# CHAPTER 2

# REVIEW OF LITERATURE

## 2.1 Corrosion Control: Coatings

It is generally accepted that surface coatings are applied to the metal substrate for decorative and protective purposes [21]. Coatings in their simplest form are a mixture of a binder, solvent, pigment and an additive [21] and [22] as shown in Figure 2.1. These components in the coatings have their own functions that will determine the properties of the coatings.

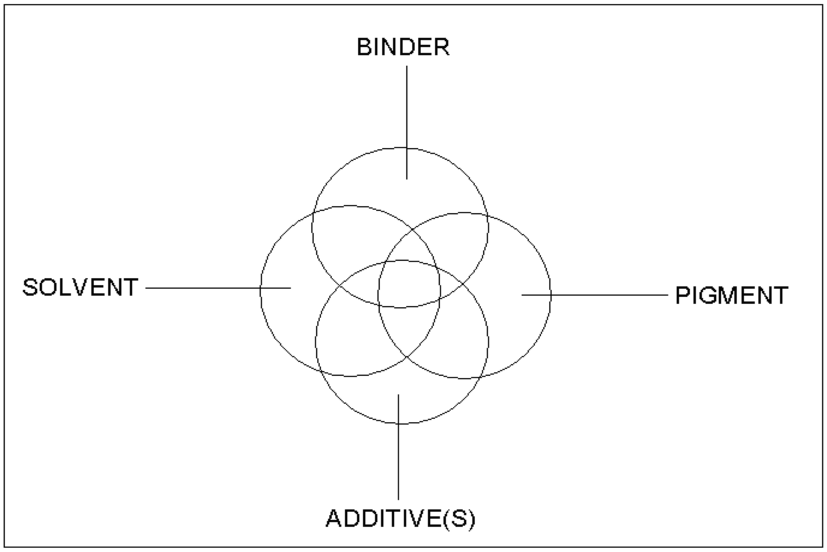


Fig. 2.1 Basic components in paints/coatings

Binder is the main element of the paints. According to Kopeliovich [22] binders are polymers that are responsible for the adhesion of the coating to the substrate. The binder holds the pigments dispersed throughout the coating. In other words, it can be said that a binder establishes most of the physical and chemical properties of a coating. The commonly used binders are alkyd resins, urethane resins, phenolic resins, epoxy resins and others.

Meanwhile, a solvent is a medium where the binder, pigment and additive are dispersed in molecular form or as colloidal dispersions. It acts as a “carrier” or “vehicle” to other elements. In addition, solvents are also used to modify the viscosity of the paint. [22]. Some of the examples of solvents used in coatings are water, toluene, xylene, alcohols and ketones.

A pigment is a solid substance dispersed throughout the coating to impart it a color. It changes the coating appearance (gloss level) and also improves the properties of the coating such as increase the hardness and decrease the ductility as mentioned in [22]. Besides, a pigment may also protect the substrate from UV light. Pigments may be natural, synthetic, organic and inorganic. Titanium dioxide ($TiO_2$), carbon black and yellow dyes are some of the examples of pigments.

Additives are small amount of substance modifying the coatings [22]. Brown [21] asserted that additives are used in the coatings for a great number of purposes to improve specific properties throughout the life-cycles of the coatings such as processing properties in manufacture, application properties, drying properties and final film performance. In general, additives are often added to the coating formulations for pH adjustment, wetting, dispersing, stabilizing purposes, to promote adhesion, to increase the durability of the coatings, as corrosion inhibitors to reduce corrosion and for rheology modifications [21]. Examples of additives are chromates, silica, phosphates and others.

Coatings should adhere well to substrate, have the correct color and level of gloss and have the desired protective properties, ideally for as long as possible [21]. Therefore, it is important to determine the elements used in the coatings as they will determine the formulations of the coatings, thus improving the properties of the coatings.

A survey on the causes of corrosion failures has shown that over 40% of the failures were due to several reasons and one of them is the non-use of efficient and durable protective coatings [23]. One of the ways to ensure the protective characteristic of a coating is by selecting the appropriate coating systems prior to the applications. The types of coating systems can be summarized as: (a) the three-layer-coating consists of a top coat, an intermediate coat and a primer (b) the two-layer-coating consists of a topcoat and a primer and (c) direct-to-metal coating (one-coat). The (a) and (b) types are usually applied as maintenance coatings. All of these systems are illustrated in Figure 2.2 as demonstrated in [7]

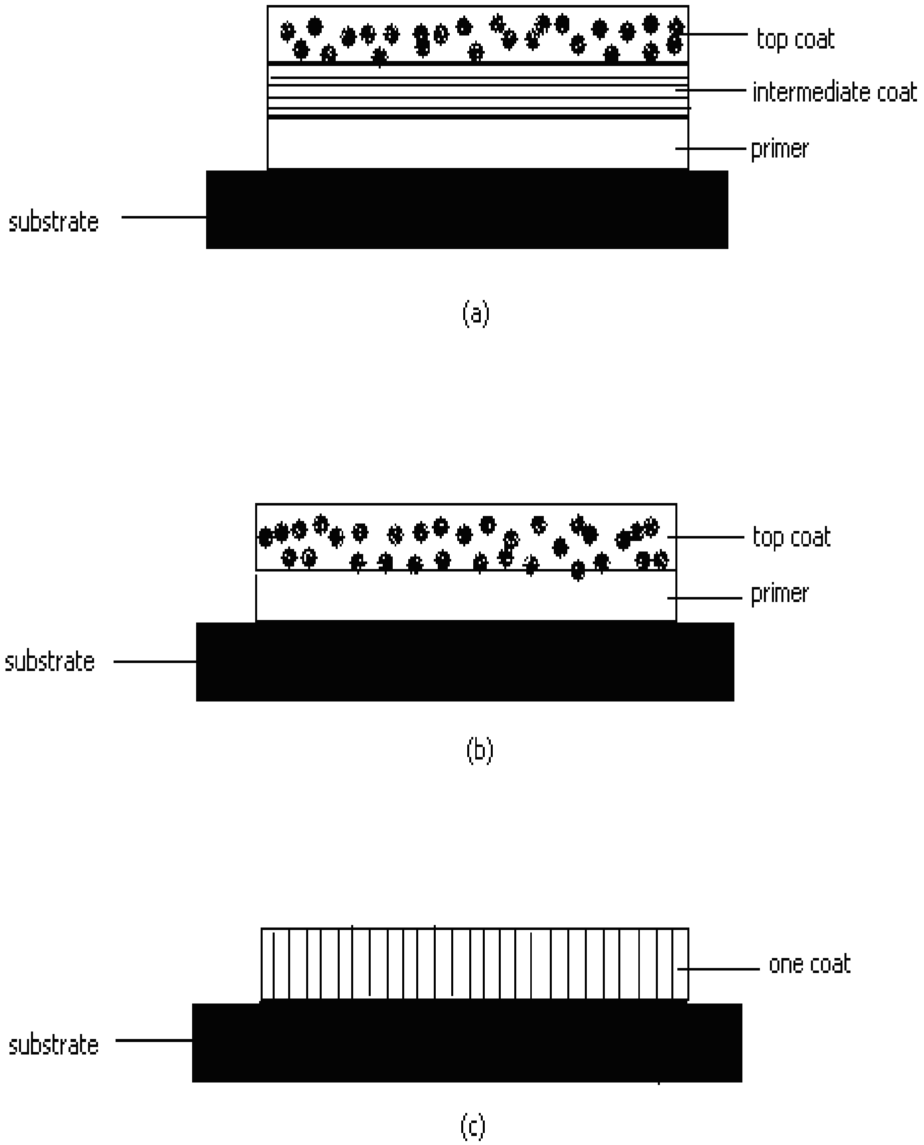


Fig. 2.2 Types of coating system [7]

## 2.2 Conventional Coatings : Solvent-borne Coatings

Several conventional coatings have been developed in order to prevent corrosion. Majority of the conventional coatings are solvent-borne coatings which basically has only 25% solids and relatively high organic solvents [24]. The common solvents used in coatings are toluene, xylene, methyl ethyl ketone and others. The usage of these solvents in coatings is getting more attention due to environmental concern.

When solvent vapor is released, they emit volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) into the atmosphere [25]. These components pose a number of risks to human health which may eventually lead to fatality. Basically, these solvents may cause acute effects such as sore throat, dizziness, eye irritation, vomiting and nausea. Chronic effects can also be derived from the release of these solvents. It may affect the central nervous system (CNS), kidneys and blood, severe chest pain and also risk of cancer (carcinogenic).

## 2.3 Alternative Coatings : Organic Coatings

Apart from the use of solvent-borne coatings, organic coatings containing corrosion inhibitors is chosen as an alternative coatings used in preventing corrosion replacing the solvent-borne coatings. As mentioned by Lin [7] the corrosion inhibitors used in the organic coatings can either be organic or inorganic inhibitors. Since organic inhibitors are not capable of providing sufficient corrosion protection to metal substrates, they are usually being used with combination of inorganic inhibitors such as chromates and phosphates in which this is undesirable as these substances are toxic and could be detrimental to the environment and human health.

