epoxy polyester containing zinc and polyaniline coated film

No.	Before	After	Classification
6			5B
7			5B
8			5B
9			5B
10			5B

Table A-2 (cont.) Adhesive results of epoxy polyester containing zinc and polyaniline coated film
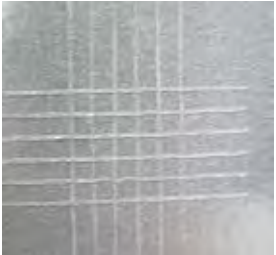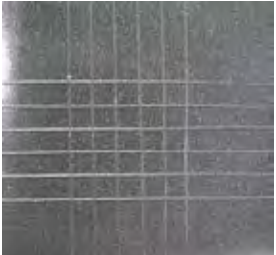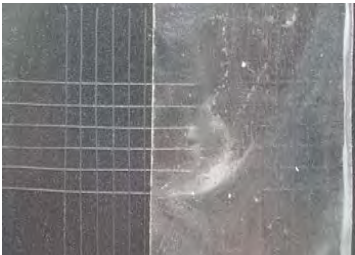
No.	Before	After	Classification
11			5B
12			5B
13			5B
14			5B
15			5B

Table A-2 (cont.) Adhesive results of epoxy polyester containing zinc and polyaniline coated film

No.	Before	After	Classification
16			5B
17			5B

*Adhesion test by tap test result: (5B) none remove, (3B) 5-15% of area remove.

Appendix B

Corrosion test by salt spray test (ASTM B 117)

Procedure

1. Preparation of coated steel sheet.

2. Edges and rear side of the coated steel sheet were properly sealed using the adhesive tape.

3. Cross scratch mark or scribed lines shall be made through the coating with a sharp instrument so as to expose the underlying metal before testing.

4. The specimen was subjected to salt spray test was carried out in a salt fog chamber following ASTM B117, in salt solution which consists of 5 wt% NaCl. The relative humidity of cabinet was 100% and temperature was 35°C.

5. Specimens scribed exposed to the salt fog were evaluated with loss of adhesion at the scribed and unscribed area.

Table B-1 Standard ASTM D1654.

Rating of failure at scribe

Representative mean creepage from scribe		
Millimeters	Inches (Approximate)	Rating Number
Zero	0	10
Over 0 to 0.5	0 to 1/64	9
Over 0.5 to 1.0	1/64 to 1/32	8
Over 1.0 to 2.0	1/32 to 1/16	7
Over 2.0 to 3.0	1/16 to 1/8	6
Over 3.0 to 5.0	1/8 to 3/16	5
Over 5.0 to 7.0	3/16 to 1/4	4
Over 7.0 to 10.0	1/4 to 3/8	3
Over 10.0 to 13.0	3/8 to 1/2	2
Over 13.0 to 16.0	1/2 to 5/8	2
Over 16 to more	5/8 to more	0

Table B-2 Failure result after exposure to salt spray of epoxy polyester powder containing zinc and polyaniline.
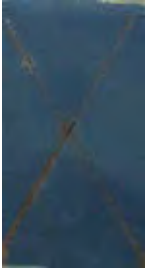
No.	Before	After
1		
2		
3		
4		
5		

Table B-2 (cont.) Failure result after exposure to salt spray of epoxy polyester powder containing zinc and polyaniline.
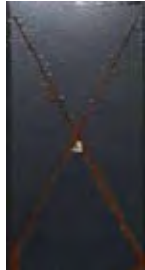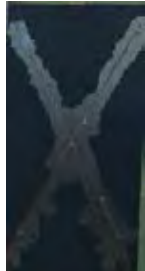
No.	Before	After
6		
7		
8		
9		
10		

Table B-2 (cont.) Failure result after exposure to salt spray of epoxy polyester powder containing zinc and polyaniline.

No.	Before	After
11		
12		
13		
14		
15		

Table B-2 (cont.) Failure result after exposure to salt spray of epoxy polyester powder containing zinc and polyaniline.

