CORROSION BEHAVIOUR OF MILD STEEL COATED WITH EPOXY-GRAPHENE FILM IN 3.5 WT.% NaCl SOLUTION

AHMAD RIDHWAN BIN AHMAD FADZI
B051410047

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2017

CORROSION BEHAVIOUR OF MILD STEEL COATED WITH EPOXY-GRAPHENE FILM IN 3.5 WT.% NaCl SOLUTION

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

by

AHMAD RIDHWAN BIN AHMAD FADZI
B051410047
930713-06-5519

FACULTY OF MANUFACTURING ENGINEERING
2017

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

Tajuk: **CORROSION BEHAVIOUR OF MILD STEEL COATED WITH EPOXY-GRAPHENE FILM IN 3.5 WT.% NaCL SOLUTION**

Sesi Pengajian: **2016/2017 Semester 2**

Saya **AHMAD RIDHWAN BIN AHMAD FADZI (930713-06-5519)**

mengaku membenarkan Laporan Projek Sarjana Muda (PSM) ini disimpan di Perpustakaan Universiti Teknikal Malaysia Melaka (UTeM) dengan syarat-syarat kegunaan seperti berikut:

1. Laporan PSM adalah hak milik Universiti Teknikal Malaysia Melaka dan penulis.
2. Perpustakaan Universiti Teknikal Malaysia Melaka dibenarkan membuat salinan untuk tujuan pengajian sahaja dengan izin penulis.
3. Perpustakaan dibenarkan membuat salinan laporan PSM ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. *Sila tandakan (√)

☐ SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysiasebagaimana yang termaktub dalam AKTA RAHSIA RASMI 1972)

☐ TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/ badan di mana penyelidikan dijalankan)

☐ TIDAK TERHAD

Disahkan oleh:

________________________ ________________________

Alamat Tetap: Cop Rasmi:

____

____

____

Tarikh: __________________ Tarikh: __________________

*Jika Laporan PSM ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan PSM ini perlu dikelaskan sebagai SULIT atau TERHAD.

DECLARATION

I hereby, declared this report entitled "Corrosion Behaviour of Mild Steel Coated with Epoxy-Graphene Film in 3.5 wt.% NaCL Solution" is the result of my own research except as cited in references.

Signature : ……………………………………

Author's Name : Ahmad Ridhwan Bin Ahmad Fadzi

Date : 22 June 2017

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 (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

……………………...............................

(Dr. Mohd Shahadan Bin Mohd Suan)

ABSTRAK

Kakisan boleh menjadi masalah utama bagi kebanyakan bahan pada masa kini dan bagi mengatasi masalah hakisan, sistem salutan telah dibangunkan. Sistem penyalutan boleh datang dalam pelbagai cara yang sesuai dengan aplikasi yang berbeza. Salutan cat merupakan salah satu langkah asas dalam membendung masalah kakisan yang boleh didapati. Penambahan pengisi dalam sistem salutan cat epoksi boleh membantu meningkatkan perlindungan kakisan bagi sistem salutan. Jenis dan kuantiti pengisi yang dipilih dalam meningkatkan salutan epoksi perlu dikaji terlebih dahulu sebelum ia boleh digunakan. Kajian ini akan memberi tumpuan kepada mengkaji tingkah laku kakisan sistem salutan epoksi-graphene ke atas keluli lembut sebagai substrate. Penyediaan bahan bagi kajian ini akan melibatkan dengan resin epoksi, pengeras dan graphene sebagai pengisi dalam sistem salutan. Lapisan cat epoksi-graphene telah digunakan pada substrat keluli lembut dengan menggunakan kaedah berusan tangan dan dibiarkan ia mengering untuk tempoh satu hari pada suhu bilik. Pengisi graphene telah ditambah ke dalam sistem salutan cat epoxy dengan berbeza rumusan kandungan yang bermula dengan 0%, 2%, 4%, 6%, 8% dan 10% mengikut berat graphene. Kelakuan kakisan pada salutan epoxy-graphene telah dijalankan dengan menggunakan ujian Litar Terbuka Potensi (OCP) dan ujian polarisasi. Sampel keluli lembut yang bersalut dengan 0% dan 2% kandungan graphene dapat memberikan perlindungan yang lebih baik sebagai penghalang terhadap aktiviti kakisan manakala lapisan sampel dengan kandungan 4%, 6%, 8% dan 10% graphene tidak dapat memberikan perlindungan yang terbaik terhadap kakisan ke atas keluli lembut. Sampel dengan tambahan sebanyak 10% kandungan graphene menunjukkan aktiviti kakisan teruk dan dapat dibuktikan melalui pemerhatian makroskopik dan mikroskopik selepas semua sampel telah menjalani ujian rendaman dalam 3.5% larutan NaCl selama 30 hari.

