Electrochemical Impedance Spectroscopy Evaluation of Non-Metallic Pipe (NMP) Degradation in CO_2 Environment

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Mechanical Engineering
With Honours

FYP II
JANUARY 2020

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CERTIFICATION OF APPROVAL

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Approved by,

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(AP Ir. Dr Mokhtar Bin Che Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2020

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(Muhammad Yusri Hafiz Bin Ab Aziz)

ACKNOWLEDGEMENT

All praise to the Almighty God for granting me the will and well-being in completing this glorious journey of my research for Final Year Project (FYP) II course. I feel blessed and very grateful for this golden chance to work on my research in corrosion perspective since I am very passionate in this critical field. I am utterly grateful for the countless blessings that He has blessed me with throughout my degree journey.

In addition, I would like to express my cordial appreciation to my supervisor, AP Ir. Dr Mokhtar Bin Che Ismail who always helps and guides me whenever I have problems with my works. He also shares a lot of knowledge and resources throughout this project which really helpful for me to gain more understanding on the concept and fundamental of the project. I am very thankful to him for believing in me to work on this project even its might be something new for me. I am very grateful for having a superb and professional lecturer as my supervisor because with his experience in this field, I believe he can develop and help me to face the real working life in future as a corrosion engineer.

Besides, I would like to express my deepest gratitude to the Research Officer (RO), Mr Haq and Mr Afif who also be there for me every time I need their help in the corrosion lab. They have guided me with full of sincerity by sharing their experience and knowledge on the required equipment and instruments for my project.

Not forgetting my beloved parents who always support me in whatever I done in my life and always be there for me through my ups and downs. Parents' prayers are majestic and with their superior blessing and prayers, my life will always be in full of bless by the Almighty God and make things easier for me to complete my research in this project. Lastly, to my friends who always backing me up whenever I am about to fall and support me every time, I really need them.

ABSTRACT

The utilization of Non-Metallic Pipe (NMP) as part of recent corrosion control and management practise has create a critical requirement in term of corrosion monitoring of the NMP as it exposed to field operating condition. Currently, there is no established method to monitor the corrosion activities in NMP. Hence, this study was initiated to evaluate the capability of an advance monitoring technology namely Electrochemical Impedance Spectroscopy (EIS) in detecting the chemical degradation of NMP when exposed to CO_2 corrosion environment. The chemical degradation process on a selected types of polymer, High-density Polyethylene (HDPE) and the electrochemical impedance analysis were conducted comprehensively. The chemical degradation process was held in an autoclave machine with fixed temperature and pressure setup. The chemical deterioration of polymer have proven by assessing under EIS which based on EIS reading such as Nyquist and Bode Plot that identify the salient characteristic of corrosion damage in polymer. As a conclusion, this project can give a practical quantitative monitoring method in future NMP application. However, the research was recommended to continue the studies by using stronger and thinner polymer in order to avoid the sample from melting and for better result.

TABLE OF CONTENT.

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil & Gas industry are generally known as the vital and critical business in producing petroleum products such as gasoline, diesel, kerosene and lubrication oil for our daily usage. The petroleum products are being distributed and transported from one location to another by using pipeline which generally laid underground and also above the ground. Oil & Gas industry also extensively acknowledged as the most hazardous and risky business since they are dealing with the flammable and poisonous chemicals in their day-to-day production. In the past century, oil and gas pipeline encountered countless failure and damage cases which led to series of catastrophic and prominent disaster and numerous personal injuries, fatalities, environmental pollution, property damage, etc. For example, the tremendous spillage of the crude oil pipeline in western Prudhoe Bay, Alaska, owned by BP Exploration, Alaska (BPXA) on 2 March 2006. BPXA operators discovered a 1⁄4" hole leak at 6 o'clock position of an oil transit pipeline above ground 34-inch in diameter and caused a spillage of 201,000 gallons (+/- 33%) of crude oil due to internal corrosion in the pipeline.

Figure 1.1: Affected wildlife due to oil spill disaster [1].

Nowadays, corrosion related issues have become the major challenges in safeguarding the integrity and reliability of oil and gas pipeline. Corrosion is defined as an irreversible interfacial reaction of a material (metal, ceramic, or polymer) with its environment resulting in the deterioration of the material or in dissolution into the material of an element of the environment [2]. By the definition, there are three key points need to be focused in characterizing any corrosion damage mechanism which are form of corrosion, type of material and environmental condition. Hence, corrosion can be controlled and prevented by studying and manipulating those key points such as by material selection, corrosion allowance application, injecting corrosion inhibitor, cathodic protection, etc. However, effective and successful corrosion management plans by having an effectual corrosion prevention technique is very critical and essential in order to minimize the corrosion attack. Thus, a detailed and thorough corrosion study need to be done by the expert before installing or designing any equipment so that it can withstand and able to handle the corrosive environment of the streamline.

In recent years, there is a new approach in designing a corrosion resistant pipeline which utilizing non-metallic material. Nowadays, Non-Metallic Pipe (NMP) has becomes one of the best option in fluid handling application due to its ability to offer a longer lifetime and promote cost-effectiveness compared to the application of corrosion-resistance alloys (CRA). Thermoplastic and thermoset are two type of polymer materials that are generally used to produce NMP [3]. Thermoplastic pipes are manufactured by extrusion method which the raw material are melted and then extruded into a long tubular profile since it has the ability to change its phase when heat source is introduced. Thus, it will melt when subjected to high temperature and then solidified back when the heating source been removed. The raw polymer materials that can be used to produce various type of thermoplastic pipe are olefin, vinyl and fluoropolymer. Thermoplastic pipes are beneficial in many ways such as superb in flexibility, easy to manufacture, high durability, lighter in weight, etc.

Meanwhile, thermoset pipe or also commonly known as fiber reinforced plastic (FRP) is being manufactured by filament winding processes which employ epoxy resins reinforced with continuous glass filaments [4]. FRP does not melt when exposed to high temperature environment which make thermoset piping become more advance in temperature and pressure rating application compared to thermoplastic piping. Thermoplastic and thermoset pipe are good in scale formation prevention and fluid hydraulic improvement since they have extremely smooth internal surface. FRP pipe is broadly used in many industries due to its light in weight, corrosion resistance, fire-resistance, etc. FRP pipe also describe as the possible competitor for 316 stainless steel pipe or other higher alloys in term of ownership cost [3]. Even though NMP is one of the best option, it also subjected to corrosion or also known as polymer degradation.

Polymer degradation been defined as the change in physical properties that caused by chemical reaction which associating bond scission in the backbone of the macromolecule [5]. There are many degradation agents that can cause the chain scission in polymer to occur such as thermal, humidity exposures, complete immersion in water at ambient and elevated temperature, etc [6]. The examples of polymer degradation are thermal degradation, mechanical degradation, chemical degradation, degradation by high energy radiation, etc. Hence, in order to detect the polymer degradation in the NMP, the monitoring techniques also must have the capability to detect early changes inside the macromolecular structure of the polymer.

1.2 Problem Statement

The application of NMP had become more acknowledged in oil and gas industry from time to time. However, corrosion damage mechanism is inevitable since they are handling corrosive product such as crude oil, acidic gaseous, petroleum products, etc. Unfortunately, not all of the monitoring technique for the metallic pipe are suitable for NMP due to the conductivity, material involve, etc. Nowadays, the industry are using corrosion coupon and mass measurement technique in order to assess the fluid permeation process inside NMP. In the author opinion, this method are not really practical in predicting the useful life for the NMP due to some limitation such as disable to monitor the sample in smaller time interval due to insignificant mass changes, disable to detect early premature process in the NMP, etc. Hence, Electrochemical Impedance Spectroscopy (EIS) method is a potential competitor in this corrosion management technique for NMP application in Oil and Gas industry.

1.3 Objectives

The objectives for this project are:

1. To study the chemical degradation process in polymer under CO_2 environment.
2. To evaluate the polymer degradation based on impedance analysis under Electrochemical Impedance Spectroscopy (EIS).

1.4 Scope of Study

This project was initiated to study the chemical degradation issue in NMP materials for In-Field Liner (IFL) application. The selected corrosive environment is CO_2 corrosion condition by having deionized water, hydrocarbon and diffused CO_2 gaseous at setup pressure of 20 bar and elevated temperature at 60°C for 72 hours. The non-metallic material used is High-density polyethylene (HDPE). This project will undergo several testing methods such as chemical deterioration process by using an autoclave machine and Electrochemical Impedance Spectroscopy (EIS) evaluation.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion in Oil and Gas Pipeline

Corrosion had caused serious problems to oil and gas pipeline. Corrosion damage activities can initiate internally or externally and even both can occur simultaneously. In general, internal corrosion in oil and gas pipeline is caused by the presence of carbon dioxide (CO_2), hydrogen sulphide (H_2S), seawater, etc. Meanwhile for external corrosion, it is caused by the external pipeline environment such as seawater, soil, microbiological activity, etc. The example of oilfield corrosion damage mechanisms are sweet corrosion, sour corrosion and microbiological induced corrosion (MIC).

2.1.1 Sweet Corrosion

Sweet corrosion or CO_2 corrosion is the most common oilfield corrosion failure that occur in oil and gas pipeline [7]. Sweet corrosion initiates when the contamination of CO_2 gas begins to dissolve in water from either condensation or seawater carryover resulting in carbonic acid (H_2CO_3) or acetic acid (CH_3COOH) being formed. Fortunately, carbonic and acetic acid are weak acid. Therefore, the corrosion attacks are not as vigorous and severe as compared to corrosion attack by strong acid such as hydrochloric acid (HCl). However within adequate concentration, it can significantly lower the pH value and caused general corrosion and/or pitting corrosion on the pipeline [8].

In general, carbon steel and low alloy steel materials are usually susceptible to sweet corrosion. The sweet corrosion mechanism will form the precipitation of iron (II) carbonate or commonly called as siderite that act as a passive layer on the metal surface. Commonly, the passive layer will stunt the corrosion damage. Yet, the integrity of the structure will decrease since the material will become thinner. The mechanism of CO_2 corrosion can be summarised as in Figure 2.1.