Basically, a coating provides protection to the metal substrates by resisting any corrosion species and preventing it from reaching the metal surface. According to Lin [7], the organic coatings protect the metal from corrosion by using one or more of the following basic concepts: barrier protection, cathodic protection (Zinc-rich coatings) and inhibition (inhibitive primers to passivate metal).

In the case of barrier protection, the barrier coatings are designed to have reduced the permeability to water and ionic species. This is achieved by introducing the lamellar pigment such as aluminum flake, graphite, kaolin and steel flake into the coatings. As mentioned in [26], this lamellar pigment can reduce the water permeability of a coating by creating a long and curvy route at which the water and dissolved electrolytes/oxygen must travel to reach the substrate as shown in Figure 2.3

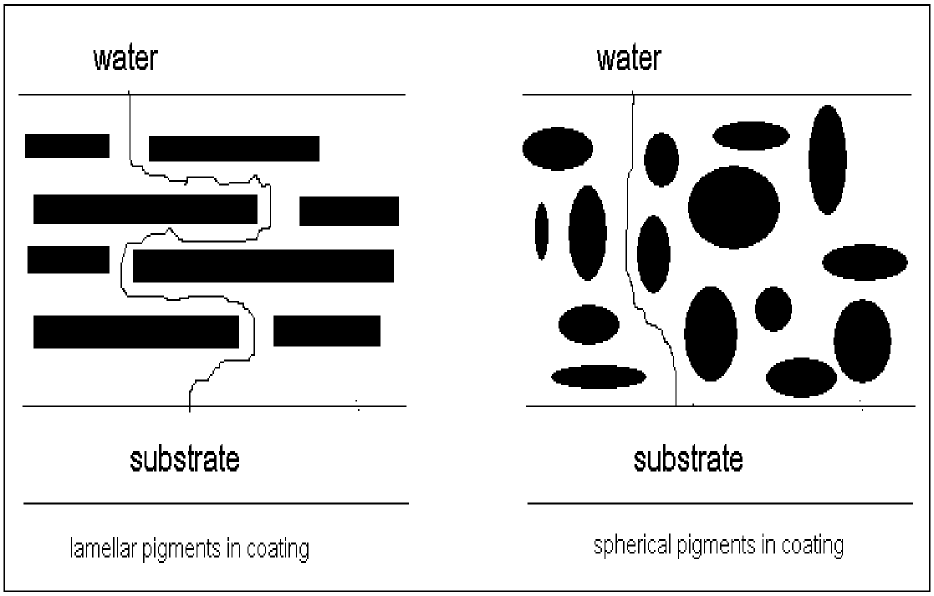


Fig. 2.3 The barrier effect created by lamellar pigments (Adapted from Lin [7])

Zinc rich coatings which incorporated zinc dust into the film as pigment is responsible for the cathodic protection. It uses the same concept as zinc galvanizing steel where zinc is more active than iron/steel, thus will sacrifice itself (as an anode) to protect steel (as cathode) [7].

For protection by using the inhibition concept, the organic coatings actually protect the steel by covering the metal surface with a passivating, metal oxide layer. This oxide layer will protect metal from corrosion [7].

Among these three concepts of corrosion protection provided by organic coatings, the most widely used concept is the inhibition concept which involves the use of corrosion inhibitors in the coatings. The corrosion inhibitors play an important role in order to ensure the corrosion protection of the steel. These corrosion inhibitors and the type of passivation provided by them will be discussed in the next section.

## 2.4 Corrosion Inhibitors

The presence of corrosion inhibitors in coatings is claimed as the main reason for the corrosion protection offered by coatings. According to Roberge [2] inhibitors can be defined as chemical substances that effectively reduce corrosion rate, when added to the coatings in certain concentrations.

Basically, there are two possible ways that an inhibitor plays its role in corrosion protection. The inhibitors can retard corrosion rate by reacting either at the anodic sites or the cathodic sites, regardless of their types (organic or inorganic) [10]. However, both ways are using the same concept where the potential of the metals are shifted to a more noble value which reduces the corrosion rate.

Anodic inhibitors cause a positive shift in corrosion potential while cathodic inhibitors cause a negative shift. When anodic inhibitors cause the anodic shift, it actually forces the metallic surface to the passive region, which reduces the corrosion rate and shifts the corrosion potential to noble values. On the other hand, cathodic inhibitors shift the corrosion potential from the active region to more reducing (negative) values in the immune region, in which corrosion is prevented [10]. In general, cathodic inhibitors act inversely from anodic inhibitors in which it will reduce the corrosion rates and shift the corrosion potential to immune region. These conditions can be well explained by the Pourbaix diagram as shown in Figure 2.4 and Figure 2.5.

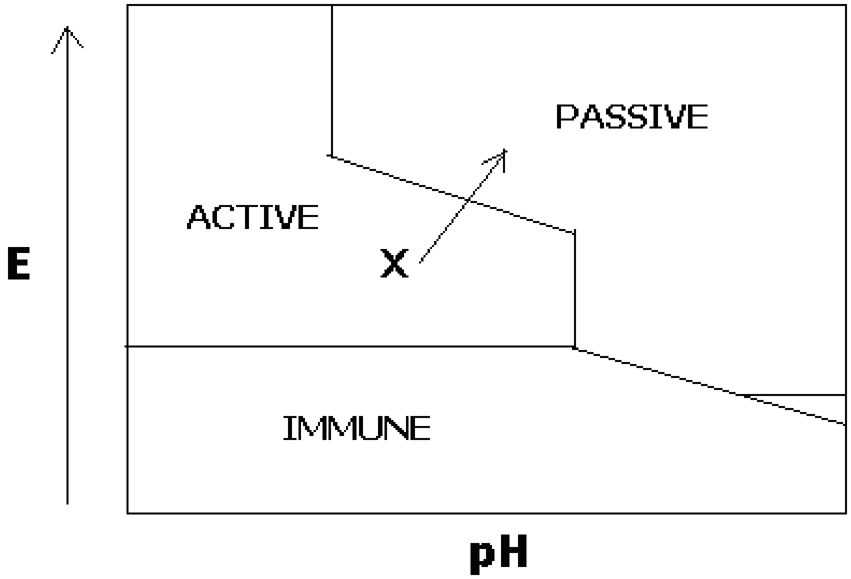


Fig. 2.4 Pourbaix diagram illustrating the mechanism of anodic inhibitors [10]

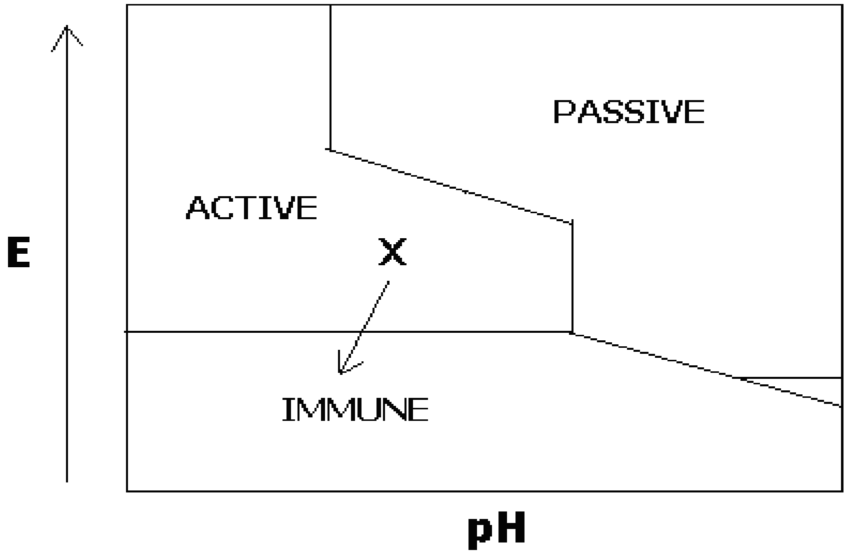


Fig. 2.5 Pourbaix diagram illustrating the mechanism of cathodic inhibitors [10]

Generally, inhibitors can be divided into two types – inorganic and organic inhibitors. Typical inorganic corrosion inhibitors for coatings are lead pigments, chromates, phosphates, borates, molybdenum and others. These inhibitors proven to be effective in inhibiting corrosion as asserted in [7]. However, most of the inorganic inhibitors are toxic carcinogens in which this could harm the environment and human health.

On the other hand, for organic inhibitors, the compound's functional groups play an important role. Among the important types of functional groups are amines, carboxyls, hydroxyls and sulfonates [27]. Lin [7] stated that a number of studies have been carried out on the use of organic inhibitors for coatings. However, the use of organic inhibitors has been very limited so far and they need to be used in combination with other inorganic inhibitors to enhance the inhibition properties in which the use of inorganic inhibitors is undesirable because of the toxicity issue mentioned earlier.

