CORROSION BEHAVIOUR OF MILD STEEL COATED WITH EPOXY-PANi-PHOSPHORUS THIN FILM IN 3.5 WT PERCENT NaCl SOLUTION

This report is submitted in accordance with the requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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Tajuk: **CORROSION BEHAVIOUR OF MILD STEEL COATED WITH EPOXY-PANi-PHOSPHORUS THIN FILM IN 3.5 WT PERCENT NaCl SOLUTION**

Sesi Pengajian: **2018/2019 Semester 2**

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Date : 26 June 2019

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

…….....

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ABSTRAK

Lapisan cat epoksi adalah salutan cat biasa yang digunakan dalam industry kerana sifatnya adalah pelekat yang baik serta penebat haba yang tinggi tetapi ianya mudah menyerap kakisan yang agresif menyebabkan kadar kakisan naik. Penambah pengisi di dalam system salutan cat epoksi digunakan untuk meningkatkan perlindungan dari system salutan daripada kakisan. Oleh itu, kajian ini dijalankan untuk menyiasat kelakuan kakisan keluli ringan yang bersalut dengan nanopartikel epoksi-polianilin-fosforus. Penyediaan bahan akan melibatkan epoksi resin, pengikat, PANi, dan F sebagai pengisi dalam sistem salutan. Salutan cat nanopartikel epoksi-PANi-F telah digunakan pada susbtrat keluli ringan dengan menggunakan kaedah berus tangan dan membiarkannya kering selama dua hari dalam suhu bilik. Pengisi nanopartikel PANi-F dimasukkan ke dalam sistem salutan cat epoksi dengan rumusan kandungan PANi-F berbeza dengan bermula dengan 0%, 2%, 4%, 6%, 8% dan 10% berat peratus nanopartikel PANi-F. tindak balas kakisan salutan epoksi-PANi-F ini akan ditentukan dengan menggunakan ujian Potensi Litar Terbuka (OCV). Penambahan sample keluli ringan 0% dan 2% berat peratus zarah epoksi-PANi-F dapat memberikan perlindungan yang lebih baik sebagai penghalang terhadapa aktiviti kakisan manakal sample salutan dengan 4%, 6%, 8% dan 10% berat peratus tidak dapat memberikan penghalang kakisan yang tepat. Sample dengan penambahan pengisi 10% berat peratus menunjukkan aktiviti kakisan terburuk dan telah dibuktikan oleh pemerhatian makroskopik dan mikroskopik selepas semua sample telah direndam dalam 3.5 berat peratus % larutan sodium klorida selama 30 hari. Ujian OCV yang dijalankan juga menunjukkan bahawa penambahan 10% berat peratus epoksi-PANi-F partikel ke dalam sistem salutan epoksi tidak dapat memberikan penghalang kakisan yang lebih baik dan menyebabkan substrat keluli ringan untuk menghakis.

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ABSTRACT

The epoxy paint coating is the common paint coating used in industries because of its properties are high thermal and good adhesions but its permeable to aggressive agent caused the corrosion rate increase. Addition of filler inside the epoxy paint coating system used to improve the corrosion protection of the coating system. Thus, this study was conducted to investigate the corrosion behaviour of the mild steel coated with epoxy-Polyaniline-Phosphorus nanoparticles. The preparation of the material will involve with epoxy resin, harderner, PANi and P particles as the filler in coating system. The epoxy-PANi-P nanoparticles paint coating was applied on the mild steel susbstrate by using hand layout method and let it cure for two days in room temperature. PANi-P nanoparticles was added into the epoxy paint coating system with different formulate of PANi-P content started with 0%, 2%, 4%, 6%, 8% and 10% weight percent of PANi-P. The corrosion behaviour of these epoxy-PANi-P was determined using Open Circuit Voltage (OCV) test. The mild steel sample coated addition of 0% and 2% weight percent of PANi-P particles able to provide better protection as a barrier against the corrosion activities while coating sample with addition of 4%, 6%, 8% and 10% weight percent of PANi-P particles was not able to provide the proper corrosion barrier. Sample with addition of 10% weight percent of PANi-P particles shows the worst corrosion activities and had being proven by both macroscopic and microscopic observation after all sample were immersed in 3.5% weight percent of sodium chloride solution for 30 days. OCV test also showed that the addition of 10% of PANi-P particles into the epoxy coating system were not able to provide better corrosion barrier and causes the mild steel substrate to corrode.

