# Corrosion Protection using Polymer Solution Coating

A
Dissertation submitted in
Partial fulfillment of the requirements for the degree of

**Master of Science in Chemistry**

Submitted by
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**301502014**

Under the Supervision of
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**July, 2017**

*Dedicated to my parents*

# Certificate

This is to certify that the dissertation entitled **"Corrosion Protection using Polymer Solution Coating"**, being submitted by Ms. Harleen Kaur in partial fulfillment of the requirements for award of the degree of Master of Science in Chemistry at School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Raj Kumar Arya and that no part of this dissertation has been submitted for the award of any other degree.

Raj Arya 21-08-17

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# Candidate Declaration

I, hereby declare that the work being presented in the dissertation entitled **"Corrosion Protection using Polymer Solution Coating"**, in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry at School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of Jan 2017 to July 2017, under the supervision of Dr. Raj Kumar Arya, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Harleen Kaur

Place: Patiala
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Date: 17-07-2017
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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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# Acknowledgement

It is a genuine pleasure to express my deep sense of thanks and gratitude to my teacher and supervisor Dr. Raj Kumar Arya, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala. His immense interest and support helped me to learn and work in a more practical way. I consider myself fortunate to have worked under him and enrich from his vast knowledge and analysis power and affection during the course of this project. Finally, I would like to thank all those who knowingly and unknowingly helped me all throughout this period.

My sincere heartfelt gratitude to my family, whose prayers, best wishes, concern and encouragement has been a constant source of inspiration.

I would like to express my deep and sincere gratitude to all other research fellows for their sincere efforts, keen interest and caring nature.

Nevertheless, I will always be grateful to my friends and batch mates for their unconditional love, care.

Harleen Kaur

Date: 17-07-2017

Place: Patiala

Harleen Kaur

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# Abstract

Solvent-based polymeric coating prepared by ex-situ addition of crosslinked poly(styrene-co-divinyl benzene) in poly(styrene)-ethyl benzene solution was used for corrosion protection of mild steel in simulated water equivalent to sea water and acid rain. Electrochemical impedance spectroscopy (EIS) technique was used to determine the corrosion resistance behavior of prepared polymeric coatings in 3.5 weight % of NaCl aqueous solution. EIS analysis suggested that the sample solution prepared by adding 1% cross-linked polymer in poly(styrene)-ethyl benzene solution, has better corrosion resistance as compared with the sample solution prepared by adding 3% and 2% of crosslinked polymer in poly(styrene)-ethylbenzene solution. Scanning electron microscopy (SEM) revealed that substrate coated with polymeric solution prepared by adding 1% of cross linked polymer in poly(styrene)-ethyl benzene solution showed less corrosion as compared with substrates coated with sample solutions prepared by adding 3% and 2% of crosslinked polymer in poly(styrene)-ethyl benzene solutions.

# Chapter 1

# Introduction

In environment, metals occur in its chemically-stable ore form. When metals are extracted from its ore, then they become unstable and want to return to their original form. The process of conversion of refined metals to stable oxide, sulphide or hydroxide form is known as corrosion. In other words, the destruction of metals by chemical or electrochemical reaction with its environment is called corrosion. Few examples related to corrosion in daily life are given below:

1. Rusting of iron
2. Copper pots containing greenish colour spots
3. White powder on zinc roofing etc.

### 1.1. Significance of corrosion management

The prevention of corrosion is very important because it can be harmful to economy and reason for several safety issues. Corrosion induces different kind of losses to economy, caused by deterioration of metals. It can be very dangerous from safety point of view. It decreases the metallic strength of components of vehicles, airplanes and ships etc. In chemical industries, corrosion of chemical containers, boilers, pressure vessels can be very detrimental. The kinds of losses caused by corrosion to economy are direct and indirect losses[1] :

**Direct losses**

Metallic components are needed to repainting, in order to prevent from rusting. In case of corroded boilers, mufflers, pipelines etc., replacement of these components is necessary. The extra money is required to galvanize zinc on the surface of steel for corrosion protection.

**Indirect losses**

It is very hard to determine indirect losses caused by corrosion. Therefore, from thorough analysis, some indirect losses are determined. For example, in soap industries, the small particles of copper from corroded copper pipes leads to contamination of large bunch of soaps. Small amount of metal particles from corroded container or pipes, results in variation of colour of dye. During reinstatement of corroded pipes in oil refinery, the production of oil has to stop which results in production loss.

Microscopic level observation of metallic surface determined that surface of metal is not uniform. There may be presence of some kind of impurities on surface. Chemical composition and structure may differ throughout the surface of metal. Anode and cathode can exit simultaneously on the surface of metal. Metallic part act as anode and impurities present on surface act as cathode. Based on the cathodic and anodic sites of metal surface, corrosion occurs in two different ways:

**1.1.1. Localized corrosion**: It is the type of corrosion in which one part of metal surface act as anode and other part act as cathode as shown in Figure 1(a).

**1.1.2. Uniform corrosion**: In this type of corrosion, cathodic and anodic part of metallic surface can't be distinguished as shown in Figure 1(b).

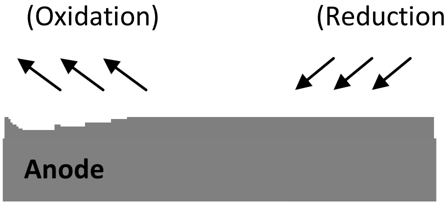


**Figure 1(a)**. Localized corrosion

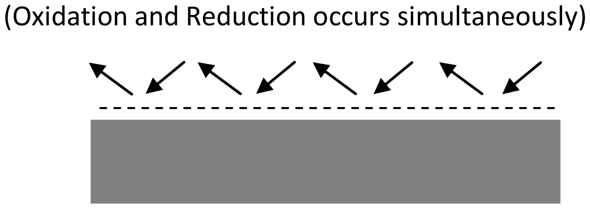


**Figure 1(b)**. Uniform corrosion

### 1.2. Electrochemistry of corrosion

Iron comes in contact with oxidizing agent like oxygen and water droplets. One part of iron surface inside water droplet act as anode and other part act as cathode. Anodic part loses electrons and releases $Fe^{2+}$ ions. Electrons move to cathodic part outside the droplet, where oxygen and water react to form hydroxide ion as shown in Figure 2[2].

**Anodic reaction**

$Fe\ (s) \longrightarrow Fe^{2+}\ (aq) + 2e^-$ ………… (1)

**Cathodic reaction**

$O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq)$ ……….... (2)

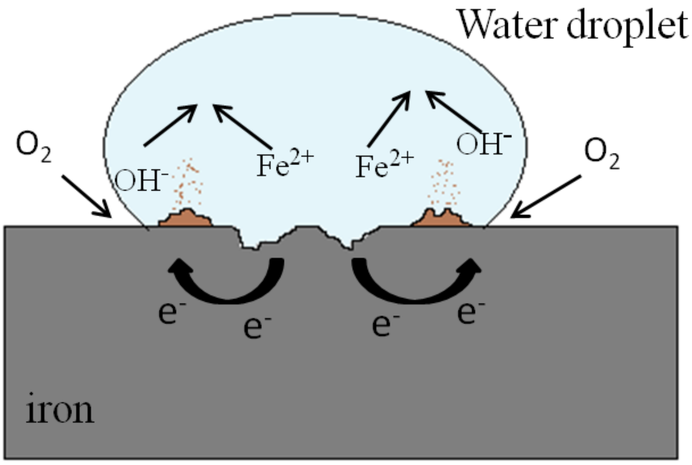


**Figure 2**. Corrosion as an electrochemical cell

These hydroxide ions produced on cathode, move inside the water droplet and react with $Fe^{2+}$ ions at anode to form iron oxide as per following reaction,

$Fe^{2+}$ (aq) + $4OH^-$ (aq) $\longrightarrow$ $Fe(OH)_2$ (s) …………(3)

Further oxidation of iron oxide results in the formation of rust.

$4Fe(OH)_2$ (s) + $O_2$ (g) $\longrightarrow$ $2Fe_2O_3.H_2O$ (s) + $2H_2O$ (l) ..……….. (4)

### 1.3.Types of corrosion

Various types of corrosion causing damage on metal and their reasons are given below.

### 1.3.1. General corrosion

In general corrosion, surface of metal is uniformly corroded by oxidizing agents present in its environment. The anodic and cathodic sites cannot be distinguished as shown in Figure 3[1].

**Figure 3.** General corrosion

### 1.3.2. Selective corrosion

It is the type of corrosion in which components of an alloy are not uniformly distributed. Component A which is less noble is dissolved at first and porous layer of nobler component B is left behind as shown in Figure 4.

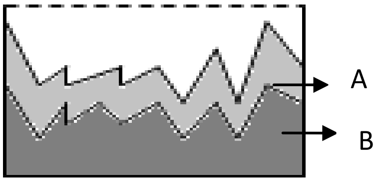


**Figure 4.** Selective corrosion

### 1.3.3. Stress corrosion

It is the type of corrosion which occurs under the influence of corrosion attack and the external or internal stress applied on metal. Cracks are formed, when mechanical stress is applied just below the tensile strength of metal as shown in Figure 5.

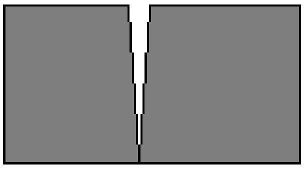


**Figure 5.** Stress corrosion

### 1.3.4. Pitting corrosion

The material like stainless steel has protective oxide layer. Small sort of damage on this protective film can initiate the corrosion. In the presence of anions like chloride ions mostly present in seawater, pH level decreases and environment becomes oxygen deficient. Under these conditions, small cavities are formed on metal surface and process is known as pitting corrosion as shown in Figure 6[3].

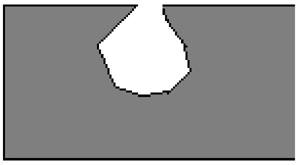


**Figure 6.** Pitting corrosion

### 1.3.5. Erosion corrosion

The process in which general corrosion is accompanied by the turbulent flow of fluid, scraping away the corroded part of metal, is known as erosion corrosion as shown in Figure 7.

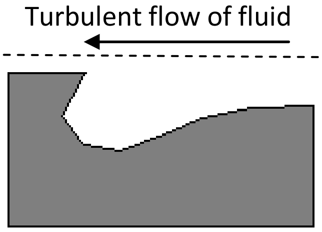


**Figure 7.** Erosion corrosion

### 1.3.6. Intergranular corrosion

When stainless steel is kept at 500-600$^{\circ}C$ temperature for long duration of time, then inside the metal at the interface of grains chromium starts reacting with carbon. This reaction leads to the formation of carbides and depletion of chromium, such type of corrosion is known as intergranular corrosion as shown in Figure 8[3].

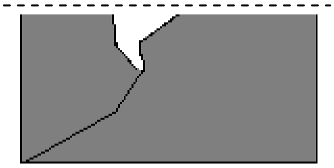


**Figure 8.** Intergranular corrosion

### 1.3.7. Crevice corrosion

It is localized type of corrosion which occurs within crevices of metal surfaces as shown in Figure 9. In these crevices corrodant can be stagnant and cause corrosion.

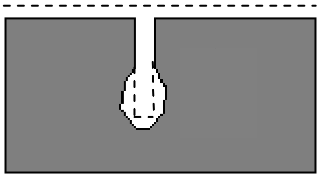


**Figure 9.** Crevice corrosion

### 1.3.8. Galvanic corrosion

When two different metals are in contact with each other, results in the formation of electrochemical cell in the presence of electrolyte like water as Figure 10. Metal having less electrode potential will act as anode and it will corrode.

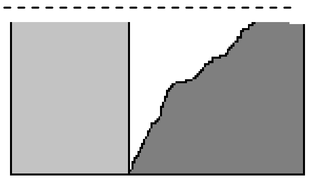


**Figure 10.** Galvanic corrosion

### 1.4. Corrosion prevention methods:

There are four types of methods to prevent corrosion of metal, which are given below:

**1.4.1. Active corrosion protection:** In this method, metallic surface is protected from corrosion by restricting the reaction involved in corrosion and the attack of corrosive agents. This process is done by fabricating anti-corrosive alloys and incorporating inhibitors to the aggressive medium.

**1.4.2. Passive corrosion protection**: It is the technique in which corrosion of metal is prevented by creating barrier in between the metallic surface and surrounding oxidizing agents, using protective layers, coatings or films etc[4].

**1.4.3. Permanent corrosion protection:** Inside industrial building, corrosive agents are less effective and temperature variation is also under control. In such condition, metallic machines are permanently protected from corrosion using galvanization, tin plating, coating etc[5].

**1.4.4. Temporary corrosion protection:** The risk of metallic corrosion is more during transportation and handling because there is more contact with corrosive environment and temperature variation. In this situation, temporary corrosion protections are helpful against corrosion[5]. Different types of temporary corrosion protection are given below:

**(a) In protective coating method:** Coatings containing anti-corrosive agents are applied on metallic surface to provide barrier in between the metallic surface and corrosive agents. Anti-corrosive agents are water-borne anticorrosive agents, solvent based anti- corrosive agents, dipping waxes and corrosion protective oils.

**(b) In desiccant method**: Metallic materials are placed inside bags, which contain desiccants like silica gel, blue gel, molecular sieves to absorb water vapours and controls humidity for corrosion protection of material.

**(c) Volatile corrosion inhibitor method**: In this method volatile corrosion inhibitors are sprayed on the metallic surface or film and then changes to vapour state making a film. This film is resistive to reactions involved in corrosion and thus protects the metallic surface from corrosion.

In present study, solvent-based polymeric coating was prepared by ex-situ addition of cross-linked poly (styrene-co-divinyl benzene) in poly (styrene)-ethyl benzene solution for corrosion protection of mild steel in pH corresponding to sea water and acidic rain. The anti-corrosive performance of resultant polymeric coating was investigated by using different techniques. The corrosion inhibition of polymeric coatings having 1%, 2%, and 3% of cross-linked poly(styrene-co-divinyl benzene) were studied by using electrochemical impedance spectroscopy.

