

CHAPTER 3

METHOD OF INVESTIGATION

3.1 Introduction

This chapter covers the procedures used for the preparation of materials and the analysis methods that were used to determine the corrosion behavior of samples. The overall experimental steps involved are as shown in Figure 3.1.

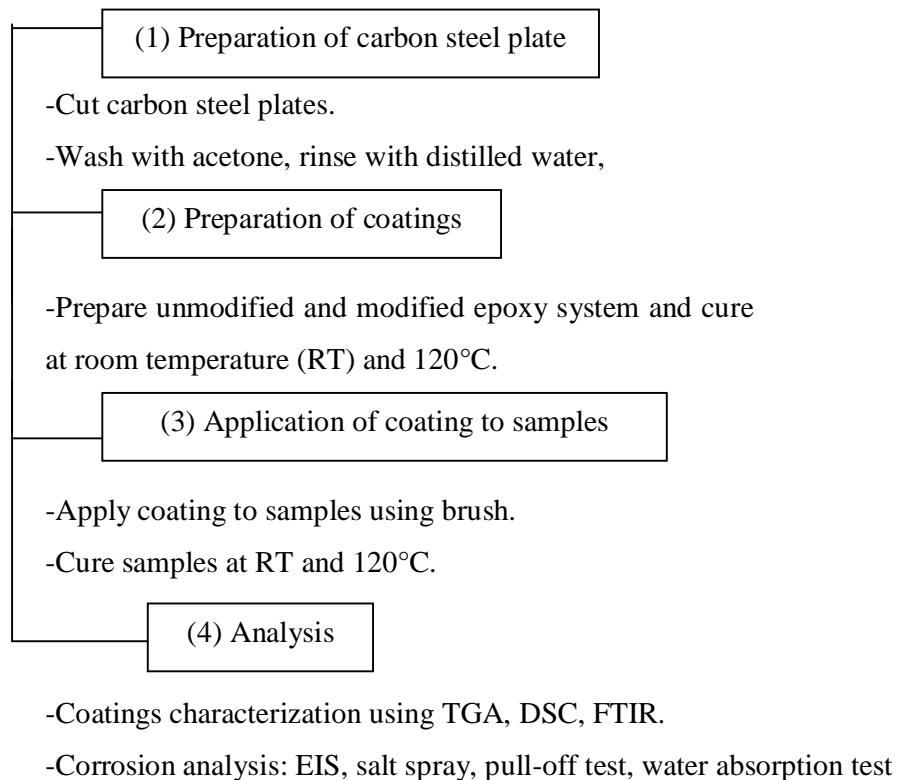


Fig. 3.1 Flow diagram of sample preparation and evaluation of unmodified and modified epoxy systems

3.2 Chemicals and Materials

Low carbon steel plates (A36 grade) were used as samples. Materials used for the preparation of the coating system are ASA 828 (provided by ASA Chem. Sdn. Bhd) as the epoxy, m-XDA (provided by Sigma Aldrich) as the hardener and Polyaniline emeraldine salt (provided by Sigma Aldrich) as the additive. The properties of PANI as provided by the supplier are shown in Table 3.1. Other chemicals that were used in this research are acetone and distilled water for the purpose of cleaning the samples and sodium chloride (3% NaCl) for electrochemical test.

Table 3.1 Properties of Polyaniline [112]

Concentration	3 wt% in xylene
Particle size	<400 nm
Conductivity	10-20 S/cm (film)
Viscosity	~3 cP (lit.)
Boiling point	116 °C (xylene)
Melting point	>300 °C (lit.)
Solubility	H ₂ O: insoluble
Density	0.90-0.95 g/mL at 25 °C