No.	Before	After
16		
17		

Appendix C

Table C-1 EIS spectra of coating no.2

	Nyquist plot	Bode plot
0day		
5days		
10days		
20days		
◇ 5days +10days *20days		
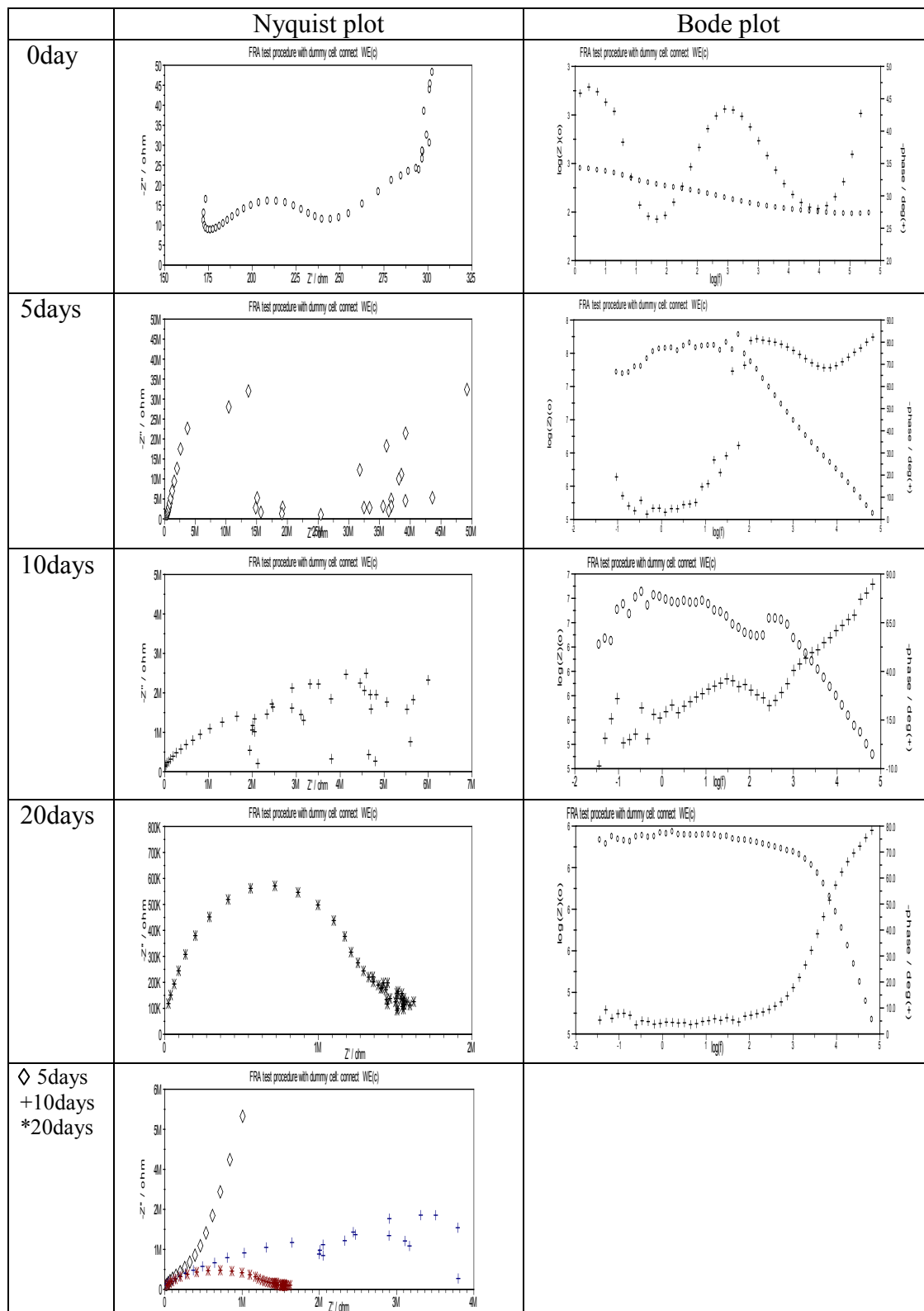
Table C-2 EIS spectra of coating no.3