ABSTRACT

Corrosion can be a major problem for most of the material nowadays and as the countermeasure for the corrosion problem, a coating system were developed. Coating system can come in many ways suitable with different application. Paint coating can be say as the one of the most basic type of coating available. Addition of filler inside the epoxy paint coating system can help improving the corrosion protection of the coating system. Type and quantity of the filler selected in improving the epoxy coating need to be studies first before it is can be applied. This study will be focus on the study of the corrosion behaviour of the epoxy-graphene coating system. The preparation of the material with involve with epoxy resin, hardener and graphene as the filler in the coating system. The epoxy-graphene paint coating was applied on the mild steel substrate by using hand-brush method and let it cure for one day in room temperature. Graphene filler was added into the epoxy paint coating system with different formulate of the graphene content started with 0%, 2%, 4%, 6%, 8% and 10% by weight of the graphene. The corrosion behaviour of these epoxy-graphene coating was determined using Open Circuit Potential (OCP) test and Polarization test. The mild steel sample coated addition of 0% and 2% of graphene able to provide better protection as a barrier against the corrosion activities while coating sample with addition of 4%, 6%, 8% and 10% of graphene content are not able to provide proper corrosion barrier. Sample with addition of 10% of the graphene shows the worst corrosion activities proven by both macroscopic and microscopic observation after all samples were undergoes with immersion in 3.5% of NaCl solution for 30 days. Both OCP and Polarization test conducted also showed that the addition of 10% of graphene into the epoxy coating system are not able to provide better corrosion barrier and causes the mild steel substrate to corrode.

DEDICATION

To my beloved parents

Ahmad Fadzi Bin Othman and Alisa Binti Mohamed

To my siblings

Nur Najwa Atikah Binti Ahmad Fadzi, Anis Amiera Binti Ahmad Fadzi, Anis Hanani Binti Ahmad Fadzi and Ahmad Aniq Syazwan Bin Ahmad Fadzi

To all my friends, lecturers and supervisor

for giving me moral support, money, cooperation, encouragement and also understandings
Thank You So Much

ACKNOWLEDGEMENT

First and foremost, praise to Allah the Almighty for the strength and hope given to me throughout doing this research project. I would like to express my gratitude to my supervisor Dr. Mohd Shahadan Bin Mohd Suan for the continuous support, guidance and knowledge with my FYP project. His guidance helped me all time of the project and writing this report.

I would like to give my gratitude to my fellow colleagues from Bachelor of Manufacturing Engineering (Material Engineering) for all the ups and downs we have been through all these semesters and all this time executed this project together.

Last but not least, I would like to express my deepest gratitude to my beloved parents, Ahmad Fadzi Bin Othman and Alisa Binti Mohamed and siblings for their supports and believe towards me throughout my studies in UTeM. Their love, care and prayers are greatly appreciated. I am highly indebted to them and may Allah repay their kindness.

TABLE OF CONTENT

CHAPTER 3: METHODOLOGY

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

NACE	-	Nation Association of Corrosion Engineers
Fe	-	Iron
H_2O	-	Water
SACP	-	Sacrificial Anode Cathodic Protection
DC	-	Direct Current
UV	-	Ultra Violet
SrCrO4	-	Strontium Chromate
HNO3	-	Nitric Acid
HCIO4	-	Perchloric Acid
HCL	-	Hydrochloric Acid
NaCl	-	Sodium Chloride
KCL	-	Potassium Chloride
Pt	-	Platinum
SCE	-	Standard Calomel Electrode
OCP	-	Open Circuit Potential
EIS	-	Electrochemical Impedance Spectroscopy
Rct	-	Coating Resistant
C_{dl}	-	Capacitance Double Layer
Ecorr	-	Corrosion Potential
Icorr	-	Corrosion Current
%	-	Percentage
Atm	-	Atmosphere
Wt.%	-	Weight Percentage
SiC	-	Silicon Carbide
FESEM	-	Field Emission Scanning Electron Microsopy
PVC	-	Polyvinyl Chloride