3.3 Preparation of carbon steel plate

The A36 carbon steel alloy composition is shown in Table 3.2 [113]. The samples were prepared in two different ways, depending on the analysis that will be done for the samples. For electrochemical analysis, the samples were cut and mounted in epoxy resin, leaving an approximate surface of 20 mm x 20 mm for exposure. Before mounting, electrical contact were made to each specimen using silver paste to attach a copper wire to the back surface of the specimen. The surface was polished sequentially on 240, 320, 400 and 600 grit SiC paper until previous coarse scratches have been removed. Finally, the specimens were degreased with acetone, rinsed in distilled water and then dried. For salt spray and pull-off test analyses, the samples were prepared using the same way as above, but the size of the specimens were cut to

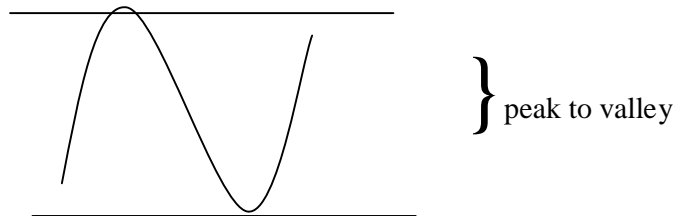
40 mm x 40 mm x 2 mm and a hole of 3 mm diameter was made on the top of the steel plate and they were not mounted.

Table 3.2 Composition of A36 carbon steel [113]

Alloy	Chemical composition (wt %)				
	C	Mn	P	S	Si
A36 steel	0.29	1.2	0.04	0.05	0.3

3.4 Surface Profile Test

This test was done according to ASTM D4417 [114]. The purpose of conducting this test is to determine whether the surfaces of the steel plates are suitable/ready to be coated after the sample cleaning process. It was done by measuring the peak to valley of the sample surface (surface roughness depth) using a profilometer.



A profilometer consists of several parts: a stylus, a rider, a part to hold the sample. All of these parts are then connected to a computer. The stylus travels along a straight line over the sample surface. It detects and traces the depth of the surface roughness. In order to highlight the roughness, the profilometer traces are recorded on an exaggerated vertical scale. The brand of the profilometer used was Mahr. Perthometer as shown in Figure 3.2.



Fig.3.2 Profilometer used : Mahr. Perthometer

3.5 Preparation of Epoxy Coating

Two epoxy systems were prepared, the unmodified epoxy and the modified epoxy. The epoxy that was used is relatively simple, unmodified diglycidyl ether of bisphenol A (DGEBA). The m-xylydiamine (m-XDA), as the curing agent, was added into the epoxy in the ratio of 2:1. The required amount of DGEBA and m-XDA can be calculated using Equation 3.1.

$$M = \left[\frac{E}{E_{n_{epoxy}}} \right] \left[\frac{E_{n_{a \min e}}}{2} \right] \quad \text{Eq.3.1}$$

Where, M is mass of m-XDA (g), E is mass of Epikote 828 (g), $E_{n_{epoxy}}$ is equivalent weight of Epikote 828 (g/mol) and $E_{n_{a \min e}}$ is equivalent weight of m-XDA (g/mol). The overall calculation is as shown in Appendix A.

The mixture was then stirred for 10 minutes using an electrical stirrer. The structures of DGEBA and m-XDA are as shown in Figure 3.3a and 3.3b respectively.

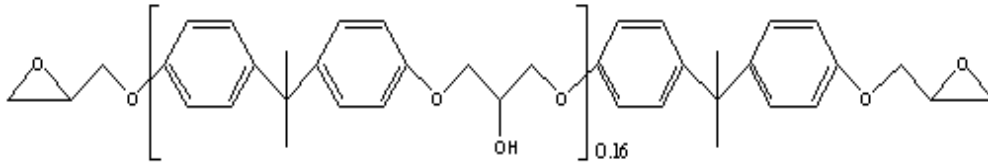


Fig.3.3a The chemical structure of diglycidyl ether of bisphenol A (Epikote 828) [86]