	Nyquist plot	Bode plot
0day		
5days		
10days		
20days		
◊ 5days +10days *20days		
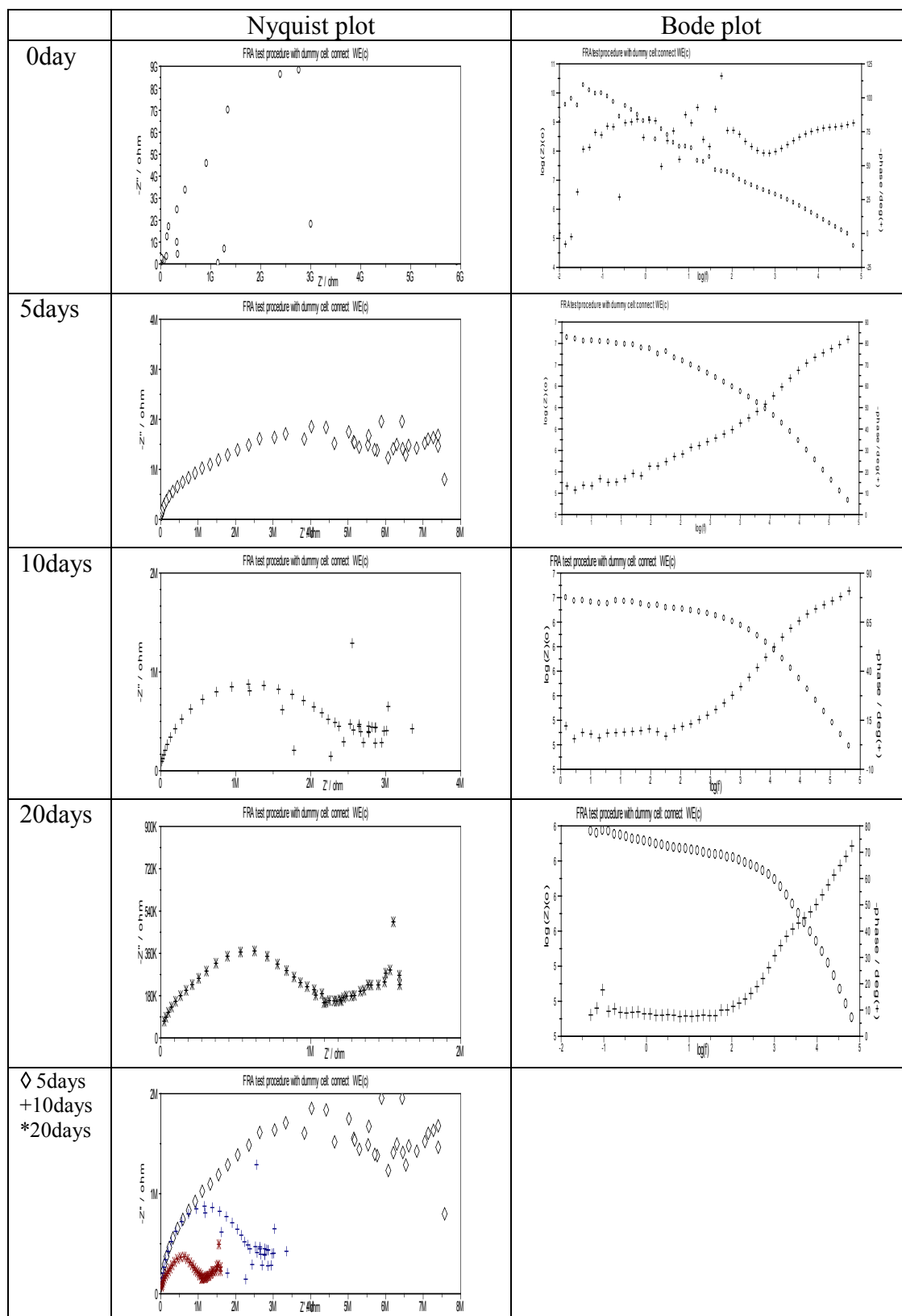
Table C-3 EIS spectra of coating no.5