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DEDICATION

To my beloved parents

Rosdie Bin Sawal and Noorliza Binti Abdullah

To my siblings

Sharifah Noorazirah Binti Rosdie, Sharifah Noorshahirah Binti Rosdie, and Muhammad Aqief Zuhair Bin Rosdie

To my supervisor

Dr Mohd Shahadan Bin Mohd Suan

To all my friends and lecturers

For giving me moral support, money, cooperation, encouragement and understandings

Thank You So Much

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

NACE	-	National Association of Corrosion Engineers
PANi	-	Polyaniline
P	-	Phosphorus
Wt.%	-	Weight Percentage
OCV	-	Open Circuit Voltage
EIS	-	Electrochemical Impedance Spectroscopy
Fe	-	Iron
H_2O	-	Water
NaCl	-	Sodium Chloride
HCL	-	Hydrochloric Acid
AgCl	-	Silver Chloride
HNO3	-	Nitric Acid
HCIO4	-	Perchloric Acid
SiC	-	Silicon Carbide
Rct	-	Coating Resistance
Cdl	-	Capacitance Double Layer
Icorr	-	Corrosion Current
Ecorr	-	Corrosion Potential
CHCl	-	Concentration of Hydrochloric Acid
SACP	-	Sacrificial Anode Cathodic Protection

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ICCP	-	Impressed Current Cathodic Protection
PVC	-	Polyvinyl Chloride
SCE	-	Standard Calomel Electrode
FRA	-	Frequency Response Analyser
DC	-	Direct Current
ICP	-	Inherently Conducting Polymers
2D	-	Two Dimensional
3D	-	Three Dimension
Pt	-	Platinum
Ag	-	Silver
Hz	-	Hertz
MHz	-	Mega Hertz
%	-	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Introduction

For many decades metal work applications had been highly demanded for helping developing infrastructure in many countries for modern development. It is widely used in the industry for bridge building, vehicle, machines and other metal work because of their structure that is hard and high tensile strength. The most common metal that used in the industry is mild steel. Mild steel is a type of carbon steel with low level of carbon and has excellent machinability that can be easily shaped in any form. Mild steel is widely used the industry because of their characteristic that is high in tensile strength, malleability, ductile, good conductor for electricity and nonetheless it is cheaper compared to other steel. Thus, mild steel is widely used in machinery parts, cookware, wire, automobile parts, structural steel and fencing because of it can easily forged in variety of shapes to meet even specific designs.

However, corrosion can be easily occurred on the mild steel because of poor resistance towards corrosion and also due to low stability of the metallic state. This destructive and unintentional degradation of metal is a natural phenomenon causes the atoms on the surface of mild steel are oxidized; as oxygen is reduced, they tend to lose electrons to oxygen forming an oxide with the metal. The incompetent protection of corrosion on metal can causes catastrophe damage not only towards the physical structure of metal but also on economical production. From NACE report, National Association of Corrosion Engineers, the total cost of corrosion for five sector categories are up to $137.9 billion such on infrastructure, utilities, government, transportation, and production on manufacturing. Thus, the deterioration of mild steel need to

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be overcome particularly towards the mild steel properties for improving the economy of industry and expanding the safety of using mild steel.

In order to overcome the corrosion, the application of coating is one of the method. By using a paint application method, the liquid or powdery substances of coating are applied in thin coats produce solid coating bonds to the substrate. This method is to protect the metal substrate against deterioration process of the metal surfaces. The effectiveness of coating has been proven by the industry in improving protective coatings and cheaper compared to other preventive method. Coating by epoxy resin are one of the coating material used in coating application.

Epoxy resins as the coating agents has been widely used in coating industry which epoxy can be classified as one of the most versatile classes of polymer to be used as the coating as their excellent in overall properties over other (Wazarkar, 2018). Epoxy resins have excellent adhesions, good in mechanical properties, and their notable chemical resistance under different aggressive environment such as wet and high humidity conditions make it suitable as the coating materials (Svendsen, 2007). Other than used in coating application, epoxy resin have make their way in wide range of applications including in use in electronic/electrical components, high tension electrical insulators, fiber-reinforced plastic material, structural and engineering adhesives.

Another one of the coating agents that are widely used in coating industry is polyaniline (PANi). PANi-representative from the family of conducting polymers-is distinguished by easy synthesis and high environmental stability (Boeva, 2014). PANi is recognized as one of the best candidates for enhancing anticorrosion properties of coating due to its environmentally friendly anticorrosion ability, ease of preparation, excellent environmental stability and interesting redox properties that are associated with the chain of nitrogen (Al-Dulaimi, 2011). Although, the application of paint coating in industry is limited due to poor impact resistance and stress cracking (Conradi, 2014). Because of the lack of preventing stress cracking, studies are carry out to improve PANi adhesive by adding additive material into PANi adhesive.