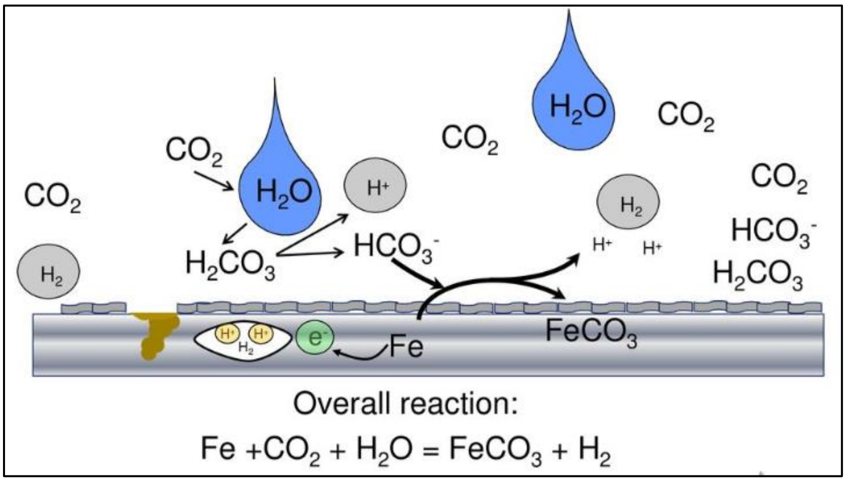

Figure 2.1: Summary of CO_2 Corrosion Mechanism [9].

From the figure, we can analyse that there are many factors that contribute to initiate and introduce sweet corrosion into the system. The critical factors that can enhance sweet corrosion to occur are partial pressure of CO_2, pH and temperature of the system [8]. When the partial pressure of CO_2 increased, it will increase the corrosion rate since the pH value becomes much lower. The transient change in the environment condition such as increase in chloride ion concentration, change in temperature and CO_2 partial pressure can initiate pitting corrosion in CO_2 condition [10]. However, based on the research from Fang, et al. [7], with an increase in NaCl concentration at 5°C, pH 4.0, the general CO_2 corrosion rate decreases strongly and non-linearly. In the author opinion, corrosion damage mechanism will always happen since they cannot completely eliminate the corrosive agents from the system.

Material selection is the most effective yet pricey choices for corrosion control technique. Even in the common international standards are highlighting the affected and the best material selection for every corrosion damage mechanism [8]. However, increase in the grade of material will cause large amount of money that they need to spend. As a result, it lessen the desire for the engineer to choose this technique and tend to find another cost-effective path. Luckily, nowadays they can find another cheaper option in corrosion resistance material which is polymer. There are many research that been made but the utilization of non-metallic materials as a sweet corrosion resistant material are not been addressed adequately. Hence, a study on the effect of absorption and permeation of CO_2 gases and low salinity brine into the polymer molecule structure will be done through this project.

2.2 Non-Metallic Pipe (NMP) Application in Oil and Gas

In Oil and Gas industry, the application of NMP can be installed in two ways either by replace the frequently corroded metallic pipe with is a solid non-metallic pipe or another way is by internally lining the pipeline with a corrosion resistant plastic pipe liner [11]. The commonly used lined material are rubber, glass, Polytetrafluoroethylene (PTFE), Polyvinylidene Fluoride (PVDF), Ethylene Tetra-Fluoroethylene (ETFE), Perfluoro Alkoxy (PFA), and Fluorinated Ethylene Propylene (FEP) [3]. In oil and gas upstream sector, there are two types of NMP application that recently practiced which are In-Field Liner (IFL) and Flexible Pipe. Those pipes are applying non-metallic liner which used to handle corrosive product such as crude oil, natural gas, etc.

2.2.1 In-Field Liner (IFL)

These days, pipelining application has been amazingly renowned among researchers and investors. For example, In-Field Liner (IFL) project which invested by Petronas in collaboration with Anticorrosion Protective System (APS) whose act as the inventor and project managers. IFL is a creative and innovative move taken by Petronas in rehabilitating their aged offshore pipeline to prolong the useful life of their assets. This idea initiated when their carbon steel sub-sea hydrocarbon pipeline were found severely corroded internally due to presence of Sulphate Reducing Bacteria (SRB) in their pipeline system [12]. Oil and gas pipeline can provide an ideal environment for SRB growth since the pipeline can unintentionally provide nutrients for them. For example, the application of oxygen scavenger injection in most crude oil pipeline is initially intended to reduce the dissolved oxygen concentration had accidently introduced nutrients for the SRB to flourish and creating an anaerobic environment that encourage the growth of SRB [13].

Nowadays, by killing the bacteria in-situ and avoiding the contamination of downstream equipment and piping is the international best practise to control the SRB [13]. Injection of corrosion inhibitor (CI) named biocide that used to kill SRB from oil and gas pipeline are widely utilized. However, CI injection system is demanding for a really effective and proper design to avoid uneven protection on the pipeline. This uneven protection only worsen the situation which the SRB will accumulate at one place and caused vigorous localized corrosion to occur. In this case, IFL program has an additional advantage over implementing CI injection technique. IFL can provide an economical trenchless relining technology that characterized by flexibility, portability, lightweight and low wall thickness while possess the strength like a steel pipe. IFL consist of three layer and the material used are as in Figure 2.2.

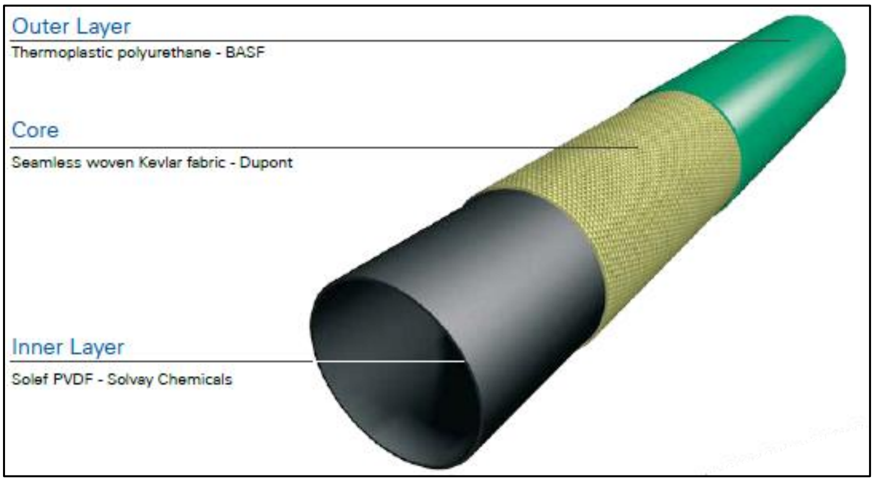

Figure 2.2: In-Field Liner Layer [14].

According to the research by Baron, et al. [11], they are evaluating plastic liner which made of High-density polyethylene (HDPE) and Polyamide – 11 (PA-11). However, the current material that been used as plastic liner is Polyvinylidene fluoride (PVDF) since the researcher are seeking for a material that can handle extremely aggressive, hot and sour hydrocarbon, and high operating temperature up to 110°C [12]. The critical factors in applying plastic liner are exposure time for the plastic to handle the fluid and temperature of the environment. HDPE was built with C-H bond while fluoropolymer such as PVDF was built with C-F bond which is a stronger bond with a stable crystalline structure compared to C-H bond [21]. An illustration on the installation of IFL inside a metallic pipe are shown in Figure 2.3.

Figure 2.3: IFL installation in a metallic pipe [15].

2.2.2 Flexible Pipe

In Oil and Gas upstream sector, the seabed flowlines and the floating production facilities are commonly connected by a dynamic riser namely flexible pipe. The flexible pipe also can be used as static and dynamic jumpers [16]. Flexible pipe become more favourable in offshore pipeline because it can withstand water depths down to 8000 ft, high pressure reaching to 10000 psi, high temperature application above 150°F and lastly withstanding large vessel motions in hostile weather condition [17]. A typical example on the application of flexible pipe for floating production systems as follow:

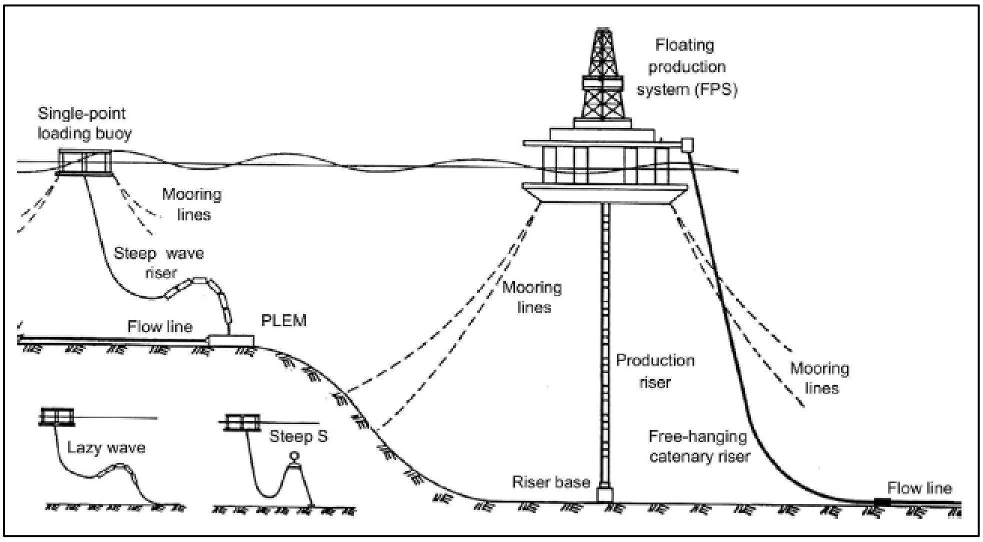

Figure 2.4: Typical flexible riser configurations [17].

