CHAPTER 9

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF HYBRID EPOXY RESIN COATING

9.1. INTRODUCTION

The deterioration of concrete structures has received significant attention in recent years. A major contributing factor to this deterioration is reinforcing steel corrosion. Corrosion of metal is one of the most challenging problems in materials science and causes huge economic losses in many applications, including the aerospace, automotive, and shipbuilding industries. Much research has been performed to investigate possible solutions to the problem.

The principal function of these corrosion-protection systems is to prevent aggressive agents, mainly chloride ions, from attacking the surface of the metal. The use of epoxy coating has been considered as one of the most cost-effective solutions to the widespread corrosion problem due to their convenient and economical application to concrete structures. Epoxy resins have excellent characteristic property of corrosion resistance [324]. Epoxy-coating provides a physical barrier to the ingress of aggressive agents, and cathodic protection electrochemically stabilizes the steel/concrete interface. They have been used as two pack systems in combination of different curing agents as protective coatings [426, 427]. However; they have poor or low fracture energy, high shrinkage, and show brittle behavior [428]. To overcome these disadvantages and due to the introduction of strict regulations in the use of volatile organic compounds (VOCs) has brought about the development of waterborne one pack hybrid emulsions.

Waterborne coatings have gained increasing importance for many applications. The degradation of a polymer-coated metal occurs after water penetrates at the coating–substrate interface, where failure mechanisms such as osmotic blistering, cathodic delamination and anodic undermining may be initiated [429, 430].

Reliable evaluation methods of organic coatings for corrosion protection are required by coating industries. For this purpose, various test methods have been developed and applied for many
years. Outdoor exposure test generally requires very long test time. On the other hand, an accelerate test very often disagress with the actual degradation mechanisms which occurred under natural conditions. In fact, in order to design an acceleration condition, it is necessary to increase the levels of natural parameters affecting the corrosion protection properties of a coating. In general, acceleration factors can be obtained by controlling the concentration of corrosive material, such as the change of pH and temperature. Many evaluation tests and techniques for coatings have been examined and applied in recent years to reduce the test time and improve their reliability. The most commonly used method is salt-spray testing following the ASTM D 117-94 standard which was introduced by modifying the chemical composition of test solution, or by introducing several degradation steps in one cycle. Salt spray and different cyclic exposure tests are widely used in the coating industry, but these tests yield essentially qualitative information. More recently, electrochemical methods, especially electrochemical impedance spectroscopy (EIS), have found increasing interest for testing of coatings, because these methods are capable to yield mechanistic data which can be quantified by using suitable models [431, 432]. The advantages of the EIS method are principally the precision with which a small sine-wave perturbation can be measured in an electrically noisy environment. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and detection of localized corrosion [433]. Polymer based coatings use barrier technology to protect substrates from corrosive chemicals and environments, particularly when in immersion service [434].

Before discussing the results of the present investigation, an attempt has been made to explain some general concepts of corrosion theory.

### 9.1.1. Corrosion Principles

Corrosion is defined as the destruction or deterioration of a material due to a chemical or an electrochemical reaction with its environment. Corrosion behavior of a material is mainly determined by its structure and composition. There are several ways of classifying corrosion, One method divides corrosion into low-temperature and high-temperature corrosion. Electrochemical corrosion reactions are conveniently divided into, Dry corrosion which is
mainly concerned with the oxidation of a dry metal surface and Wet corrosion in which the reactions occur in an environment which, under normal conditions, is predominantly composed of water.

The importance of corrosion studies is threefold:
(i) Economic factor which is the prime motive for much of the current research in corrosion
(ii) Improved safety in the design of the operating equipment,
(iii) Conservation of energy and resources

9.1.2. Corrosion Rate
Corrosion behaviour of a material is quantitatively expressed in terms of corrosion rates. Corrosion rates have been expressed in a variety of ways in the literature, such as percent weight loss, grams per square inch per hour and milligrams per square decimeter per day (mdd). Corrosion rates can be determined by the,

(1) Non-electrochemical method and
(2) Electrochemical method

(1) Non-Electrochemical Method
Non-electrochemically, the rate of corrosion is determined by the conventional weight loss/gain technique. Using this technique, the loss of a metal due to corrosion is measured by exposing the metal specimen of known area to the corrosive environment for a particular period and finding the difference in weight before and after exposure.

The expression 'mils per year' (mpy) is the most widely used way of expressing the corrosion rate Corrosion rate is calculated using the formula,

\[
\text{Corrosion Rate (mpy)} = \frac{534W}{DAT}
\]

Where, \( W \) = weight loss in mg, \( D \) = density of the specimen in g/cm\(^2\), \( A \) = Area of the specimen in sq inch, \( T \) = exposure time in hr

Corrosion rate in mpy can also be calculated by using the formula,

\[
Mpy = \frac{0.129 \times a \times icorr}{n \times D}
\]
Where,

\[ a = \text{atomic weight} \]
\[ n = \text{valence charge} \]
\[ i_{\text{corr}} = \text{corrosion current density in uA/cm}^2 \]
\[ D = \text{density in g/cm}^* \]

The weight loss method yields the average rate for the exposure period and is inherently inaccurate when it involves measuring small differences between initial and final weights of corroded specimens.