Phosphorus (P) is the most common material in the used as retardant to its distinctive structures and useful properties. It is thermodynamically stable form of phosphorus at room temperature with heat of formation. P has a unique structure and is the reactive allotrope, a result of its interlinked double bond where each atom is bonded to two other atoms. P have excellent properties in both optical, mechanical properties and also high charge mobility. It is also believed that P can be used in coating application as the enhancement material. P can also

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be a promising candidate for solar water splitting which is the chemical reaction in which water is broken down into oxygen and hydrogen. With this properties, P is suitable for coating.

PANi- P combination can be known as composite coating that can provide protection effectively. P enhance the weakness of PANi coating due to mechanical properties of P. P can provide the repellent of water, act as water splitting while PANi act as conducting polymer. Systems coating which developed for a variety of applications such as static charge dissipation, antistatic coatings and space heating known as electrically conductive coating. It will prevent dangerous discharge sparks by providing low surface resistance which effectively bleed-off the electric charge build up from the frictional contact between the dielectric substrates.

1.2 Problem Statement

Corrosion is a natural process with the procedure of degradation which metal disintegrates due to oxidation produces a concoction response that made oxides chip formed from the base of the metal. This natural phenomenon is a serious problem that can commit carnage of material especially for industries that involving metal work applications. The corrosion can be prevented by various methods where covering metal with the coating material is the easiest and lowest cost but yet it is highly effective. The protective materials used to cover the mild steel must have good adhesion to the surfaces, and able to withstand particular working environmental conditions. Thus, epoxy film attracted most attention to be selected as protective materials on the mild steel surface since it had all of the properties that suitable as a protective materials. Epoxy is known as the thermoset material which have excellent resistance against moist water and high temperature environment. It is applicable on many surfaces and easily available at low cost.

There are many types of coating material that have been used to prevent corrosion from occurred such as paint coating and using epoxy-graphene film. However, due to certain limitation of the properties and applications, the study of new coating material is needed, where PANi and P is an interesting material. PANi exists in a number of forms that differ in the degree of oxidation or protonation (Sathiyanarayanan, 2007). PANi itself has redox properties that can be used in the protection against corrosion. PANi also is a green protonated emeraldine that is important for conducting electricity that enable by the presence of cation-radicals in its structure. PANi has been added with various particles to enhance its electrical, thermal and physical properties while Black P has been reported to increase its thermoelectric properties.

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P is a single-elemental layered crystalline material consisting of only phosphorus atoms. P properties are beyond graphene. It is one step ahead of coating for prevention of corrosion due to its excellent mechanical properties, tunable band structures, anisotropic thermal, electrical and optical properties. Enhancement of the PANi and P coating can bring the capability of coating to another stage of coating for better protection of corrosion in future. Hence, in order to increase the physical properties of epoxy film, PANi-P nanoparticles were added with several composition into epoxy coating film and further improve corrosion protection of mild steel by discharging out the static ion.k

1.3 Project Objectives

The objectives of this work are as follows:

i. To develop epoxy added with polyaniline (PANi) and Phosphorus (P) nanoparticles as advanced coating film on the mild steel.
ii. To characterize the structural and electrical properties of epoxy with PANi-P film.
iii. To investigate the corrosion behaviour of the mild steel coated with epoxy-PANi/P film.

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1.4 Scope of Study

1. Develop mild steel coated with epoxy-PANi-P nanoparticles (PANi-P wt%: 0, 2, 4, 6, 8, and 10)
2. Characterize the microstructure of the developed film by using optical microscope.
3. Investigate the corrosion behaviour of mild steel in solution 3.5wt% NaCl solutions by using open circuit voltage (OCV) test.
4. Observing the physical and microstructural of the mild steel surface after the corrosion test by using optical microscope.

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CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion

Corrosion is a process where erosion is occurred on metal. Rusting occurred when iron is exposed to the atmosphere where there is a presence of moisture on the surface of the metal oxidizes with atmospheric oxygen. This phenomenon has become a serious problems to the worldwide industries. Thus, to overcome the corrosion a prevention control need to be applied in metal work industries in order to overcome and save the cost of damage. According to NACE, is state the implementing corrosion prevention helps to save the cost damage between $375 - $875 billion (USD) (Nation Association of Corrosion Engineers, 2016).

2.2 Corrosion Mechanism

Corrosions occurs by the electrochemical process which is consist of anode which acts as the negative electrode and cathode that act as the positive electrode, electrolyte which can be the present water or soil, and a circuit that connected both anode and cathode as the requirements for the corrosion occurs. In time the corrosion current entering the electrolyte and flowing to the cathode, the dissolution of metal occurs at the anode. Metallic material that exposed to water or aqueous will involve the interactions of iron (Fe) and water (H20). From this interactions, the reaction amount of the cathodic areas will chemically equivalent to the metal ions that will go into solution at anodic areas. The reaction at anode is shown below in Equation 2.1.