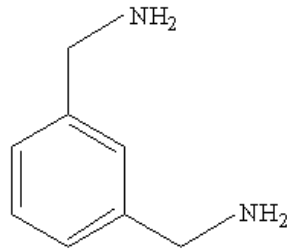


Fig. 3.3b The chemical structure of *m*-xylylenediamine (*m*-XDA) [86]

For modified epoxy, three samples containing various amount of Polyaniline (0.5%, 1.0% and 1.5%) were prepared. Polyaniline was mixed together with the DGEBA by direct mixing. Then *m*-XDA was added into the Polyaniline/epoxy mixtures, and the mixtures were stirred for 10 minutes using the same method as above. The amount of PANI added to the epoxy system was calculated using Equation 3.2 and the composition is shown in Table 3.3 and the overall calculation is as shown in Apendix B.

$$\text{PANI} = \frac{x(E + M)}{(1 - x)} \quad \text{Eq. 3.2}$$

Where, PANI is mass of Polyaniline (g), E is mass of ASA 828 (g), M is mass of *m*-XDA (g) and *x* is mass fraction of PANI.

Table 3.3 Composition of unmodified and PANI modified epoxy resin

Sample Codes	Sample	Composition %wt
E/M	ASA 828/ <i>m</i> -XDA	85.15/14.85
E/M/0.5 PANI	ASA 828/ <i>m</i> -XDA /0.5 % PANI	84.72/14.78/0.5
E/M/1.0 PANI	ASA 828/ <i>m</i> -XDA /1.0 % PANI	84.30/14.70/1.0
E/M/1.5 PANI	ASA 828/ <i>m</i> -XDA /1.5 % PANI	83.87/14.63/1.5

3.6 Application of Coatings to the Substrates

The coatings were applied to the carbon steel plates using a brush. The thickness of coatings was set to be in the range of 60-80 μm and it was measured using a micron meter. For salt spray analysis the carbon steel plates were dipped into the coating so that both sides of the carbon steel plates were coated. Finally, the coated carbon steel plates were cured at two different conditions (room temperature for 24 hrs and 120° C for 3 hrs) before proceeding with other analyses.

3.7 Sample Characterization

3.7.1 Differential Scanning Calorimetry (DSC)

DSC is a technique that is used to study the thermal transition of a polymer. Thermal transitions are the changes that take place when a polymer is heated. The melting of a crystalline polymer and glass transition temperature (T_g) are examples of thermal transitions.

The basic instrumentation used for thermal analysis usually consists of four parts as shown in Figure 3.4 [115]:

- a. Sample/sample holder (aluminium, stainless steel, platinum sample pans).
- b. Sensors to detect and measure the property of the sample and also temperature (usually thermocouples).

- c. An enclosure within which the experimental parameters may be controlled.
- d. A computer for data collection and processing.