(2) Electrochemical Theory of Corrosion

The electrochemical theory of corrosion states that corrosion proceeds by electrochemical reactions involving an anodic or oxidation reaction and a cathodic or reduction reaction. Usually corrosion consists of a set of redox reactions that are electrochemically in nature, which for a given metal M given as:

\[
M \rightarrow M^{2+} + 2e^- \tag{1}
\]

and hydrogen is reduced at the cathodic sites,

\[
2H^+ + 2e^- \rightarrow H_2 \tag{2}
\]

Eqs (1) and (2) are partial reactions and both of them must occur simultaneously and at the same rate on the metal surface, otherwise the metal would become charged which is impossible. This leads to the most basic principle of corrosion "During corrosion, the rate of oxidation equals the rate of reduction". So any reaction that can be divided into two or more partial reactions of oxidation and reduction is termed electrochemical. During corrosion, more than one oxidation and one reduction may occur. Since these reactions are mutually dependent, it is possible to reduce corrosion by reducing the rates of either of these reactions. The interpretation of corrosion processes by superimposing electrochemical partial processes was developed by Wagner and Traud, which is the well known 'Mixed potential theory'. The two hypotheses of this theory are:

(i) Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions
(ii) There can be no net accumulation of electric charge during the electrochemical reaction.

In general the following are the commonly employed electrochemical techniques to measure corrosion rates.

(a) Polarization and (b) AC Impedance Spectroscopy

The theoretical background and experimental procedures of the above methods to determine the corrosion rates are described below:

(a) Polarization Studies

During electrochemical corrosion the anode and cathode are not at their equilibrium potential at the surface of the metal. This deviation from equilibrium potential is called polarization. Polarisation can be defined as the extent of potential difference or the displacement of electrode potential caused by net current flow to or from an electrode measured in volts, commonly known as over voltage or over potential represented by $\eta$. Polarization is an extremely important corrosion parameter, which enables one to understand the corrosion rate processes.

There are three types of polarization:

1. **Activation polarization**: This refers to an electrochemical process that is controlled by the sequence of reaction taking place at the metal-electrolyte interface. In other words, activation polarization is caused by a slow electrode reaction because the reaction at the electrode requires activation energy. Both anodic and cathodic reactions can be under activation polarization.

2. **Concentration polarization**: This is observed when the electrochemical reactions occur that are controlled by the diffusion in the electrolyte. This behaviour usually occurs when the concentration of reducible species in the environment is small, e.g. corrosion in aerated salt solutions.

3. **Resistance polarization**: This usually includes an ohmic potential drop through either a portion of the electrolyte surrounding the electrode or through a metal reaction product film on the surface or both. Resistance polarization may be written as:

$$\eta = RI = yi$$

Where,

$R = $ film resistance of electrode surface in ohms
I = current in amperes
y = film resistance for 1 cm2 area in ohm/cm'
i = current density in amp/cm

In electrochemical corrosion testing, two different approaches are apparent.
1. Control of current (i.e., corrosion rate) and
2. Control of potential (i.e., the oxidizing power) and measuring the resulting current
In each case the potential of an electrode in a conducting medium is changed by the flow of current in the electrolytic cell. The formation of the mixed potential of a corroding metal surface is illustrated in the polarization diagram sometimes called Evans diagrams. The determination of these polarization curves and the corrosion rate of a specimen can be done very quickly. A complete curve can be determined in an hour in laboratory setup, whereas the conventional method to determine corrosion rate, i.e., by weight loss measurements takes several days or weeks.

(b) AC Impedance Spectroscopy method
A polarization resistance method often gives erroneous results for systems in which the electrolyte resistance is very high Impedance technique has been proved to be effective in these cases. AC impedance measurements, when applied to the study of electrochemical systems can provide a wealth of kinetic and mechanistic information. For this reason, the technique is becoming very popular in the study of corrosion. AC impedance approach offers some distinct advantages over DC techniques:
1) The AC impedance technique uses very small excitation amplitudes, generally in the range of 5 to 10 mV peak to peak. Excitation amplitudes of this magnitude cause only minimal perturbation of the electrochemical test system, thus reducing errors caused by the measurement technique itself.
2) Since AC impedance experiments can provide data on both electrode capacitance and charge transfer kinetics, the technique offers valuable mechanistic information.
3) Because the method does not involve a potential scan, measurements can be made in low conductivity solutions where DC techniques are subject to serious potential-control errors. In
fact, the AC impedance method can be used to determine the uncompensated resistance of an electrochemical cell.

The object of an AC impedance experiment may be to determine the values of the various elements in the equivalent circuit or simply to confirm that a given electrochemical system fits a particular equivalent circuit model. This is done experimentally by studying the response of the electrochemical system to an AC excitation over a wide range of frequencies. The excitation can be applied as an AC voltage or an AC current. The measured response will be, respectively, an AC current or an AC voltage, from which the system impedance can be calculated. A full description of the electrochemical system's behavior requires both in-phase and quadrature components of impedance at a number of frequencies over the desired range. These can be calculated from the real and imaginary components of the excitation and response waveforms using the following equation.

\[ Z_{\text{TOTAL}} = Z' + Z'' \]

Where,

- \( Z_{\text{TOTAL}} \) is the resultant AC impedance vector,
- \( Z' \) and \( Z'' \) are the real and imaginary parts of the impedance vector.

Most electrochemical systems can be characterized by impedance data over a range of 0.001 to 10,000 Hz.