# Chapter 2

# Literature review

This work is mainly focused on protection of metallic surfaces using polymeric coatings. The latest literature related the corrosion protection using polymeric coatings have been discussed in this chapter.

## 2.1. Literature review

Reinhard et al.[6] studied the application of corrosion inhibitors in water-borne coatings. They used water-borne coatings for corrosion protection of mild steel instead of using toxic organic solvents. They substituted mercapto compounds as corrosion inhibitors in acrylate- based dispersion. These mercapto compounds reduced the early rusting during film formation without altering the properties of acrylate dispersion. The acrylate-based dispersion was prepared by using copolymer of butyl esters of (acrylic acid, styrene and methacrylic acid). It also contained acrylic acid, monoesters and polymerization initiator ammonium persulphate $(NH_4)_2S_2O_8$ . Corrosion inhibitors present in acrylate dispersion were investigated by using modal electrolyte (0.03M $KNO_3$ in double distilled water + 0.01M acrylic acid). They determined using electrochemical impedance spectroscopy (EIS) that anticorrosive property of mercapto compounds increased with the increase in pH values. EIS also showed that mercapto compounds were involved as a cross linking agent during layer formation.

Perrin et al.[7] synthesized and characterized waterborne corrosion protection coating using poly(aniline) nanoparticles. They used aqueous amphiphile solution of phosphonic acid. Polyaniline dispersion was prepared in the presence of oxidizing agent i.e. ammonium peroxydisulphate (APS) and a surfactant i.e. n-decylphosphonic acid (DPA). DPA acted as dopant anion. Energy dispersive X-ray spectroscopy revealed that when surface of DPA doped polyaniline coating scratched, then dopant anion released to further protect the metal surface from corrosion. Surfactant concentration was kept higher than critical micelle concentration (cmc) for the preparation of water/DPA solution. DPA has property to form vesicles in water and these vesicles coexited with vesicles of aniline and n-decylphosphonic acid . Precipitates of polyaniline were formed due to unstable reaction mixture. DPA to aniline molar ratio was kept greater than 1 in all poly(aniline) dispersions because at higher surfactant concentration no precipitates were obtained. Higher value of electrical conductivity obtained at molar ratio 1.25 of APS/aniline. FT-IR analysis showed that the polyaniline was doped efficiently with DPA. Thermo gravimetric analysis showed that the DPA doped PANI has good thermal stability at least up to $260^{\circ}C$. The interlayer distance of polyaniline increased with higher concentration of DPA as shown by the DPA-Polyaniline XRD analysis in emerlidine salt. This shows the effective penetration of dopant.

Baskar et al.[8] synthesized poly((E)-(1-(5-(4-(3-(4-chlorophenyl)-3-oxoprop-1-enyl) phenoxy)decyl)-1H-1,2,3-triazol-4-yl)methyl acrylate) and poly((E)-(1-(5-(4-(3-(4-chlorophenyl)-3-oxoprop-1-enyl)phenoxy) pentyl)-1H-1,2,3-triazol-4-yl) methyl acrylate) , which are cross-linkable on photo irradiation. These polymers were coated on mild steel to protect it from corrosion in 1.0 M HCl solution. FT-IR analysis showed the presence of photo sensitive chalcone moieties. The spectra given by H-NMR results confirmed the formation of polymer. Cross-linking of polymer under the influence of photo illumination was confirmed by absorption spectroscopy. The morphology given by SEM analysis confirmed that these photo crosslinking polymers can protect mild steel from corrosion.

Pour-Ali et al.[9] suggested that direct addition of polyaniline particles in epoxy matrix results in aggregation of the particles. Thus, polymer was synthesized using different way. Epoxy matrix was modified using polyethylene glycol (PEG) and polyaniline-camphorsulphonate particles were prepared in epoxy network. Mild steel was coated using this prepared polymeric coating, in order to protect it from corrosion in 3.5% NaCl medium. The prepared characteristic description of polymeric coating was characterized by FT-IR and TEM. Anticorrosive nature of polymeric coating in 3.5% NaCl solution was determined using several techniques like EIS and salt spray test etc.

Baldissera and Ferreira [10] prepared different epoxy matrix (EM) based coatings by incorporating different forms of polyaniline (PANI). These coating were utilized for protecting mild steel substrates from corrosion in 3.5% NaCl solution. Different forms of PANI like PANI sulphonate, PANI-fibers, PANI-emerlidine salt, PANI-emerlidine base, PANI-zinc phosphate, PANI-zinc chromate were prepared. Different coatings prepared by incorporating these forms of PANI in epoxy matrix showed better anticorrosive nature as compared to simple epoxy coating. Electrochemical impedance spectroscopy determined that coating prepared by incorporating PANI sulphonate in epoxy matrix showed more desirable anticorrosive behavior than other coatings.

Behzadnasab et al.[11] fabricated polymeric coating for protection of mild steel from corrosion in 3.5% NaCl solution. The polymeric coating was prepared using $ZrO_2$ nanoparticles which were modified using amino propyl trimethoxy silane (APS). Further, these modified $ZrO_2$ particles were added in epoxy matrix. APS helped to form chemical bonds in between epoxy matrix and $ZrO_2$ particles and these particles got properly distributed in epoxy matrix. The anticorrosive nature of resulted polymeric coating was enhanced at 2-3 wt. % of $ZrO_2$. The salt spray test and electrochemical independence spectroscopy were used to determine the corrosion resistance of polymeric coating.

Kocijan et al.[12] studied the comparison and characterization of biocompatible polymer coating on AISI316L stainless steel. Biofouling reduces the efficiency of materials and contributes to corrosion of metal and alloys. PDMS (Polydimethylsiloxane) and PEG (polyethylene glycol) were used for surface modification of AISI316L stainless steel. PDMS induced the hydrophobic nature in the substrate by changing the surface wetting properties. PDMS has water contact angle greater than $90^{\circ}$and decreased the free energy of the surface. It acted like a water repellent and protected the surface from the corrosion. On the other hand, the contact angle of PEG and water was less than $90^{\circ}$ which induced the hydrophilic nature to the system. The free energy of the substrate surface was also increased. PEG has anticorrosive properties, but less than PDMS. X-ray photoelectron spectroscopy determined that PEG coating is slightly thicker than PDMS. Their electrochemical impedance spectroscopy data confirmed that PDMS coatings applied on stainless steel has superior anticorrosion properties than PEG.

El-Mahdy et al.[13] prepared corrosion resistant coatings of magnetite/ acryl amide-co-sodium acrylate nano-composite and these coatings were tested on mild steel substrate in HCl solution. Preparation of nanocomposite coating was based on core-shell system. The magnetite nanoparticles were modified using NMA (polyoxyethylene 4-nonyl-2-propyl-phenyl/Maleic anhydride adducts). These magnetite/NMA nanoparticles were used as a core. The cross-linked acryl amide-co-sodium acrylate containing magnetite nanoparticles was used as shell. Transmission electron microscopy results confirmed that magnetite nanoparticles were dispersed inside polymeric matrix in the presence of magnetite/NMA nanoparticles. The characteristic properties of coating were investigated using UV-VIS spectroscopy, Fourier transform-infrared spectra.

Xu et al. [14] studied the facile fabrication of super hydrophobic polyaniline structures and their anticorrosive properties. They used different surfactants i.e. SDBS (sodium dodecylbenzene sulphonate), PEG (polyethylene glycol) and CTAB (cetyltrimethyl ammonium bromide) to modify polyaniline to make it super hydrophobic. SEM and water contact angle measurements showed that when polyaniline interacted with surfactant, then it made the hydrophobic alkyl chain of surfactant going out. This kind of interaction decreased the free energy of surface. Surfactant modified the polyaniline to super hydrophobic polyaniline, which has water contact angle greater than $150^{\circ}$. Super hydrophobic polyaniline acted as water repellant and showed anticorrosive properties. The super hydrophobic nature introduced by PEG on polyaniline was better than the CTAB and SDBS due to huge hydrophobic alkyl chain of PEG. Larger is the hydrophobic alkyl chain of surfactant, greater is the water contact angle of modified polyaniline. These methods to produce the super hydrophobic polyaniline are cheap, easy, an environmentally friendly as compared to toxic fluoride.

Voevodin et al.[15] studied the nanostructured coatings approach for corrosion protection. Chromate based treatment of aluminium aerospace alloy release $Cr^{6+}$ which is extremely carcinogenic in nature. Self-assembled nanophase particles (SNAP) coatings were successfully replaced the chromate based coatings. SNAP solution was prepared by mixture of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetramethoxysilane (TMSO) in 3:1 ratio. Corrosion inhibitors such as aminopiperidine (APD), aminopiperazine (APZ) and tetraethyl dimethylenediphosphate (TMD) + mercaptobenzotriazole (MTZ) were added in SNAP solution immediately before the film application. SNAP coating was prepared by sol-gel process. This process includes formation of silica nanoparticles by hydrolysis and condensation of silanes with epoxy functionalities. They used potentiodynamic scan (PDS) to analyze the barrier properties of SNAP coatings with different organic inhibitors i.e. APD, APZ and TMD +MTZ. PDS indicated that all of given organic inhibitors show good barrier properties. Electrochemical impedance spectroscopy (EIS) showed good hydrolytic stability of SNAP film applied on aluminium alloy. When the paint systems containing SNAP coating and chromated primers were kept in salt spray system for 2000 h. Up to 2000 h paint system showed sufficient corrosion protection.

Schreiber et al. [16] prepared the plasma polymerized (PP) polymeric coatings which surpass the conventional polymeric coatings in corrosion protection. They were highly cross linked and adhere to a wide range of substrates, but they adhere well to the substrates above a specific critical substrate temperature. Films did not adhere well to the substrate below critical temperature ($T_S$). Simple peeling and scratch tests were conducted with sharp tool. Attenuated total reflection infra-red spectra revealed that with increasing the substrate temperature, Si-O-Si bonds intensities were increased. The PP coating film had greater dimensional stability and there was absence of any discontinuities at molecular level (pin holing) because of high cross linkage. As $T_S$ was increased the film density resembled density of vitreous silica and not that of conventional polymers. This also made them stable at temperatures as high as 800-1000ºC. PP polymeric coatings also had outstanding deformation tolerance due to high cohesive strength of the cross linkage.

Pourhashem et al.[17] prepared solvent based epoxy coatings containing graphene oxide (GO) nanosheets. Mild steel substrate protected was using this polymeric coating to protect it from corrosion. Corrosion resistance property of polymeric epoxy coating was affected by varying concentration of GO nanosheets. At 0.1wt.% weight of GO nanosheets in epoxy coating showed best anticorrosive nature of coating, when compared with 0.3wt.%, 0.5wt.% and 0.05wt.% of GO nanosheets. FE-SEM analysis determined that at 0.1wt. % of GO, there was no sign of agglomeration of GO nanosheets. Polymeric coating was prepared using two different ways. In first method, GO was directly added to epoxy resins and then polyamide hardener was added. In second method, GO was directly added to polyamide harder and then mixed with epoxy matrix. Coatings prepared by second one method showed better corrosion resistance because GO nanosheets were well distributed in polymeric matrix.

Cho et al.[18] studied the self-healing polymeric coatings. The thermo gravimetric analysis (TGA) of the self-healing system showed primary weight loss beginning near chlorobenzene's boiling point ($131^{\circ}C$) and secondary weight loss about $225^{\circ}C$ exhibiting thermal decomposition of polyurethane (PU) shell. The coating showed self-healing property only when both the catalyst (5% wt. dimethyldineodecanoate tin (DMDNT) in chlorobenzene capsules) and the healing agent Polydimethylsiloxane (PDMS) were present. Scanning electron microscopy showed that about 40% of the scribed damage was self-healed in the sample with self-healing coating. Electrochemical testing showed large magnitudes of current passing through the scribed control sample (26.6-58.6 mA/cm$^2$) as compared to the scribed and self-healed sample (12.9 µA/cm$^2$-1.4µA/cm$^2$) with no gas evolution. All control samples showed rust formation on exposure to brine whereas, the self-healed sample, allowed to heal for 24 h at 50ºC showed no rust formation. Self-healing readily occur around 20ºC without any requirement of moisture when Si [OSn (n-$C_4H_9)_2OOCCH_3]_4$ (TKAS) was used as instead of DMDNT.

Shi et al.[19] studied the mechanical and corrosion resistant properties of epoxy nanoparticle coatings. Separate epoxy coating sample doped with nanoparticles of $SiO_{2,}$ $Fe_2O_{3,}$ Zn and hallyosite nanoclay along with one undoped epoxy resin coating were prepared. FE-SEM images of coating samples depicted that cured plain epoxy and epoxy coating doped with $SiO_2$ were homogeneous and showed no agglomeration as compared to the coating having $Fe_2O_3$ nanoparticles. The potentiodynamic weak polymerization showed the corrosion rate decreased to a great extent because of the nanoparticles and increased the polarization resistance ($R_p$) of the epoxy coated steel. This incorporation decreased the coating porosity. Epoxy coating having $Fe_2O_3$ nanoparticles showed maximum Rp. EIS curves of these samples depicted that the resistance of coating increased with decrement in capacitance with $Fe_2O_3$ nanoparticles in epoxy coating as reported by them. The increase in capacitance and decrease in resistance after sometime explained the penetration of corrosive electrolyte through the film.

Zandi-Zand et al. [20] studied the use of organic-inorganic hybrid coating to protect the aluminium alloy. The coatings were applied using dip coating method. Hybrid coating was fabricated from 3-glycidoxypropyl-trimethoxysilane (GPTMS) and tetramethoxysilane (TMOS) by two step acid catalysis. In the first step, there was hydrolysis and condensation of GPTMS and TMSO to form organo- silica nanoparticles. In second step, organo-silica nanoparticles cross linked in the presence bisphenol as a cross-linking agent. ATR-IR Spectroscopy showed that the coating of hybrid sol on aluminium alloy resulted in superior cross-linked density of silane as the aluminium alloy had formed networks with silicates. Electrochemical results revealed that the silane content in coating influences the corrosion resistance. More is the silane content in the coating, lesser it will be corrosion resistive.