Although there are some drawbacks of using the organic inhibitors, a new finding has been discovered. Recent literature and patent activity indicate an increasing interest in using a conducting polymer called polyaniline as a new organic inhibitor in the organic coatings [7]. Polyaniline is claimed to have the ability to act as corrosion inhibitor in the coating thus providing sufficient corrosion protection to the metals.

## 2.5 Conducting Polymers (CPs) as an Alternative to Inorganic Inhibitors

Conducting polymers is also known as "synthetic metals" was first discovered by Shirakawa, Heeger and MacDiarmid. In 2000, they won the Nobel Prize in chemistry for the discovery and development of conducting polymers [28].

The main characteristic of conducting polymers is the presence of the conjugated double bonds along the backbone of the polymer. Conjugated double bonds mean that the bonds between the carbon atoms are alternately single and double. Every bond contains a localized sigma ($\sigma$) bond which forms strong chemical bond. In addition, every double bond also contains localized pi-bond ($\pi$) which is weaker. However, conjugation does not guarantee the electrical conductivity properties of the polymer. Polymers need to be doped for the electron flow to occur.

When polymers are doped, it allows the movement of the pi-bond along the polymer chain and allowing charge to migrate a long distance [29].

The unique properties of conducting polymers such as mechanical strength, electrical conductivity, corrosion stability and possibility and of both chemical and electrochemical synthesis make it suitable for various applications [30-32]. Conducting polymers have been studied extensively for various applications such as light emitting diodes, sensors and actuators, catalysts, energy conversion systems and corrosion protection [8].

For the application of corrosion protection, at least two mechanisms for corrosion protection by conducting polymers have been proposed. According to Jain et al. [33], conducting polymers will generate an electric field when a metal is in contact with them. This electric field will restrict the flow of electrons from the metal to an outside oxidizing species thus preventing corrosion. A second mechanism proposed by most researchers, states that conducting polymers can cause the formation of protective metal oxide films on the metal surface, thus preventing corrosion [31], [34-37].

Some examples of conducting polymers that has opened a new dimension in the field of anti-corrosive organic coatings are polythiopene (Pth), polypyrrole (Ppy), polyaniline (PANI) and others. Among the large numbers of conducting polymers, polyaniline and polypyrrole are the most promising conducting polymers for corrosion protection [38]. The lower aniline monomer compared to pyrrole is one of the reasons why PANI is more preferable than Ppy [38]. In addition, unlike polypyrrole, polyaniline can be doped to a highly conducting regime in acidic media without removing electrons from the polymer backbone (non-oxidative doping) as mentioned in [39] and [40]. Furthermore, the polymer can also undergo oxidative doping which is a reversible process within the potential range that the polymer is stable [41-43] and this ability enables polyaniline to act as a versatile polymer in anticorrosion studies [44]. The ease of synthesis, easy preparation by both electro polymerization and chemically oxidation of aniline, chemical and electrical stability and good environmental stability possess by polyaniline are another reasons for the usage of PANI in most studies [29] and [45]. When a study on a comparison of these two conducting polymers was carried out, polyaniline also showed better performance as corrosion inhibitor as compared to polypyrrole [46]

## 2.6 Polyaniline (PANI) - Background and Characteristics

Polyaniline was first synthesized in 1834 by Runge. At that time, the real identity of polyaniline was unknown. Polyaniline was only known as “aniline blacks”. Later, Fritche tried to analyze these aniline blacks. PANI was not recognized as conducting polymers until early 1980’s and 1990’s when conducting polymers were discovered, and polyaniline was recognized as one of them [47].

Polyaniline is a molecular structure that is formed from the polymerization of a monomer unit called aniline. The general formula of polyaniline is:

$$[(\text{-B-NH-B-NH-})_y\,(\text{-B-N=Q=N-})_{1\text{-}y}]x$$

in which y represents the oxidation states, while B and Q represent the $C_6H_4$ rings in the benzenoid and quinonoid forms, respectively [48]. The structure of polyaniline is as illustrated in Figure 2.6.

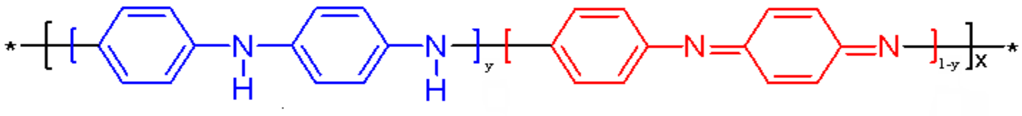


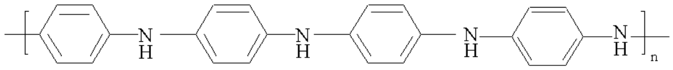
Fig. 2.6 Main polyaniline structure (Adapted from Kang et al. [48])

Polyaniline exists in three oxidation states: leucoemeraldine, pernigraniline and emeraldine. The emeraldine form of polyaniline is often referred to as emeraldine base and emeraldine salt. Among all forms, only emeraldine is electrically conductive [49]. All forms of polyaniline are as shown in Figure 2.7. The oxidation states and forms of polyaniline can be distinguished by the colors represented by them as tabulated in Table 2.1.

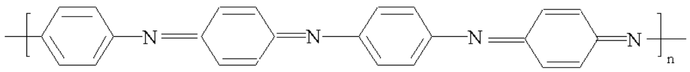
Table 2.1 Various oxidation states of polyaniline [48] and [50].

| **Oxidation states (y)** | **Conditions** | **Colors** | **PANI forms** |
|---|---|---|---|
| If y = 1 | fully reduced | colorless/clear | leucoemeraldine |
| If y = 0 | fully oxidized | purple/violet | pernigraniline |
| If y = 0.5 | partially oxidized | green or blue | emeraldine |

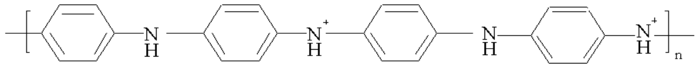
leucoemeraldine



pernigraniline



emeraldine salt



emeraldine base

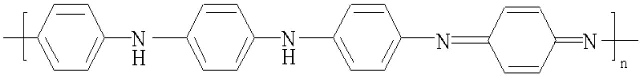


Fig. 2.7 Molecular structures of few polyaniline forms [49]

Figure 2.8 illustrates the synthesis of polyaniline. In Figure 2.8, step (a) is the polymerization process of aniline to form PANI-ES. Usually, this polymerization process is prepared by direct oxidative polymerization using a chemical oxidant [51]. Then, the PANI-ES can be converted to PANI-EB and this is the process shown in step (b).

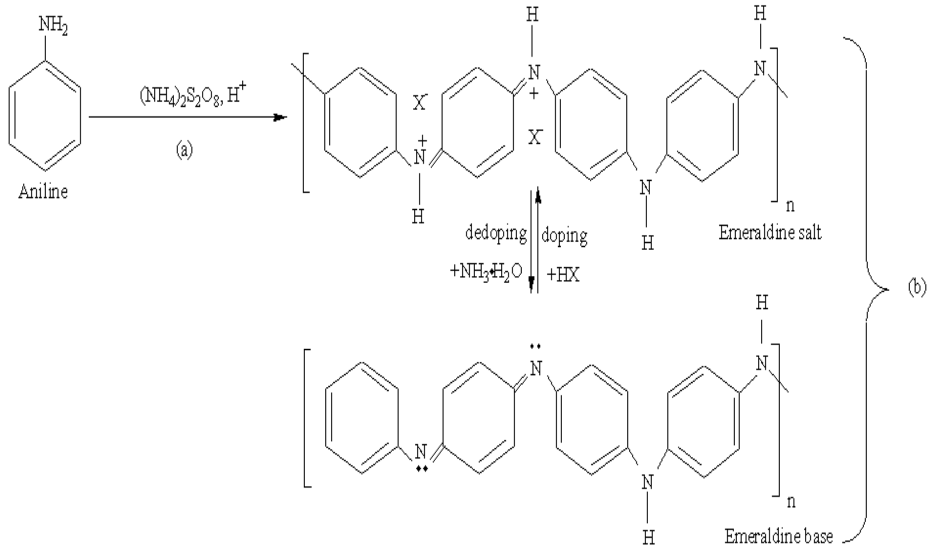


Fig.2.8 Step (a) Polymerization of aniline, (b) conversion of PANI-ES to PANI-EB (Adapted from Kalendova et. al [51])

The polymerization of aniline with the presence of the oxidant can be carried out only in an acidic environment (e.g: 1M HCl). In an acidic environment, aniline exists as an anilinium cation, and the aniline cation radical is the first product of the oxidation reaction of aniline as illustrated in Figure 2.9 [51].