A variety of formats can be used to plot the impedance data. Each format offers specific advantages for revealing certain characteristics of a given test system.

i) Nyquist plot

This form of the plot is also known as Cole-Cole plot or a complex impedance plane diagram. The imaginary component of impedance (\( Z'' \)) is plotted against the real component of impedance (\( Z' \)) at each excitation frequency. This plot could be used to compute the values of the uncompensated resistance between the working electrode and the reference electrode (\( R_\Omega \)), the polarization resistance of electrode/solution interface (\( R_p \)), and double layer capacitance at this interface (\( C_d \)). Knowledge of \( R_p \) permits the calculation of electrochemical corrosion reaction rates.
ii) Bode plot

The Bode plot is a useful alternative to the Nyquist plot to avoid longer measurement times associated with low frequency. Rp determinations as this is a plot of log |Z| vs log ω. It allows a more effective extrapolation of data from higher frequencies. This form of the plot permits examination of the absolute impedance |Z| and the phase shift as calculated by the following equation of the resultant waveform, each as a function of frequency

\[ |Z| = \sqrt{(z')^2 + (z'\prime)^2} \quad \text{and} \quad \tan \phi = \frac{z'\prime}{z'} \]

The log |Z| vs log ω curve can yield values of R_P and R_Ω. At intermediate frequencies, the "break-point" of this curve should be a straight line. Extrapolating this line to the log |Z| axis at ω= 1 (log ω = 0) yields the value of C_d from the relationship

\[ Z = \frac{1}{C_d} \]

There are several methods of measuring the true, instantaneous rate of corrosion and many of these are electrochemical methods. They rely on measuring changes in the half cell potential as it is perturbed, and use electrochemical theory to calculate the corrosion current and hence the rate of corrosion. Linear polarization technique has proven itself to be useful in measuring corrosion rates. The corrosion density can be determined by the concept of reaction rates and polarization of electrochemical reactions at the metal surface.

9.2. OBJECTIVES

The corrosion research and testing provides information about the reasons for corrosion processes and their mechanism. Since corrosion processes are mostly of an electrochemical nature, electrochemical methods play an important role in corrosion research and testing.

The objective of the present work was to develop an experimental method using electrochemical impedance spectroscopy (EIS) to measure the frequency response of steel Panels coated with hybrid epoxy resin subjected to electrolyte environments. EIS has been shown to be a sensitive technique for monitoring non-stationary behavior, which proved to be ideal for exploring corrosion systems where film formation contributes to influence reaction kinetics and transport properties over time.
Polarization resistance method, based on electrochemical concepts, enables determination of instantaneous interfacial reaction rates such as corrosion rates and exchange currents densities from a single experiment. The estimation of corrosion rate based on polarization resistance measurements has been used more and more extensively.

This chapter reports the results of an investigation of the corrosion resistance of the hybrid coatings using EIS techniques. The hybrid emulsion coatings with increasing resin content was applied on metal surface and analyzed with electrochemical impedance spectroscopy. The effects of coating thickness on water absorbance and ultimately on corrosion resistance were also studied. Nyquist and bode plots was analyzed to predict the corrosion performance of hybrid coatings. SEM analysis of the specimen was performed after immersion to get a closer view of coating degradation.

9.3. EXPERIMENTAL METHODOLOGY

9.3.1. Preparation of specimen for testing
Specimens in the form of mild steel strips with 1000 × 700 × 0.5 mm size was used for analysis. The panels were chemically washed with acetone to remove any oil, grease and other organic contaminants before the application of coatings. The steel panels used had the following composition:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Chemical composition (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Mild steel</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Hybrid epoxy coatings were applied to specimen surfaces and they were left to dry for 24 hours at 28 °C. Specimens were prepared with varying thickness of hybrid coatings to study the effect of coating thickness on corrosion performance. Two specimens were tested as soon as they were immersed in testing solution and were considered as time zero. Data were collected from specimens immersed in 3.5% NaCl solution periodically for 12 days at room temperature.
9.3.2. Electrochemical Impedance Tests

Well-controlled experiments were designed to assure the generation of reliable data suitable for regression of process models. To guarantee symmetric current and potential distributions, an electrochemical cell was designed and constructed with a cylindrical geometry. The EIS cell was built by a glass tube of 4 inches height and cross sectional area of 7 cm$^2$. A representative cell for EIS measurement was similar, as shown in Figure 9.1.

![Electrochemical Impedance Spectroscopy Diagram](image)

**Figure 9.1: Block diagram of electrochemical impedance spectroscopy**

Two techniques, namely Tafel plots and AC polarization curves were used to study the corrosion behavior of the hybrid coatings. The first technique allowed the determination of corrosion potential $E_{corr}$ and corrosion current $I_{corr}$. Corrosion current $I_{corr}$ was determined by the Tafel extrapolation method by carrying out scans in both the positive and negative directions with respect to the corrosion potential. As a result, a polarization curve consisting of both anodic and cathodic segments was obtained. Based on $I_{corr}$ values, the corrosion rate of the hybrid coatings was calculated. The potentiodynamic polarization curves of all the specimens were generated after conducting the scan below $E_{corr}$ (versus saturated calomel electrode) at a scan rate of 1.66 mV/min. The potentiodynamic plots were produced directly using the data acquisition system. All tests were performed at room temperature.

The measurements are usually made employing a potentiostat. This instrument automatically maintains the desired potential between the working and reference electrodes by passing an
appropriate current between the working and counter electrodes. A basic circuit for a potentiostat is schematically shown in Figure 9.2. A potentiostat is a controller circuit that maintains the potential between the working and the reference electrodes equal to the value $E$. If there is a small difference $\Delta E$ volts, this is sensed, amplified and a current $I$ flows. This process continues till the difference $\Delta E$ becomes zero. The direction of the current flow depends upon the sign of $\Delta E$. Since the input impedance is very high, very low current flows through, and the reference electrode is not polarized. Using the potentiostat, polarization may be accomplished either potentiostatically (in steps) or potentiodynamically (continuously).