## 2.2. Research Gap of Earlier Work

1. All literature reported here showed the application of some special chemical to get the special coating for protection.
2. In few research papers[8, 16] polymeric solution solutions are being cross linked in order to enhance the corrosion resistance properties.
3. Few researches [15, 19] used the doping of nanoparticles to decrease the porosity of the film, hence high corrosion protection.

In the proposed work, polystyrene has been selected to study the corrosion resistance property of metal. The coating was prepared using dip coating technique. The cross-linked poly (styrene-co-divinyl benzene) having 1% crosslinking has been used as a doping agent. The detailed methodology has been given in next chapter i.e. materials and method.

# Chapter 3

# Materials & Method

## 3.1. Materials

Mild steel specimens of dimensions 5mm×5mm×1mm and 1cm×1cm×1mm have been purchased from local market, polystyrene [molecular weight=192000; density=1.05 g/cm$^3$] and poly(styrene-co-divinyl benzene) (PDB) [density=0.29 g/cm$^3$] were purchased from Sigma Aldrich (Germany), ethyl benzene [molecular weight=106.17; density=0.866 g/cm$^3$] was purchased from Spectrochem (India), emery paper of 1200 grade, sulphuric acid (98%), hydrochloric acid (37%), acetone [molecular weight=58.08] was purchased from Rankem, Faridabad, India.

Chemical structure of polystyrene, ethyl benzene and poly(styrene-co-divinyl benzene) are given in Figure 11.

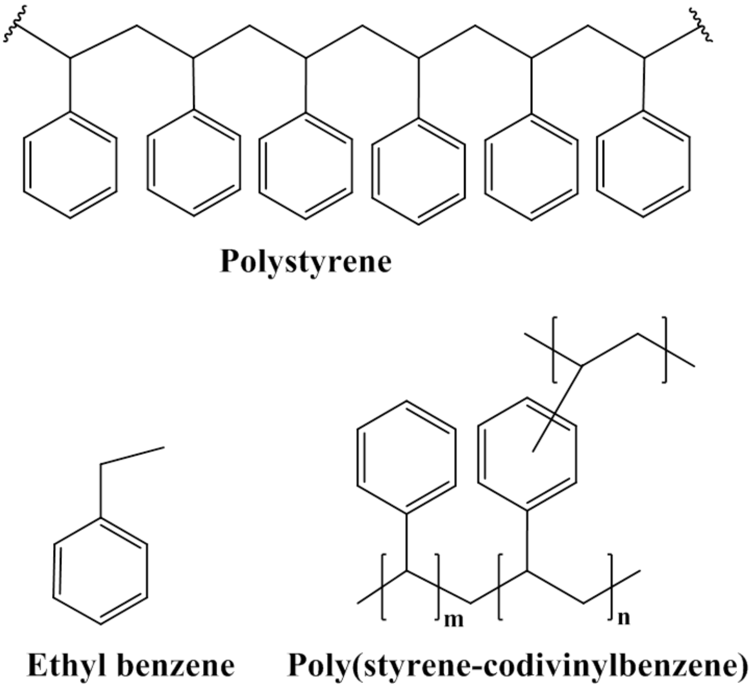


**Figure 11.** Chemical structures of polystyrene, ethyl benzene and poly (styrene-co-divinyl benzene).

### 3.2. Preparation of coating solution

Six sample solutions were prepared by dissolving different amounts of ethyl benzene (EB), polystyrene, poly (styrene-co-divinyl benzene) (PDB) in six reagent bottles shown in Table 1. These sample solutions were mechanically shaken in incubator for 4 hours at $40^{\circ}C$ to get the homogenous solutions.

**Table 1**: Chemical composition of sample prepared.

| Sample No. | Ethyl benzene , wt % | Polystyrene , wt % | PDB , wt % |
|---|---|---|---|
| 1 | 94 | 5 | 1 |
| 2 | 93 | 5 | 2 |
| 3 | 92 | 5 | 3 |
| 4 | 82 | 15 | 3 |
| 5 | 83 | 15 | 2 |
| 6 | 84 | 15 | 1 |

### 3.3. Surface preparation of mild steel (MS)

Cleansing of surface of MS specimen is necessary before their coating. Carbon black, dirt, oil and grease were removed from surface of MS by dipping them in 30% HCl solution. Remaining oxidation particles were removed using emery paper of 1200 grade. Specimen were washed using distilled water, degreased using acetone and dried in oven at $50^{\circ}C$ .

### 3.4. Preparation of polymeric coating

There are several methods for preparation of coating like dip coating, spin casting[21], thermal spraying[22], pinned-drop casting[22] etc. In the present work, coatings were prepared by using dip coating technique. Dip coating is defined as the method in which, substrate is dipped into the solution of coating and withdrawn at a particular rate to obtain a thin coating on its surface. Steps involved in this process are given below:

(a) *Immersion*: Substrate is dipped at constant rate into the chemical solution.

(b) *Dwell time*: Substrate is kept entirely dipped and left for some time in a solution.

(c) *Withdrawal*: Substrate is withdrawn at constant rate from solution without shaking. The thickness of coating on surface of substrate is directly proportional to the rate at which it is withdrawn from solution.

Dip coating method is mostly used in industries and labs because these methods are not much expensive and easy to control. During this method, there is very less wastage of paint or material. This coating technique is used in laboratories for the preparation of thin layer of chemical compound like polymer or nanoparticles dissolved in volatile solvent. This method is also used in industrial sector for preparation of coated fabrics, grips for hand tools etc. There are some materials in industries which require quick coating of their entire surface. In such condition dip coating technique is helpful[23].

### 3.5. Coating Procedure

MS substrates were weighed before applying the coating. These substrates were immersed in sample solutions 1, 2, 3, 4, 5 and 6 and manually withdrawn at very slow speed. Then, the coated substrate was dried for few minutes and again immersed in the same polymeric solution. In this way, substrates were coated thrice. Thin multilayer coatings were formed on the surface of substrate. These substrates were dried at $30^{\circ}C$ for overnight. After coating was dried, substrates were again weighed. The difference in two weights divides by density of polymer will give the volume of coating on the substrate. The volume of coating divided by cross-section area of substrate will give the average coatings thickness on the substrate.

### 3.6. Preparation of Synthetic Sea/Rain water

Acidic solutions of pH 3, 4 and 5 were prepared by diluting 98% of sulphuric acid using distilled water. Dried coated substrates were dipped in prepared acidic solutions for corrosion tests. Weight loss of substrates after corrosion was measured after one week.

# Chapter 4

# Results and Discussion

## 4.1. Weight gain of MS substrates after coating

Mild steel substrates were weighed before applying polymeric coating and after the coating were dried. Substrate were weighed after coating, weight gain is given in Table 2. The difference in dried coated substrate weight and initial substrate weight will give the mass of coating on the substrate. The volume of coating can be calculated from the mass of the coated film divided by density of coating. The thickness of coating will be equal to coating volume divided by surface area of the initial substrate.

$$\textbf{Volume of coating }(\mathbf{V_c}) = \frac{(\mathbf{B-A})}{\boldsymbol{\rho_{ps}}}$$

$$\textbf{Coating thickness (T)} = \frac{\mathbf{V_c}}{\mathbf{0.5\times0.5}} \times \mathbf{10^4}$$

A = Substrate weight before coating, B = Substrate weight after drying coating,
(B-A) = Weight gain of substrate after corrosion, $\rho_{ps}$ = Density of poly(styrene)

**Table 2**: Weight gain of substrate after coating

| **Sample solution** | **Substrate No.** | **A (mg)** | **B (mg)** | **(B-A) (mg)** | **Coating Volume, $V_c$ ($cm^3$)** | **Thickness, T, (μm)** |
|---|---|---|---|---|---|---|
| 4 | 1 | 242.50 | 248.50 | 6 | $5.769\times10^{-3}$ | 231 |
|  | 2 | 225.06 | 228.11 | 3.05 | $2.933\times10^{-3}$ | 117 |
|  | 3 | 229.30 | 231.56 | 2.26 | $2.173\times10^{-3}$ | 87 |
| 5 | 1 | 271.84 | 275.39 | 3.55 | $3.413\times10^{-3}$ | 137 |
|  | 2 | 247.27 | 250.33 | 3.06 | $2.942\times10^{-3}$ | 118 |
|  | 3 | 252.27 | 254.52 | 2.25 | $2.163\times10^{-3}$ | 87 |
| 6 | 1 | 294.07 | 296.94 | 2.87 | $2.759\times10^{-3}$ | 110 |
|  | 2 | 247.27 | 251.85 | 4.58 | $4.404\times10^{-3}$ | 176 |
|  | 3 | 244.08 | 247.15 | 3.07 | $2.951\times10^{-3}$ | 118 |

## 4.2. Weight loss of substrates after corrosion

Corrosion test was carried out by immersing the dried coated substrates for one week in sulphuric acid solution of pH 3, 4 and 5 as shown in Figure 12. After corrosion test, substrates were withdrawn from the containers containing acidic solution. Then, substrates were dried in oven for 3 hours and weighed. Substrates were weighed after corrosion and weight loss is given in Table 3.

C = Substrate weight after corrosion

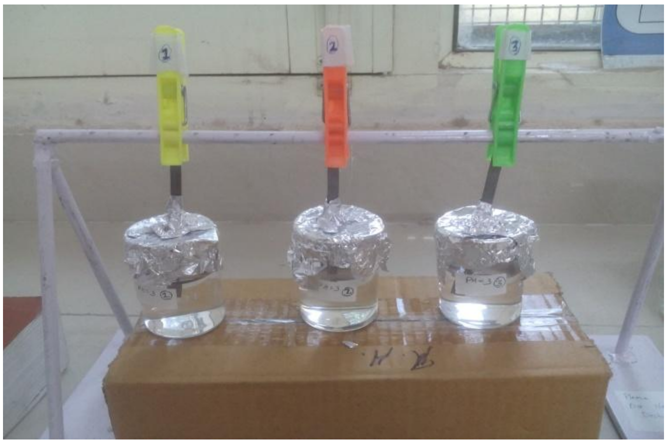


**Figure 12.** Substrates immersed in acidic solution of pH 3, 4 and 5

**Table 3**: Weight loss of substrate after corrosion

| Sample solution | Substrate No. | Ph | B (mg) | C (mg) | (B-C) (mg) | % Wt loss |
|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 248.50 | 248.04 | 0.46 | 0.19 |
| | 2 | 4 | 228.11 | 227.30 | 0.81 | 0.36 |
| | 3 | 5 | 231.56 | 231.05 | 0.51 | 0.22 |
| 5 | 1 | 3 | 275.39 | 275.00 | 0.39 | 0.14 |
| | 2 | 4 | 250.33 | 248.57 | 1.76 | 0.7 |
| | 3 | 5 | 254.52 | 253.85 | 0.67 | 0.26 |
| 6 | 1 | 3 | 296.94 | 296.66 | 0.28 | 0.09 |
| | 2 | 4 | 251.85 | 246.98 | 4.87 | 1.93 |
| | 3 | 5 | 247.15 | 251.76 | -4.61 | -1.87 |

Substrates coated by using sample solution 6 having 1% of crosslinked polymer showed less weight loss as compared with the substrate coated with sample solution 4 and 5 having 3% and 2% of crosslinked polymer respectively.

### 4.3. Electrochemical Impedance Spectroscopy (EIS) study

EIS plots were drawn by using simple equivalent electric circuit model shown in Figure 13. Figure 14 (a) and (b) shows EIS Nyquist and Bode plots of MS substrates coated with different solutions. This model contains parameters like $R_S$ (solution resistance), $R_p$ (polarization resistance) and $C_{dl}$ (coating capacitance)[24]. Constant phase element (CPE) tells about the behaviour of polymeric coatings. The formula used to calculate the impedence value is given below,

$$\textbf{Impedance } (Z_{CPE}) = R_S + \frac{Q}{R_P}$$

Q = Constant phase element, $R_S$ = Solution resistance, $R_P$ = Polarization resistance
The calculated values of these parameters are shown in Table 4.

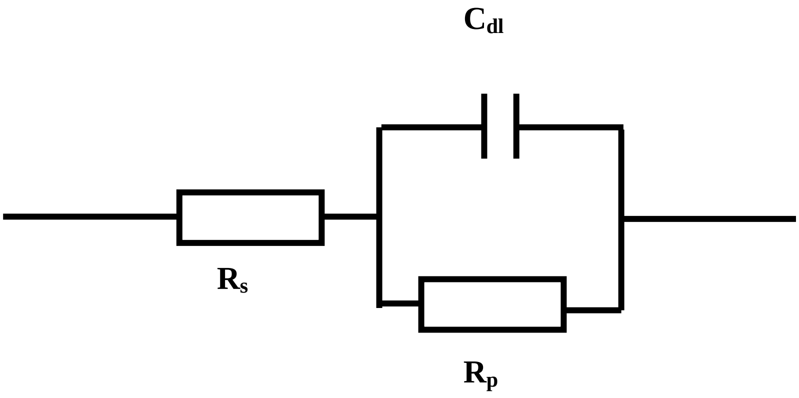


**Figure 13**. Equivalent circuit model

Figure 14 (a) shows the Nyquist plots of corrosion of different electrodes in 3.5 % NaCl solution. These electrodes were mild steel substrates coated by using different solutions. Capacitive loops of different diameter were obtained for solutions 1, 2 and 3. Semi-circles shown in Nyquist plot are not very perfect. Capacitive loops represents the corrosion of mild steel substrates, which is regulated by the charge tranfer process of corrosion. Diameter of semi-circles decreased by increasing the concentration of cross linked polymer in sample solutions as shown in Figure 14 (a). Diameter of capacitive loop of sample solution 3 having 1% of cross linked polymer is greater than sample solutions 1 and 2 having 3% and 2% of cross linked polymer respectively. Therefore, the sample solution 3 showed more corrosion resistance as compared with the sample solutions 1 and 2 as shown in Table 4. Greater the diameter of capacitive loop, more will be the corrosion resistance of sample solution[13]. The results are in agreement with earlier findings[13].