	Nyquist plot	Bode plot
0day		
5days		
10days		
20days		
○ 0 days ◇ 10days +10days		
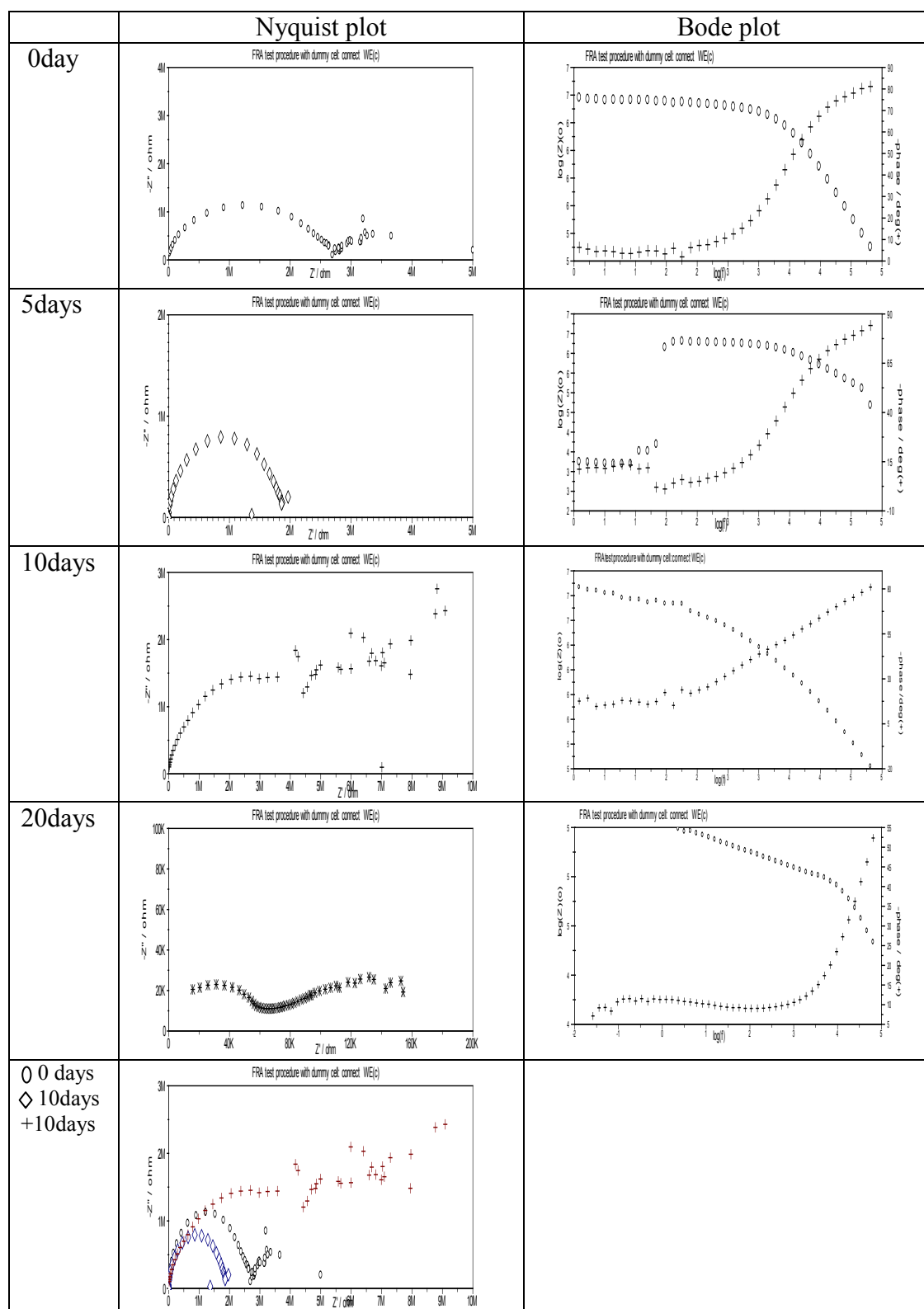
Table C-4 EIS spectra of coating no.6