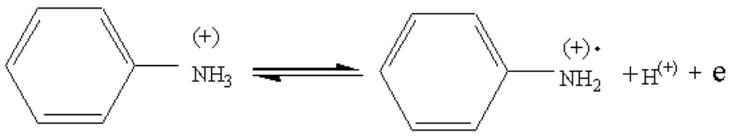


Fig. 2.9 Aniline cation radical (Adapted from Kalendova et al. [51])

According to step (a) in Figure 2.8, polyaniline emeraldine salt (PANI-ES) is produced by mixing the monomer, aniline in the aqueous solution of ammonia peroxodisulfate [$(NH_4)_2S_2O_8$] which acts as the chemical oxidant. Step (b) as shown in Figure 2.8 is a reversible reaction for the conversion of polyaniline emeraldine salt (PANI-ES) to polyaniline emeraldine base (PANI-EB), and vice versa. The protonated polyaniline (PANI-ES) is transformed to deprotonated polyaniline (PANI-

EB) in an alkaline environment at pH 6-7. This process is also known as dedoping. On the other hand, the conversion of PANI-EB to PANI-ES occurs in a quite acidic environment and this process is known as doping.

Other forms of polyaniline like leucoemeraldine (LM) and pernigraniline (PNA) can be achieved through few reactions. The conversion among that various forms of polyaniline is shown in Figure 2.10.

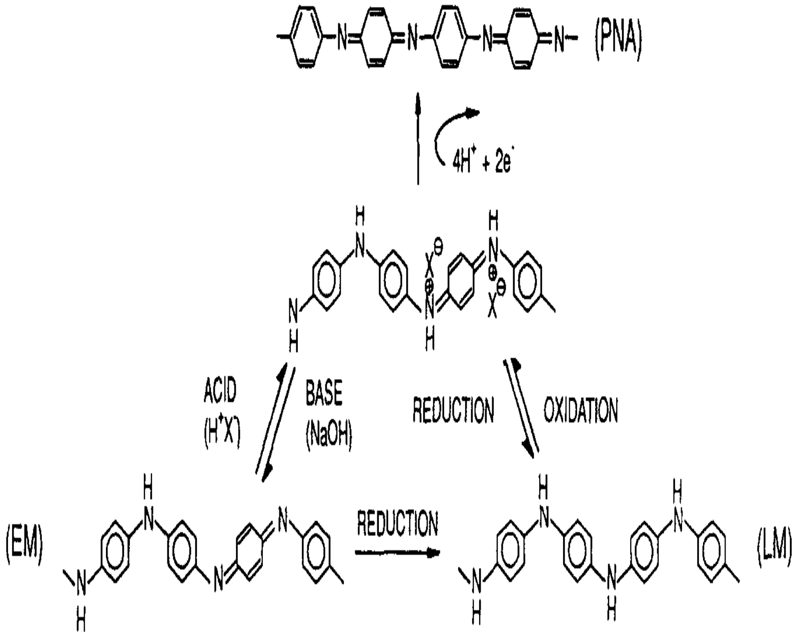


Fig.2.10 The conversion among various forms of PANI oxidation states [48]

Leucoemeraldine (LM) is produced from the reduction of emeraldine with phenylhydrazine or hydrazine. Leucoemeraldine is an electrically non-conducting substance and it is colorless. If oxidized, emeraldine yields pernigraniline. Strong oxidants like ammonium peroxodisulfate or hydrogen peroxide are required for the oxidation process to occur. The transformation to pernigraniline can occur either in acidic environment or a basic environment. However in acidic environment, the transformation is completed in several seconds, whereas a complete transformation in basic environment will take several hours. If emeraldine is oxidized in an acidic environment, pernigraniline salt which is blue in color will be produced; while a purple pernigraniline base will be produced if the oxidation takes place in a basic environment [51].

## 2.7 Polyaniline Coatings

Because of the health issues related to conventional coatings, several alternative coatings have been developed to ensure better quality coatings that can comply the environmental guidelines. These coatings contain pigments or additives that are more environmental friendly, but still maintaining good corrosion protection qualities. Among these alternative coatings, polyaniline coating has emerged as one of the most promising and effective alternative coatings for corrosion prevention.

For the application of polyaniline in coatings, only the two-layer coating and one-coat systems are used. According to Dominis et al. [52] and Armelin et al. [53], there are three different configurations of polyaniline applications have been reported: (i) polyaniline coatings as a primer alone; (ii) polyaniline coatings as primer with a conventional topcoat and (iii) polyaniline blended with a conventional polymer coating.

The application of polyaniline as primer alone is actually a method where polyaniline is electrochemically deposited directly on the metal surface [53]. In 1985, DeBerry [15] found out that PANI electrochemically deposited on steel reduces the corrosion rates. Camalet et al. [54] stated that the electrodeposition of polyaniline on mild steel exhibit very promising properties against corrosion. Although polyaniline provided excellent protection when applied as primer alone, there are few challenges faced by the researchers. The main problem related to the electrochemical polymerization of PANI on steel is the dissolution of bare metal in the beginning of the process [54] and [55]. They also claimed that the adherent of polyaniline to metal surface is also hard to achieve. Furthermore, in recent studies, improvements have been made to this approach in which a relatively small concentration of anticorrosive inorganic inhibitors was added to the primer [53]. Although this will enhance the corrosion inhibition properties of the primer, the use of inorganic inhibitors are undesirable due to strict environmental regulations on the use of these inhibitors in paints.

On the other hand, a number of studies has shown that polyaniline primers combined with conventional topcoats provide better protection than topcoat only and some primer-topcoat systems containing inorganic inhibitors in the primer (such as zinc) [52], [56] and [57]. Dominis et al. [52] demonstrated that the use of polyaniline increased the corrosion protection of steel when polyaniline was used with conventional top coats. Schauer et al. [57] also asserted that polyaniline primer with a combination of conventional topcoat exhibits the most effective corrosion protection. When comparisons are made, a number of studies have shown that this approach is superior compared to the other two approaches [52]. However, this approach also has several drawbacks. The performance of PANI/topcoat systems has shown to be dependent upon the properties of the topcoat [57]. This will actually restrict the evaluation of the actual ability of PANI in inhibiting corrosion. Besides, as mentioned in [57], the role of the topcoat is mainly on slowing down the water and ions diffusion in which without the use of the topcoat, polyaniline was also proven to be capable of restricting the diffusion of water and ions. In addition, the application of several layers of coatings needs to be avoided to make it more practical for coatings application.

An interesting alternative to avoid multilayer coatings is the mixing of polyaniline with conventional resins to prepare blend materials for corrosion protection [53]. Many researchers obtained good results by means of corrosion protection provided by this system. For instance, Akhbarinezhad et al. [58] found out that polyaniline epoxy blend coating was able to provide protection to the carbon steel. Similar findings were also obtained by Talo et al. [59] and few other researchers as mentioned in [8] and [46]. Talo et al. [59] even mentioned that polyaniline blended coatings was chosen in order to avoid the need to use several coating layers for different purpose.

Over the years, a great number of works on the protection of steels by polyaniline have been patented [60]. In 1985, De Berry [15] first discovered the inhibition properties of polyaniline. He found that the corrosion rate of stainless steel in acidic media was lowered when polyaniline was electrochemically deposited on the stainless steel. In 1996, Camalet et al.[54], found that the formation of a passive Fe(II)-oxalate layer in oxalic acid, resulted in strongly adherent PANI films in which the layer provided good protection to steel in acidic chloride solutions. In the same year, Ahmad and MacDiarmid [61] discovered that chemically deposited PANI was able to protect stainless steel in acidic chloride environments.

In 2001, Bernard et al. [62] have also proven that PANI deposited from metanilic acid yielded a superior copolymer coating. This is due to the incorporation of metanilate into the polymeric backbone. Later, Moraes et al. [60] in their study found out that after the electrodeposition of polyaniline on stainless steel, act as corrosion inhibitor in 3% NaCl solution which is indicated by large shift of the corrosion potential to noble values. Over the years, a number of the same important patents have appeared [60]. However, the direct application of PANI onto the metal surface through electrodeposition is the main issue face by most researchers. This is because, the electrodeposition of PANI on metals needs a very low pH where an acidic medium is required and to attain the adherent of PANI on the metal surface is also another challenge in the electrodeposition of polyaniline as being stressed in [54]

In 1997, Sheur et al. [57] studied on the protection of iron against corrosion by using polyaniline primers. In addition, a topcoat was also applied above the polyaniline primer. They found out that the combination of polyaniline primer and an epoxy topcoat provided excellent corrosion protection. In 1998, Wessling and Posdorfer [63] studied the performance of polyaniline when applied as primer and sealed with different top coats using EIS and found out that the steel was highly corrosion resistant. They have also been many other works demonstrated on the use of polyaniline as primer which when combined with an epoxy or other topcoats give good corrosion protection [64]. However, Talo et al. [59] asserted that blending of polyaniline with topcoat is a more practical approach and multiple layer coatings should be avoided. They discovered that different types of polyaniline blended in epoxy coatings provided effective corrosion protection of mild steel in saline solution. Huh et al. [65] also agreed with Talo et al. [59] to not use multiple layer coatings in their coating formulations. They found out that polyaniline blend coating turned out to be excellent coating materials for corrosion protection of iron. Aroujo et al. [66] also provided evidence that the adhesion of PANI onto mild and galvanized steels were poor and this lack adhesion leads to bad performance even when PANI was applied with a top coat. This shows that direct application of PANI to the metal surface produces poor adhesion which will affect its performance in inhibiting corrosion. Better adhesion could be achieved by blending PANI with epoxy as epoxy improves the adhesion of the coating to the substrates due to the existence of OH-bonds.