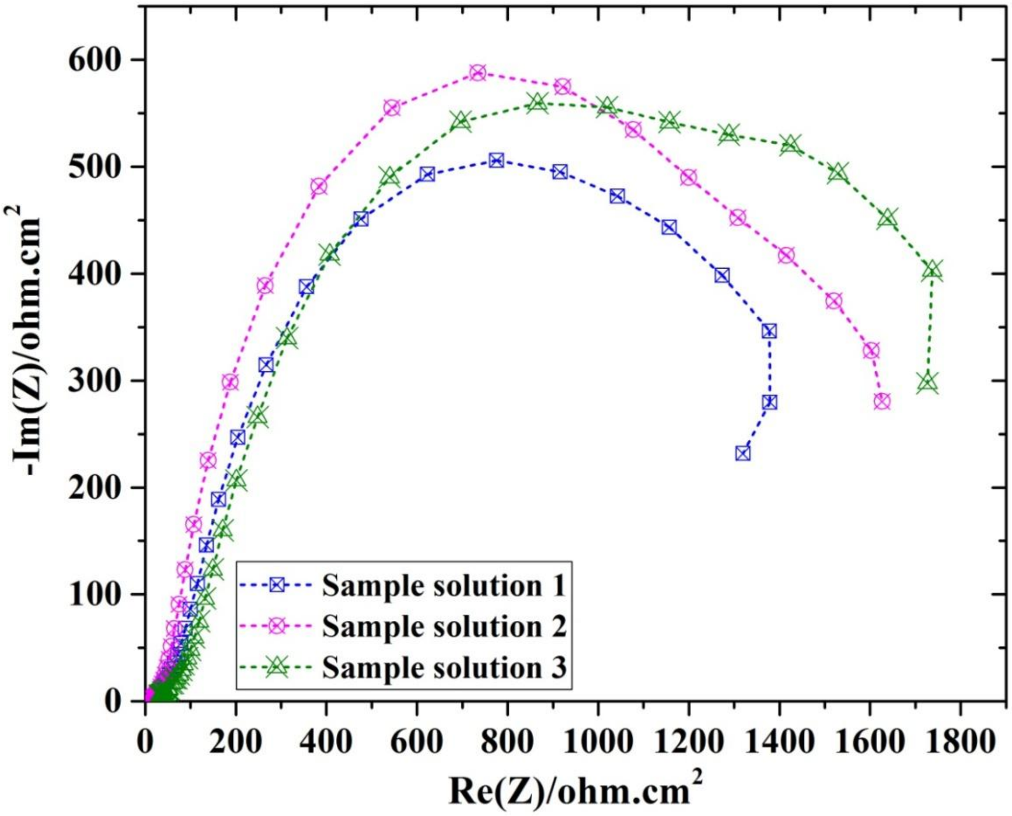


**Figure 14** (a). Nyquist plots of corrosion of different electrodes in 3.5% NaCl solution

Figure 14 (b) showed the Bode plots of corrosion of mild steel substrates coated with sample solution 1, 2 and 3 in 3.5% NaCl solution. The breakpoint frequency technique was used to estimate area of delamination of different polymeric coatings on mild steel substrates in acidic solution. The breakpoint frequency is the frequency corresponding to the $45^\circ$ of phase angle[25]. Mathematically, it can be expressed as given below,

$$\textbf{Breakpoint frequency } (\mathbf{f_{45}}) = \mathbf{K}\frac{\boldsymbol{A_d}}{\boldsymbol{A}}$$

$$\mathbf{K} = \frac{\mathbf{1}}{\boldsymbol{2\pi\varepsilon\varepsilon_o\,\rho_o}}$$

Where, $A_d$ = Area of delamination, K = Material constant for polymeric coating, A = Total area of sample, $\varepsilon$ = Vaccum permittivity, $\varepsilon_o$ = Dielectric constant of polymeric coating, $\rho_o$ = Specific ionic resistance of moist polymeric coating.

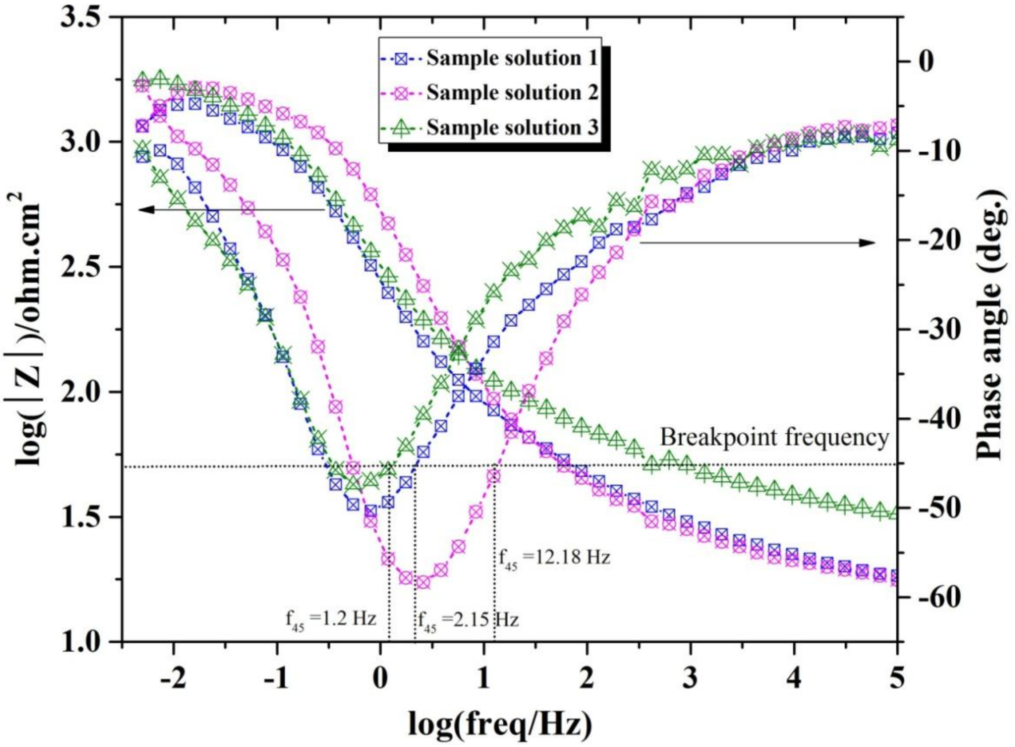


**Figure 14** (b). Bode plots of corrosion of different electrodes in 3.5% NaCl solution

The breakpoint frequency is directly proportional to the area of delamination of polymeric coating in corrosive solution. The breakpoint frequency ($f_{45}$) is 1.2 Hz for sample solution 3 having 1% of cross linked polymer, which is lesser than $f_{45}$ values of sample solutions 1 and 2 containing 3% and 2% of cross linked polymer respectively. So, the area of delamination of polymeric coating prepared by using sample solution having 1% cross inked polymer is lesser than the area of delamination of polymeric coating prepared by using sample solution 3% and 2% of cross linked polymer.

**Table 3**: Parameters of corrosion and impedance kinetics

| | **Impedance kinetics** | | | |
|---|---|---|---|---|
| **Sample solution** | **$R_s$ (ohm cm$^2$)** | **CPE (F.s$^{n-1}$)** | **n** | **$R_p$ (ohm cm$^2$)** |
| 1 | 21.5 | 1.75e-3 | 0.725 | 1600 |
| 2 | 21.4 | 1.5e-3 | 0.752 | 1821 |
| 3 | 37.88 | 1.3e-3 | 0.602 | 2200 |

**Parameters for EIS study**

Solution: 3.5 wt. % NaCl

Impedance parameters:

fi =100 kHz

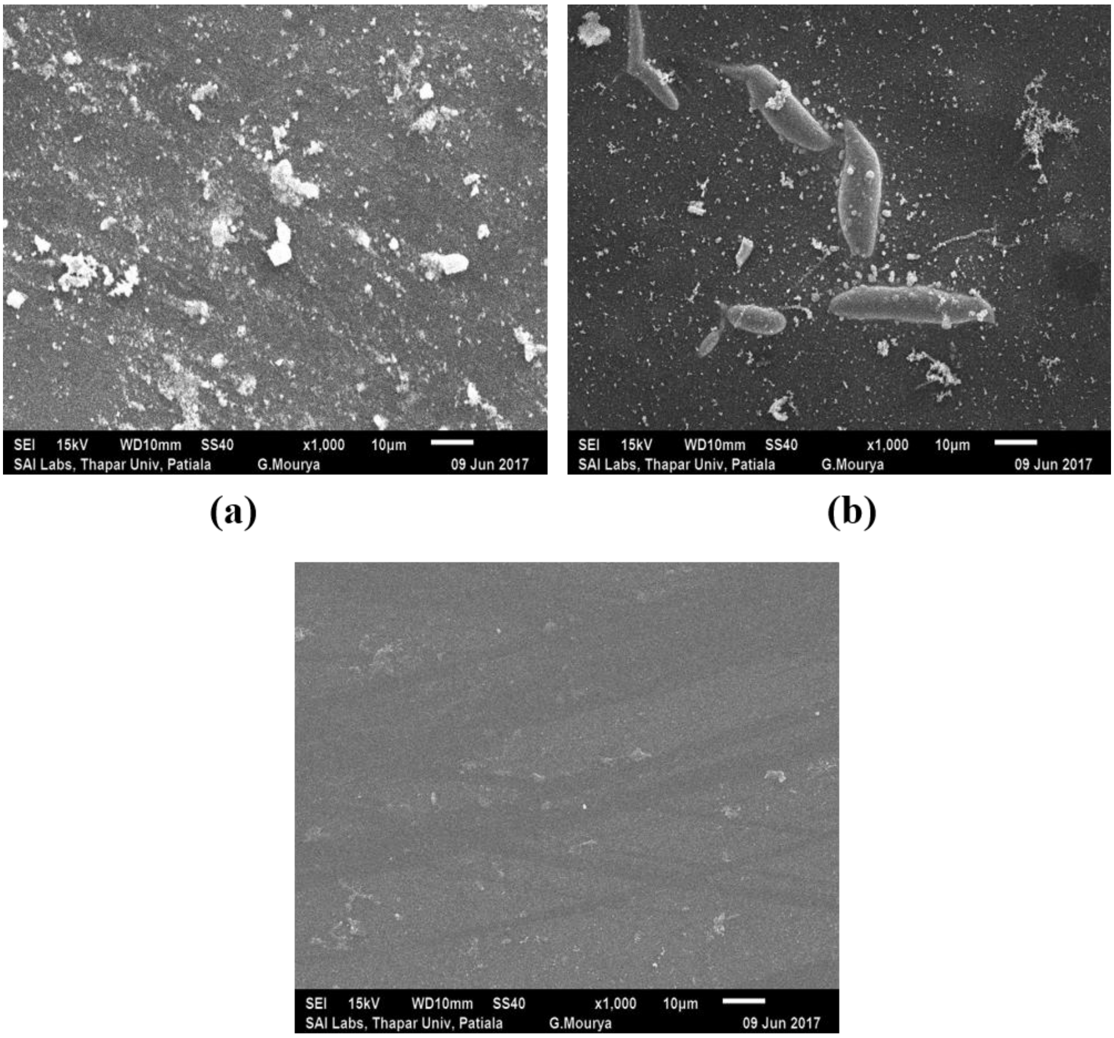
fz =0.5 mHz

Sinus amplitude: 10 mV

### 4.4. Scanning Electron Microscopy (SEM) Analysis

*(i) Surface morphology of MS substrates with coating*

After performing the corrosion test, the surface morphology of MS substrates with coating of sample solution 4, 5 and 6 were studied using scanning electron microscopy (SEM). Substrate coating with polymeric solution 6 containing 3% of cross linked polymer has maximum aggregation of particles as shown in Figure 15 (a). Substrate coated with polymeric solution 5 having 2% of cross linked polymer showed intermediate aggregation of particles and some balloon type air gaps as shown in Figure 15 (b). Substrate coated with polymeric solution 4 containing 1% of cross linked polymer showed very less aggregation of particles as shown in Figure 15 (c).