![Figure 9.2: Schematic of a basic circuit for a potentiostat.](image)

$C$ = Counter electrode, $R$ = Reference electrode, $W$ = Working electrode

9.3.3. Experimental assembly for AC impedance spectroscopy of polymer coated metal

The corrosion behavior of the specimens was monitored using electrochemical impedance spectroscopy (EIS) during immersion in 3.5% NaCl solution open to air and at room temperature for up to 12 days. A three-electrode set-up was used to record corrosion potential of coating. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Pt wire to reduce the phase shift at higher frequencies. The open circuit potential (OCP) was measured between reference electrode and working electrode in artificial sea water (3.5% w/v NaCl) before each scan within a 50 seconds initial delay. The impedance
measurements were performed at the OCP using a sine wave of 10mV amplitude peak to peak for each panel. Electrochemical impedance tests were carried out by using Versa STAT 3 provided with frequency response analyzer, frequency in the range from 1 Hz to 1 kHz to collect data with a total number of 40 readings for the whole range. The amplitude of the sinusoidal voltage signal was 50 mV. Data were collected by means of Frequency Response Analyzer software developed by Princeton Applied Research instruments and were in the form of Nyquist plots.

9.3.4. Model for simulation and analysis of EIS data for hybrid coatings

The equivalent circuit for polymer coated steel can be represented by the model shown in Figure 9.3. Where, Cdl is the double layer capacitance, and Cc is the capacitance of the polymer coating given by:

\[ C_c = \varepsilon \varepsilon_0 A/d \]

Where, \( \varepsilon \) is the dielectric constant of polymer, \( \varepsilon_0 \) is the dielectric constant of free space (8.85 \times 10^{-14} \text{ F/cm} ), A is the exposed area of the electrode and d is the thickness of coating. \( R_S \) is the solution resistance, \( R_P \) is the pore resistance which is due to the formation of ionically conducting paths across the coating, \( R_T \) is the charge transfer resistance of the metal / solution interface at which corrosion occurs.

Since, the impedance for coated metals changes over many orders of magnitude, between the value for \( R_S \) at the very highest frequencies to that of \( R_S + R_P + R_T \) at very lowest frequencies. The EIS data are better displayed as bode plot in which the magnitude of the logarithm of the impedance modulus \(|Z|\) and the phase angle \( \Phi \) are plotted vs. the logarithm of the applied frequency.

![Figure 9.3. Equivalent RC circuit for organic coating/metal systems.](image-url)
### 9.3.5. DC electrochemical polarization study

Most metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. A thin film of moisture on a metal surface forms the electrolyte for atmospheric corrosion. Corrosion normally occurs at a rate determined by an equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often O$_2$ or H$^+$) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. The two reactions can take place on one metal or on two dissimilar metals (or metal sites) that are electrically connected. Figure 9.4 diagrams this process, vertical axis is potential and the horizontal axis is the logarithm of absolute current. The theoretical current for the anodic and cathodic reactions are shown as straight lines. The curved line is the total current which is sum of the anodic and cathodic currents. This is the current that, you measure when you sweep the potential of the metal with your potentiostat. The sharp point in the curve is actually the point where the current changes signs as the reaction changes from anodic to cathodic, or vice versa. The sharp point is due to the use of a logarithmic axis. The use of a log axis is necessary because of the wide range of current values that must be displayed during a corrosion experiment. Because of the phenomenon of passivity, it is not uncommon for the current to change by six orders of magnitude during a corrosion experiment.

The potential of the metal is the means by which the anodic and cathodic reactions are kept in balance. Refer to Figure 9.4. Notice that, the current from each half reaction depends on the electrochemical potential of the metal. Suppose the anodic reaction releases too many electrons into the metal. Excess electrons shift the potential of the metal more negative, which slows the anodic reaction and speeds up the cathodic reaction. This counteracts the initial perturbation of the system. The equilibrium potential assumed by the metal in the absence of electrical connections to the metal is called the Open Circuit Potential, $E_{oc}$. In most electrochemical experiments, the first step is the measurement of $E_{oc}$. The terms $E_{oc}$ (Open Circuit Potential) and $E_{corr}$ (Corrosion Potential) are usually interchangeable, but $E_{oc}$ is preferred.

It is very important that, the Corrosion Scientist measures the Eoc and allows sufficient time for the $E_{oc}$ to stabilize before beginning the electrochemical experiment. A stable $E_{oc}$ is taken to indicate that the system being studied has reached "steady state", i.e., the various corrosion
reactions have assumed a constant rate. Some corrosion reactions reach steady state in a few minutes, while others may need several hours. Regardless of the time required, a computer-controlled system can monitor the $E_{oc}$ and begin the experiment after it has stabilized.

![Diagram of corrosion process showing anodic and cathodic current components.](image)

**Figure 9.4: Corrosion Process Showing Anodic and Cathodic Current Components.**

The value of either the anodic or cathodic current at $E_{oc}$ is called the Corrosion Current, $I_{corr}$. If we could measure $I_{corr}$, we could use it to calculate the corrosion rate of the metal. Unfortunately, $I_{corr}$ cannot be measured directly. However, it can be estimated using electrochemical techniques. In any real system, $I_{corr}$ and Corrosion Rate are a function of many system variables including type of metal, solution composition, temperature, solution movement, metal history, and many others.

Because corrosion occurs via electrochemical reactions, electrochemical techniques are ideal for the study of the corrosion processes. In electrochemical studies, a metal sample with a surface area of a few square centimeters is used to model the metal in a corroding system. The metal sample is immersed in a solution typical of the metal's environment in the system being studied.
Additional electrodes are immersed in the solution, and all the electrodes are connected to a device called a potentiostat. A potentiostat allows you to change the potential of the metal sample in a controlled manner and measure the current flow as a function of potential.