Although many of the studies were done on blending polyaniline in epoxy coatings, these studies involve the use of high concentration of polyaniline. Iribarren et al. [67] studied the corrosion protection of carbon steel by blending polyaniline in alkyd resins and the concentration of polyaniline added was varied up to 6wt.%. Samui et al. [68] did a study of polyaniline containing paint for corrosion prevention using up to 20 wt.% of PANI in the paint formulations. It was mentioned in [57] that one of the reasons for the long delay in a practical application of polyaniline was its insolubility where adequate doping and production of stabilized polyaniline dispersion in coatings need to be considered in order to pave the way for the usage of high concentration of polyaniline in coatings. Armelin et al. [53] asserted that the addition of conducting polymer (CP) in a very low concentration (less than 1 wt.%) is already sufficient in providing sufficient corrosion resistance to the substrates. This is proven in their study as mentioned in [46] that a modified PANI provided the best corrosion protection even under very low concentration of PANI was used (0.3 wt.%). However, they did not vary the amount of PANI in the coatings and the epoxy used also contains mixture of solvents and anticorrosive additives (Zn dust) in which the release of these substances to the environment is undesirable as they are not environmental friendly. Akhbarinezhad et al. [58] also stated that only 1 wt.% of PANI was added in the PANI epoxy blend coating and this coating formulation was proven to be effective in inhibiting corrosion of steel in sodium chloride solution. Kamaraj et al. [69] also added the same amount of benzoate doped polyaniline in their paint formulations in their study on corrosion protection of iron and discovered that the coating is able to protect steel in neutral media better than in acid media. Obviously, previous researchers did not vary the amount of PANI in their coating formulations. So, the exact range of amount of PANI that may offer sufficient corrosion protection is not known. Therefore, in this study, even the same approach is used (polyaniline blended with epoxy and low concentration of PANI is also preferred to be added to the epoxy), the amount of PANI were varied (0.5-1.5 wt.%) to investigate the effects of corrosion protection offered by PANI when varying the concentrations of PANI in the epoxy. In addition, the epoxy used was free from any other anticorrosive additives.

On the other hand, most of the studies did not emphasize on the curing condition of the epoxy in which curing temperature of the epoxy actually affects the performance of the coatings especially regarding water absorption. Armelin et al. [70] in their studies, observed that coating cured at room temperature was not fully cured when the DSC analysis was performed. This will actually affect the performance of the coatings as there are some drawbacks of uncured epoxy which will be discussed later in section 2.10.

## 2.8 The Corrosion Protection Mechanism of Polyaniline

Although polyaniline has been proven as capable of preventing corrosion, the exact corrosion protection mechanisms provided by polyaniline are still in debate and not well explained. Researchers have come up with several different theories on how polyaniline protects steels from corroding.

Among all of the suggested theories, the theory that is agreed by most researchers proposes that the reaction of polyaniline on the metal surface will induce the formation of a protective metal oxide layer, which is thought to passivate the metal surface [11]. This mechanism is well explained by Kinlen et al. [35]. They proposed that polyaniline anodizes exposed iron (Fe) surface, while the dopant complexes with the iron to form the passive layer. This mechanism is illustrated in Figure 2.11.

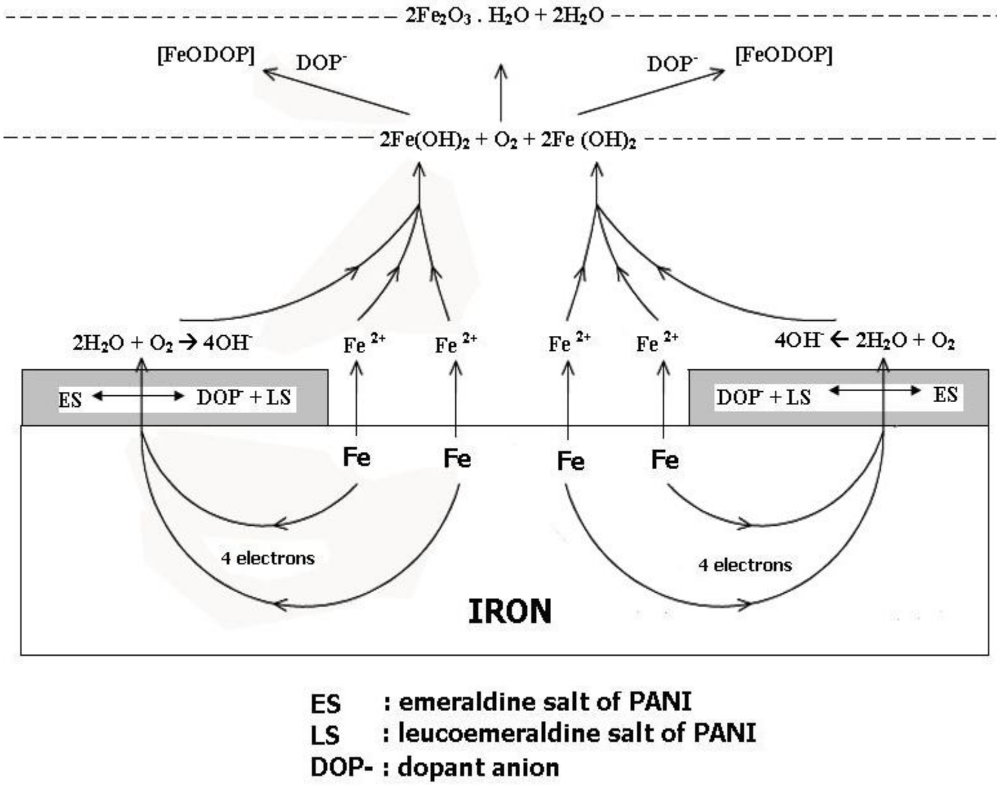


Fig. 2.11 PANI corrosion protection mechanism proposed by Kinlen et al. [35].

Saravanan et al. [71], who used polyaniline epoxy coating for corrosion protection of steel in their research, agreed with the corrosion protection mechanism suggested by Kinlen et al. [35]. They claimed that redox reactions take place simultaneously both at the metal/polymer interface and at the polymer/solution interface. In theirs study, the polyaniline used was doped with HCl. The redox reactions that occur at the metal/polymer interface can be expressed as in Equations 2.1 and 2.2.

<u>At metal/polymer interface</u>

$Fe \rightarrow Fe^{2+} + 2e$ Eq.2.1

Emeraldine salt(ES) + 4e $\rightarrow$ Leucoemeraldine (LS) + $2Cl^-$ Eq.2.2

The oxidized metal ions can be converted into a protective oxide layer, incorporating oxygen diffusion into the coating. On the other hand, at the polymer/solution interface, the following redox reaction can compensate for the consumption of an electron in the polyaniline coating [71].

At polymer/solution interface

$O_2 + 2H_2O + 4e \rightarrow 4\ OH^-$ Eq.2.3

Leucoemeraldine + $2Cl^- \rightarrow$ Emeraldine salt + 4e Eq.2.4

Besides Kinlen et al. [35], a similar mechanism was also proposed by Wessling [72]. He stated that there was a formation of an iron oxide layer on the metal surface, and claimed that it is the passive oxide layer that passivates the metal surface. In addition, conversions of the polyaniline forms also occurred, which contributed to the corrosion protection properties of polyaniline as well. This mechanism is clearly illustrated in Figure 2.12 [72].

Lu et al. [73], who ran XPS analysis confirmed the formation of a passivating oxide layer that consists of $\gamma$-$Fe_2O_3$ layer and also $Fe_3O_4$. Fahlman et al. [74] who studied the interaction between polyaniline and steel using XPS found similar results as obtained by Lu et al. [73].

Radhakrishnan et al. [75] also, proposed a similar mechanism. They claimed that the conducting PANI liberates the dopant near the bare area which creates a passivating layer on the substrate, thus preventing further corrosion. They also suggested that PANI gives the self healing effect in the intentionally damaged samples, and this is due to the redox characteristics of PANI which prevents the corrosion reaction to progress. This mechanism is clearly illustrated in Figure 2.13.