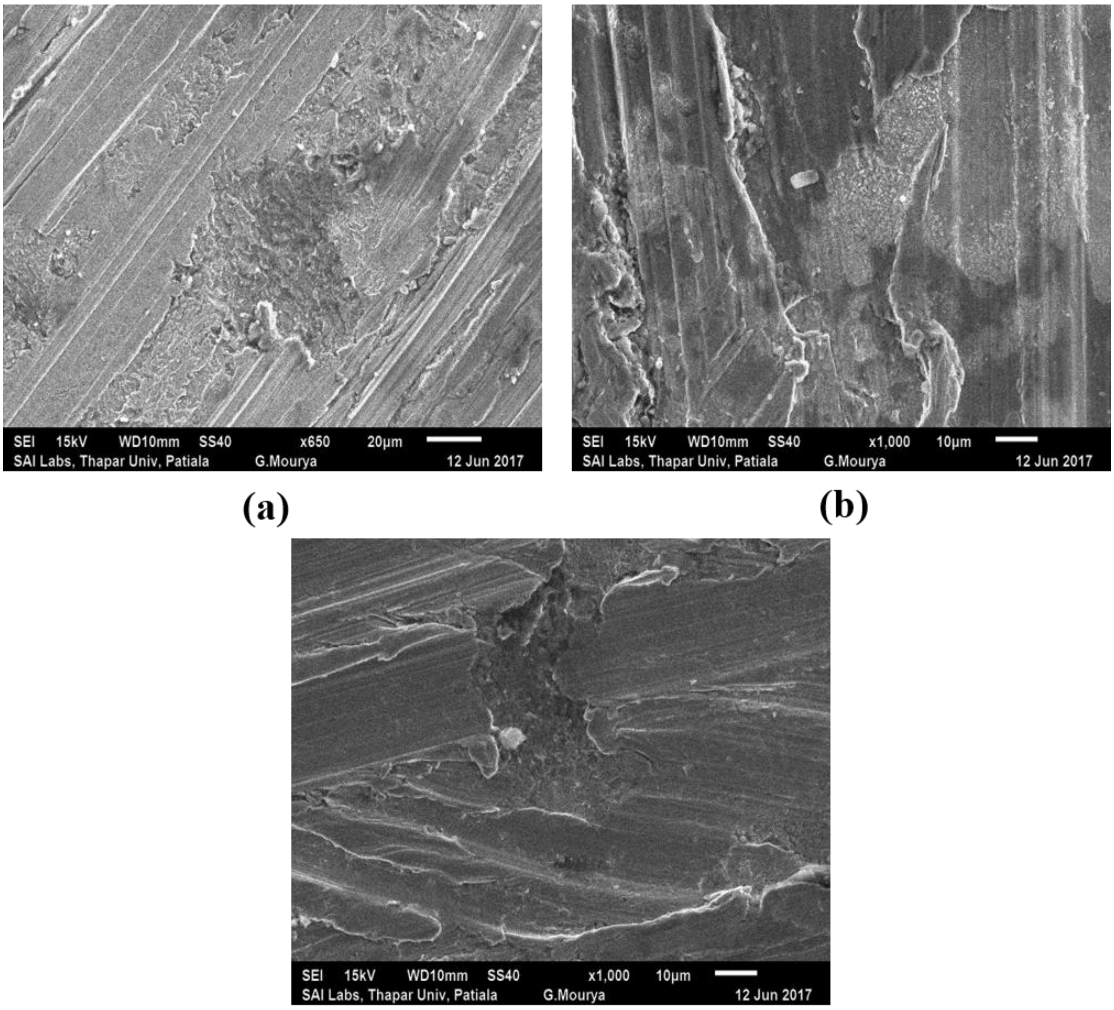
(a) (b)

(c)

**Figure 15.** SEM images of MS substrates coated with polymeric solution having (a) 3%, (b) 2% and (c) 1% of cross linked polymer.

*(ii) Surface morphology of corroded MS substrates without coating*

After corrosion test, polymeric coating of MS substrates was removed. Then, surface morphology of MS substrates determined using SEM analysis. SEM analysis determined that substrate coated with polymeric solution having 1% of cross linked polymer as shown in Figure 16 (c) shows less corrosion as compared with substrates coated with sample solution having 3% and 2% as shown in Figure 16 (a) and (b) respectively.



**(a)** **(b)**

**(c)**

**Figure 16.** SEM images of corroded MS substrates after removing the polymeric coating containing (a) 3%, (b) 2% and (c) 1% of cross linked polymer.

# Conclusions

Poly(styrene)-ethyl benzene coatings has been used for corrosion protection of mild substrates in acidic mediums equivalent to rain water and sea water. The effects of coating compositions have been studied. The coatings doped with crosslinked polymer were tested for corrosion resistant properties. The weight loss analysis of coated substrates suggests that coatings with less percentage of crosslinked polymer have better corrosion resistance. These findings are in agreement with EIS study. The surface morphology of tested substrates were performed using scanning electron microscopy. The SEM result shows the high percentage of aggregation of crosslinked polymer, which give rise to porosity to these coatings and these findings are further justified by polarization resistance value given by EIS.

The measurement of substrate weight before and after corrosion test, concluded that Substrates coated by using sample solution having 1% of cross linked polymer showed less weight loss as compared with substrates coated by using sample solutions having 3% and 2%. EIS study revealed that substrate coated with sample solution containing 1% of cross linked polymer has maximum value of coating resistance ($R_P$ = 2200 ohm.cm$^2$) as compared with sample solution having 2% and 3% of cross linked polymer. SEM analysis determined that substrate coated with polymeric solution containing 1% of cross linked polymer showed less corrosion as compared with substrate coated with sample solution having 3% and 2% of cross linked polymer.

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# Harleen_14-07-2017

*by* Harleen Kaur

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# Abstract

The aim of this study was to use solvent-based polymeric coating prepared by ex-situ addition of cross-linked Poly (styrene-co-divinyl benzene) in polystyrene-ethyl benzene solution for corrosion protection of mild steel in pH corresponding to sea water and acidic rain. Electrochemical impedance spectroscopy (EIS) technique was used to determine the corrosion resistance behavior of prepared polymeric coatings in 3.5% of NaCl aqueous solution. EIS study investigated that that sample solution prepared by adding 1% cross linked polymer in polystyrene-ethyl benzene solution, has better corrosion resistance as compared with the sample solution prepared by adding 3% and 2% of crosslinked polymer in polystyrene-ethyl benzene solution. Scanning electron microscopy (SEM) revealed that substrate coated with polymeric solution prepared by adding 1% of cross linked polymer in polystyrene-ethyl benzene solution showed less corrosion as compared with substrates coated with sample solutions prepared by adding 3% and 2% of cross linked polymer in polystyrene-ethyl benzene solutions.

# Chapter 1
# Introduction

In environment, metals occur in its chemically-stable ore form. When metals are extracted from its ore, then they become unstable and want to return to their original form. The process of conversion of refined metals to stable oxide, sulphide or hydroxide form is known as corrosion. In other words, the destruction of metals by chemical or electrochemical reaction with its environment is called corrosion. Basically, corrosion is derived from Latin word 'corrodere' which means 'to chew away'. According to IUPAC, "Corrosion is a reaction of metallic surface with its surrounding, results in its consumption or one of the components of environment getting dissolved in it".

Few examples related to corrosion in daily life are given below:

1. Rusting of iron
2. Copper pots containing greenish colour spots
3. White powder on zinc roofing etc.

## 1.1. Significance of corrosion management

The prevention of corrosion is very important because it can be harmful to economy and reason for several safety issues. Corrosion induces different kind of losses to economy, caused by deterioration of metals. It can be very dangerous for safety point of view. It decreases the metallic strength of components of vehicles, airplanes and ships etc. In chemical industries, corrosion of chemical containers, boilers, pressure vessels can be very detrimental. The kinds of losses caused by corrosion to economy are direct and indirect losses.(Landolt, 2007)

1. *Direct losses*: Metallic components are needed to repainting, in order to prevent from rusting. In case of corroded boilers, mufflers, pipelines etc., replacement of these components is necessary. The extra money is required to galvanize zinc on the surface of steel for corrosion protection.

2. *Indirect losses*: It is very hard to determine indirect losses caused by corrosion. Therefore, from thorough analysis, some indirect losses are determined. For example, in soap industries, the small particles of copper from corroded copper pipes leads to contamination of large

bunch of soaps. Small amount of metal particles from corroded container or pipes, results in variation of colour of dye. During reinstatement of corroded pipes in oil refinery, the production of oil has to stop which results in production loss.

Microscopic level observation of metallic surface determined that surface of metal is not uniform. There may be presence of some kind of impurities on surface. Chemical composition and structure may differ throughout the surface of metal. Anode and cathode can exit simultaneously on the surface of metal. Metallic part act as anode and impurities present on surface act as cathode. Based on the cathodic and anodic sites of metal surface, corrosion occurs in two different ways:

1. *Localized corrosion*: It is the type of corrosion in which one part of metal surface act as anode and other part act as cathode as shown in Figure 1(a).

2. *Uniform corrosion*: In this type of corrosion, cathodic and anodic part of metallic surface can't be distinguished as shown in Figure 1(b).

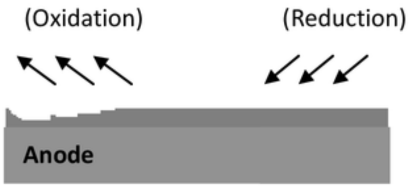


**Figure 1(a). Localized corrosion**

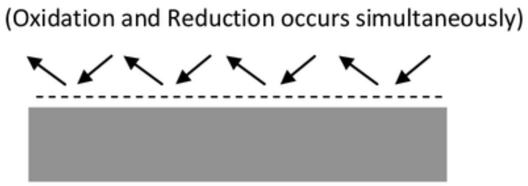


**Figure 1(b). Uniform corrosion**

### 1.2. Electrochemistry of corrosion

Iron comes in contact with oxidizing agent like oxygen and water droplets. One part of iron surface inside water droplet act as anode and other part act as cathode. Anodic part loses electrons and releases $Fe^{2+}$ ions. Electrons move to cathodic part outside the droplet, where oxygen and water react to form hydroxide ion as shown in Figure 2.(Hill and Kolb, 2007)

*Anodic reaction*

$$Fe\ (s) \longrightarrow Fe^{2+}\ (aq) + 2e^{-} \qquad \ldots\ldots\ldots\ (1)$$

*Cathodic reaction*

$O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-\,(aq)$ …………..... (2)

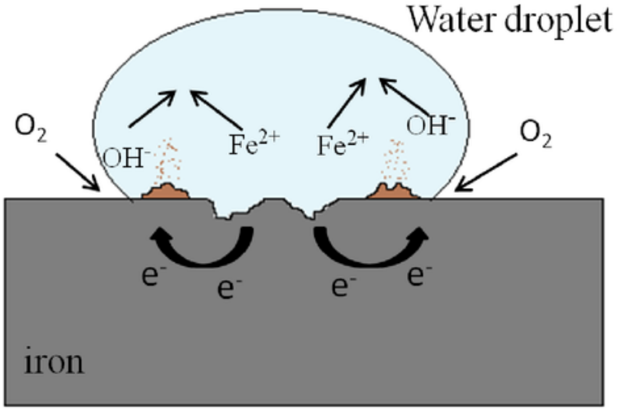


**Figure2. Corrosion as an electrochemical cell**

These hydroxide ions produced on cathode, move inside the water droplet and react with $Fe^{2+}$ ions at anode to form iron oxide as per following reaction,

$Fe^{2+}\,(aq) + 4OH^-\,(aq) \longrightarrow Fe\,(OH)_2\,(s)$ …………… (3)

Further oxidation of iron oxide results in the formation of rust.

$4Fe\,(OH)_2\,(s) + O_2\,(g) \longrightarrow 2Fe_2O_3.H_2O\,(s) + 2H_2O\,(l)$ ……………. (4)

### 1.3.Types of corrosion

Various types of corrosion causing damage on metal and their reasons are given below.

#### 1.3.1. General corrosion

In general corrosion, surface of metal is uniformly corroded by oxidizing agents present in its environment. The anodic and cathodic sites can't be distinguished as shown in figure 3.(Landolt, 2007)

**Figure 3. General corrosion**

### 1.3.2. Selective corrosion

It is the type of corrosion in which components of an alloy are not uniformly distributed. Component A which is less noble is dissolved at first and porous layer of nobler component B is left behind as shown in figure 4.

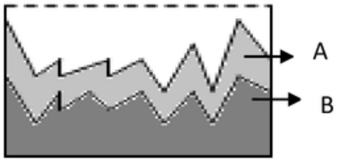


**Figure 4. Selective corrosion**

### 1.3.3. Stress corrosion

It is the type of corrosion which occurs under the influence of corrosion attack and the external or internal stress applied on metal. Cracks are formed, when mechanical stress is applied just below the tensile strength of metal as shown in figure 5.

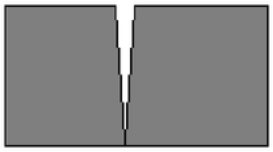


**Figure 5. Selective corrosion**

### 1.3.4. Pitting corrosion

The material like stainless steel has protective oxide layer. Small sort of damage on this protective film can initiate the corrosion. In the presence of anions like chloride ions mostly present in seawater, pH level decreases and environment becomes oxygen deficient. Under these conditions, small cavities are formed on metal surface and process is known as pitting corrosion as shown in figure 6. (Revie, 2008)

**Figure6. Pitting corrosion**

### 1.3.5. Erosion corrosion

The process in which general corrosion is accompanied by the turbulent flow of fluid, scraping away the corroded part of metal, is known as erosion corrosion as shown in figure 7.

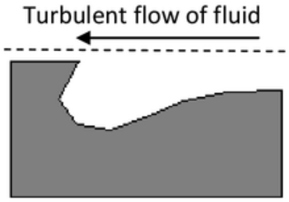


**Figure7. Erosion corrosion**

### 1.3.6. Intergranular corrosion

When stainless steel is kept at 500-600°C temperature for long duration of time, then inside the metal at the interface of grains chromium starts reacting with carbon. This reaction leads to the formation of carbides and depletion of chromium, such

**Figure8. Intergranular corrosion**

type of corrosion is known as intergranular corrosion as shown in figure 8.(Revie, 2008)

### 1.3.7. Crevice corrosion

It is localized type of corrosion which occurs within crevices of metal surfaces. In these crevices corrodant can stagnant and cause corrosion.

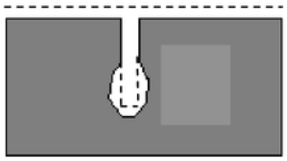


**Figure9. Crevice corrosion**

### 1.3.8. Galvanic corrosion

When two different metals are in contact with each other, results in the formation of electrochemical cell in the presence of electrolyte like water. Metal having less electrode potential will act as anode and it will corrode.

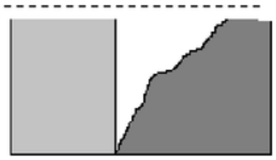


**Figure10. Galvanic corrosion**

### 1.4. Corrosion prevention methods:

There are four types of methods to prevent corrosion of metal, which are given below:

**1.4.1. Active corrosion protection:** In this method, metallic surface is protected from corrosion by restricting the reaction involved in corrosion and the attack of corrosive agents. This process is done by fabricating anti-corrosive alloys and incorporating inhibitors to the aggressive medium.