The term of "Flexible" refers to these pipes, which are really stiff compared to a garden hose, yet more flexible compared to steel pipe with identical dimension [18]. and flexible pipe, they are using a non-metallic internal sheath inside the pipe to maintain the integrity of the pipe since polymer is a good corrosion resistant. The critical factor that been considered in material selection are the exposure concentration and temperature of the fluid [17]. Thermoplastic materials of API 17 such as HDPE, PVDF and PA-11 are used for the internal sheath [16]. HDPE and PA-11 can withstand the temperature up to 65°C while PVDF can tolerate higher temperature up to 130°C [17]. Thus, PVDF will be more desirable in high temperature application compared to HDPE and PA-11. The flexible pipe are constructed with several layer which shown in Figure 2.5.

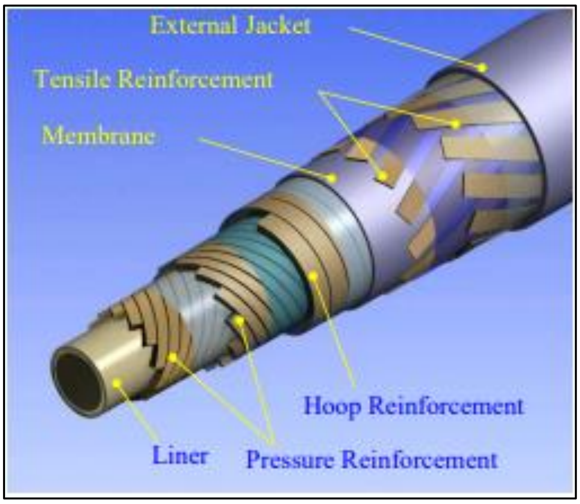

Figure 2.5: Typical structure of flexible pipe [16].

2.3 Polymer Degradation in NMP

During design stage, there are a lot of parameters that can influence the selection of polymer to control the corrosion activities. For example, the nature of the service fluid and the environment condition during service such as temperature, pressure, flow, stress, etc [18]. There are many types of polymer degradation yet for this project, the author will only cover chemical degradation which caused by fluid permeation into the polymer structure.

2.3.1 Chemical Degradation

Thermoplastic materials that undergo chemical degradation involves specific chemical reaction by the fluid with the most common failure mode are being hydrolysis by water, acids and alkalis [6]. As also mentioned by Waterton, the limitation of non-metallic materials are the permeation and absorption by gases and liquids which susceptible to physical transformation and chemical degradation [19]. Fluid permeation issue can cause chain scission in the polymer structure. The chain scission process will result in reduction of molecular weight which lead to reduce the toughness and fracture strain of the polymer. NMPs also subjected to stress which can enhance the chain scission process and at the same time encourage the rate of fluid permeation into the polymer. A summary of common hydrolysis process on a polymer are shown in Figure 2.6.

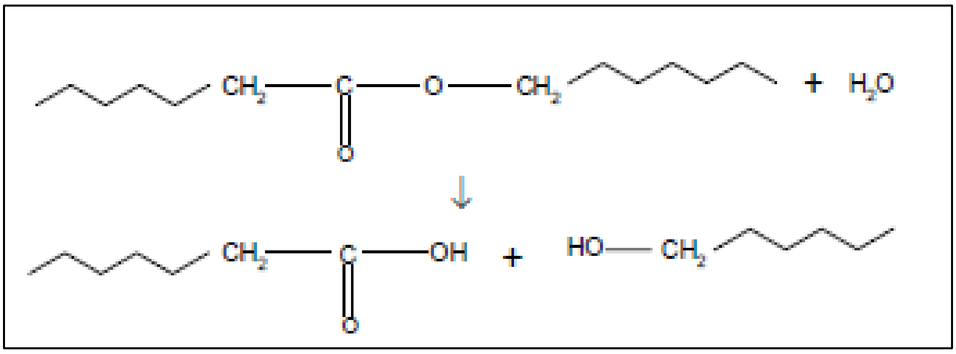

Figure 2.6: Summary of general hydrolysis scheme [6].

The driving force for fluid to permeate into the material is usually quantified by the concentration gradient [18]. For gas or vapour service such as natural gas and condensate, the concentration gradient will depend on the partial pressure of the fluid. According to Maxwell, et al. [6], the water absorption will result in swelling, reduction of glass transition temperature, T_g and reduction of mechanical and physical properties. In many cases, the fluid that permeate into the material will react with the polymer matrix and resulting in irreversible chemical changes and reduce the material performance. As a result, the change in mass and volume of the elastomer and thermoplastic can be significantly observed from time to time. Those correlation also mentioned by Waterton in Figure 2.7 and 2.8 below [19].

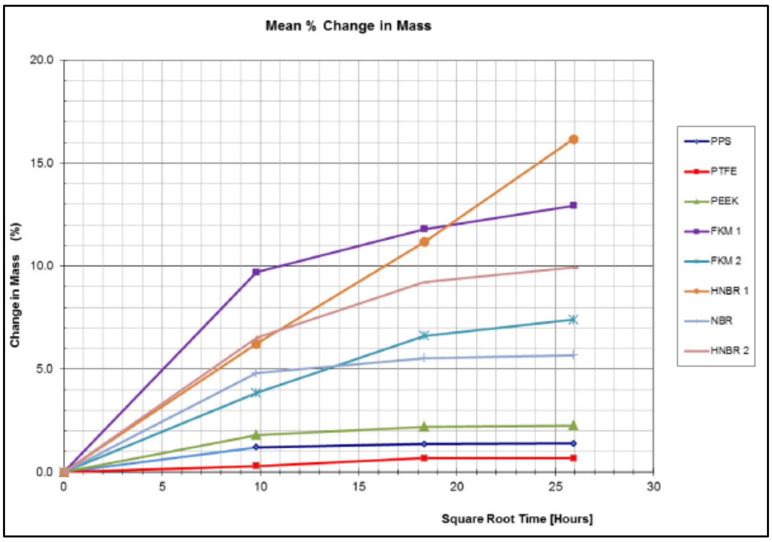

Figure 2.7: Percent change in mass versus exposure time at HP&HT [19]

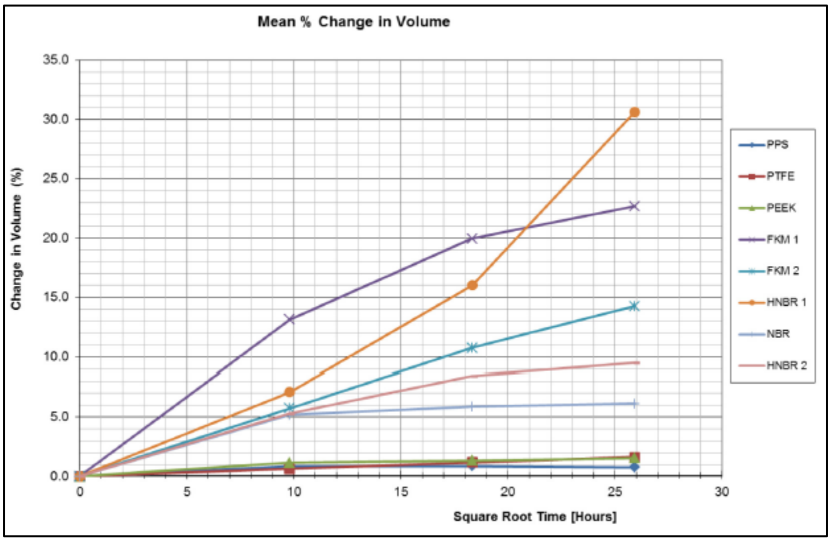

Figure 2.8: Percent change in volume versus exposure time at HP&HT [19]

2.4 Test Method

There are many literature that explaining on the test method in evaluating the effect of fluid permeation toward polymer performance. Since fluid permeation phenomenon will reduce the mechanical properties of the material, some literature might have some testing method in common. The test method is by performing tensile test, hardness test, water absorption test, etc [6][11][18]. However, there are no significant amount of literature that mentioned on change in impedance of polymer when exposed to the oil and gas environment. Hence, this experiment was set up to investigate the practicality of measuring the impedance in polymer as a condition and integrity monitoring method.

2.4.1 Sample Degradation Method

In general, there is standard procedure and experimental setup to inspect the fluid permeation activity in polymer. ISO 175 and ASTM D543 cover the absorption of chemical reagents in polymer while ISO 62 and ASTM D570 cover the absorption of water [6]. Those current international standards are using common immersion and weight measurement technique. The sample will be immersed for specific time interval and the weight of the sample are been monitored from time to time. Then, absorption can be developed by having the percentage of water absorbed versus time. However, the standard method will consume a lot of time to obtain a significant results. Hence, the author planned to accelerate the process by manipulating the test parameters.

The test parameters that need to be considered are temperature, pressure, exposure time, concentration of active impurities, pH value, etc [19]. For example the research by Baron, et al. [11], the temperature variation for HDPE are 23°C, 40°C and 60°C while for PA-11 are 22°C, 40°C, 60°C, 80°C and 100°C, with the exposure time is three and six months. However, the suggested exposure time for water absorption test is too long for this project. Thus, the author were accelerating the chemical degradation process by putting the polymer into autoclave machine. This method are widely implemented for high temperature and pressure application with mentioned exposure time for 2, 7 and 21 days [18][19]. Thus, in predicting the useful life of NMP, the author used EIS machine to detect and monitor the fluid absorption in the material.