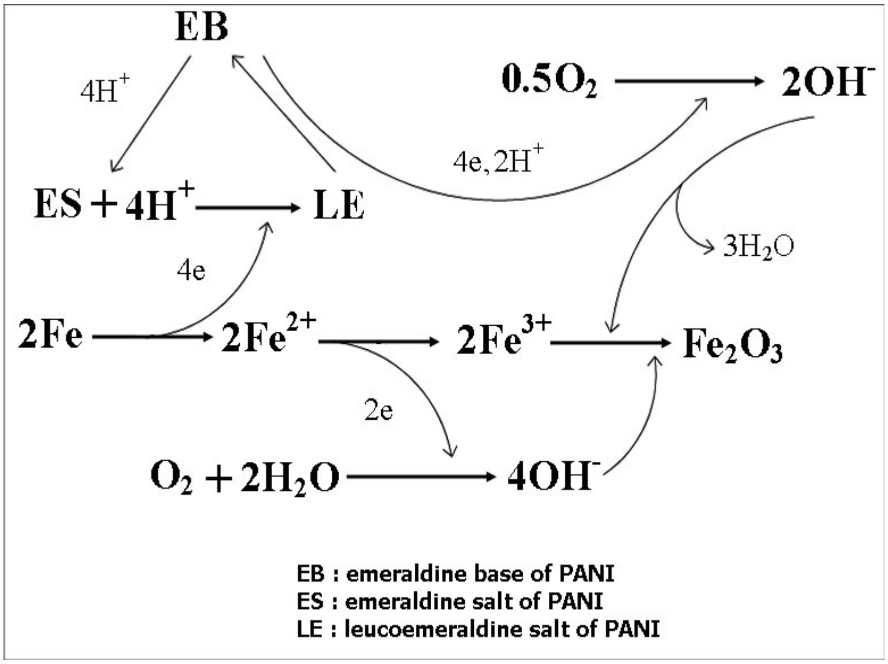


Fig.2.12 The mechanism of PANI corrosion protection as proposed by Wessling [72]

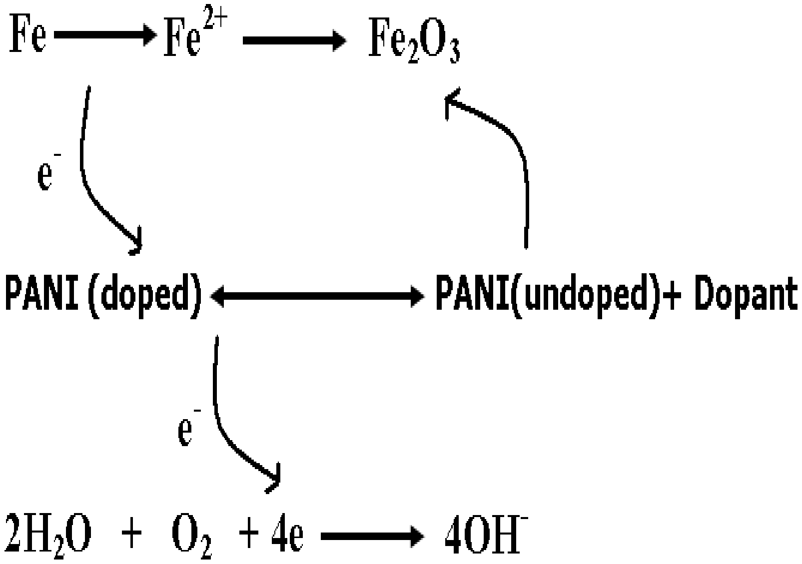


Fig.2.13 Reaction scheme indicating the self healing process for coatings containing PANI which goes through doping and undoping cycle during exposure to corroding ions [75]

Most of the applications of coating are done at room temperature. For examples, the coatings applied for the rig, building and most structures are done and cured at room temperature in which these coatings are exposed to weather conditions such as rain and moisture after 1-2 days of coatings. This may cause the permeation of water into the coatings, thus leading to corrosion. Therefore, it is important to study how curing temperature with respect to water absorption may affect the corrosion rate. It is also important to determine how PANI may inhibit the corrosion due to water permeation for no study has been reported.

### 2.9 Water Absorption in Organic Coatings

Scientist and industries have been trying to find methods to estimate when their coatings/paints should be replaced [76]. This shows that it is crucial to increase the durability or lifetime of organic coatings and in order to achieve this, the factors that lead to the degradation of the coatings need to be discovered. Nguyen et al. [77] and Zhang et al. [78] in their studies mentioned that, the degradation of organic coatings depends on many factors but the permeation of water into the coatings plays an important role.

Organic coatings provided protection to the metals by acting as a barrier between the metals and its environment [55]. However, organic coatings are not permanently impenetrable and to some extent become permeable to corrosion species such as water, ions, and oxygen. Moreover, water is actually the main vehicle for the penetration of the aggressive ions and water soluble gases [79].

Water is an element that is commonly related to the loss of adhesion of coatings. A weak hydrogen bonding of a metal/coating interface may be easily displaced by water. When water has successfully penetrated through the coating, it will accumulate even easier in the coating especially at the less adherent site. These conditions are illustrated in Figure 2.14. There are three factors which are responsible for the transport of water through coatings [7], namely moisture vapor transfer rate, osmotic pressure and electroendosmosis.

According to Lin [7], when there is a difference in moisture vapor pressure between two sides of the coatings, the rate at which moisture vapor will transfer through a coating is called moisture vapor transfer rate. The vapor transfer rate (water permeability) is different for each coating; if a coating has low water permeability, it will give better protection against corrosion. Generally, water will penetrate into coatings through hydrophilic groups, and it is capable of passing through the layers of polymer due to kinetic energy of the water molecule.

Kitteelberger and Elm [80], on the other hand, asserted that the migration of water through a coating is due to osmotic gradients between two sides of the coating film. The external phase has a lower osmotic pressure compared to the internal. So, water tends to 'press' the paint and dissolve soluble impurities such as chlorides and sulfates, and finally causes blistering or delamination to the substrates.

Another factor that caused the absorption of water is by electroendosmosis in which it occurs only when corrosion has already taken place at the interface [81]. At this point, water transport by the coating may be driven by an electrical potential gradient between the anode and cathode where the film bears a negative charge. The defect areas will become the anode and water will be directed to the cathodic areas. High alkalinity and water expansion will eventually cause damage to the paint film and this is known as cathodic delamination.

When water penetrates into the coatings, it will cause the degradation and delamination of the coatings. Adhesion of the coatings will be reduced and eventually destroyed [82]. As a result, corrosion reaction of metallic structures will occur [79]. Destreri et al. [83] concluded that water absorption into the coatings will cause three phenomena in the coatings. First is the loss of adhesion which eventually leads to the corrosion reaction. Secondly, absorbed water may recall further water by osmotic processes due to the soluble impurities with a self-amplifying effect and lastly, the paths that have been covered by water through the coating can be accessed by other solvated ions which accelerate the corrosion process.

So, it can be said that the efficiency of the coating in protecting metals from corrosion is actually related to the barrier effect provided by the coatings. Weigang et al. [79] mentioned that one may to a great extent improves the protection efficiencies by reducing the water absorption. Zhang et al. [84] also stated that the corrosion protection of the coatings can be improved by reducing the water absorption of the cured epoxy. Water absorption thereby is an important factor that needs to be considered in determining the durability and reliability of the coating towards protecting metals against corrosion. The influence of water to the adherence of coatings to the substrate is as illustrated in Figure 2.14.