**1.4.2. Passive corrosion protection**: It is the technique in which corrosion of metal is prevented by creating barrier in between the metallic surface and surrounding oxidizing agents, using protective layers, coatings or films etc.(Tong, 2014)

**1.4.3. Permanent corrosion protection:** Inside industrial building, corrosive agents are less effective and temperature variation is also under control. In such condition, metallic machines are permanently protected from corrosion using galvanization, tin plating, coating etc.(Maaß, 2011)

**1.4.4. Temporary corrosion protection:** The risk of metallic corrosion is more during transportation and handling because there is more contact with corrosive environment and temperature variation. In this situation, temporary corrosion protections are helpful against corrosion.(Maaß, 2011) Different types of temporary corrosion protection are given below:

(a) In protective coating method, coatings containing anti-corrosive agents are applied on metallic surface to provide barrier in between the metallic surface and corrosive agents. Anti-corrosive agents are water- borne anticorrosive agents, solvent based anti- corrosive agents, dipping waxes and corrosion protective oils.

(b) In desiccant method, metallic materials are placed inside bags, which contain desiccants like silica gel, blue gel, molecular sieves to absorb water vapours and controls humidity for corrosion protection of material.

(c) The method in which volatile corrosion inhibitors are sprayed on the metallic surface or film and then changes to vapour state making a film, the given method is known as volatile corrosion inhibitor method. This film is resistive to reactions involved in corrosion and thus protects the metallic surface from corrosion.

In present study, solvent-based polymeric coating was fabricated by ex-situ addition of cross-linked Poly (styrene-co-divinyl benzene) in polystyrene-ethyl benzene solution for corrosion protection of mild steel in pH corresponding to sea water and acidic rain. The anti-corrosive performance of resultant polymeric coating was investigated by using different techniques. The corrosion inhibition of polymeric coatings having 1%, 2%, and 3% of cross-linked Poly (styrene-co-divinyl benzene) were studied by using electrochemical impedance spectroscopy.

# Chapter 2
# Literature review

This work is mainly focused on common protection of metallic surfaces using polymeric coatings. The latest literature related the corrosion protection using polymeric coatings have been discussed in this chapter.

## 2.1. Literature review

Reinhard et al.(Reinhard et al., 1992) studied the application of corrosion inhibitors in water-borne coatings. They used water-borne coatings for corrosion protection of mild steel instead of using toxic organic solvents. They substituted mercapto compounds as corrosion inhibitors in acrylate- based dispersion. These mercapto compounds reduced the early rusting during film formation without altering the properties of acrylate dispersion. The acrylate-based dispersion was prepared by using copolymer of butyl esters of (acrylic acid, styrene and methacrylic acid). It also contained acrylic acid, monoesters and polymerization initiator ammonium persulphate $(NH_4)_2S_2O_8$ . Corrosion inhibitors present in acrylate dispersion were investigated by using modal electrolyte (0.03M $KNO_3$ in double distilled water + 0.01M acrylic acid). They determined using electrochemical impedance spectroscopy (EIS) that anticorrosive property of mercapto compounds increased with the increase in pH values. EIS also showed that mercapto compounds were involved as a cross linking agent during layer formation.

Perrin et al.(Perrin et al., 2015) have studied the synthesis and characterization of polyaniline nanoparticles in phosphonic acid amphiphile aqueous micellar solutions for waterborne corrosion protection coatings. Polyaniline dispersion was prepared in the presence of oxidizing agent i.e. ammonium peroxydisulphate (APS) and a surfactant i.e. n-decylphosphonic acid (DPA). DPA acts as dopant anion. Energy dispersive X-ray spectroscopy revealed that when surface of DPA doped polyaniline coating scratched, then dopant anion released to further protect the metal surface from corrosion. Surfactant concentration was kept higher than critical micelle concentration (cmc) for the preparation of water/DPA solution. DPA has property to form vesicles in water, so the DPA vesicles and

DPA-aniline salt vesicles started coexisting. Precipitates of polyaniline were formed due to unstable reaction mixture. Polyaniline dispersion was prepared at DPA/aniline molar ratio greater than 1, because at higher surfactant concentration no precipitates were obtained. Higher value of electrical conductivity obtained at molar ratio 1.25 of APS/aniline. FT-IR analysis showed that the polyaniline was doped efficiently with DPA. Thermo gravimetric analysis showed that the DPA doped PANI has good thermal stability at least up to 260°C temperature .X-ray diffraction patterns of DPA-Polyaniline in emerlidine salt form showed that interlayer distance of polyaniline increased with higher concentration of DPA and dopant was penetrated effectively.

Baskar et al.(Baskar et al., 2014) fabricated poly((E)-(1-(5-(4-(3-(4-chlorophenyl)-3-oxoprop-1-enyl)phenoxy)decyl)-1H-1,2,3-triazol-4-yl)methyl acrylate)and poly((E)-(1-(5-(4-(3-(4-chlorophenyl)-3-oxoprop-1-enyl)phenoxy)pentyl)-1H-1,2,3-triazol-4-yl)methyl acrylate) , which are cross- linkable on photo irradiation. These polymers were coated on mild steel to protect it from corrosion in 1.0 M HCl solution. FT-IR analysis showed the presence of photo sensitive chalcone moieties. The spectra given by H-NMR results confirmed the formation of polymer. Cross-linking of polymer under the influence of photo illumination was confirmed by absorption spectroscopy. The morphology given by SEM analysis confirmed that these photo crosslinking polymers can protect mild steel from corrosion.

Pour-Ali et al.(Pour-Ali et al., 2014**)** suggested that direct addition of polyaniline particles in epoxy matrix results in aggregation of the particles. Thus, polymer was synthesized using different way. Epoxy matrix was modified using polyethylene glycol (PEG) and polyaniline-camphorsulphonate particles were prepared in epoxy network. Mild steel was coated using this prepared polymeric coating, in order to protect it from corrosion in 3.5% NaCl medium. The prepared characteristic description of polymeric coating was characterized by FT-IR and TEM. Anticorrosive nature of polymeric coating in 3.5% NaCl solution was determined using several techniques like EIS, salt spray test etc.

Baldissera and Ferreira et al.(Baldissera and Ferreira, 2012) prepared different epoxy matrix (EM) based coatings by incorporating different forms of polyaniline (PANI). These coating were utilized for protecting mild steel substrates from corrosion in 3.5% NaCl solution. Different forms of PANI like PANI Sulphonate, PANI-fibers, PANI-emerlidine salt, PANI-emerlidine base, PANI-zinc phosphate, PANI-zinc chromate were prepared. Different coatings fabricated by incorporating these forms of PANI in epoxy matrix showed better anticorrosive nature as compared to simple epoxy coating. Electrochemical impedance spectroscopy determined that coating prepared by incorporating PANI sulphonate in epoxy matrix showed more desirable anticorrosive behavior than other coatings.

Behzadnasab et al.(Behzadnasab et al., 2011) fabricated polymeric coating for protection of mild steel from corrosion in 3.5% NaCl solution. The polymeric coating was manufactured using $ZrO_2$ nanoparticles which were modified using amino propyl trimethoxy silane (APS). Further, these modified $ZrO_2$ particles were added in epoxy matrix. APS helped to form chemical bonds in between epoxy matrix and $ZrO_2$ particles and these particles got properly distributed in epoxy matrix. The anticorrosive nature of resulted polymeric coating was enhanced at 2-3 wt. % of $ZrO_2$. The salt spray test and electrochemical independence spectroscopy were used to determine the corrosion resistance of polymeric coating.

Kocijan et al.(Kocijan et al., 2015) have studied the comparison and characterization of biocompatible polymer coating on AISI316L stainless steel. Biofouling reduces the efficiency of materials and contributes to corrosion of metal and alloys. PDMS (Polydimethylsiloxane) and PEG (polyethylene glycol) were used for surface modification of AISI316L stainless steel. PDMS induced the hydrophobic nature in the substrate by changing the surface wetting properties. PDMS has water contact angle greater than $90^\circ$and decreased the free energy of the surface. It acted like a water repellent and protected the surface from the corrosion. On the other hand, the contact angle of PEG and water was less than 90 degree which induced the hydrophilic nature to the system. The free energy of the substrate surface was also increased. PEG has anticorrosive properties, but less than PDMS. X-ray photoelectron spectroscopy determined that PEG coating is slightly thicker than PDMS. Their electrochemical impedance spectroscopy data confirmed that PDMS coatings applied on stainless steel has superior anticorrosion properties than PEG.

El-mahdy et al.(El-Mahdy et al., 2014) prepared magnetite/ acryl amide-co-sodium acrylate nanocomposite coating for corrosion protection of mild steel in HCl solution. Preparation of nanocomposite coating was based on core-shell system. The magnetite nanoparticles were modified using NMA (polyoxyethylene 4-nonyl-2-propyl-phenyl/Maleic anhydride adducts). These magnetite/NMA nanoparticles were used as a core. The cross-linked acryl amide-co-sodium acrylate containing magnetite nanoparticles was used as shell. Transmission electron microscopy results confirmed that magnetite nanoparticles were dispersed inside polymeric matrix in the presence of magnetite/NMA nanoparticles. The characteristic properties of coating were investigated using UV-VIS spectroscopy, Fourier transform-infrared spectra.

Xu et al. (Xu et al., 2016) studied the facile fabrication of super hydrophobic polyaniline structures and their anticorrosive properties. They used different surfactants i.e. SDBS (sodium dodecylbenzene sulphonate), PEG (polyethylene glycol) and CTAB (cetyltrimethyl ammonium bromide) to modify polyaniline to make it super hydrophobic. SEM and water contact angle measurements showed that when polyaniline interacted with surfactant, then it made the hydrophobic alkyl chain of surfactant going out. This kind of interaction decreased the free energy of surface. Surfactant modified the polyaniline to super hydrophobic polyaniline, which has water contact angle greater than $150^{\circ}$. Super hydrophobic polyaniline acted as water repellant and showed anticorrosive properties. The super hydrophobic nature introduced by PEG on polyaniline was better than the CTAB and SDBS due to huge hydrophobic alkyl chain of PEG. Larger is the hydrophobic alkyl chain of surfactant, greater is the water contact angle of modified polyaniline. These methods to produce the super hydrophobic polyaniline are cheap, easy, an environmentally friendly as compared to toxic fluoride.

Voevodin et al.(Voevodin et al., 2003) studied the nanostructured coatings approach for corrosion protection. Chromate based treatment of aluminium aerospace alloy release $Cr^{6+}$ which is extremely carcinogenic in nature. Self-assembled nanophase particles (SNAP) coatings were successfully replaced the chromate based coatings. SNAP solution was prepared by mixture of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetramethoxysilane (TMSO) in 3:1 ratio. Corrosion inhibitors such as aminopiperidine (APD), aminopiperazine (APZ) and tetraethyl dimethylenediphosphate (TMD) + mercaptobenzotriazole (MTZ) were added in SNAP solution immediately before the film application. SNAP coating was prepared by sol-gel process. This process includes formation of silica nanoparticles by hydrolysis and condensation of silanes with epoxy functionalities. They used potentiodynamic scan (PDS) to analyze the barrier properties of SNAP coatings with different organic inhibitors i.e. APD, APZ and TMD +MTZ. PDS indicated that all of given organic inhibitors show good barrier properties. Electrochemical impedance spectroscopy (EIS) showed good hydrolytic stability of SNAP film applied on aluminium alloy. When the paint systems containing SNAP coating and chromated primers were kept in salt spray system for 2000 h. Up to 2000 h paint system showed sufficient corrosion protection.

Schreiber et al. (Schreiber et al., 1980) prepared the plasma polymerized (PP) polymeric coatings which surpass the conventional polymeric coatings in corrosion protection. They were highly cross linked and adhere to a wide range of substrates, but they adhere well to the substrates above a specific critical substrate temperature. Films did not adhere well to the substrate below critical temperature ($T_S$). These tests were conducted by simple empirical peel tests and scratch test with sharp tool. Attenuated total reflection (ATR) IR spectra revealed that with increasing the substrate temperature, Si-O-Si bonds intensities were increased. The PP coating film had greater dimensional stability and there was absence of any discontinuities at molecular level (pin holing) because of high cross linkage. As $T_S$ was increased the film density resembled density of vitreous silica and not that of conventional polymers. This also made them stable at temperatures as high as 800-1000° C. PP polymeric coatings also had outstanding tolerance to extreme deformations of the substrate because of high cohesive strength of the cross linkage.

Pourhashem et al.(Pourhashem et al., 2017) prepared solvent based epoxy coatings containing graphene oxide (GO) nanosheets. Mild steel substrate protected was using this polymeric coating to protect it from corrosion. Corrosion resistance property of polymeric epoxy coating was affected by varying concentration of GO nanosheets. At 0.1wt.% weight of GO nanosheets in epoxy coating showed best anticorrosive nature of coating, when compared with 0.3wt.%, 0.5wt.% and 0.05wt.% of GO nanosheets. FE-SEM analysis determined that at 0.1wt. % of GO, there was no sign of agglomeration of GO nanosheets. Polymeric coating was prepared using two different ways. In first method, GO was directly added to epoxy resins and then polyamide hardener was added. In second method, GO was directly added to polyamide harder and then mixed with epoxy matrix. Coatings prepared by second one method showed better corrosion resistance because GO nanosheets were well distributed in polymeric matrix.

Cho et al.(Cho et al., 2009) studied the self-healing polymeric coatings. The thermo gravimetric analysis (TGA) of the self-healing system showed primary weight loss beginning near chlorobenzene's boiling point (131℃) and secondary weight loss about 225 ℃ exhibiting thermal decomposition of polyurethane (PU) shell. The coating showed self-healing property only when both the catalyst (5% wt. dimethyldineodecanoate tin (DMDNT) in chlorobenzene capsules) and the healing agent Polydimethylsiloxane (PDMS) were present. Scanning electron microscopy showed that about 40% of the scribed damage was self-healed in the sample with self-healing coating. Electrochemical testing showed large magnitudes of current passing through the scribed control sample (26.6-58.6 mA/cm$^2$) as compared to the scribed and self-healed sample (12.9 µA/cm$^2$-1.4µA/cm$^2$) with no gas evolution. All control samples showed rust formation on exposure to brine whereas, the self-healed sample, allowed to heal for 24hrs at 50 $^{o}$ C showed no rust formation. Self-healing readily occur around 20 $^{o}$ C without any requirement of moisture when Si [OSn (n-$C_4H_9$)$_2$OOCCH$_3$]$_4$ (TKAS) was used as instead of DMDNT.