CHAPTER 1

INTRODUCTION

1.1 Introduction

Protection of the surfaces especially on the metalwork application need more attention particularly in projects which involved with large areas of exposed steel. The exposed surfaces may deteriorate due to the chemical reaction of the surfaces with the ambient surrounding which also can be known as corrosion attack (Alhumade et al., 2015). Corrosion in steel can be an expensive problem when it is happened which it also can contributed to significantly high portion of loss and can causes lost production, inefficient operation and high maintenance (Karthik et al., 2015). Corrosion also becomes the major causes of energy and material loss. It has been reported that 1/5 of energy globally and average 4.2% of gross national product (GNP) is lost each year due to corrosion (Nguyen et al., 1991). And it is estimated that the impact of the corrosion greater than $100,000,000,000 per year in the United State alone (Mentroke et al., 2001).

Application of coating on the metals surfaces has long been developed as the countermeasure for the corrosion problem. In principle, application of coating can help in prevention of the deterioration process of the metal surfaces which involves with the chemical reactions of the metal with the surrounding atmosphere. As an oil-based (alkyd) coating had been applied regardless of the surface characteristics and exposure conditions in the early 1990s, corrosion prevention in the industry has become popular (Chew et al., 2000). 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 (Balgude et al., 2016). 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 et al., 200). Other than being used in coating application, epoxy resins have make their ways in wide range of applications including in use in electronic/electrical components, high tension electrical insulators, fiber-reinforced plastic material, structural and engineering adhesives etc (Malshe et al., 2008).

Graphene is a new generation material which it is an allotrope of carbon element first isolated by simple mechanical exfoliation in 2004 by Novoselov and Geim by using simple adhesive tape (Novoselov et al., 2004). Graphene is a two-dimensional honey comb which contain of single layer lattice formed by the tightly packed sp^2 bonded carbon. Graphene forms an excellent electrons carrier space which graphene can provide high electron mobility at room temperature (250,000 cm^2/V) which makes them has extraordinary electrical properties (Singh et al., 2001). Besides, graphene also excellent in both optical and mechanical properties. Due to the excellent properties graphene have, it is believed that graphene also could be used in coating application as the enhancement material. Graphene also has been regards as the highly water and oil repellent material while graphene oxide is hydrophilic material (Hsieh et al., 2011). This properties makes graphene suitable as coating which can provides resistance to water and oil.

Epoxy coating can suffer from brittleness and poor resistance to crack propagation and due to contains of hydrophilic hydroxyl group and free volumes in their structure, they are permeable to an aggressive agents such as water which can cause the corrosion rate of the metal accelerate over time (Pourhashem et al., 2016). As for improving the corrosion resistance of the epoxy as the coating material, nanocomposite coating seems to be promising in enhancement of the epoxy coating. There are recent studies on graphene improvise epoxy coating to the corrosion resistance (Chang et al., 2014). Monetta et al., (2015) stated in their report that the addition of graphene nanoflakes significantly changes the barrier properties of epoxy resin and it also improves the barrier properties of neat epoxy resin in water contact angle measurement.

This combination of epoxy-graphene coating also can be known as composite coating can provide protection to the metal effectively due to the mechanical properties that graphene has which enhance the weaknesses from the epoxy coating. Graphene can provide strong repellent of water and oil in the coating application. Besides that, graphene also has good mechanical properties which can improvise the epoxy coating to become conductive type coating. Electrically conductive coating are new classes of coating systems which developed for a variety of applications such as static charge dissipation, electromagnetic/radio frequency interference shielding, antistatic coatings and space heating (Azim et al., 2006). This conductive type coating provided low surface resistance which effectively bleed-off the electric charge build up from the frictional contact between the dielectric substrates and other materials which also can help prevent dangerous discharge sparks.