	Nyquist plot	Bode plot
0day		
5days		
10days		
20days		
◊ 5days +10days *20days		

Table C-5 EIS spectra of coating no.11

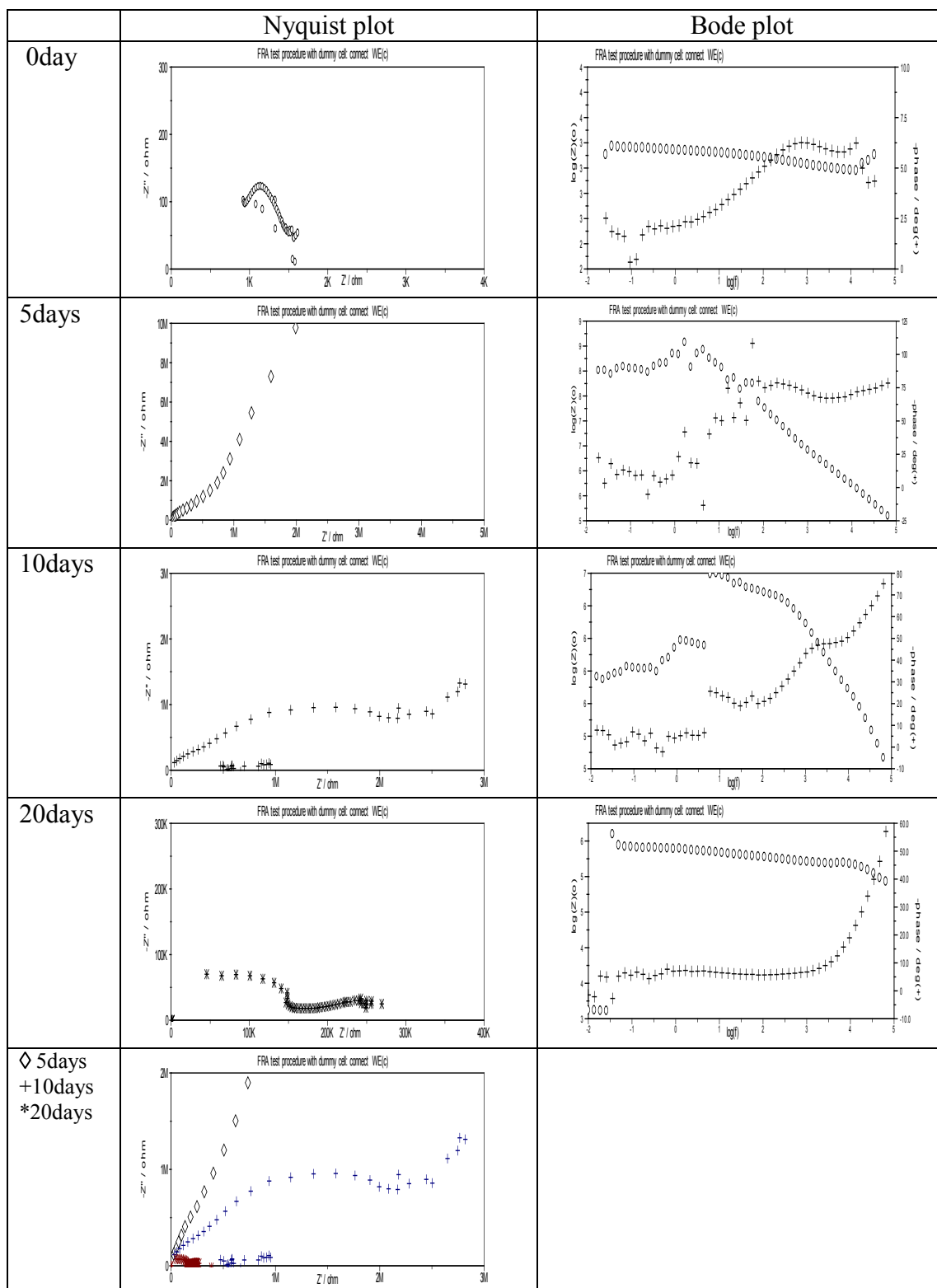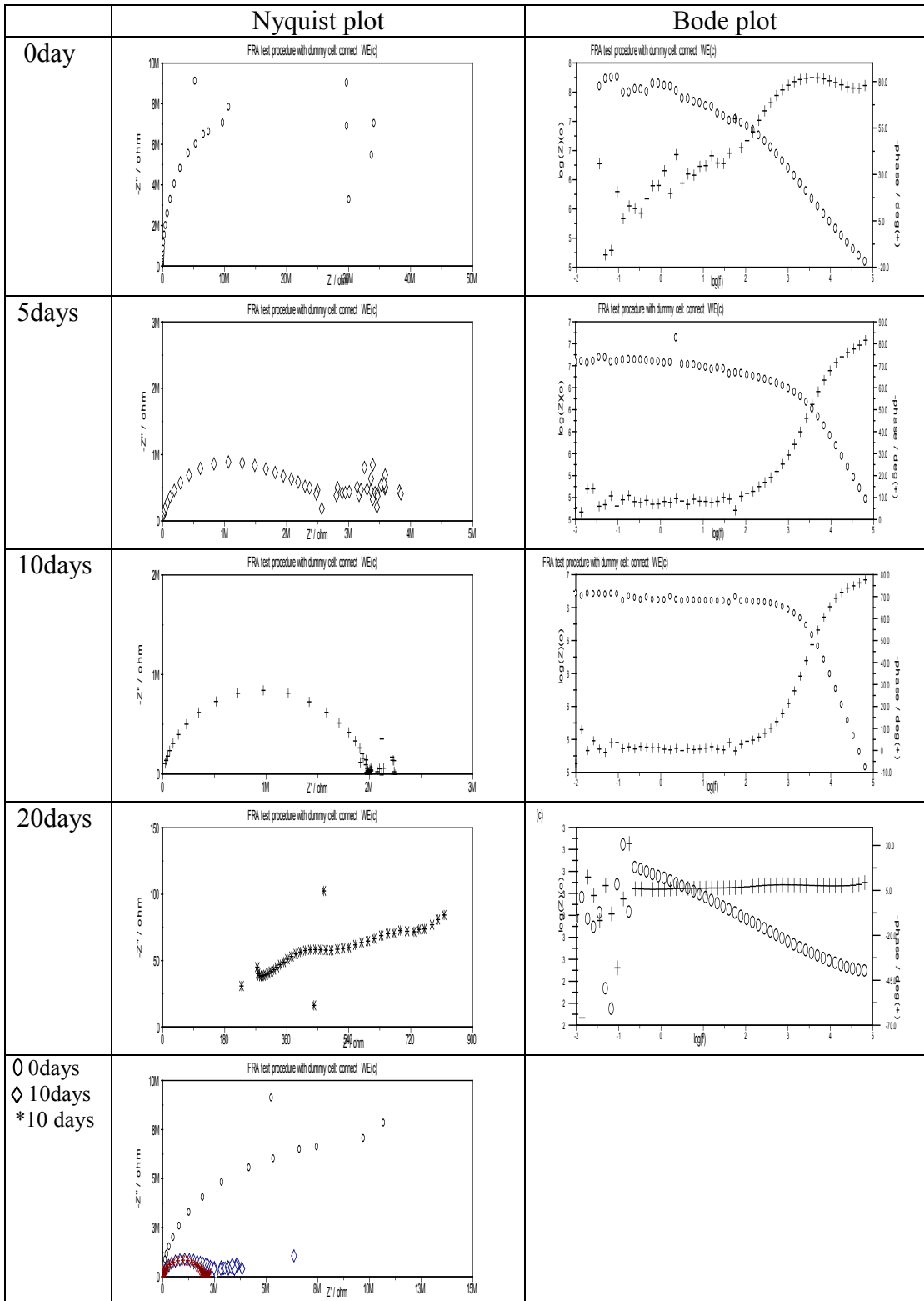|	Nyquist plot	Bode plot
0day		
5days		
10days		
20days		
0 0days ◊ 10days *10 days		

VITAE

Miss Sureerat Tipoo was born on December 5, 1981 in Nakornpanom, Thailand. She graduated with a Bachelor's Degree of Science from Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang. She has worked in Nippon Paint (Thailand) Company. She has studied for Master Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2010 and finished her study in 2012. Presentation in Pure and Applied Chemistry International Conference 2013.