2.4.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a broadly used method in evaluating protective coating. EIS was an upgraded equipment during the 1970’s that resulted in wide laboratory application as a quantitative coating evaluation technique. As illustrated before in Figure 2.1, CO_2 corrosion damage mechanism is involving electron transfer between one element to another which introducing quantifiable current flow in the system. From Ohm’s Law, the relation between electric current, potential different and resistance were clarified.

$$R = \frac{V(t)}{I(t)} \tag{2.1}$$

However in AC circuit, the signal become cyclic and alternates which results in creating a more complex mathematic relationship. Thus, impedance was introduced which representing the resistance, capacitance and inductance in an AC circuit. In electrochemical experiment, the working electrode will experience a sinusoidal potential signal $V(t)$ with frequency, f. The voltage signal can be expressed in the Equation 2.2. The current response will be a sinusoid at same frequency as voltage system but being “shifted in phase” as in Figure 2.9 below which can be determined by the ratio of resistive and capacitive element of the output current.

$$V(t) = V_A \sin(2\pi f t) = V_A \sin(\omega t) \tag{2.2}$$

$$I(t) = I_A \sin(\omega t + \varphi) \tag{2.3}$$

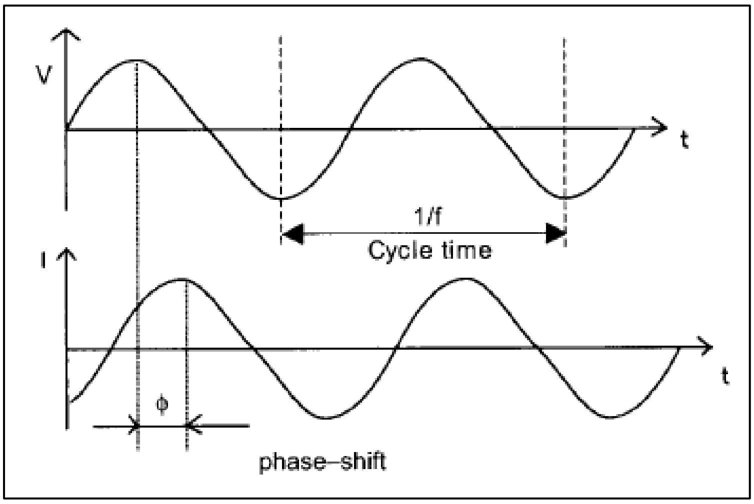

Figure 2.9: Sinusoidal voltage input, V(t) at a single frequency, f and current response, I(t) [20]

The impedance of the system can be calculated by relating to Ohm's Law, where:

$$Z = \frac{V(t)}{I(t)} = \frac{V_A \sin(\omega t)}{I_A \sin(\omega t + \varphi)} \quad (2.4)$$

The impedance also can be represented as a complex function which expressed as a combination of "real" or "in-phase" (Z_{REAL}), and "imaginary" or "out-of-phase" (Z_{IM}) [20].

$$Z = Z_{real} + jZ_{img} \quad (2.5)$$

The magnitude of the impedance and phase angle, φ can be calculated by using formula as follow.

$$|Z| = \sqrt{(Z_{real})^2 + (Z_{img})^2} \quad (2.6)$$

$$\varphi = tan^{-1}\left(\frac{Z_{img}}{Z_{real}}\right) \quad (2.7)$$

In general, the EIS results are represented in two graphical approach namely Nyquist and Bode Plot. In Nyquist plot, the imaginary impedance, Z_{img} is plotted against the real impedance, Z_{real}. Every point that plotted in the graph is representing the impedance value at one frequency. The impedance magnitude and phase angle also can be obtained from Nyquist plot as in Figure 2.10. After that, for Bode plot as in

Figure 2.11, it will present the impedance magnitude and phase angle are plotted separately against the logarithm of frequency [20].

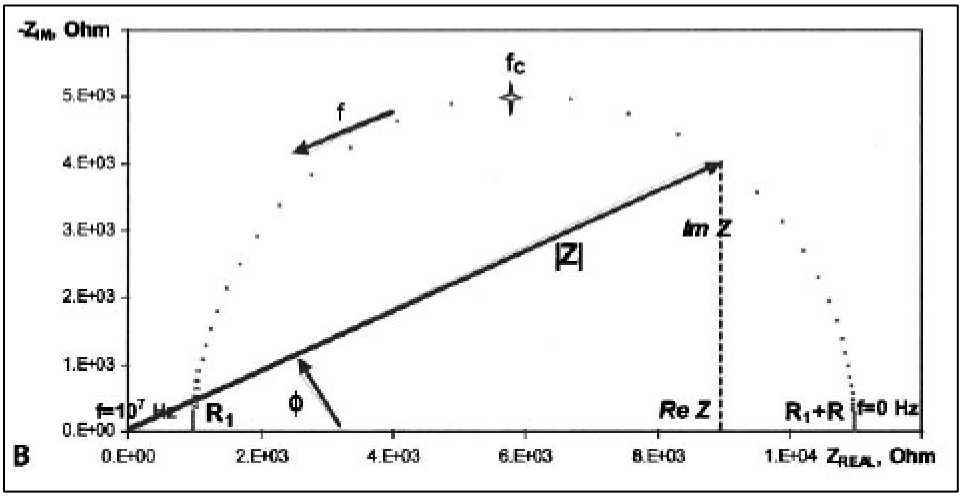

Figure 2.10: Example of Nyquist plot [20]

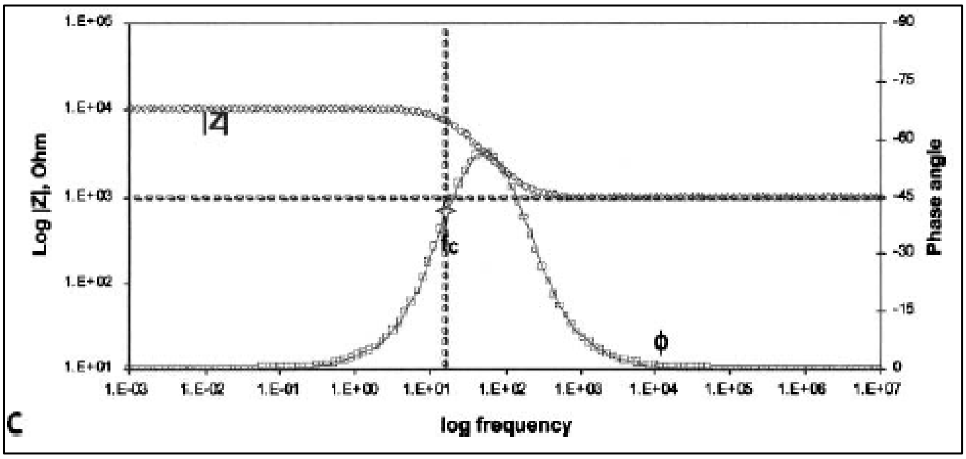

Figure 2.11: Example of Bode plot [20]

Dielectric is a non-conducting medium or material such as polymer coating and pipelining. However, the electron may diffuse through the material when placed in an electric field and this so-called electric polarization. There are two parameters needed to scrutinise the abilities of any material to store electrical energy and transmit electron charge which are permittivity and conductivity. In dielectric analysis, those parameters are measured as a function of time, temperature and AC radial frequency, w [20]. For this project, the author was using HDPE as the dielectric material. The permittivity value of HDPE was evaluated and tabulated in Figure 2.9.

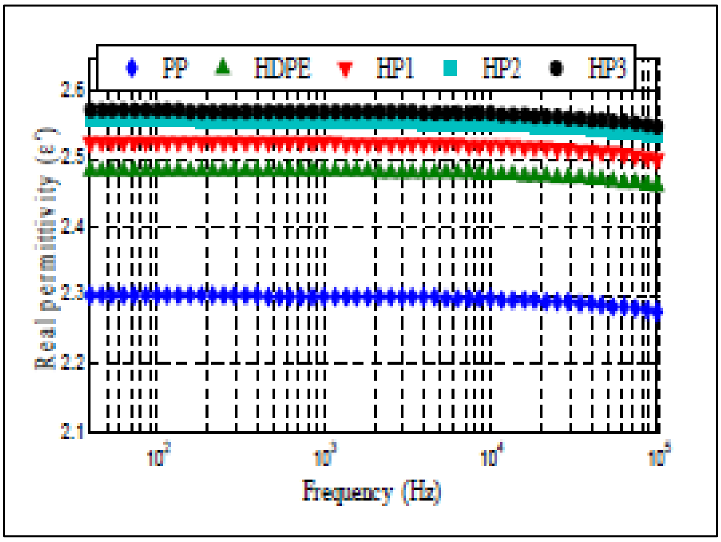

Figure 2.12: Permittivity real component of HDPE [21]

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, the author will discuss on the material and instrument utilised throughout this experiment, experimental design study, overall research flow of the project, sample and solution preparation, physical and impedance change measurement.

3.2 Material and Instrument

The materials and instruments utilised throughout this project are mentioned in Table 3.1 and Table 3.2 below.

Table 3.1: Material / chemical used for the experiment

No	Material / Chemical	Application
1	Deionized water + Sodium Chloride (NaCl)	Solution for EIS evaluation
2	Deionized water + Hydrocarbon + Carbon Dioxide (CO_2)	Solution and gaseous medium for chemical deterioration process
3	High Density Polyethylene (HDPE)	Polymeric sample for degradation analysis
4	Commercial epoxy adhesive	Adhesive substance between polymer and metallic surface for EIS evaluation
5	Low alloy metallic plate	Conductive surface for EIS evaluation

Table 3.2: Instrument used for degradation and impedance study

No	Instrument	Application
1	Potentiostat	Used to control the potential difference between the three electrodes
2	Reference electrode (Ag/AgCl electrode)	Used as cathode in the electrochemical circuit
3	Counter electrode (Stainless Steel)	Used to balance the reaction at the working electrode
4	Working electrode (Low alloy Steel)	Use as anode in the electrochemical circuit
5	Autoclave machine	Used to accelerate the chemical degradation process

3.3 Experimental Design Study

This project consists of two different work process which are EIS evaluation and chemical degradation of polymer in high pressure and temperature application. For the first work process, the author was assessing the polymer degradation based on the impedance variation that indicate the fluid permeation process was occur in the sample. The experiment been carried out by referring to the common standards such as ASTM D570 - 98 – Standard Test Method for Water Absorption of Plastics and equivalent standard, ISO 63:2008 Plastics - Determination of Water Absorption.