1.2 Problem Statement

Corrosion is a natural process which the process of something such as metal deteriorates because of oxidation which a chemical reaction that created oxides that flake away from the base of the materials (Alhumade et al., 2015). This process can contribute to the destructions of the material which become a serious problem faced by industries especially industries that involving with metalwork application. Corrosion can come in many types such as uniform corrosion, galvanic corrosion, concentration cell corrosion, pitting corrosion and etc. By applying a coating, the corrosion can be controlled.

The used of epoxy as the coating material has widely been used on the various of application in preventing the corrosion problem but there are some weaknesses in epoxy coating such as poor resistance of crack propagation and permeable to aggressive agent which can increased the corrosion rate (Hsieh et al., 2011).

There are been studies on improving epoxy coating with various means possible such as natural renewable resources which has been done by El-Fattah et al., (2006). His studies in improvement of the epoxy coating corrosion resistance, antimicrobial activity, mechanical and chemical properties by using chitosan which is also known as marine polymer as the enhancement material. The incorporation of chitosan into epoxy coating led to an improvement in alkali, acid and solvent resistance of epoxy coating based on the result obtained by El-Fattah et al., (2006). Enhancement of the epoxy coating with other materials can bring out the capability of the coating itself into another level which it is can provide better protection for the applications in future.

1.3 Project Objective

The objectives of this work are as follows:

I. To develop epoxy-graphene film as coating material on mild steel.

II. To study the effect of graphene + epoxy as the coating material against corrosion.

1.4 Scope of Study

In this study, an epoxy-graphene coating system is develop by using 2.0, 4.0, 6.0, 8.0, and 10.0 wt.% of combination of epoxy and graphene, as these formula will later provide different result of the corrosion behaviour on the mild steel as which the follow one of the stated objective of this study. The corrosion behaviour of these five different sample later will be evaluate by using corrosion test which is open circuit potential (OCP), and polarization test on the sample. Macro and microscopy observations on the morphology and cross section of each coated sample will be perform to confirm the occurrence of corrosion.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion

Corrosion can be defined as the deterioration of a material, which usually metal due to the interaction of the metal with the surrounding environment. Common examples of metal corrosion are rusting of irons, tarnishing of silver, dissolution of metals in acid solutions and growth of patina in copper. Corrosion has become one of the serious threads to the worldwide industries significantly. The annual cost of corrosions and corrosions protections in the United States is estimated by the Nation Association of Corrosion Engineers (NACE) to be excess of 10 billion dollars (Roberge et al., 1990).

2.2 Corrosion Mechanisms

Corrosions occurs by the electrochemical process which is consists 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 requirement for the corrosion to occurs (Scully et al., 2000). The dissolution of metal occurs at the anode which the corrosions current entering the electrolyte and flowing to the cathode. Most of the metallic material commonly exposed to the water or aqueous corrosion will involve on the interactions of iron (Fe) with water (H2O).

During the interactions occurs, the metal ions will go into solution at anodic areas in an amount which chemically equivalent to the reaction at cathodic areas. For iron-based alloys case, following reaction of the iron usually takes place at the anodic areas (Roberge et al., 1990).

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

The loss of electrons leaves positively charged ions at the anode which travel from the anode to cathode via the electrolyte such as water and carry the positive current. The electrons which are released on the anode travel from the anode to the cathode via the metallic circuit. These electrons are utilized in the reduction of oxygen present in water which is in contact with the cathode. Thus, following reactions may occur at the cathode.

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \text{ (if the water is acidic)} \qquad \text{Equation 2.2}$$

$$O_2 + 2H_2O + 4e \rightarrow 4H^+ \text{ (if the water is basic)} \qquad \text{Equation 2.3}$$

In neutral solutions, the reduction of oxygen is of considerable importance for many metals and in such cases which the amount of oxygen dissolved in the water will determine the corrosion rate. Table 2.1 shows the corrosions rate of ions in an aqueous solution is affected by the amount of oxygen content of the water.

Table 2.1: Corrosion rate of iron exposed to 3.5% NaCl solutions containing various concentrations of dissolved Oxygen (Scully et al., 2000).