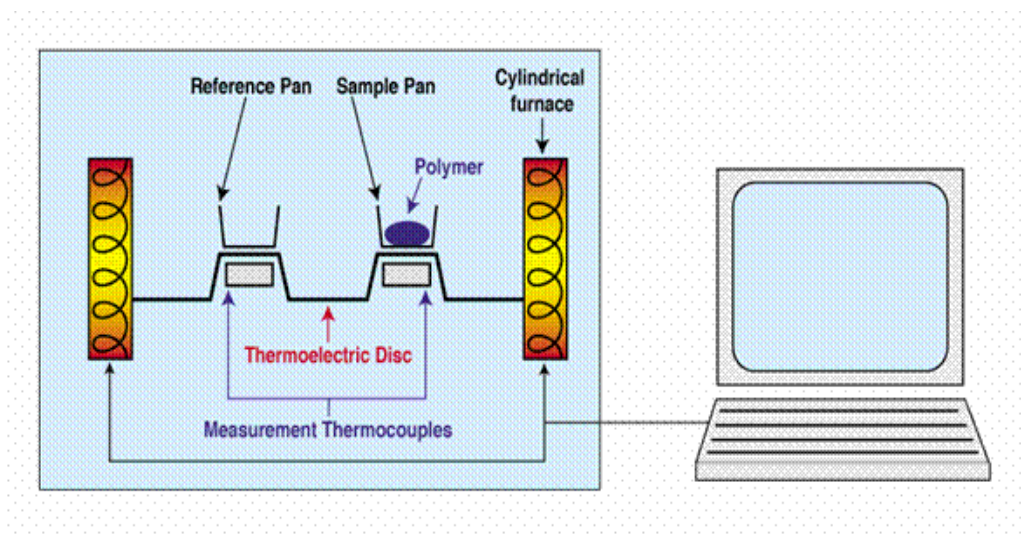


Fig. 3.4 Schematic diagram of a DSC [115]

This device consists of two pans. In one pan, the polymer sample is loaded while the reference pan is normally left empty. These pans are placed on top of a heater. The computer assembly will turn on the heaters and the heating rate of the two pans is accurately controlled. The computer programs the heating rate to stay exactly the same throughout the experiment. The two pans are heated at the same rate.

The presence of a polymer material in the sample pan results in an uptake of more heat in order to keep the temperature of the sample pan increasing at the same rate as the reference pan. This means that the heater underneath the sample pan will provide more heat energy than the heater under the reference pan. So, basically, a DSC analysis is about how much heat the sample pan heater has to produce as compared to the reference pan heater. The amount of heat required to obtain to a certain temperature increase in a material is called heat capacity, C_p . (Figure 3.5a). When the polymeric material is heated a little more after a certain temperature, the temperature plot will shift downward suddenly, and that indicates the glass transition temperature (Figure 3.5b).

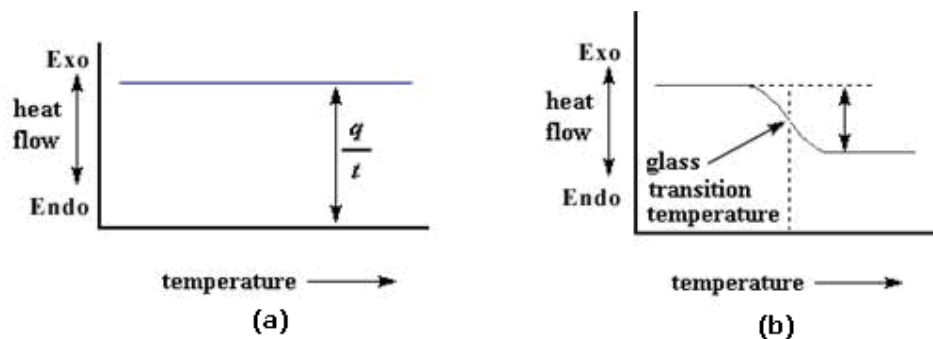


Fig. 3.5 Plots of heat flow against temperature (a) a graphical illustration of heat capacity phenomena and (b) definition of glass transition temperature [115]

This analysis was done according to ASTM D3418 [116]. Samples of cured unmodified and modified epoxy resin were weighed between 5-10 mg and encapsulated in an aluminium pan. Before conducting the experiment, the equipment needs to be pre-heated and the temperature of the DSC cell must be set at 20°C. Then the pan containing the sample was placed on the left side next to an empty reference cell. For uncured sample, the samples were heated at 10° C/min until 200° C under a nitrogen flow of 20 ml/min. The glass transition, T_g was measured straight from the 1st heating. On the other hand, the cured samples were first heated to 150° C at 10°C/min under a nitrogen flow of 20 ml/min and maintained for 1 min at 150° C. Then they were cooled to -50° C at a cooling rate of 20° C/mins and the glass transition temperature was determined also after the 1st cycle of heating. The DSC instrument used was Perkin Elmer Pyris I.

