CHAPTER 1

INTRODUCTION

1.1 Background

Corrosion can be best described as the deterioration of materials because of their reactions with the environment [1]. It is one of the major problems faced by most industries around the world. Generally, corrosion failures cause plant shutdowns, waste of valuable resources, high maintenance costs and others [2]. Many incidents due to corrosion failures have been reported in [3] and some examples of the incidents are listed in Table 1.1.

Table 1.1 Examples of incidents caused by corrosion [3]

Year	Incident	Location	Cause	Effects
2006	Crude oil spillage	Prudhoe Bay, Alaska	Corroded pipeline caused leakage for 5 days	-approximately 1 million litres of crude was lost -pollution
2004	Pipe rupture	Japan	Carbon steel pipe carrying 300° C steam at high pressure has ruptured due to corrosion	- 5 fatalities - 6 people injured - cost (repair)
1998	Sinking of Erika (tanker)	France	Corrosion caused the Erika tanker to break into two-19,800 tons of heavy fuel oil were spilled.	-water pollution -cost -ban on the trade of sea products

Based on the incidents happened, obviously, corrosion failures may not just affect the safety and environmental aspects but might as well affect the economics. According to available data provided by NACE [4], between 4 to 6% of Gross Domestic Product (GDP), is lost to corrosion. This is equal to $1.6 trillion dollars lost every year from the world's economy. In the Malaysian context, 4% of GDP would mean a loss of around RM30 billion every year [5].

Since corrosion causes many problems, it needs to be prevented. There are many ways to prevent corrosion. Coatings are one of the most efficient ways of protecting against corrosion [6]. A coating system may vary depending on the amount of layers applied to the substrates which are primer, secondary (intermediate) and topcoat layers. Basically, there are three types of coating systems: three-layer coating, two-layer coating and direct-to-metal coating (one layer) as mentioned in [7]. The amount of layers applied depends on the needs of the application. In many cases, coatings are applied to improve the surface properties of the substrates such as adhesion, appearance (cosmetics), corrosion resistance and others.

In organic coating applications, the use of some corrosion inhibitors as primers in the conventional coatings have been restricted due to the toxicity issues [7]. For example, the inorganic inhibitors such as chromates, phosphates etc. are not environmental friendly and cause detrimental effects to human health [8].

Since many inhibitors used in the coatings are not environmental friendly, other anticorrosive inhibitors are being introduced to substitute them. Many researchers have agreed that a conducting polymer called Polyaniline (PANI) is the most reliable inhibitor to be used as primer to replace those inorganic inhibitors due to its ability to inhibit corrosion.

1.2 Corrosion mechanism

In general, corrosion processes consist of a series of electrochemical reaction occurring at the metal surface in contact with the metal and its constituents. The metal (Fe) is converted into ferrous solids (e.g: $Fe(OH)_2$) which may be converted to ferric solids (e.g: $Fe_2(OH)_3$) after reaction with oxygen [9]. It is actually a process where metal is converted to its original ore where they are more thermodynamically stable [7]. An example of a corrosion process is shown in Figure 1.1 [10]

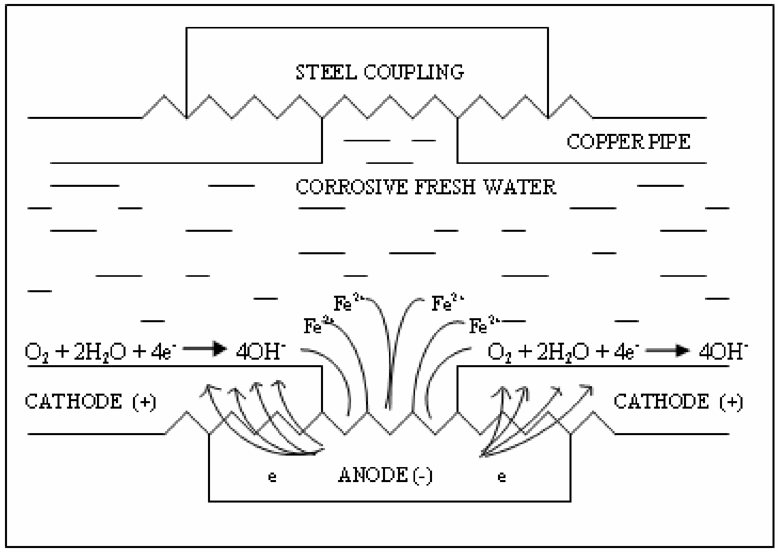

Fig. 1.1 example of corrosion process [10]

In corrosion process, dissolution of metal occurs at the anode in which it involves electron transfer through redox reactions. Oxidation reactions occur at the anode are coupled with reduction reactions at the cathode. [11]. The general reaction that occurs at the anode is actually the dissolution of metal as ions.

$M \rightarrow M^{n-} + e^{n-}$ Eq.1.1

where M is the metal involved, n is the valence of the corroding metal species and e is the electrons.