9.3.6. Experimental assembly for DC impedance spectroscopy of polymer coated metal
The DC polarization study was performed during immersion in 3.5% NaCl solution open to air and at room temperature for up to 12 days. A Pyrex glass cell with a capacity of 300 ml was used for the electrochemical corrosion tests. A three-electrode set-up was used with impedance spectra being recorded at the corrosion potential $E_{corr}$. The system was composed of a working electrode, counter electrode, and reference electrode. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a counter electrode made of platinum wire to reduce the phase shift at high frequencies. The probe tip was easily adjusted to bring it at a distance of about 2 mm from the working electrode. A potentiostat (Versa STAT 3, by Princeton Applied Research) was used for the electrochemical measurements. VersaStudio corrosion analysis software was used to analyze the data and calculate the Tafel constants. DC polarization tests of specimens previously immersed in 3.5% NaCl solution were made at a scan rate of 1.66 mV/sec in the applied potential range from -1.5 V to 0.2 V with respect to $E_{corr}$. The exposed surface area was 7 cm$^2$. The corrosion rate of hybrid coatings was reported as millimeter per year (mmpy).

9.4. CHARACTERIZATION

9.4.1. Dry film thickness
Dry film thickness of coatings was measured with a dry film thickness meter. DFT meter was calibrated to zero reading before testing. The average of successive three readings has been reported as film thickness.

9.4.2. Crosshatch adhesion
Adhesion of the cured coatings was determined by this test according to ASTM D3359-02. Six parallel cuts of about 20mm in length and 2mm apart from each other were made on the coated panel using a sharp blade having a cutting edge angle between 15°. Additional number of cuts at
90° to the original cuts was made. The grid area was brushed and a pressure sensitive tape about 75 mm long was placed over the grid and inspected according to the standards. The grid area was examined for any flaking of the coating. More the coated material removed from the tape, poorer the adhesion of the coating to the substrate. The adhesion is reported as a percentage of the grid area retained.

9.4.4. Gloss

Gloss is a measure of ability of coated surface to reflect light at a particular angle without scattering. Gloss was determined according to ASTM D523-67. Gloss of the cured sample was measured at 45° and 60° of reflectance using a digital mini gloss meter calibrated against internal standard i.e. refractive index (Komal Scientific Co. Mumbai, India) and the results are reported in terms of gloss unit (GU).

9.4.5. Morphology

The morphology of hybrid coatings were with ZEISS SUPRA 40 Scanning electron microscope. Tested specimens were washed with distilled water, and then gold coated to examined under scanning electron microscope. Electrolyte penetration through the hybrid coating was analyzed with SEM images.
9.5. RESULTS AND DISCUSSION

The hybrid epoxy resin coatings were applied on metal surface and tested with an EIS technique for corrosion resistance. The composition of hybrid films used for analysis were indicated in Table 9.2. Effect of the increasing epoxy resin content and thickness of hybrid coatings was studied with impedance spectroscopy.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
<th>H7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy: Acrylics (%)</td>
<td>0:100</td>
<td>20:80</td>
<td>30:70</td>
<td>40:60</td>
<td>50:50</td>
<td>60:40</td>
<td>70:30</td>
</tr>
<tr>
<td>DFT (µm)</td>
<td>75</td>
<td>75</td>
<td>74</td>
<td>75</td>
<td>76</td>
<td>75</td>
<td>72</td>
</tr>
<tr>
<td>Adhesion (%)</td>
<td>50</td>
<td>70</td>
<td>75</td>
<td>80</td>
<td>100</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>Gloss 60°</td>
<td>85</td>
<td>82</td>
<td>83</td>
<td>81</td>
<td>80</td>
<td>82</td>
<td>65</td>
</tr>
</tbody>
</table>

The corrosion resistance of the hybrid Ep-Ac coating was tested with salt spray (ASTM-117) method for 500hr. Analysis reveals that, with increasing percentage of epoxy resin the corrosion resistance of the coating improves. The improvement in the corrosion resistance of the hybrid coating with the content of the epoxy resin was attributed to the hydrophobic nature of resin. There is increasing trend in corrosion resistance properties up to H6 but for H7 formulation the corrosion resistance is not satisfactory. Poorest corrosion resistance of H7 is attributed to the presence of unreacted epoxy resin which will affect the uniform distribution of polymer coating on metal surfaces.

9.5.1. DC POLARIZATION STUDY

DC polarization studies were performed to study the corrosion behavior of hybrid coatings with increasing percentage of epoxy resin. Figure 9.5-9.11, represents tafel plot for hybrid coatings with increasing epoxy resin content and Figure 9.12, represents an overlay of tafel plots for
hybrid coatings with epoxy resin concentration varying from 0 to 70% with respect to acrylate monomers.

Table 9.3, shows the electrical parameters for hybrid coatings. The $E_{corr}$ values for hybrid coating moves towards more negative, while $I_{corr}$ and corrosion rate decreases with increasing resin content. However, the parameters for hybrid with more than 60% resin content does not follow the trend. Figure 9.12, represents tafel overlay of hybrid coatings which shows that, the corrosion resistance of coatings improves with resin content. Results obtained with EIS study are in good argument with salt spray results discussed in chapter 3.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_{corr}$ mV</th>
<th>$I_{corr}$ µA/cm²</th>
<th>C.R. mmpy</th>
<th>$\beta_{anodic}$ mV/decade</th>
<th>$\beta_{cathodic}$ mV/decade</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>-61.33</td>
<td>3.169</td>
<td>0.0526</td>
<td>2.0717e+05</td>
<td>801.09</td>
</tr>
<tr>
<td>H2</td>
<td>-159.73</td>
<td>1.273</td>
<td>0.00185</td>
<td>1.7261e+05</td>
<td>549.73</td>
</tr>
<tr>
<td>H3</td>
<td>-161.84</td>
<td>0.721</td>
<td>0.00018</td>
<td>57011</td>
<td>604.78</td>
</tr>
<tr>
<td>H4</td>
<td>-373.14</td>
<td>0.191</td>
<td>0.00119</td>
<td>83.641</td>
<td>109.06</td>
</tr>
<tr>
<td>H5</td>
<td>-599.13</td>
<td>0.113</td>
<td>0.00031</td>
<td>8534.7</td>
<td>2125</td>
</tr>
<tr>
<td>H6</td>
<td>-951.37</td>
<td>0.009</td>
<td>0.000016</td>
<td>73.12</td>
<td>81257</td>
</tr>
<tr>
<td>H7</td>
<td>-275.24</td>
<td>0.219</td>
<td>0.00211</td>
<td>1.2557e+05</td>
<td>252.82</td>
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</tbody>
</table>