Shi et al.(Shi et al., 2009) studied the effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coatings. Separate epoxy coating sample doped with nanoparticles of $SiO_2$, $Fe_2O_3$, Zn and hallyosite nanoclay along with one undoped epoxy resin coating were prepared. FE-SEM images of coating samples depicted that cured plain epoxy and epoxy coating doped with $SiO_2$ were homogeneous and showed no agglomeration as compared to the coating having $Fe_2O_3$ nanoparticles. The potentiodynamic weak polymerization showed the corrosion rate decreased to a great extent because of the nanoparticles and increased the polarization resistance ($R_p$) of the epoxy coated steel. This incorporation decreased the coating porosity. Epoxy coating having $Fe_2O_3$ nanoparticles showed maximum Rp. EIS curves of these samples depicted that the resistance of coating increased with decrement in capacitance with $Fe_2O_3$ nanoparticles in epoxy coating as reported by them. The increase in capacitance and decrease in resistance after sometime explained the penetration of corrosive electrolyte through the film.

Zandi-Zand et al. (Zandi-Zand et al., 2005) studied the use of organic-inorganic hybrid coating to protect the aluminium alloy. The coatings were applied using dip coating method. Hybrid coating was fabricated from 3-glycidoxypropyl-trimethoxysilane (GPTMS) and Tetramethoxysilane (TMOS) by two step acid catalysis. In the first step, there was hydrolysis and condensation of GPTMS and TMSO to form organo- silica nanoparticles. In second step, organo-silica nanoparticles cross linked in the presence bisphenol as a cross-linking agent. ATR-IR Spectroscopy showed that the coating of hybrid sol on aluminium alloy resulted in superior cross-linked density of silane as the aluminium alloy had formed networks with silicates. Electrochemical results revealed that the silane content in coating influences the corrosion resistance. More is the silane content in the coating, lesser it will be corrosion resistive.

### 2.2. Research Gap or Short coming of earlier work

1. All literature reported here showed the application of some special chemical to get the special coating for protection.
2. In few research papers(Baskar et al., 2014; Schreiber et al., 1980) polymeric solution solutions are being cross linked in order to enhance the corrosion resistance properties.
3. Few researches(Shi et al., 2009; Voevodin et al., 2003) used the doping of nanoparticles to decrease the porosity of the film, hence high corrosion protection.

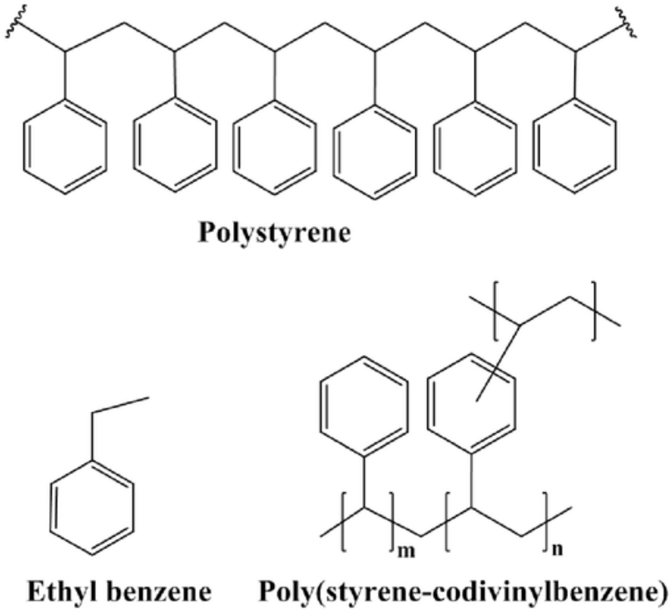
In the proposed work, polystyrene has been selected to study the corrosion resistance property of metal. The coating was prepared using dip coating technique. The cross-linked Poly (styrene-co-divinyl benzene) having 1% crosslinking has been used as a doping agent. The detailed methodology has been given in next chapter i.e. materials and method.

# Chapter 3
# Materials & Method

## 3.1. Material

Mild steel specimens of dimensions 5mm×5mm×1mm and 1cm×1cm×1mm have been purchased from local market, polystyrene [molecular weight=192000; density=1.05 g/cm$^3$] and poly(styrene-co-divinyl benzene) (PDB) [density=0.29 g/cm$^3$] were purchased from Sigma Aldrich (Germany), ethyl benzene [molecular weight=106.17; density=0.866 g/cm$^3$] was purchased from Spectrochem (India), emery paper of 1200 grade, sulphuric acid (98%), hydrochloric acid (37%), Acetone.

Chemical structure of polystyrene, ethyl benzene and poly (styrene-co-divinyl benzene) are given in Figure 11.



**Polystyrene**

**Ethyl benzene** **Poly(styrene-codivinylbenzene)**

**Figure11. Chemical structures of polystyrene, ethyl benzene and poly (styrene-co-divinyl benzene)**

### 3.2. Preparation of coating solution

Six sample solutions were prepared by dissolving different amounts of ethyl benzene (EB), polystyrene, poly (styrene-co-divinyl benzene) (PDB) in six reagent bottles shown in Table 1. These sample solutions were placed in incubator for 4 hours at 40 °C for shaking.

**Table 1**: Chemical composition of sample prepared

| Sample no. | EB (g ) | Polystyrene (g) | PDB (g) |
|---|---|---|---|
| 1 | 94 | 5 | 3 |
| 2 | 93 | 5 | 2 |
| 3 | 92 | 5 | 1 |
| 4 | 82 | 15 | 3 |
| 5 | 83 | 15 | 2 |
| 6 | 84 | 15 | 1 |

### 3.3. Surface preparation of mild steel (MS)

Cleansing of surface of MS specimen is necessary before their coating. Carbon black, dirt, oil and grease were removed from surface of MS by dipping them in 30% HCl solution. Remaining oxidation particles were removed using emery paper of 1200 grade. Specimen were washed using distilled water, degreased using acetone and dried in oven at 50 °C.

### 3.4. Preparation of polymeric coating

There are several methods for preparation of coating like dip coating, spin casting(Flack et al., 1984), thermal spraying(Vyawahare, 2006), pinned-drop casting(Li et al., 2012) etc. In the present work, coatings were prepared by using dip coating technique. Dip coating is defined as the method in which, substrate is dipped into the solution of coating and withdrawn at a particular rate to obtain a thin coating on its surface. Steps involved in this process are given below:

(a) *Immersion*: Substrate is dipped at constant rate into the chemical solution.

(b) *Dwell time*: Substrate is kept entirely dipped and left for some time in a solution.

(c) *Withdrawal*: Substrate is withdrawn at constant rate from solution without shaking. The thickness of coating on surface of substrate is directly proportional to the rate at which it is withdrawn from solution.

Dip coating method is mostly used in industries and labs because these methods are not much expensive and easy to control. During this method, there is very less wastage of paint or material. This coating technique is used in laboratories for the fabrication of thin layer of chemical compound like polymer or nanoparticles dissolved in volatile solvent. This method is also used in industrial sector for preparation of coated fabrics, grips for hand tools etc. There are some materials in industries which require quick coating of their entire surface. In such condition dip coating technique is helpful.(Scriven, 1988)

### 3.5. Coating Procedure

MS substrates were weighed before coating. These substrates were immersed in sample solutions 1, 2, 3, 4, 5 and 6 and withdrawn at constant speed. Then, the coated substrate was dried for few minutes and again immersed in the same polymeric solution. In this way, substrates were coated thrice. Thin multilayer coatings were formed on the surface of substrate. These substrates were dried at room temperature (30°C) for overnight. After coating was dried, substrates were again weighed. The difference in two weights divides by density of polymer will give the volume of coating on the substrate. The volume of coating divided by cross-section area of substrate will give the average coatings thickness on the substrate.

### 3.6. Preparation of Synthetic Sea/Rain water

Acidic solutions of Ph 3, 4 and 5 were prepared by diluting 98% of sulphuric acid using distilled water. Dried coated substrates were dipped in prepared acidic solutions for corrosion tests. Weight loss of substrates after corrosion was measured after one week.

# Chapter 4
# Results and Discussion

## 4.1. Weight gain of MS substrates after coating

Mild steel substrates were weighed before applying polymeric coating and after the coating were dried. Substrate were weighed after coating, weight gain is given in Table 2.
A = Substrate weight before coating
B = Substrate weight after drying coating

**Table 2**: Weight gain of substrate after coating

| Sample solution | Substrate No. | A (mg) | B (mg) | (B-A) (mg) |
|---|---|---|---|---|
| 4 | 1 | 242.50 | 248.50 | 6 |
| | 2 | 225.06 | 228.11 | 3.05 |
| | 3 | 229.30 | 231.56 | 2.26 |
| 5 | 1 | 271.84 | 275.39 | 3.55 |
| | 2 | 247.27 | 250.33 | 3.06 |
| | 3 | 252.27 | 254.52 | 2.25 |
| 6 | 1 | 294.07 | 296.94 | 2.87 |
| | 2 | 247.27 | 251.85 | 4.58 |
| | 3 | 244.08 | 247.15 | 3.07 |

## 4.2. Weight loss of substrates after corrosion

Corrosion test was carried out by immersing the dried coated substrates for one week in sulphuric acid solution of pH 3, 4 and 5 as shown in figure1. After corrosion test, substrates were withdrawn from the containers containing acidic solution. Then, substrates were dried in oven for 3 hours and weighed. Substrates were weighed after corrosion and weight loss is given in Table 3.

**Figure12. Substrates immersed in acidic solution of pH 3, 4 and 5**

**Table 3**: Weight loss of substrate after corrosion

| **Sample solution** | **Substrate No.** | **pH** | **B (mg)** | **C (mg)** | **(B-C) (mg)** |
|---|---|---|---|---|---|
| 4 | 1 | 3 | 248.50 | 248.04 | 0.46 |
| | 2 | 4 | 228.11 | 227.30 | 0.81 |
| | 3 | 5 | 231.56 | 231.05 | 0.51 |
| 5 | 1 | 3 | 275.39 | 275.00 | 0.39 |
| | 2 | 4 | 250.33 | 248.57 | 0.55 |
| | 3 | 5 | 254.52 | 253.85 | 0.67 |
| 6 | 1 | 3 | 296.94 | 296.66 | 0.28 |
| | 2 | 4 | 251.85 | 246.98 | 0.17 |
| | 3 | 5 | 247.15 | 251.76 | 0.01 |

Substrates coated by using sample solution 6 showed less weight loss as compared with 4 and 5.

### 4.3. EIS study

Figure14. showed EIS Nyquist and Bode plots of MS substrates coated with different sample solutions. These plots were drawn by using simple equivalent electric circuit model shown in figure15. This model contains parameters like $R_S$ (solution resistance between reference electrode and working electrode), $R_P$ (polarization resistance) and $C_{dl}$ (coating capacitance). Constant phase element (CPE) tells about the behaviour of polymeric coatings. The formula used to calculate the impedence value is given below,

$$\textbf{Impedance } (\mathbf{Z_{CPE}}) = \mathbf{R_S} + \frac{Q}{R_P}$$

Q = Constant phase element
$R_S$ = Solution resistance
$R_P$ = Polarization resistance
The calculated values of these parameters are shown in table4.

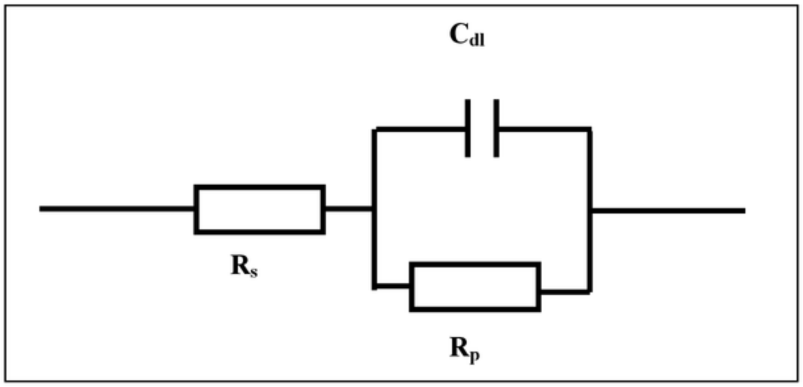


**Figure13**. Equivalent circuit model

Figure14 (a). showed the Nyquist plots of corrosion of different electrodes in 3.5 % NaCl solution. These electrodes were mild steel substrates coated by using different sample solutions.

Capacitive loops of different diameter were obtained for sample solutions 1, 2 and 3. Semi-circles shown in Nyquist plot are not very perfect. Capacitive loops represents the corrosion of mild steel substrates, which is regulated by the charge tranfer process of corrosion. Diameter of semi-circles decreased by increasing the concentration of cross linked polymer in sample solutions as shown in figure14 (a). Diameter of capacitive loop of sample solution 3 having 1% of cross linked polymer is greater than sample solutions 1 and 2 having 3% and 2% of cross linked polymer respectively. Greater the diameter of capacitive loop, more will be the corrosion resistance of sample solution. Therefore the sample solution 3 showed more corrosion resistance as compared with the sample solutions 1 and 2 as shown in Table 4.