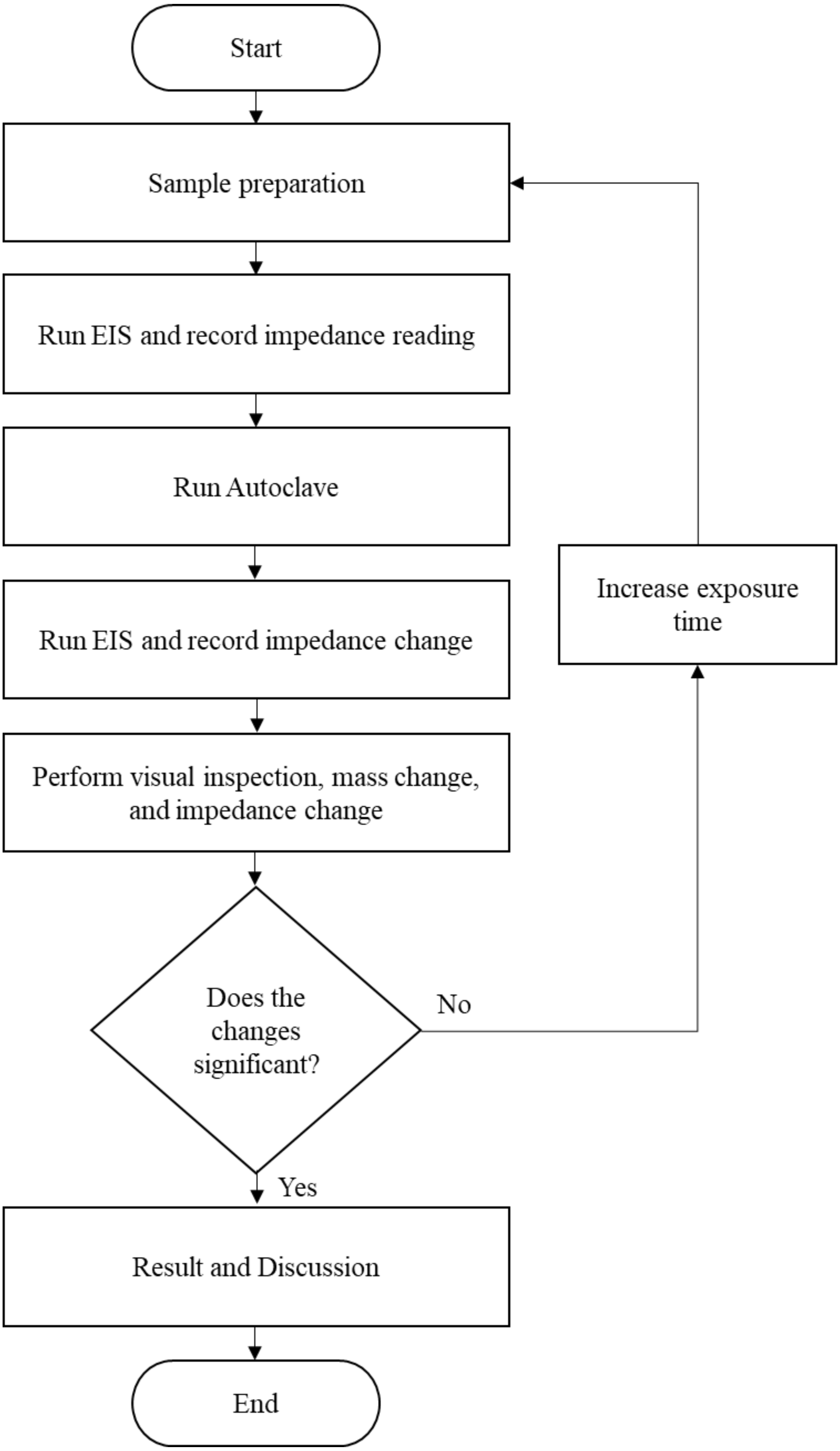

Figure 3.1: Flowchart of the FYP Project

3.3.1 Sample and Solution Preparation

For sample preparation, the polymer was cut into 6 pieces with the dimension of 25mm X 25mm X 3mm. Then, the author chose to use 10 small low alloy steel plates with the dimension of 20mm X 20mm X 3mm as conductive material for EIS evaluation. Three of the metal plates were applied with commercial epoxy adhesive on one of its side and maintained the thickness between 100 – 120 microns. Another three metal plates were coupled with the polymer samples by the same commercial epoxy adhesive in between. Before applying the epoxy, the author made some profile on the metal surface by using a coarse hand file since the epoxy will peel off easily when applied on a smooth surface. The metal plates also been grinded to remove the corroded surface before putting under EIS machine.

Next for the solution preparation, there were two type of solutions used in this project. The solution used for EIS evaluation process was combination of deionised water and 3.5% of NaCl. For the autoclave method, the author used the solution with a mixture of deionised water, hydrocarbon and diffused CO_2 gaseous.

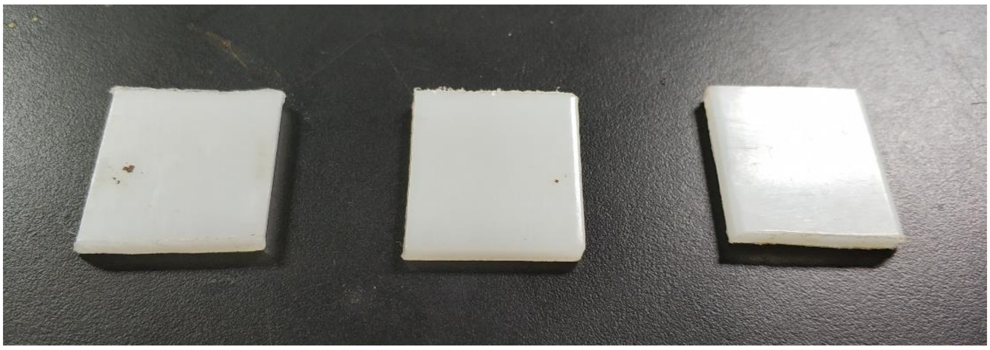

Figure 3.2: Polymer samples

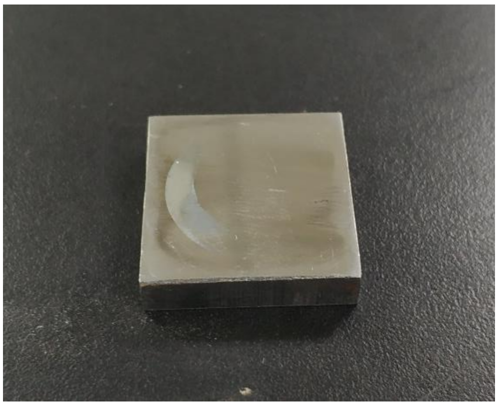

Figure 3,3: Small metal plate

Figure 3.4: Metal plate applied with epoxy

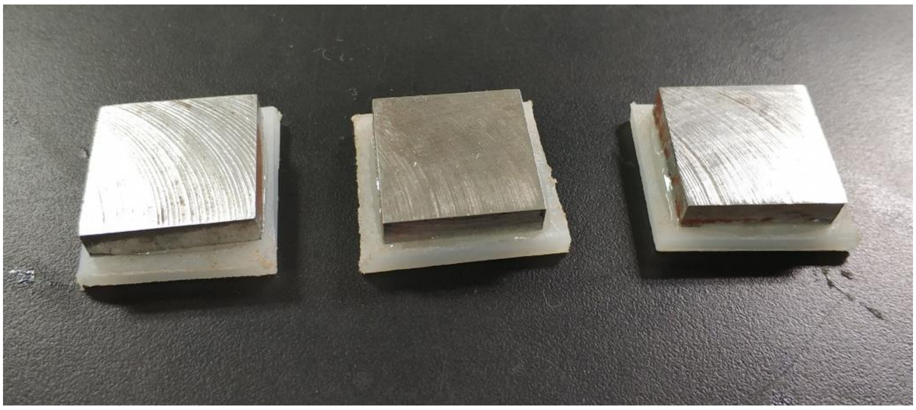

Figure 3.5: Metal plate and polymer sample with epoxy adhesive

3.3.2 Electrochemical Impedance Spectroscopy (EIS) Evaluation

As mentioned before, the current standard methods are using common coupon immersion technique but for this experiment the researcher was using an advanced technology namely Electrochemical Impedance Spectroscopy (EIS). This technology is widely utilised to evaluate rapidly, quantitatively and non-destructively the performance of protective coating on a metal. EIS can detect the impedance that produced by diffusing reactants which called Warburg impedance and by the coating capacitance. The polymer sample used for this project is High Density Polyethylene (HDPE). All of the prepared samples were initially evaluated under EIS to get the initial impedance value for each sample. After running through the autoclave, the samples were evaluated again in order to detect the changes of impedance due to chemical degradation. The setup of the EIS instrument is shown in Figure 3.6.

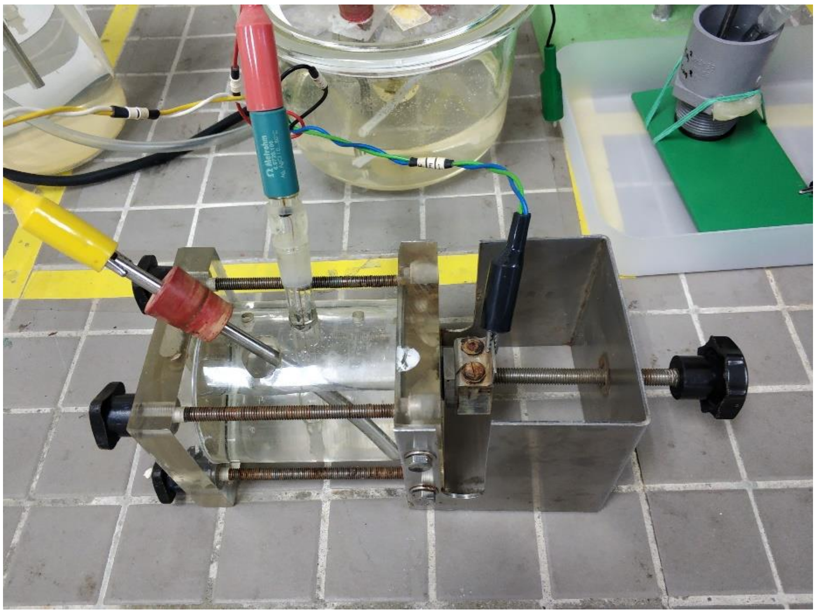

Figure 3.6: The setup for EIS evaluation

3.3.3 Chemical Degradation Process

As for accelerated study purposes, the samples were immersed in the solution and put into the autoclave machine at 20 bar and 60°C for 72 hours. Then, the exposed polymer sample were measure for its dimension and mass changes. The autoclave machine that been used was as in Figure 3.7.