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Anodic reaction:

$$Fe \longrightarrow Fe^{2+} + 2e^{-} \qquad \text{Equation 2.1}$$

The loss of electron occur at anodic reaction, the electron travel from anode to cathode leaving positively charged ions at the anode, moving by the electrolyte and carry the positive current. Hence, the corrosion is occurs at anode as electrode at anode has loss some weight due to loss of electron to other higher concentration of ion. Then, the cathode will received the electron released by the anode via metallic circuit. These electrons are utilized in the reduction of oxygen present in water which is in contact with the cathode. Following below are the reaction at cathode as shown in Equation 2.2 and Equation 2.3.

Cathodic reaction:

$$O_2 + 4H^{+} + 4e \longrightarrow 2H_2O \text{ (in acidic solution)} \qquad \text{Equation 2.2}$$

$$O_2 + 2H_2O + 4e \longrightarrow 4H^{+} \text{ (in basic solution)} \qquad \text{Equation 2.3}$$

The reduction reaction will took place at cathode causes reducing of number oxidation at cathode. By depending on the type of electrolyte contact with metal, the number of oxidation will be different. During the electrochemical process, a film layer call electrodeposited will form on cathode due to positive ion in electrolyte attach at the cathode.

2.3 Forms of Corrosion

Variety of the corrosion form can be determined by its degradation on the appearance of the corroded metal. Each one of the types of corrosion can be identified by observing the corroded metal with naked eye. There are five main forms of corrosions which is general corrosion, intergranular corrosion, galvanic corrosion, crevice corrosion and pitting corrosion.

2.3.1 General Corrosion

General corrosion or uniform corrosion is a type of deterioration of material that more or less uniformly distributed on the entire surface of material. This type of corrosion formed when the surface of material experience electrochemical process when surrounded with corrosive environment. This will effecting the surface of material by decreasing in the thickness constantly and definitely break down due to corrosions occur as shown in Figure 2.1(a). This general corrosion can be stopped or shortened with proper materials including coatings, inhibitor or cathodic protection.

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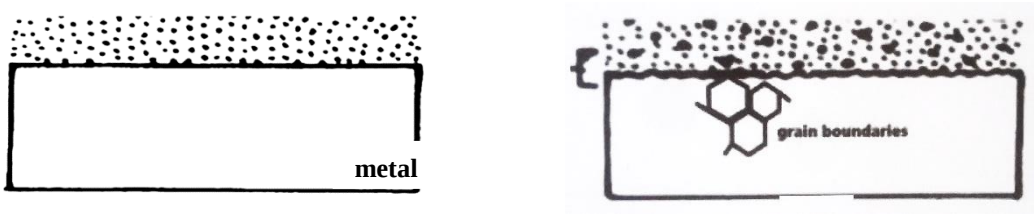
2.3.2 Intergranular Corrosion

Metals and alloys is made up of grains that separated by grain boundaries and the bulk of the grains remain largely unaffected. Intergranular corrosion specialized type of attack that takes place at the grain boundaries of a metal. The grain boundary material acts as an anode and larger area of grains acts as cathodes. This result in the flow of energy from the small anode area to the larger cathode area causing rapid attack penetrating deeply into the metal as shown in Figure 2.1(b).



(a) (b)

Figure 2.1: Corrosion types; (a) Uniform corrosion, and (b) Intergranular corrosion.

2.3.3 Galvanic Corrosion

Galvanic corrosion or also known as dissimilar metal corrosion is the reaction of two metals in the same electrolyte. The reaction is more active where one acts as anode and corrodes while the less active one is cathode (Xiao-qing DU, 2013). This rate of reaction occur causes by the combination of large cathodic area and a small anodic area is undesirable. The less noble metal will act as anode due to its less corrosion resistant and protected by the galvanic current as shown in Figure 2.2(a), while cathode is the noble part where it is resistance to corrosion that take place in the presence of electrolyte.

2.3.4 Crevice Corrosion

Crevice corrosion is a localized type of corrosion occurring within or adjacent to narrow gaps or opening formed by metal-to-metal or metal-to-non-metal contact. This type of corrosion normally occurred within crevices or at shielded surfaces with the presence of stagnant solution where the present of aqueous or moisture is not moving. The progress of the corrosion is very rapid as it is more frequently intense on chloride environments. The higher

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