The increase in epoxy resin leads to lowering of the corrosion current and shift of the corrosion potential of about 890 mV from acrylate to hybrid with 60% epoxy resin. The cathodic $\beta_{cathodic}$, does not systematic variation with increasing epoxy resin content, though hybrid coatings with epoxy resin exhibits lower values than an acrylate coating. However, examination of the cathodic curves of Figs 9.5-9.11 reveal that, the cathodic reaction most likely the $H_2$ evolution has a higher reaction rate of acrylate coating. This is inferred from the fact that, the tafel curves are shifted towards the left side, such a tendency is possible only when the exchange current density for the $H^+/H$ equilibrium decreases with epoxy resin content. In contrast to $\beta_{cathodic}$ there is a significant increase in $\beta_{anodic}$, with epoxy resin content, These observations emphasize the fact that, hybrid coatings provide better resistance towards corrosion than an acrylate coating.
Figure 9.5: Tafel plot for specimen coated with hybrid H1 at 30°C

Figure 9.6: Tafel plot for specimen coated with hybrid H2 at 30°C
Figure 9.7: Tafel plot for specimen coated with hybrid H3 at 30°C

Figure 9.8: Tafel plot for specimen coated with hybrid H4 at 30°C
Figure 9.9: Tafel plot for specimen coated with hybrid H5 at 30°C

Figure 9.10: Tafel plot for specimen coated with hybrid H6 at 30°C
Figure 9.11: Tafel plot for specimen coated with hybrid H7 at 30°C

Figure 9.12: Overlay of tafel graph with increasing ratio of epoxy resin
9.5.2. AC POLARIZATION STUDY

An equivalent electrical circuit was fitted to the AC impedance spectroscopy measurement data using a frequency-response analysis software. Then the numerical values of the electrical elements of the coated mild steel panels were extracted. Coating resistance, coating capacitance, OCP (open circuit potential) after exposure were evaluated (Table 9.4). Nyquist and bode plots are analyzed for corrosion resistance study of metal surface after exposure to salt solution.

Table 9.4: Coating impedance, Coating capacitance and Open circuit potentials

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Coating impedance</th>
<th>Coating capacitance</th>
<th>OCP (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>00 day</td>
<td>10 day</td>
<td>00 day</td>
</tr>
<tr>
<td>H1</td>
<td>5.542257e+04</td>
<td>6.500804e+02</td>
<td>1.423002e-08</td>
</tr>
<tr>
<td>H2</td>
<td>4.071049e+05</td>
<td>1.287102e+02</td>
<td>5.283194e-09</td>
</tr>
<tr>
<td>H3</td>
<td>5.015030e+06</td>
<td>1.103162e+03</td>
<td>1.643518e-09</td>
</tr>
<tr>
<td>H4</td>
<td>9.522445e+06</td>
<td>7.217372e+02</td>
<td>8.455699e-10</td>
</tr>
<tr>
<td>H5</td>
<td>4.582417e+05</td>
<td>4.128327e+02</td>
<td>1.117673e-10</td>
</tr>
<tr>
<td>H6</td>
<td>2.127438e+05</td>
<td>3.860423e+02</td>
<td>3.726407e-12</td>
</tr>
<tr>
<td>H7</td>
<td>1.078813e+04</td>
<td>2.310121e+01</td>
<td>1.543841e-09</td>
</tr>
</tbody>
</table>

The effect of epoxy resin content on coating capacitance, impedance value and open circuit potential were summarized in Table 9.4. The variation of parameters on immersion in salt solution can be analyzed from table. The coating resistance values at 00 days for hybrid coating indicates that, corrosion resistance improves with increasing epoxy resin content. The EIS analysis after immersion in salt solution shows decreasing coating resistance values for all specimens, arising due to penetration of electrolyte into hybrid coatings.

9.5.2.1. Coating Capacitance (Cc)

The capacitance of polymer film is an important parameter to measure its integrity. While an ideal film acts like a perfect capacitor, a purely capacitive behavior is characteristic of an effective barrier film. Upon initial exposure to an electrolyte film with excellent barrier properties acted as an almost perfect capacitor. The capacitance value is dependant on the thickness and its dielectric constant.
Coating capacitance for the different specimens are shown in Table 9.4. The coating capacitance determines the total amount of water in the coating. After 10 days immersion in an electrolyte, the value of the coating capacitance of the specimens is higher indicating that, the absorption of water in the coating. Absorption of water causes an increase in the dielectric constant of the coating with a corresponding increase in the coating capacitance. There are corrosion products which absorb more water through the film and increases the dielectric constant of the coating for the specimens.

As shown in Table 9.4, the change of coating capacitance from $3.726407 \times 10^{-12}$ to $1.329454 \times 10^{-09}$ for hybrid coating H6 after exposure of 10 days was a result of water absorption. Hence, the swelling of the film which resulted in the increase of film thickness.