Figure 3.7: The autoclave machine

Table 3.3: Experimental test matrix

Test Coupon	
Material	HDPE
Dimension, mm (Length*Width*Thickness)	25mm * 25mm * 3mm
Number of Sample	10 samples
Test Condition	
Electrical Impedance Spectroscopy (EIS) Evaluation	
Environment (Electrolyte)	1) Pressure: 1 atm 2) Temperature: 25°C 3) Contaminant: 3.5% of NaCl,
Duration of Exposure	2 hours
Chemical Degradation Process Using Autoclave Machine	
Environment (Electrolyte)	1) Pressure: 20 bar 2) Temperature: 60°C 3) Contaminant: 50% deionized water, 50% hydrocarbon, CO_2
Duration of Exposure	1) 72 hours
Test Information	
Standard	1) ASTM D570 - 98
Characterisation Method	1) Visual – dimension (swelling) 2) Chemical degradation - Autoclave 3) Impedance measurement – EIS

CHAPTER 4

RESULT AND DISCUSSION

This chapter presents and confers the results from the experimental work and analysis of chemical degradation in HDPE when exposed to CO_2 environment. The results were presented according to the chronology of the research methodology which explained in previous chapter.

4.1 Chemical Degradation Analysis by EIS

4.1.1 Initial Impedance Reading

Before the samples were going through the chemical degradation process in the autoclave machine, the initial mass of the polymer were recorded since the author intended to examine the water uptake in the polymer. The initial impedance readings for all samples were examined and the results are as follows:

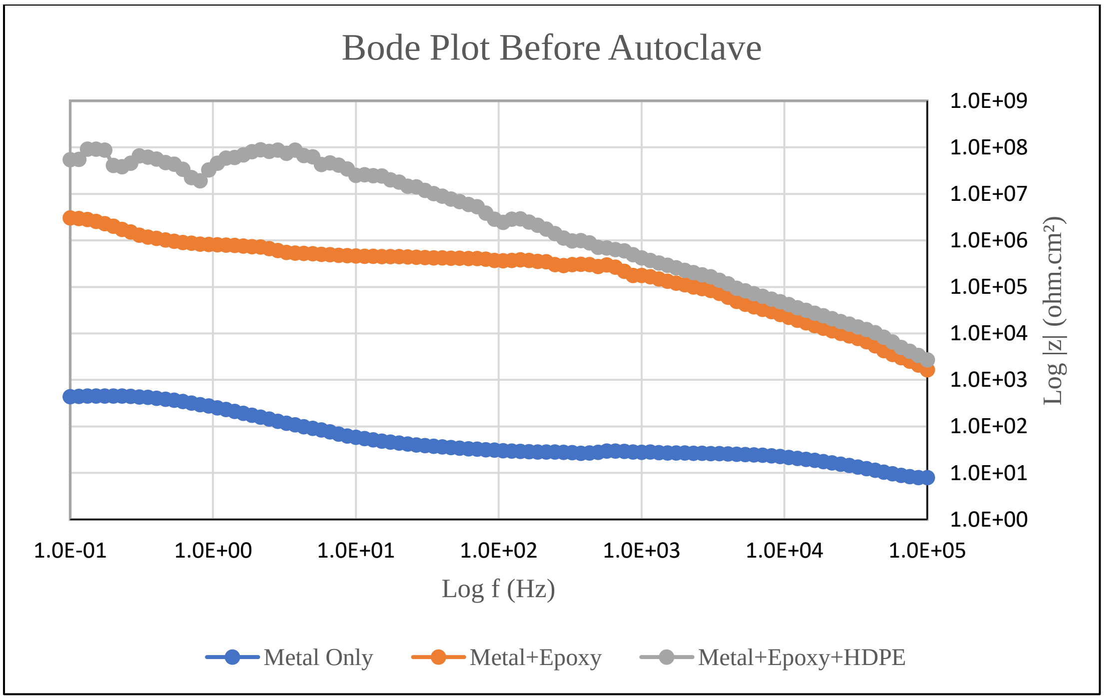

Figure 4.1: Bode plot for initial impedance reading

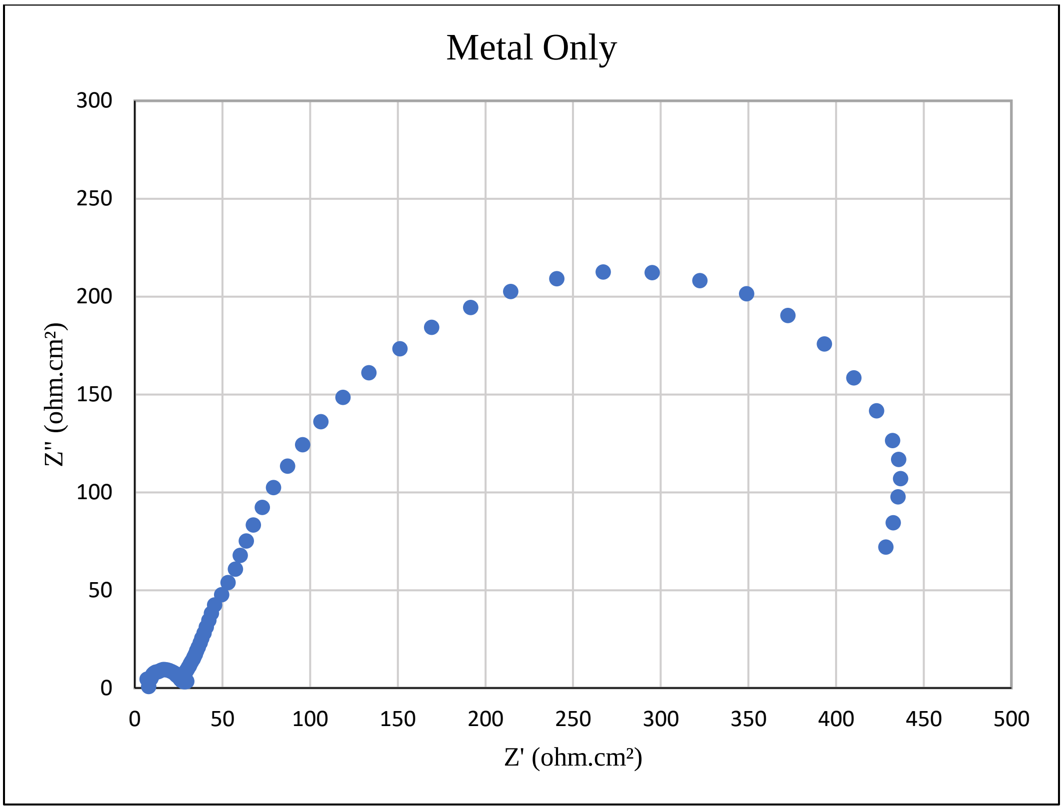

Figure 4.2: Initial Nyquist plot for metal plate

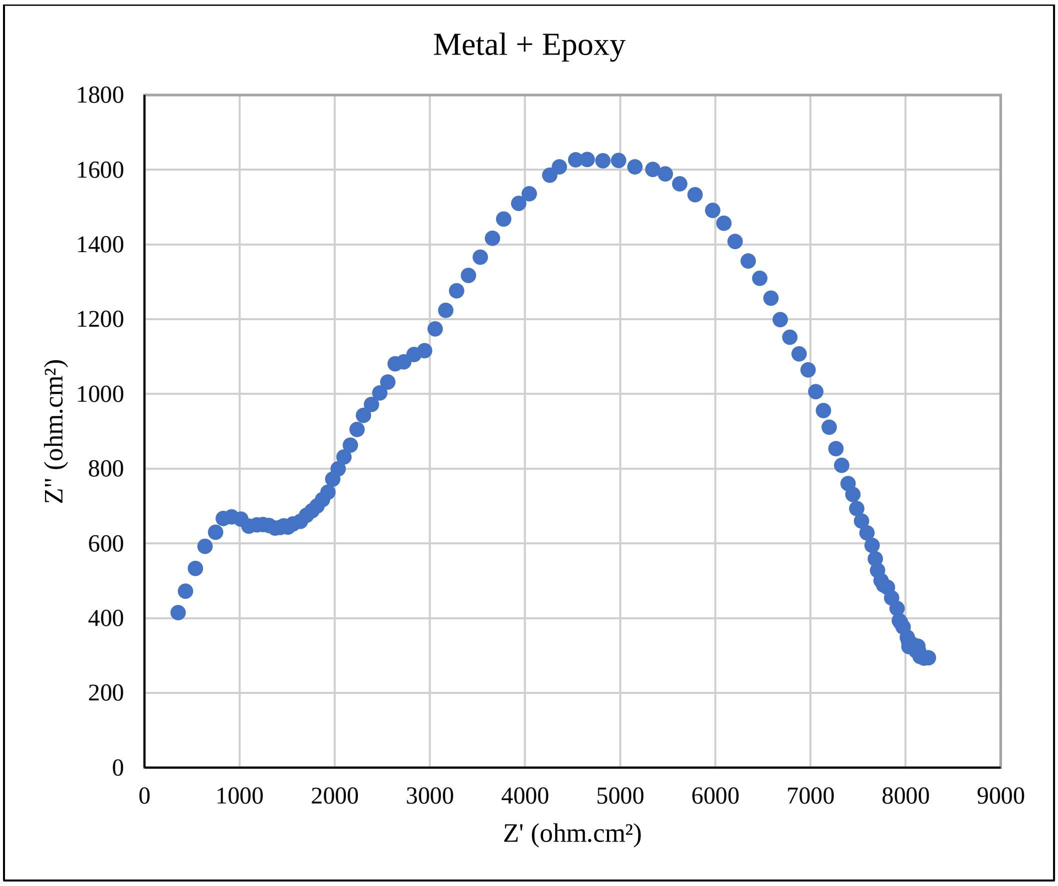

Figure 4.3: Initial Nyquist plot for metal plate and applied epoxy

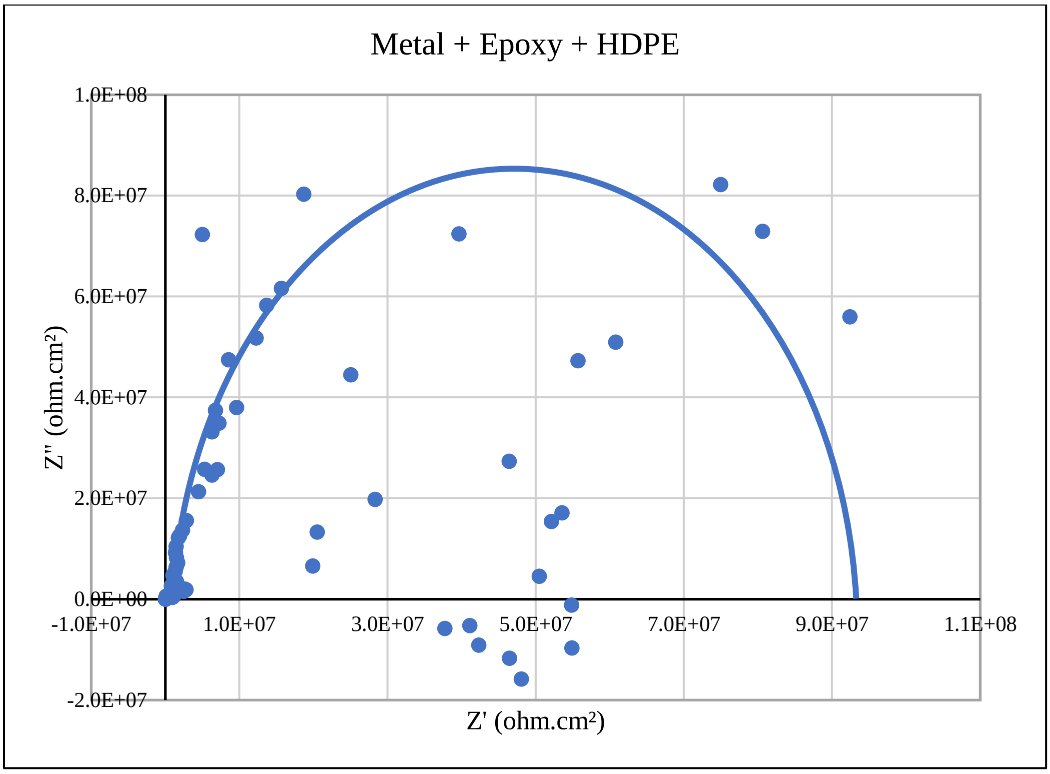

Figure 4.4: Initial Nyquist plot for metal plate and HDPE with epoxy adhesive

From the bode plot shown in Figure 4.1, the impedance of the samples were inversely proportional to the frequency. When the frequency decrease, the sample impedance will increase and vice versa. The impedance patterns and measurements for each type of samples also difference due to the present of additional capacitance and resistance into their system. This also indicates that there are some additional surface or material added on the metal plate. For example for this project, the appliances of epoxy and polymer had increased the capacitive element into the system's circuit element.

In Figure 4.2, the Nyquist plot shows a semicircle due to the present of double layer capacitance between the solution and metal surface. The Nyquist plot in Figure 4.3 shows two semicircle which represent the present of two capacitances when an epoxy adhesive layer was introduced. Lastly, in Figure 4.4 the impedance pattern was not clear and scattered. This might be due to some noises and thickness of the polymer. The polymer used was 3 mm in thickness which equivalent to 3000 microns of coating layer. As a result, the capacitance of the dielectric material will be decrease since the distance between the electrolyte and metal surface was increased.

4.1.2 Chemical Degradation Result

The chemical degradation process was done by using autoclave machine at 20 bar and 60°C. All of the samples were immersed into the solution and exposed for 72 hours. The condition of the samples after 72 hours were shown in Figure 4.5.

Figure 4.5: The samples after putting into autoclave machine

As shown in Figure 4.5, all of the epoxy adhesive which applied on the metal surface and used to attach the HDPE were peeled off. Two of the HDPE sample were melted. The metal specimens were lightly corroded. This incident occur due to the machine’s malfunction. The temperature of the solution was increased up to 100°C by the machine. The event occur not during working hour and the author just realised the changes in the next morning. After some adjustment, the temperature goes down to 30-35°C and maintained until the end of 72 hours even the setting temperature is 60°C. The author believes that the experiment can be repeated by reducing the temperature and increase the exposure time. However, the heater on the autoclave was broken and need to go through some repair work.

4.1.3 Final Impedance Reading

Since the heater could not be in place by the end of the semester due to global disease, the author decided to analyse and study the impedance change based the remaining samples. The final impedance readings for all remaining samples were recorded as follow:

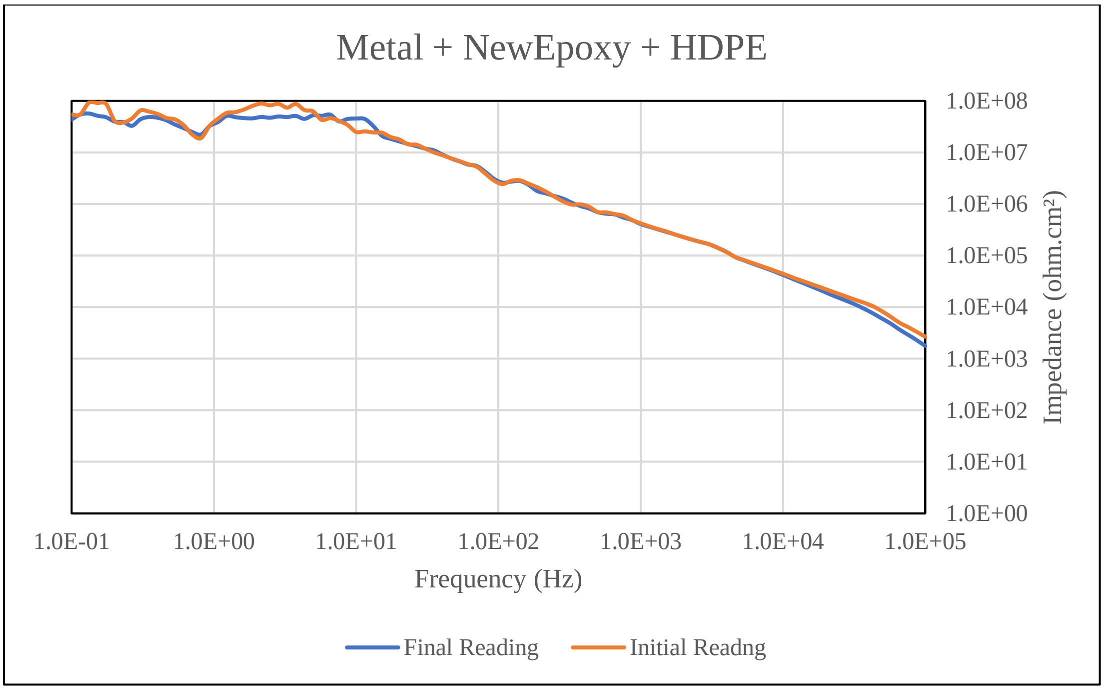

Figure 4.6: Bode plot for final impedance reading

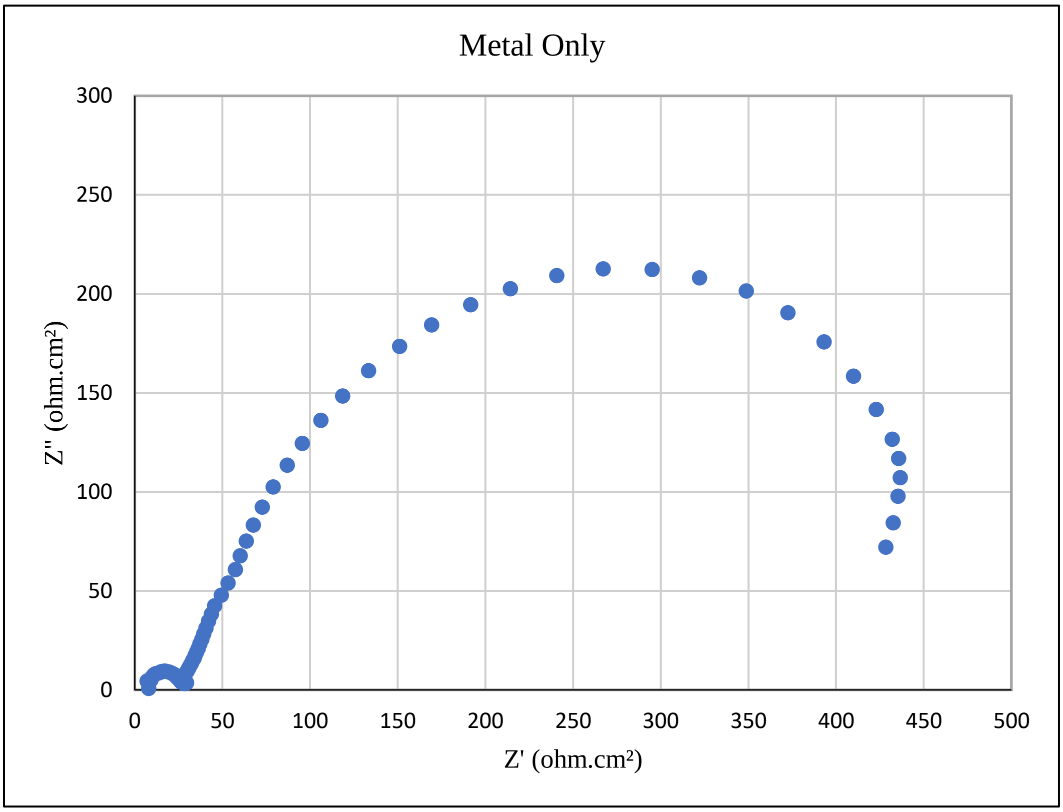

Figure 4.7: Final Nyquist plot for exposed metal plate

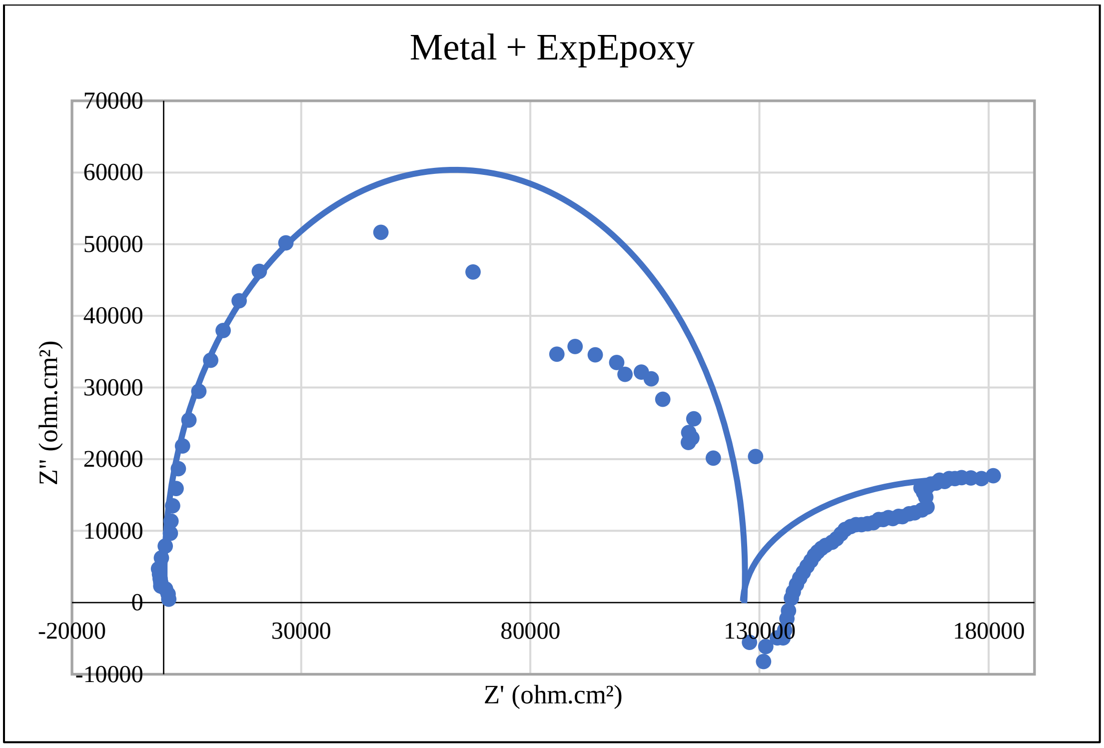

Figure 4.8: Final Nyquist plot for exposed metal plate and epoxy

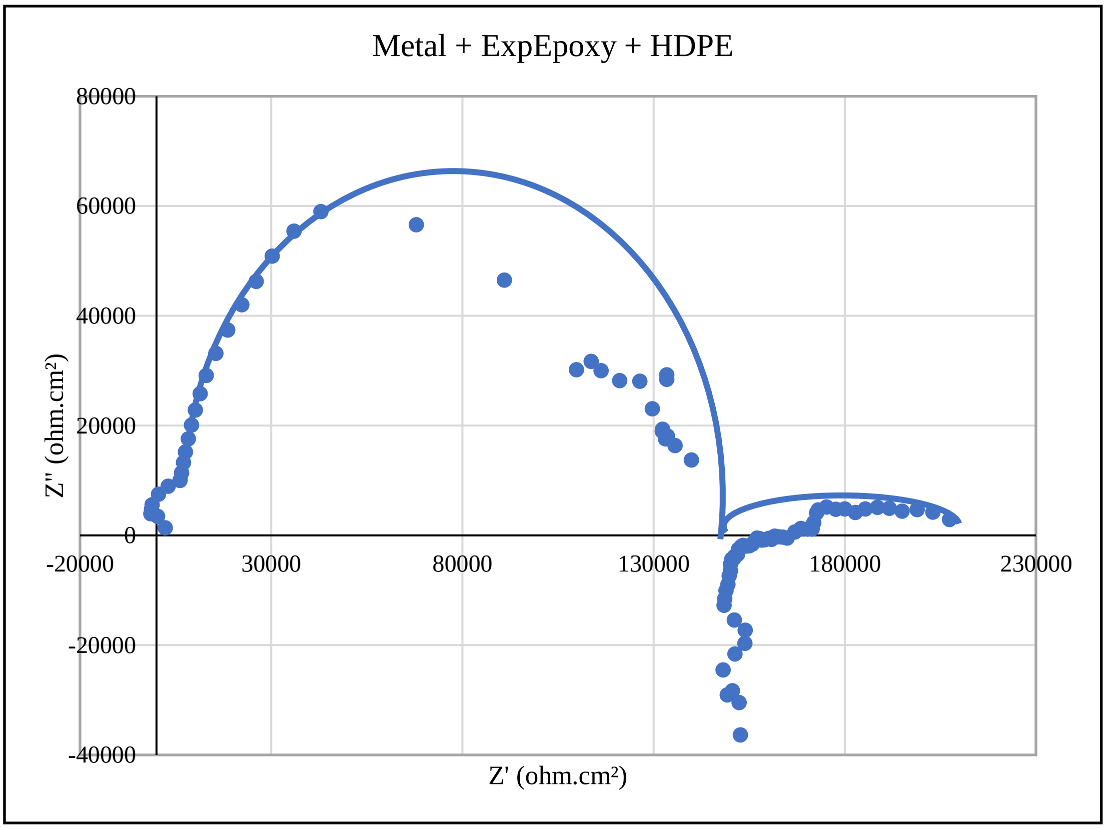

Figure 4.9: Final Nyquist plot for exposed metal plate and HDPE with exposed epoxy adhesive

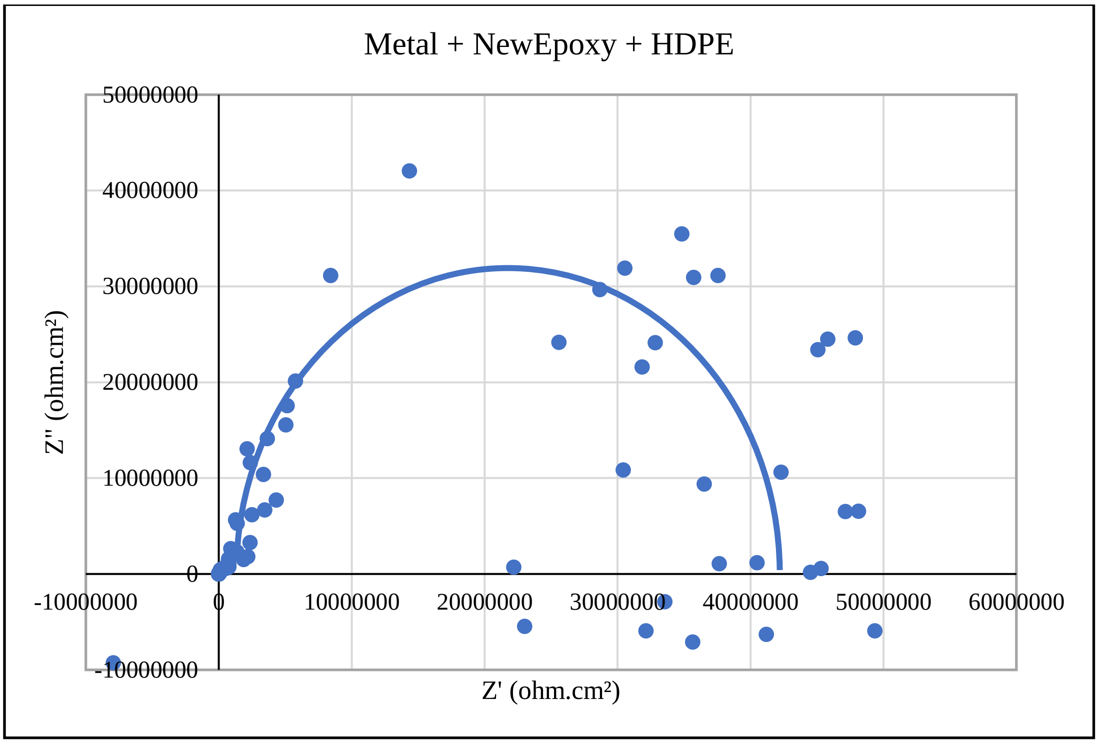

Figure 4.10: Final Nyquist plot for exposed metal plate and HDPE with new epoxy adhesive

Firstly, from the Bode plot in Figure 4.6 above, the author observed some impedance reduction at the lower frequency reading. As mentioned by Lvovich [20], the determined polarization can be ionic or displacement of the ions with respect to each other when the frequency was from Hz to kHz. However in the metal plate, the impedance remained the same. This is because the resistance in the metallic plate was remained the same, since the exposure time of 72 hours was not adequate to reduce its thickness or changing other properties. Secondly, in Figure 4.8 and 4.9, the Nyquist plots shows two semicircles which intercepted on the Z' axis. These can be interpreted such that some air gap or disbondment were present between the epoxy and metal plates. This might be due to action taken by the author which slipped on the exposed epoxy in between the samples. Lastly, the Nyquist plot in Figure 4.10 was showing a semi-circular pattern since new epoxy layer was applied on the exposed samples even the plotting was not certain and scattered due to some noises, etc. Unfortunately, for mass and volume changes, the author could proceed the analysis since the samples were melted and the labelling for the samples are wiped out in the autoclave machine.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, the fluid permeation process can cause many defects in polymer materials. Reduction of impedance is one of the defect for pipelining material since they need to prevent the metallic pipe from corrosion. EIS method can be implemented to evaluate the performance of pipelining material or NMP. In term of the sample used in this project, the appliances of epoxy adhesive and polymer are greatly increased the impedance measurement. Even the changes in sample impedance were not really impressive and significant, but the author manage to prove that EIS can detect the premature defect in polymer.

As for recommendation, the author prefer to use thinner and stronger film of polymer since the capacitance for the dielectric material will become greater. We also can avoid the sample from any damage due to stronger bond in the polymer. This can give a better pattern in the Nyquist plot. Conductive tape also can used instead of using metal plate but do not put it into the autoclave machine. Otherwise it going to ruined.

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