3.7.2 Thermal Gravimetric Analysis (TGA)

TGA is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or batch, knowledge of the magnitude and temperature range of those

reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

The analysis is usually performed by placing a sample of the test material in a high alumina cup that is either supported on, or suspended from an analytical balance located outside the furnace chamber. Then the balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve is plotted from the TGA signal, which has been converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

The thermal stability of Polyaniline and epoxy resin was determined using Setaram Instrument Model SETSYS 1750. The tests were conducted in a nitrogen environment at two temperature ranges: 30° C to 600° C and 30° C to 800° C, and 10° C/min of heating rate.

3.7.3 Fourier Transform Infrared (FTIR)

IR spectroscopy is a very powerful method for the identification of functional groups. For each spectroscopic method, it is helpful to understand how much energy corresponds to each wavelength and how this relates to the physical process after absorption of radiation. Organic molecules can absorb IR radiation between 4000 cm^{-1} and 400 cm^{-1} which corresponds to absorption of energy between 11 kcal/mole and 1 kcal/mole. This amount of energy initiates transitions between vibrational states of bonds contained within the molecule.

The samples measured were Polyaniline and Polyaniline/DGEBA mixtures which were cured at room temperature (RT) and 120 °C. During sample preparation, the samples were milled with KBr to obtain a fine powder. Then they were compressed into thin pallets. Finally, the samples were placed in the sample holder and were analyzed by Shimadzu Fourier Transform Infrared Spectrophotometer 8400-S. The spectra were analyzed using Spectrum One data acquisition system.

3.8 Corrosion analysis

3.8.1 Electrochemical Impedance Spectroscopy (EIS) Measurement

A beaker with a capacity of 1000 ml was used to place the samples and electrodes for the impedance measurement. The system configuration consists of three electrodes: a working electrode, an auxiliary electrode and a reference electrode, and a potentiostat. The auxiliary electrode is made of platinum while the reference electrode used is a Ag/AgCl electrode. This reference electrode was adjusted until it was facing the working electrode as close as possible. The sample acted as the working electrode and the electrolyte used was 3% sodium chloride (NaCl) solution. The potentiostat used was the Autolab ver. 4.9.7 model and the data were analyzed using FRA software. The schematic diagram for the experimental setup of the EIS measurement is as shown in Figure 3.6.

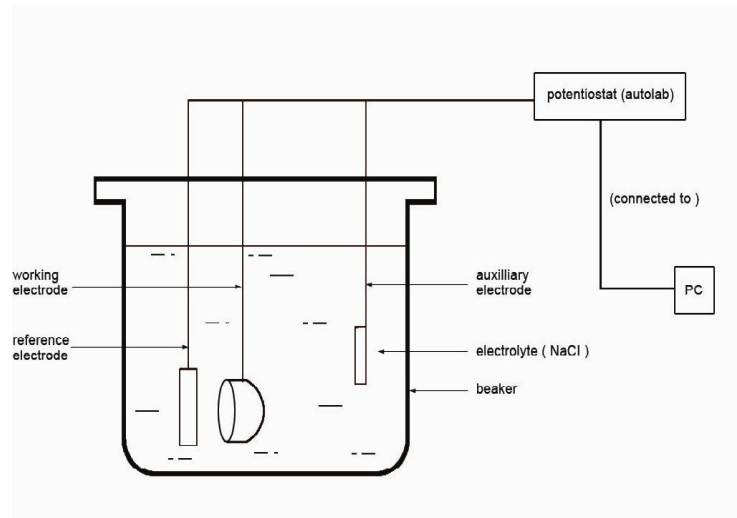


Fig. 3.6 Experimental setup for impedance measurement

3.8.2 Salt-spray Test

This test is an accelerated corrosion test that produces a corrosive attack to the coated samples in order to predict its suitability for use as a protective finish. This was done in the laboratory in accordance to the ASTM B117-02 [117]. The specimens were

scribed using sharp tool and placed in the salt spray chamber as shown in Figures 3.7 and Figure 3.8. The salt solution was prepared by dissolving 5 parts by weight of sodium chloride in 95 parts of water. The salt used was a 5% sodium chloride (NaCl) substantially free of nickel and copper, and containing on the dry basis not more than of 0.1% of sodium iodide. The exposure zone of the salt spray chamber was maintained at 35° C.