9.5.2.2. Open Circuit Potential

The open circuit potential is a parameter which indicates the thermodynamically tendency of a material to electrochemical oxidation in a corrosive medium. The OCP measurement is a simple additional tool that provides complementary information to EIS results regarding the corrosion undergone by the steel substrate after exposure to aggressive solutions. Figure 9.13, presents the OCP variation over time for the metal panel coated with hybrid polymer. The evolution of the curve trend was clearly related to the performance of hybrid film protectiveness. Table 9.4, represents OCP values for hybrid coatings with increasing epoxy resin content. The initial OCP value was the representation of film protectiveness but the decrease in OCP value, shift of potential towards more negative values indicates a fast damage produced by an accelerated corrosion process due to the loss of adherence of the film from substrate.

The Figures 9.14-9.20, represents the bode plots for hybrid epoxy coating with increasing resin content. The overlay of bode plots for hybrid coating with different thickness are presented in the Figure 9.22, while Figure 9.21 represents an overlay with increasing epoxy resin content. From which it can be predicted that hybrid coating possesses good corrosion resistance properties.
Figure 9.13: Variation of open circuit potential with days of immersion.

Figure 9.14: Bode plot of hybrid H1 at the time of immersion (30ºC)
Figure 9.15: Bode plot of hybrid H2 at the time of immersion (30°C)

Figure 9.16: Bode plot of hybrid H3 at the time of immersion (30°C)
Figure 9.17: Bode plot of hybrid H4 at the time of immersion (30°C)

Figure 9.18: Bode plot of hybrid H5 at the time of immersion (30°C)
Figure 9.19: Bode plot of hybrid H6 at the time of immersion (30°C)

Figure 9.20: Bode plot of hybrid H7 at the time of immersion (30°C)
Figure 9.21: Overlay of bode plot with increasing resin content

Figure 9.22: Overlay of Bode plot for hybrid coatings with different thickness
The Nyquist plots for hybrid coatings with increasing resin content are represented in Figures 9.23-9.29. Nyquist plots take shape of a semi-circle with increasing corrosion resistance with resin percentage. The impedance values of hybrid coatings for different resin content before and after immersion in 3% Nacl are shown in Table 9.4. From the impedance values it can be predicted that, the hybrid coating gives higher corrosion resistance with increasing resin content. Figures 9.30-9.34, represent the Nyquist plots for the impedance of specimens E tested after immersion in 3% Nacl solution at room temperature for a period of 12 days. Figure 9.30 shows, the Nyquist plot for the specimen tested at the time of immersion, the behavior takes a shape of a part of a semicircle with high capacitive and resistive values.

Figure 9.23: Nyquist plot for specimen H1 tested before immersion in the testing solution.
Figure 9.24: Nyquist plot for specimen H2 tested before immersion in the testing solution.

Figure 9.25: Nyquist plot for specimen H3 tested before immersion in the testing solution.
Figure 9.26: Nyquist plot for specimen H4 tested before immersion in the testing solution.

Figure 9.27: Nyquist plot for specimen H5 tested before immersion in the testing solution.
Figure 9.28: Nyquist plot for specimen H6 tested before immersion in the testing solution.

Figure 9.29: Nyquist plot for specimen H7 tested before immersion in the testing solution.
Figure 9.30: Nyquist plot of the specimen E just after immersion in the testing solution.

Figure 9.31: Nyquist plot of the specimen E after 4 days of immersion
Figure 9.32: Nyquist plot of the specimen E after 8 days immersion

Figure 9.33: Nyquist plot of the specimen E after 10 days immersion.
Figure 9.34: Nyquist plot of the specimen E after 12 days immersion.

The effect of exposure time on the impedance behavior of hybrid epoxy coatings can be seen from Figures 9.35-9.36, a severe change in capacitance and resistance values just after immersion for 4 days. Further immersion had also a great effect on the behavior of hybrid epoxy coatings. Immersion for 12 days and above, yielded a double semicircle, Nyquist plot with an indication about the failure of hybrid coating and the interaction of metal surfaces with a solution. Figures 9.35-9.36 show, the values of Capacitance (Cd) and Resistance (Rc) for specimen E as a function of immersion time. The capacitance values of the samples were very low, these values increased gradually as they were immersed in the solution. In the case of hybrid epoxy coatings, the value of Cd increases after immersion in the electrolyte, reaching a constant value. The plateau period of Cd indicates the beginning of detachment of the coating from the substrate due to adhesion loss.

In the case of specimen E, a low value of Cd were obtained of epoxy coating just after immersion in salt water, the gradual increase in the value of Cd can be due to solution penetration between the coating and the steel surface. This penetration can be through breakdown sites of the coating. The high viscosity of salt water compared to water may make water uptake a time consuming process.
Figure 9.35: The value of Cd Versus Immersion time for specimen E

Figure 9.36: Rc versus Immersion time for specimen E
The other parameter, \( R_c \), gives an indication about the corrosion process at the steel surface. This parameter can be used to study the effectiveness of some coating in the protection of metals. Figure 9.36, shows the decrease in the value of \( R_c \) with respect to immersion time. Scanning Electron Micrographs taken from specimens tested after 10 days of immersion show a clear coating degradation in the form of holidays and rupture. This can be seen from Figures 9.40. The effect of immersion time on the performance of epoxy coating is clear, and can be seen from the values of \( C_d \) and \( R_c \).