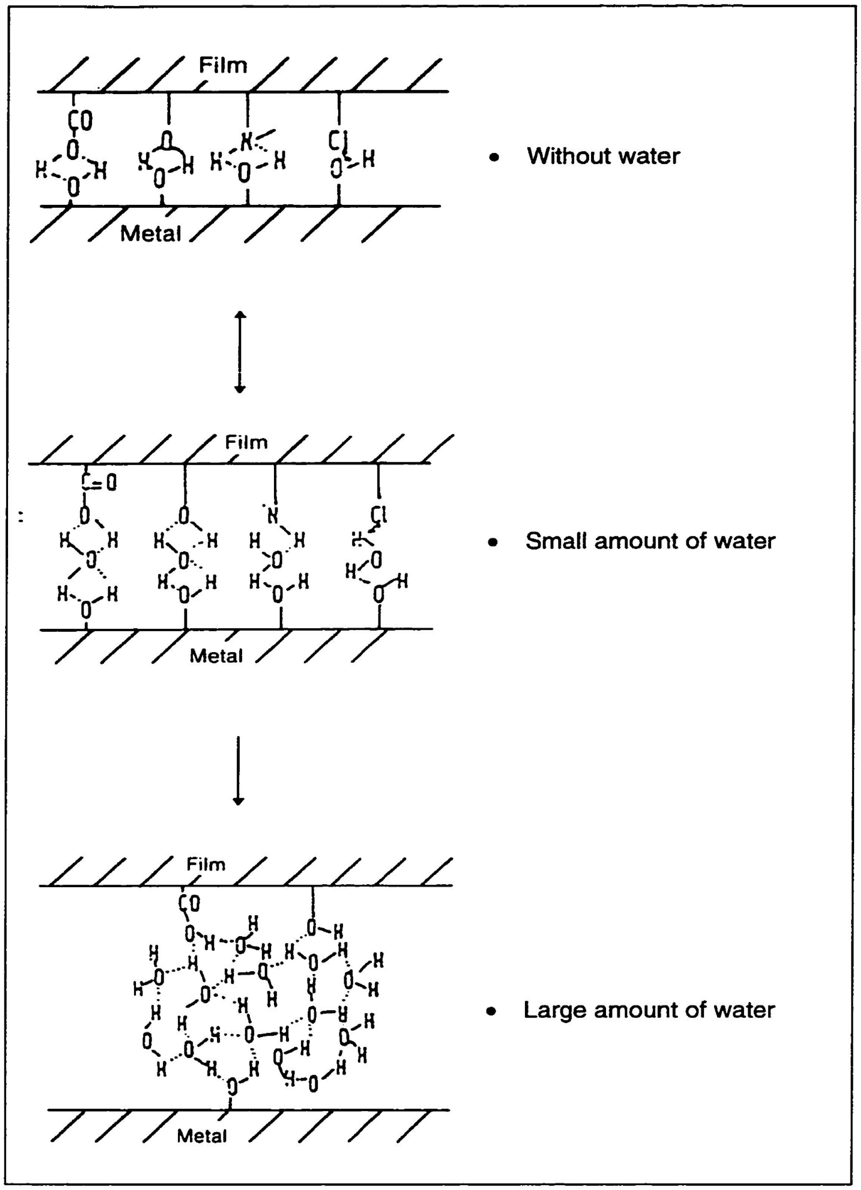


Fig. 2.14 Influence of water on adherence of coatings to metals [7]

## 2.10 Epoxy Resin and Its network Formation

Basically, epoxy resins are copolymers as they are formed from two different chemicals: a resin and a hardener. The resin consists of monomers or short chain polymers with an epoxide group at either end while the hardener consists of polyamine monomers [85]. The most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A and the formed product is known as diglycidyl ether bisphenol A (DGEBA) as shown in Figure 2.15.

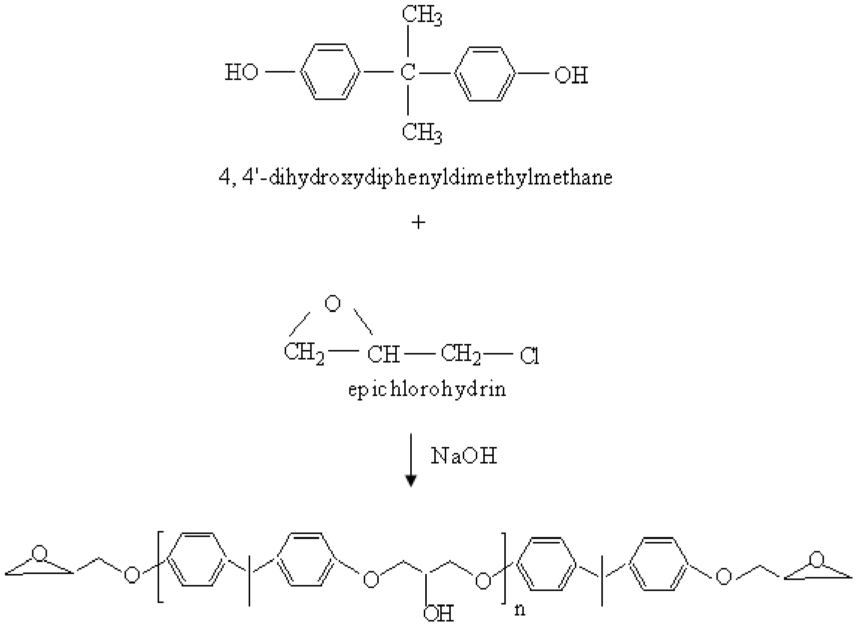


Fig. 2.15 Formation of diglycidyl ether of bisphenol A (DGEBA) [84]

The hardener is typically mixed with the resin to cause it to cure or set [87]. According to Jain et al. [88], curing is a process where linear epoxy resins are converted to three-dimensional crosslinked network. The ratio of hardener to resin varies among the type of epoxy used but it is usually set to the stoichiometric ratio calculated by supposition of full reaction for both epoxide groups and amine groups [87]. When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond, resulting in a polymer which is heavily crosslinked, rigid and strong [85] Curing is an important process as it will determine the properties of the formed epoxy resin network. Jain et al. [88] in their study stated that various chemical reactions that take place during cure determine the resin morphology, which, in turn, determines the properties of the cured formulation. A typical curing reaction that occurs between epoxy and amine during cure is shown in Figure 2.16 [86].

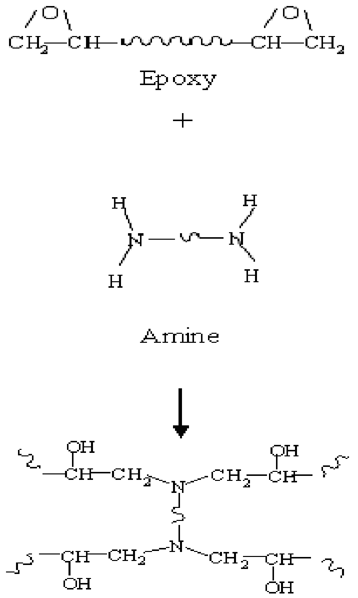


Fig. 2.16 Lightly crosslinked epoxy resin [86]

In this study, diamine hardener (m-XDA) is employed, so four epoxy prepolymers are tied to one diamine molecule and the formation of epoxy network occurs as depicted in Figure 2.17 [86].

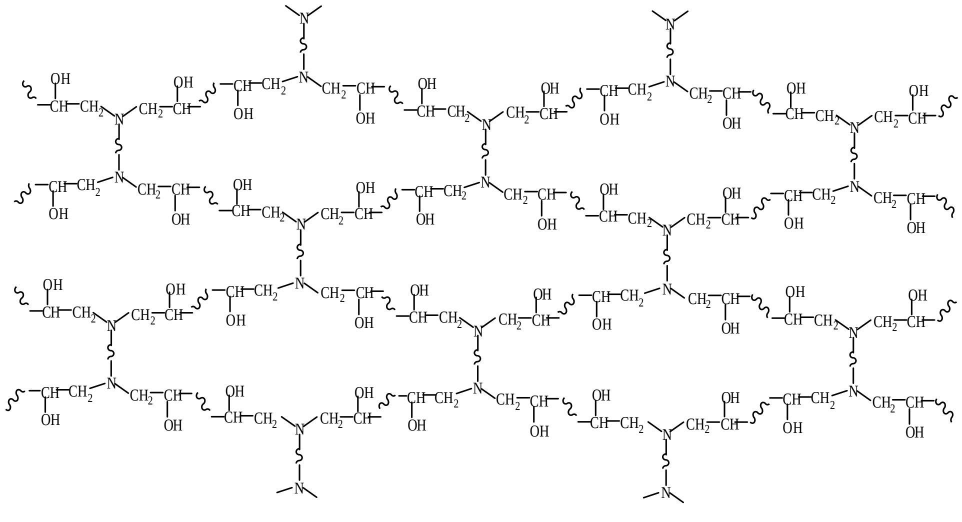


Fig. 2.17 Epoxy resin network of DGEBA/diamine [86]

Some examples of the DGEBA/amine systems using different types of amine particularly isophorone diamine (IPD), triethylenetetramine (TETA) and 1-(2aminoethyl)piperazine (AEP) are shown in Figure 2.18 [89].

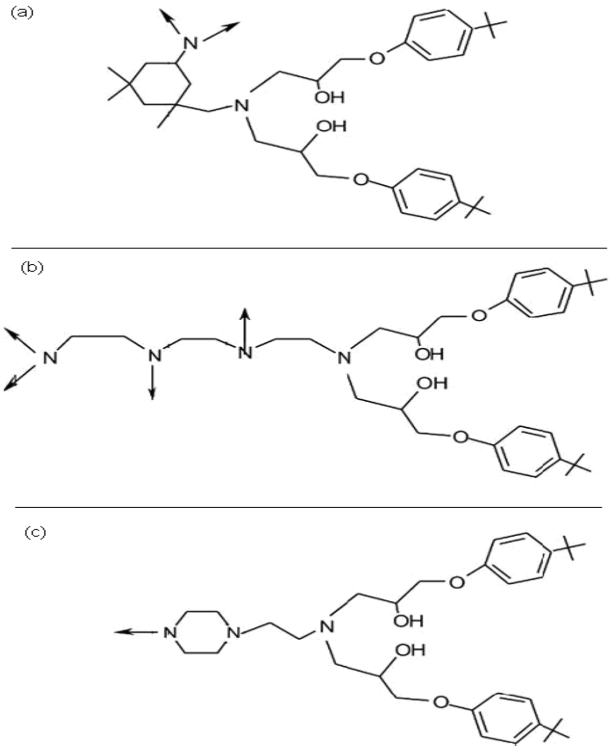


Fig. 2.18 Chemical structures of the networks (a) DGEBA/IPD (b) DGEBA/TETA and (c) DGEBA/AEP [89]

In organic coatings, the use of epoxy resin dominates over other synthetic resins [21]. Epoxy resin is well known for its superior strength, low shrinkage, good thermal and mechanical stability, better bonding with different substrates, long term corrosion and chemical resistance, etc [23], [79], [89] and [90]. However, one of the major drawbacks of epoxy resin is the high moisture absorption. Epoxy resins are susceptible to water absorption due to the presence of hydrophilic hydroxy group in the cured epoxy resins network [79] and [90]. Besides, Wu et al. [87] asserted that the cured network formed will also influence the water absorption. According to Wang et al. [90], epoxy resins can absorb water from surrounding (1-7 wt.%) in which this may affect the properties and confines its applications.