Fig.3.7 Salt spray chamber

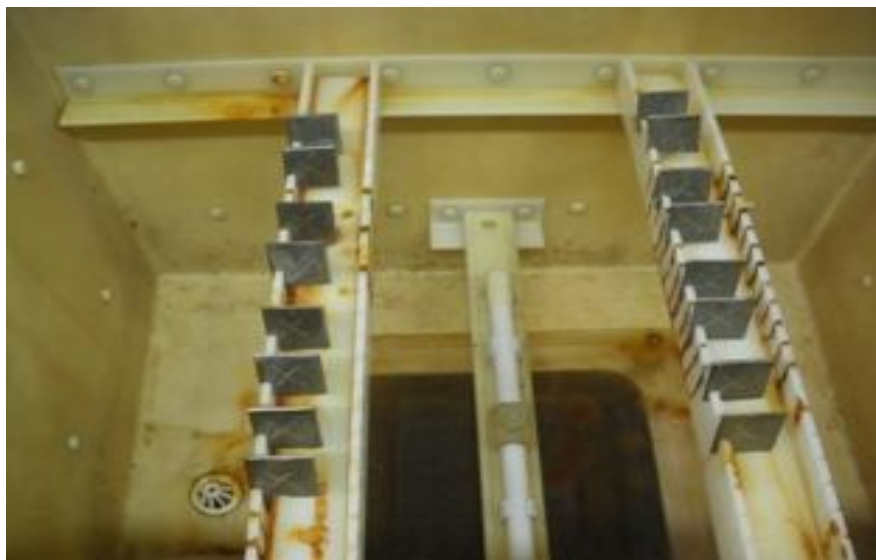


Fig. 3.8 Samples placed in chamber

3.8.3 Pull-off Tests

Pull-off tests were performed to determine the adhesion strength. The tests were performed using a portable adhesion tester (as shown in Figure 3.9a) in accordance to the ASTM D 4541-95 [118]. It was done by securing a loading fixture (aluminum test dolly) perpendicular to the surface of the coating with adhesive as shown in Figure 3.9b. After the adhesive has cured, the adhesion tester was attached to the loading fixture and aligned to apply normal tension to the test surface. The force was applied to the loading fixture until the dolly was detached from the samples. When the dolly has detached, the exposed surface represents the plane of limiting strength within the system. The nature of failure is qualified by the percentage of adhesive and cohesive failures. The pull-off test equipment model used was Elcometer 106.



Fig. 3.9a Adhesion Tester



Fig. 3.9b Dolly attached to samples

3.9 Water Absorption Test

The cured unmodified and modified epoxy resins were cut into small specimen of 20 mm x 20 mm x 2 mm. All samples were polished to ensure a flat surface. Then they were dried in atmosphere (at room temperature) for half an hour to create fully-dried specimens, and their initial weights were measured. The samples were then immersed in water at room temperature. Then, they were periodically taken out, wiped, air dried and weighed before immersing the samples again. These steps were repeated until a constant weight was obtained. Samples were weighted for 30 days. Each sample was repeated 5 times. Finally, the amount of water absorbed by the sample was then calculated using the following Equation 3.2 [119]:

$$M_t (\%) = \frac{W_t - W_0}{W_0} \times 100 \quad \text{Eq.3.2}$$

Where,

M_t is water content at any given time,

W_t is sample weight at the time of measurement,

W_0 is initial sample weight.

3.10 Surface Morphology Analysis

The morphology of the samples was determined before and after the electrochemical test using a digital microscope, Dino-Lite AM 413ZT supplied by Dutech Scientific Sdn.Bhd. Samples were placed on a flat surface and were directly analysed using the equipment mentioned above. Before analysing, the required resolution and magnification were set.