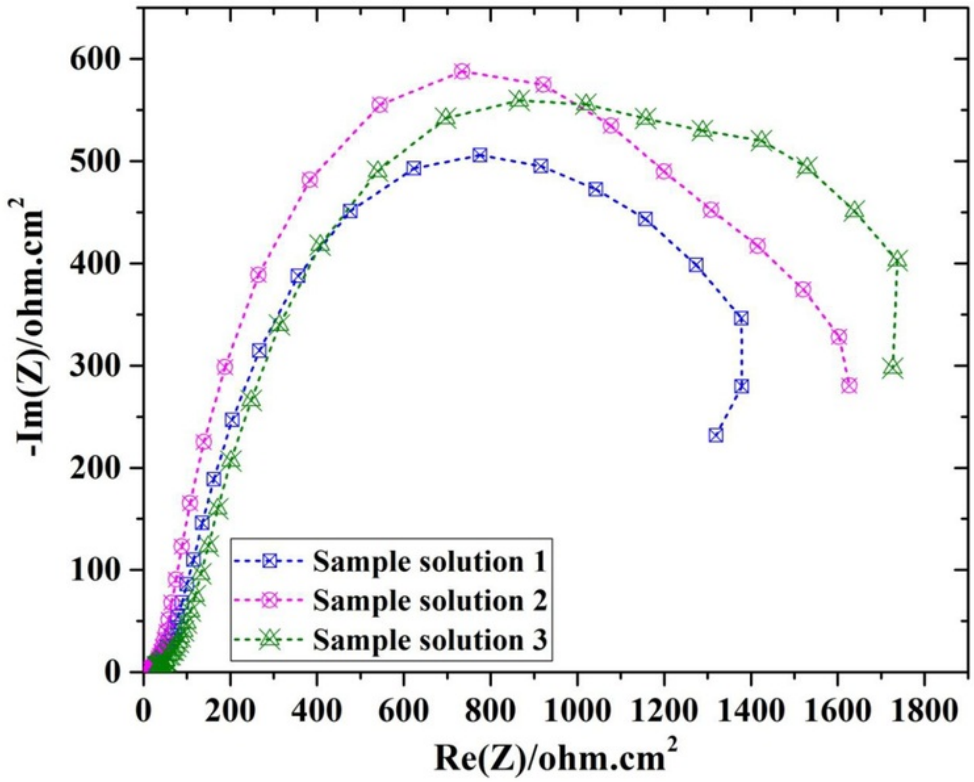


**Figure14** (a). Nyquist plots of corrosion of different electrodes in 3.5% NaCl solution

Figure 14 (b). showed the Bode plots of corrosion of mild steel substrates coated with sample solution 1, 2 and 3 in 3.5% NaCl solution. The breakpoint frequency technique was used to estimate area of delamination of different polymeric coatings on mild steel substrates in acidic solution. The breakpoint frequency is the frequency corresponding to the 45 degree of phase angle. Mathematically, it can be expressed as given below,

$$\textbf{Breakpoint frequency } (\mathbf{f_{45}}) = \mathbf{K}\frac{A_d}{A}$$

$A_d$ = Area of delamination

K = Material constant for polymeric coating

A = Total area of sample

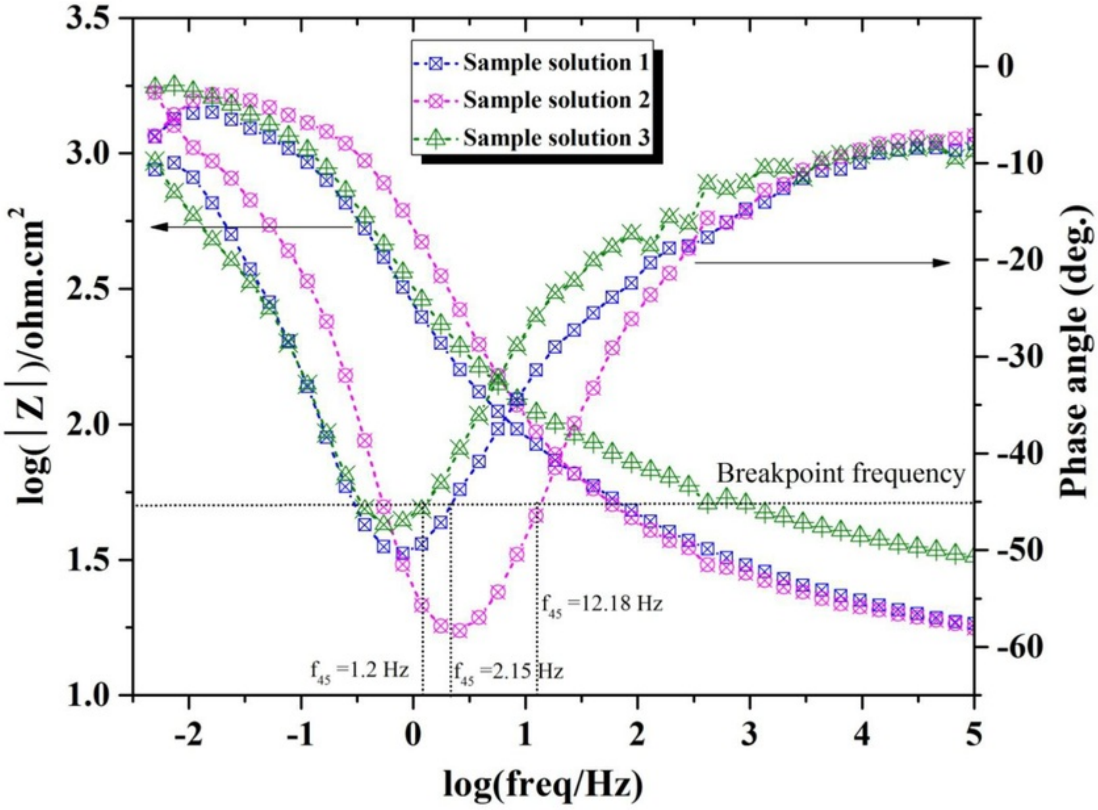


**Figure14** (b). Bode plots of corrosion of different electrodes in 3.5% NaCl solution

$$K = \frac{1}{2\pi\varepsilon\varepsilon_o\,\rho_o}$$

ε = Vaccum permittivity

$\varepsilon_o$ = Dielectric constant of polymeric coating

$\rho_o$ = Specific ionic resistance of moist polymeric coating

The breakpoint frequency is directly proportional to the area of delamination of polymeric coating in corrosive solution. The breakpoint frequency ($f_{45}$) is 1.2 Hz for sample solution 3 having 1% of cross linked polymer, which is lesser than $f_{45}$ values of sample solutions 1 and 2 containing 3% and 2% of cross linked polymer respectively. So, the area of delamination of polymeric coating prepared by using sample solution having 1% cross inked polymer is lesser than the area of delamination of polymeric coating prepared by using sample solution 3% and 2% of cross linked polymer.

**Table 4**: Parameters of corrosion and impedance kinetics

| | Impedance kinetics | | | |
|---|---|---|---|---|
| | $R_s$ (ohm cm$^2$) | CPE (F.s$^{n-1}$) | n | $R_p$ (ohm cm$^2$) |
| Sample solution 1 | 21.5 | 1.75e-3 | 0.725 | 1600 |
| | | | | |
| Sample solution 2 | 21.4 | 1.5e-3 | 0.752 | 1821 |
| | | | | |
| Sample solution 3 | 37.88 | 1.3e-3 | 0.602 | 2200 |
| | | | | |

Solution: 3.5 wt. % NaCl

Impedance parameters:

fi =100 kHz

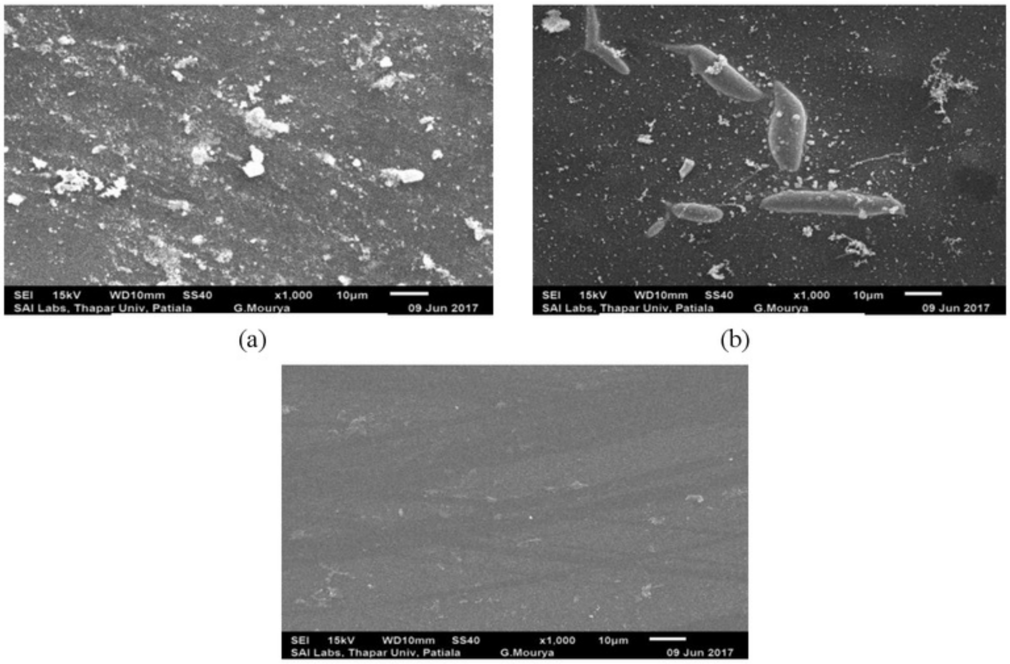
fz =0.5 mHz

Sinus amplitude: 10 mV

### 4.4. SEM Analysis

*(i) Surface morphology of MS substrates with coating*

After performing the corrosion test, the surface morphology of MS substrates with coating of sample solution 4, 5 and 6 were determined using scanning electron microscopy (SEM). Substrate coating with polymeric solution 6 containing 3% of cross linked polymer has maximum aggregation of particles as shown in figure17 (a). Substrate coated with polymeric solution 5 having 2% of cross linked polymer showed very intermediate aggregation of particles and some balloon type air gaps as shown in figure17 (b). Substrates coated with polymeric solution 4 containing 1% of cross linked polymer showed very less aggregation of particles as shown in figure17 (c).

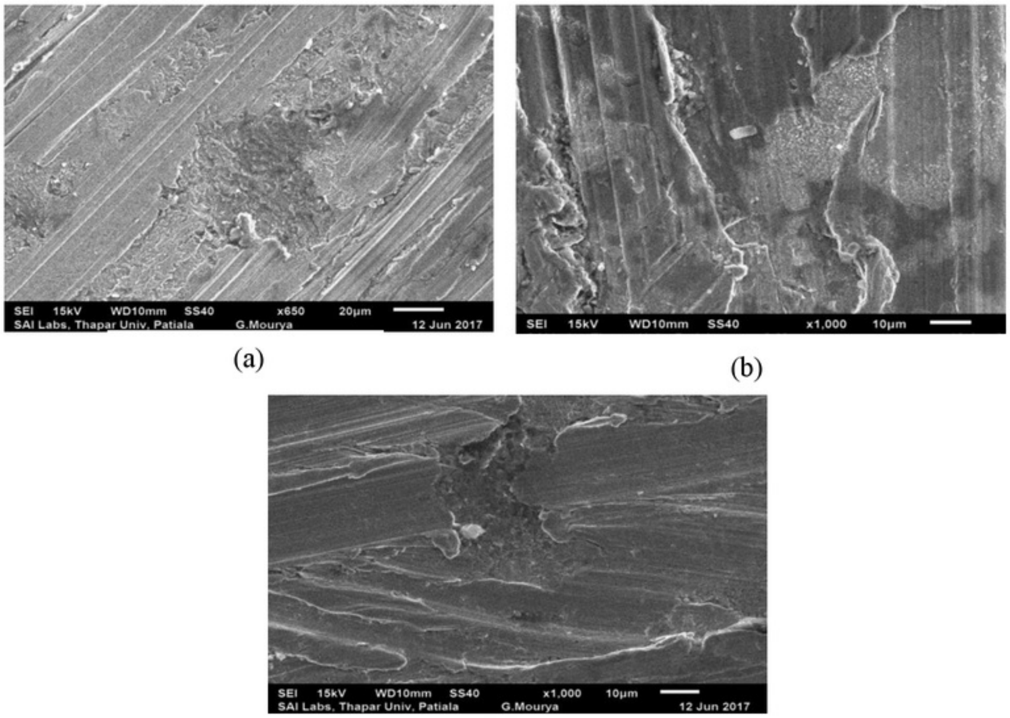


(a) (b) (c)

**Figure17**. SEM images of MS substrates coated with polymeric solution having (a) 3%, (b) 2% and (c) 1% of cross linked polymer.

*(ii) Surface morphology of MS substrates without coating*

After corrosion test, polymeric coating of MS substrates was removed. Then, surface morphology of MS substrates determined using SEM analysis. SEM analysis determined that substrate coated with polymeric solution having 1% of cross linked polymer as shown in figure18 (c) showed less corrosion as compared with substrates coated with sample solution having 3% and 2% as shown in figure18 (a) and (b) respectively.



(a) (b)

(c)

**Figure18**. SEM images of MS substrates after removing the polymeric coating containing (a) 3%, (b) 2% and (c) 1% of cross linked polymer

# Conclusion

Solvent based polymeric coatings were prepared by ex-situ addition of cross linked polymer in order to inhibit corrosion of mild steel (MS) substrates at pH 3, 4 and 5. The measurement of substrate weight before and after corrosion test, concluded that Substrates coated by using sample solution having 1% of cross linked polymer showed less weight loss as compared with substrates coated by using sample solutions having 3% and 2%. EIS study revealed that substrate coated with sample solution containing 1% of cross linked polymer has maximum value of coating resistance ($R_P$ = 2200 ohm.cm$^2$) as compared with sample solution having 2% and 3% of cross linked polymer. SEM analysis determined that substrate coated with polymeric solution containing 1% of cross linked polymer showed less corrosion as compared with substrate coated with sample solution having 3% and 2% of cross linked polymer.

# Harleen_14-07-2017

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PRIMARY SOURCES

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| 7 | Quan, Xiaodong, Jixiao Wang, Song Zhao, Zhi Wang, and Shichang Wang. "Preparation of multifunctional conductive polymers with-C=N-conjugated system and amino groups and application as active coating additives", Reactive and Functional Polymers, 2016.<br>Publication | <%1 |
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