On the other hand, the reaction that occurs at the cathode depends on the type of environment. In alkaline and neutral aerated solutions, the predominant cathodic reaction is:

$O_2 + 2H_2O + 4e \rightarrow 4\,(OH)$ Eq. 1.2

In aerated acids, the cathodic reaction is:

$O_2 + 4H+ + 4e \rightarrow 2H_2O$ Eq.1.3

In deaerated acids, the cathodic reaction is:

$2H + 2e \rightarrow H_2$ Eq.1.4

Basically, after dissolution, ferrous ions (Fe^{2+}) is generally oxidized to ferric ions (Fe^{3+}), in which these will combine with the hydroxide ions (OH^-) formed at the cathode. This combination produces a corrosion product called rust (FeOOH or Fe_2O_3. H_2O).

1.3 Problem Statement

Organic coatings containing epoxy resins are widely used to prevent the corrosion of metallic structures because they are easy to apply at a reasonable cost [12]. However, the main problem related to organic coatings is the absorption of water into the coatings; thus affecting its performance as anti-corrosion coatings. When water penetrates into a coating, it will also reduce the adhesion and durability of the coating.

There are a few studies on the effect of curing temperature on the performance of epoxy, but not many works on the effect of curing temperature on water absorption in epoxy have been reported. Curing temperature has been reported to have quite a significant effect on the water absorption phenomena, in which the amount of water absorbed by the epoxy differs when the curing temperature is varied. The effect of curing temperature on water absorption by epoxy resin has not been a subject of intensive research and still remains a grey area. However, this information is important to corrosion studies especially in humid countries as Malaysia. In addition, Aliband et al. [13] in their studies found out that after 40 years, there is still some amine not reacted in the epoxy system which resulted in operation failures. This proved that curing is an important aspect that needs to be considered when dealing with epoxy systems as it will determine the properties of the epoxy systems thus affecting its performance.

Many studies have provided strong indications that coatings based on PANI improve the resistance of steel against corrosion [14]. Although conducting PANI has been proven to have the capability to protect metals from corroding, there are a few challenges associated with PANI especially regarding the understanding on the protection mechanisms. From the beginning, it was stressed that the corrosion protection by polyaniline is its ability to passivate the metal surface [15]. Moreover, several researchers have proposed some theories on the protection mechanism, but the subject is still being debated and the mechanisms are still not well explained and understood [14]. In addition, according to Samli et al. [16], low loaded PANI paint has been discovered to be effective in inhibiting corrosion. However, the reasons for this and how PANI could affect adhesion and water absorption are not known and have not been reported before.

Electrochemical analysis like EIS is a reliable method compared to other analysis such as salt spray and pull-off test when evaluating corrosion phenomena, because it can provide both types of information – qualitative and quantitative results, whereas salt spray and pull-off tests only provide qualitative results. Since pull-off test and salt-spray test only allow qualitative evaluations, the use of EIS is essential to predict the behavior of a particular coating system. However, all analyses need to be done as each of the analysis has its own essentiality and purposes. Most of the researchers provided EIS, salt spray test and pull-off test results in their studies, but there were no correlation among those results. Discussions on the results were done separately. Correlations of the three types of information would give a better understanding of the protection mechanism provided by PANI.

1.4 Objectives of Research

The main goal of this work is to develop a coating formulation that is capable of inhibiting corrosion to carbon steel. The work has been carried out to meet the following specific objectives:

1. To investigate the effect of curing temperature on water absorption in epoxy coatings.
2. To determine the effect of conducting PANI in inhibiting corrosion when one-coat epoxy coating system is applied.
3. To characterize the corrosion inhibition properties using EIS analysis.
4. To correlate the EIS analysis results with the results from other corrosion analysis: salt spray test pull-off test and water absorption test in order to predict corrosion behavior.

1.5 Scope of research

To fulfill the objectives of this study, the scope of work has been subdivided into four stages:-

Firstly, the unmodified coatings were developed by mixing an appropriate amount of epoxy and curing agent. The epoxy used was Epikote 828 (DGEBA) while m-XDA was used as the curing agent. The DGEBA was chosen due to its fluidity, low shrinkage during cure and ease of processing whereas the selection of m-XDA is because of its lower viscosity compared to other curing agents [17-20]. This characteristic offers complete mixing process with epoxy resin. Then, the modified coatings were prepared using the same way but this time, Polyaniline (PANI) was added to the mixture of DGEBA/m-XDA. In recent studies, it is reported that the lower polyaniline loaded paint has been found to be more corrosion resistant [16]. Therefore, in this study, the amount of PANI was varied from 0.5% to 1.5%, and the effect on inhibition properties at the various amount of PANI was investigated. Both unmodified and modified epoxy systems were cured at room temperature and 120°C.

After the coatings have been prepared, they were characterized using DSC, TGA and FTIR analysis to determine the properties of the coatings.

The third stage was to apply the coatings to the carbon steel. In this case, coatings were applied in one-coat coating system in which polyaniline was blended with the epoxy. The one-coat system has been chosen as the coating system to investigate the effectiveness of PANI in inhibiting corrosion. Besides, the one-coat system is also economical and will minimize cost, time, energy and health effects.

Finally, few tests were carried out to analyze the corrosion behaviors, namely EIS, salt spray test, pull-off test and water absorption test. The measurement for each test was carried out for 30 days. The duration of 30 days was chosen so that prediction of the corrosion behavior of the coated samples within short period using EIS can be done. After completion of these tests, morphological analysis was performed using digital microscope to determine the morphology of the coatings.