Oxygen Pressure (atm)	Corrosion Rate (mm/year)
0.2	2.2
1	4.5
10	86.4
61	300

Dissolved oxygen reacts with hydrogen atoms adsorbed at random on the iron surface, independent of the presence or absence of impurities in the metal. The oxidation reaction proceeds as rapidly as oxygen reaches the metal surface. These reaction as shown in Equation 2.4 (Roberge et al., 1990)

$$2Fe^{+} + 2H_2O + O_2 \rightarrow 2Fe^{2+}\ 4(OH^{-}) \qquad \text{Equation 2.4}$$

After dissolution, ferrous ions (Fe^{++}) generally oxidize to ferric ions (Fe^{+++}) and will combine with hydroxide ions (OH^-) formed at the cathode to give a corrosion product called rust (Fe_2O_3).

2.3 Forms of Corrosion

Classification of the corrosions form can be identified by the which it manifested itself which is the classification on the appearance of the corroded metal. Each corrosion form can also be identified by observation with naked eye. There are eight basic forms of the corrosions forms which is general corrosion, galvanic corrosion, crevice corrosion, pitting, intergranular corrosion, erosion corrosion, stress corrosion cracking, and selective leaching corrosion (Fontana et al., 1967).

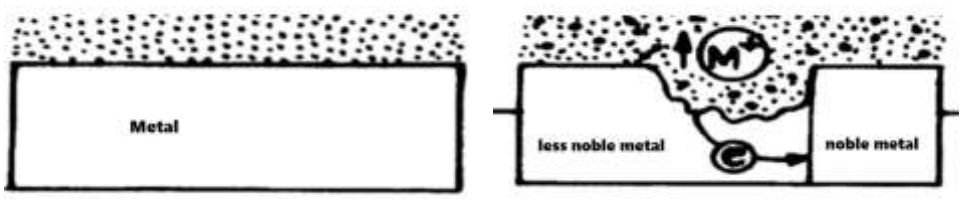
2.3.1 General Corrosion

General corrosion or also can be known as uniform corrosion is the most common form of corrosion which it is normally being characterized by a chemical or electrochemical reaction that proceeds in uniform matter on the exposed surface area (Fontana et al., 1967). The material decreasing in the thickness constantly and finally fails or destructions due to the corrosions occurs as shown in Figure 2.1a. Microscopic anodes and cathodes are continuously changing their electrochemical behaviour from anode to cathode in uniform attack. This general corrosion can be prevented or reduced with proper materials including coatings, inhibitor or cathodic protection.

2.3.2 Galvanic Corrosion

Galvanic corrosion which occurs due to the dissimilar metals metallically connected with each other and exposed to the corrosion environment, this differences in potential produce electron flow between them (Fontana et al., 1967). The less noble metal will act as anode due to its less corrosion resistant and suffers accelerated attack while more noble metal act as cathode because of their more corrosion resistant material (Figure 2.1b) were cathodic protected by the galvanic current. The tendency of a metal to corrode in a galvanic cell is determined by its positions in the "galvanic series" of metals and alloys (Sastri et al., 2007).

The order may vary with both temperature and composition of the electrolyte. As for example, the galvanic corrosion cell of the combination of copper lines and galvanized steel water mains which the soil as the electrolyte, copper line as the cathode and the water main is the anode.



(a) (b)

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

2.3.3 Crevice Corrosion

Crevice corrosion also can be called as concentration-cell corrosion occurs because of the environment differences surrounding the metal. Also, can be referred as the deposit or gasket corrosion (Figure 2.2a). This type of corrosion attack commonly occurs in localized areas which associated with small volumes of stagnant solutions (Evans et al., 1976). Normal mechanical construction can create crevices at sharp corners, spot welds, lap joint, fasteners and tube sheet supports. There are at least five type of concentration cell exist and the most common of the fives are “oxygen” and “metal ion” cells. The area become cathodic when there are high oxygen concentration on the areas on the surface which in contact with the electrolyte compare to area which have less concentration of oxygen. Same applies to the metal ions concentration cell which area on surface with higher concentration of metal ions in the electrolyte, it tend to become cathodic.

2.3.4 Pitting Corrosion

Pitting corrosion is form of corrosion which extremely localized attack resulted holes on the metal surface and randomly occur that the holes may be small or large in diameter which the depth penetration may greater than the diameter of the holes (McKay et al., 1936).