9.5.3. Water absorbance study of Hybrid Coating

The pore resistance, \( R_p \), which represents the ability of coating to protect the substrate, can be determined in the low frequency region in which the coating impedance is independent of frequency. The results show that, hybrid coatings have their well-defined pore resistance, Table 9.5, summarizes the coating impedance at 0.1 Hz obtained in this investigation as a function of immersion time for coatings of varying thickness.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Coating thickness (µm)</th>
<th>Impedance @ 0.1Hz (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 Day</td>
<td>4 Day</td>
</tr>
<tr>
<td>A</td>
<td>32</td>
<td>7.401841e+03</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>1.046800e+04</td>
</tr>
<tr>
<td>C</td>
<td>54</td>
<td>4.012673e+04</td>
</tr>
<tr>
<td>D</td>
<td>66</td>
<td>2.079440e+05</td>
</tr>
<tr>
<td>E</td>
<td>75</td>
<td>2.127438e+05</td>
</tr>
</tbody>
</table>

Figure 9.37, plots the IZI at 0.1 Hz as a function of coating thickness for a hybrid which are of the same coating type but at different thicknesses.
The results demonstrated that, the coating impedance increased with thickness. As shown in Figure 9.37, the coating impedance at 0.1 Hz decreased by one order of magnitude after 8 days of immersion. Further decrease was observed during further immersion up to 12 days. During the EIS measurements, no significant corrosion or coating degradation was observed during 8 days of testing. The decreases of coating impedance during the immersion tests is most likely due to the intrusion of moisture and ions into the structures in the coatings, which in turn increased the pore conductance. This can be explained with the structural orientation of hybrid coatings during film formation.

Figure 9.38 demonstrates the representative FTIR spectra for the air-facing side and metal-facing side of the hybrid containing. The peak at 1508 cm\(^{-1}\) for stretching of paraphenyl of epoxy resin and 1729 cm\(^{-1}\) for the absorption of carbonyl group of acrylates. Absorbance intensity of 1508 cm\(^{-1}\) peak at the metal facing side is higher than those at air-facing side, suggesting that the epoxy resin part in emulsion tends to move to the metal facing side. The driving force of this movement could be attributed to the difference in the surface free energy between the epoxy resin and the acrylic copolymer. The critical surface tensions of poly butyl acrylate, polyacrylic acid, poly methyl methacrylate and poly 2-hydroxyl ethyl methacrylate are around 31, 11.1, 39 and 37 mN/m, respectively [336], so the critical surface tension of the acrylic...
copolymers should be between 11 and 37 mN/m, which is lower than that of the epoxy resin, which is around 44 mN/m.

![Figure 9.38: FTIR-ATR of hybrid (a) Air facing, (b) Metal facing](image)

Thus, during the process of casting and drying the hybrid films, the acrylic-copolymer segments tried to segregate near the air-facing layer and the epoxy segments moved to the mold-facing side to minimize the surface energy. This migration is very beneficial because epoxy resins have excellent adhesion to substrates improving corrosion resistance, while acrylic copolymers remaining on the air-facing side have very good weatherability and appearance.

The water absorbance of coatings due to the presence of hydrophilic acrylate monomers affects the capacitance of coatings. The measurement of the water absorption using EIS techniques is based on the determination of the changes of coating capacitance. The coating capacitance can be calculated from the EIS data $C = 1/|Z|$ at the frequency of $1/2\pi$ Hz. The water absorption can be calculated by the formula given by Hartshorn [435].

$$\omega = \frac{[\log (C_t / C_0)]}{[\log \varepsilon_{H2O}]}$$

Where, $\omega$ is the volume fraction of the absorbed water, $C_t$ is the coating capacitance at time $t$, $C_0$ is the capacitance at $t = 0$, and $\varepsilon_{H2O}$ is the dielectric constant of water. In this investigation, the coating capacitance measured immediately after immersion is taken as $C_0$. The calculated $\omega$ using the capacitance values obtained in this work are summarized in Table 9.6.
Table 9.6: Water absorption $\omega$ as a function of immersion time

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Coating thickness ($\mu$m)</th>
<th>Water Absorption, $\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4 Day</td>
</tr>
<tr>
<td>A</td>
<td>32</td>
<td>0.00465</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>0.00615</td>
</tr>
<tr>
<td>C</td>
<td>54</td>
<td>0.30368</td>
</tr>
<tr>
<td>D</td>
<td>66</td>
<td>0.15323</td>
</tr>
<tr>
<td>E</td>
<td>75</td>
<td>0.09285</td>
</tr>
</tbody>
</table>

Figure 9.39: Plot of water absorbance $\omega$ against immersion time

A close examination of the data in Tables 9.5 and 9.6 reveals that, correlation between IZI and $\omega$ during the immersion tests, indicating that the decrease of IZI was due mainly to the water absorption in the coatings. For the thin hybrid epoxy coatings tested in this investigation, the rapid water absorption in the first four days of immersion could be best explained by the
capillary action in the micro pore/defect structures, which was followed by a slow water dissolution in the coatings.

**Figure 9.40: SEM micrograph of hybrid coating (E) after 10 Days of immersion**

The water absorption for thicker coatings during 10 days of testing suggested that, the rates of homogeneous water dissolution into the coatings were slow. The high performance of this type of coating has been reflected by EIS data measured during 10 days of immersion. **Figure 9.40**, represents SEM micrograph for specimen after immersion test. Micrograph showing the degradation of hybrid coatings after 10 days of immersion test.
9.6. CONCLUSION

- Study of tafel, bode and Nyquist plots show that, Hybrid one pack epoxy coating is effective as a protective coating against corrosion.
- Corrosion of substrate by the ingress of ionic species through coating, increases disbonding between coating and substrate, which promotes the degradation of coating by the dual action of chemicals and mechanical processes.
- For the hybrid coating impedance increased with increasing epoxy resin content and also with coating thickness.
- For the hybrid epoxy coatings, the quick water absorption at early immersion stage could be explained by the structure of coatings.
- It is concluded that, EIS data will be useful in predicting lifetime expectancy of coatings in immersion service.