### 2.10.1 Effects of Curing Temperature of Epoxy Resin on Water Absorption

According to Zhao et al. [91] water absorbed into the epoxy can be classified into two types: (a)“bound” water which is trapped at the polar sites, usually bonded to the hydroxyl groups in epoxy network. (b) “free” water that is clustered in free volume or “voids” inside epoxy.

There are several factors that will influence the water absorption rate in epoxy. Johncock and Tudgey [92] and Abdelkader and White [93] found out that the rate of water absorption depended on the temperature used in the curing process of the epoxy which is related to the extent of curing. Zhao et al [91] and Weigang et al. [79] in their work stated that water absorption rate in epoxy is closely related to the glass transition temperature, Tg. This shows that water absorption is closely related to the curing temperature of the epoxy as it will determine the extent of curing where a fully reacted epoxy during curing needs to be achieved. Grave et al. [94] stated that a complete reaction during cure is only achieved if the system is raised close to its glass transition temperature, Tg where Tg is actually related to the crosslinking degree of the epoxy. The higher the degree of crosslinking, the higher the Tg [79]. In other words, we can say that higher Tg indicates higher degree of crosslinking and higher degree of crosslinking will result in a fully reacted epoxy where a fully reacted epoxy will reduce the amount of water being absorbed by the epoxy systems.

Furthermore, Karasz and coworkers [95] and [96] observed that the reduction of Tg cause the increment of water absorbed by an epoxy. Wu et al. [97] discovered that many applications of epoxy are usually cured at room temperature. As a result, only a low glass transition can be obtained and this increases the sensitivity of the epoxy to the environment especially humidity where higher amount of water may be absorbed. So, curing at room temperature should be avoided as it will affect the characteristics of the epoxy thus affecting its performance.

Enns and Gilham [98] studied the water absorption of the epoxy as a function of cure. They found out that epoxy cured with the extent of room temperature resulted in the increase of water absorption after a long exposure and this may be attributed to an increase in the free volume occurring upon curing. Therefore, the extent of curing is important and needs to be considered as it will determine the crosslinking of the epoxy network thus affecting the water absorption into the epoxy.

### 2.11 Corrosion Testing Methods

There are many testing methods used to evaluate the corrosion behavior of metals. These methods include exposure test methods (salt spray test, water fog test, etc), adhesion test (pull-off test) and also electrochemical test using the electrochemical impedance spectroscopy (EIS) technique. However, electrochemical test is more reliable as they provide not just qualitative, but also quantitative results. Exposure tests and adhesion test only provide information based on visual evaluation in which they do not provide information on the corrosion behavior of the samples. Therefore, EIS is required. Furthermore, results can be obtained from the EIS analysis within short period.

#### 2.11.1 Electrochemical Impedance Spectroscopy (EIS)

Scully [99], Jones [100] and Loveday et al. [101] claimed that EIS has been widely used to characterize corrosion for coated materials. It is a non-destructive technique and takes only few minutes to run compared to exposure tests which need to be run for several weeks.

Since impedance is described as the ability of an electrical circuit to resist the flow of electrical current [102], the purpose of running EIS is to actually determine the resistance of the coatings towards corrosion attacks. Sere et al. [103], mentioned that one of the advantages of EIS is its ability to provide information about reaction mechanisms, and/or the possibility that associated faradic process parameters such as charge transfer resistance, electrochemical double layer as well as the resistive and capacitive contributions.

Generally, EIS measures the electrochemical response to a small AC voltage applied over a range of frequencies. The electrochemical response is interpreted in terms of an electrical circuit and this circuit consists of electrical components with the same frequency response as the electrochemical reaction [104]. This equivalent circuit is to quantify the chemical and physical processes involved [102].

There are many equivalent circuit models that can be proposed for coated materials. However, the most applied model to describe the corrosion response for polymer coated materials are as shown in Figure 2.19. Akhbarinazad et al. [58]. Sathiyaranan et al. [105] in their studies for example, used the same equivalent circuit to predict the corrosion behaviors of the pigmented coated steel.

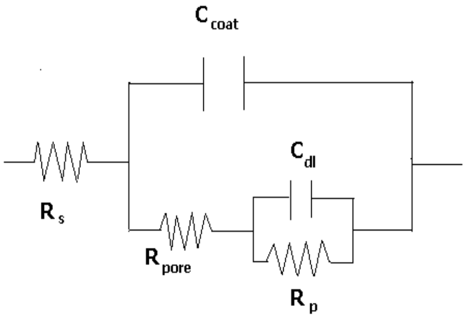


Fig.2.19 Typical equivalent circuit used to describe polymer-coated metals [102] and [104]

This equivalent circuit can be explained by the major concepts where each of the components can be clarified as follows: Rs is the uncompensated solution resistance. It depends on resistivity of the solution ad the location of the electrode with respect to the working electrode. Ccoat is the capacitance of the polymer coating. This parameter is used to monitor water absorption in the coating.

Rpore is the resistance to charge transport through pores, voids and other defects in the coating, while Cdl is the double layer capacitance that arises from dipole interactions on the metal surface. Lastly, Rp is known as the polarization resistance.

Many researchers have carried out electrochemical analysis and also other corrosion testing analysis (salt spray test and pull-off test) in their studies, however, there is no correlation among the corrosion analysis made by them. Galliano and Landolt [106] run the pull-off test and EIS to evaluate the corrosion protection properties of epoxy coatings on steel but discussions of the analysis were done separately and no correlation was made between the pull-off test and EIS. The same issue was also observed in [107] and [108] in which pull-off test results were not correlated with the EIS results obtained by them. On the other hand, Sathiyanarayanan et al. [109] and Riaz et al. [110] in their work run the salt spray test and EIS analysis but they did not relate the results of salt spray test to EIS results or vice versa.

## 2.12 Summary

The selection of a conducting polymer namely polyaniline has emerged as one of the most promising and reliable inhibitor to replace those non-environmental friendly inorganic inhibitors in the coating formulations. The method of blending the polyaniline together with epoxy has been applied by most researchers in their coating formulations. However, the formulation of this coating also contains other inorganic inhibitors and additives. The role of PANI and its effectiveness as corrosion inhibitor is not known and so far, no work has been reported on the coating formulation containing only PANI and epoxy. Moreover, the mechanism for explaining the corrosion protection by polyaniline remains a controversial issue particularly on the formation of passive oxide layer that has been claimed to passivate the protected metals from corroding.

Other than that, water absorption into organic coatings is another issue that most of the researchers need to deal with as coatings are very susceptible to water absorption and failure in preventing the absorption of water into the coatings will result in corrosion. Literature review indicates that curing temperature of the epoxy is claimed to be one of the factors that influenced water absorption. However, focuses have only been made on the effects of curing temperature on water absorption but no work has been done to relate this issue with corrosion. Therefore, a study on water absorption in epoxy by considering the curing condition of the epoxy and relating this issue towards corrosion need to be done. Curing at room temperature may need to be avoided as it will result in a not fully cured epoxy system and this will affect the performance of the system towards water absorption.

There is a need to integrate the aspects that will determine the characteristics of the coatings (i.e: curing temperature of the epoxy and water absorption) with the compatibility of the coating formulations, so that coatings containing polyaniline can offer sufficient protection to the metals. In addition, salt spray test, pull-off test and EIS are the most preferable corrosion analysis test done by the researcher in order to predict corrosion behavior of the metals. However, there were no work done to correlate the electrochemical test (EIS) and other analysis (salt spray test and pull-off test). Since pull-off test and salt spray test only provide qualitative information while EIS is capable of providing both qualitative and quantitative information, it is therefore important and beneficial to do the correlation among the corrosion analysis (EIS, salt spray test and pull-off test) as this will give better understandings on the corrosion behavior of the tested samples and it will allow us to understand the corrosion behavior by only using single equipment within short period.