ANTI-CORROSION BEHAVIOUR OF BARRIER, ELECTROCHEMICAL AND SELF-HEALING FILLERS IN POLYMER COATINGS FOR CARBON STEEL IN A SALINE ENVIRONMENT

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

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ABSTRACT

Coatings serve many purposes on metallic surfaces, including tribological coating, anti-static coating, electromagnetic shielding coating, anti-reflective coating, and anti-corrosion. Polymer coatings for corrosion protection of metallic substrates are mostly related to long-term performance needs. In addition to the barrier effect, the coating must have the ability to inhibit the corrosion process if the protective barrier is disrupted. Incorporating fillers, such as metallic oxides, layered fillers and conducting polymer, improves long termed anti-corrosion along with barrier, mechanical, electrical and optical, rheological, and adhesion properties, and resistance to the environmental degradation. The mechanism of protection of incorporated fillers can be divided into different types: barrier, electrochemical, and self-healing. Further, the anticorrosive paints, containing lead or hexavalent chromium as active pigments, represent a risk to human health and the environment. Furthermore, restrictions imposed by national and international agencies on the use of classical red lead, lead chromate, and zinc chromate, have led towards the development of non-toxic organic and inorganic anticorrosion pigments incorporated in the polymer.

In this thesis, three anti-corrosion fillers were investigated for the protection of carbon steel: (1) Graphene as a barrier filler, (2) Nickel Zinc Ferrites as electrochemical filler, (3) and Poly (ortho-anisidine) doped with heteropolyanions as the self-healing filler.

Poly (vinyl butyral) (PVB)/graphene coatings showed improved barrier protection and short-term electrochemical properties for carbon steel. The PVB/graphene nanocomposite coating exhibited lower long-term electrochemical protection due to water uptake. On the other hand, functionalized graphene/PVB coatings improved both electrochemical and barrier
properties. Large increase in pore resistance of the functionalized graphene/PVB coatings indicated lower water penetration through the coatings. Furthermore, Polyaniline-functionalized graphene (PA-G)/PVB coatings showed better protection for carbon steel for very long times, compared to unmodified graphene/PVB and functionalized graphene/PVB coatings.

The long-term electrochemical properties of ferrites were studied both in solution, and polymer coatings. In solution, the corrosion inhibition was inversely proportional to increasing concentration of cations in ferrites (Zn and Ni). The increased corrosion was attributed to the galvanic corrosion of steel due to the adsorption of metallic cations from the ferrites. In polymer composite coating, increased corrosion protection was observed with increasing ferrite concentration up to 1 wt. percent of ferrites. A mechanism of corrosion protection of steel with ferrites in polymer coatings was demonstrated. The metallic cations traveled to the surface of the polymer coating, forming a protection layer which stopped further corrosion of the substrate.

The self-healing coatings were developed by doping poly (o-anisidine) (PoA) with hetero-atoms such as Tungsten silicic acid (TSA), and phosphomolybdic acid (PMA). The doped PoA were further incorporated in PVB to manufacture a composite coating for steel protection. The doped-PoA/PVB coating exhibited increased positive open circuit potential after 45 hours of immersion compared to that of neat PVB coating. The open circuit profile of doped-PoA/PVB coating further indicated the self-healing mechanism corresponding against the corrosion process.
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CHAPTER-1 INTRODUCTION

The corrosion process is an electrochemical reaction between metals with its environments which results their deterioration. During this process, the transfer of charge from one species to another which results in impairment of metal as shown in Figure 1.1 for sodium chloride aqueous media where chloride ions accelerate the corrosion process. The accelerating corrosion process involves the dissolution of an iron oxide film with the aid of chloride ions and also sodium and chloride ions enhance the transportation of electrons.

![Figure 1.1 Schematic diagram of iron corrosion process, production, and consumption of electrons resulting corrosion products](image)

Generally, during corrosion, the oxidation of metals (anodic reaction) and reduction (cathodic reaction) of other groups e.g. oxygen, hydrogen ion or water depends on the surroundings including humidity, salty environments, acidic rains, and natural waters. The possible corresponding cathodic reactions to an anodic reaction are given as

Anodic reaction.

\[ M \rightarrow M^{n+} + ne^- \text{AcidicSolution} \]

Cathodic reactions

\[ 2H^+ + 2e^- \rightarrow H_2 \text{AcidicSolution} \]
Corrosion process can be slowed down using many methods such as cathodic protection, material selection, environmental alteration, design, and coatings. Effective physical barriers to corrosion such as coatings are the most suitable route to protect the metallic surfaces. These kind of coatings provide suitable barrier which further provide resistance to the corrosive species to reach at the surface. To enhance the performance of these barrier coatings, anti-corrosion fillers are added which further interfere with the metal surface during corrosion and provide protection. Anticorrosive paints contain lead or hexavalent chromium as active pigments. The restriction on the use of classical red lead, lead chromate, and zinc chromate is due to the increasing environmental and rigorous national and international rules, as these pigments foul the environment and represent a risk to human health.

Reinforcement with nanometer size fillers can overcome many of the weaknesses in polymers. Additionally, property enhancements (mechanical and anti-corrosion) can be achieved at significantly lower weight percent of the nano fillers (filler loadings) than conventional micron-sized fillers. Higher is the surface-to-volume ratio can lead towards the larger number of atoms to exist on the surface than inside the particle itself. Present scenario of application of nanotechnology in the area of corrosion inhibition of metals has achieved considerable attention and importance. Many authors have already shown nanoparticles ability to perform better.

\[
4H^+ + O_2 + 4e^- \rightarrow 2H_2O \text{Acidic Solution with oxygen}
\]

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{Neutral of Alkaline Solution}
\]

\[
2H_2O + O_2 + 4e^- \rightarrow 4OH^- \text{Neutral of Alkaline Solution with oxygen}
\]

\[
M^{2+} + e^- \rightarrow M^+ \text{Metal ions with multiple valency}
\]

1.1 Polymeric coatings and Anti-corrosion pigments
performance in composites of coatings of polymers. Nanocomposites are defined as having, at least, one dimension of the dispersed particles in the nanometer range.

1.2 Inorganic anti-corrosions pigments

Inorganic pigments are also extensively used in coatings for enhancement of anti-corrosion, barrier, mechanical, optical, rheological, adhesion properties and resistance against environmental degradation etc owing to their structural features. Polymer/Al$_2$O$_3$nanocompsites dispersion coated on carbon steel which showed improved scratch and wears resistance along with hardness of the hybrid whereas corrosion inhibition properties are shown by electrochemical testing were almost the similar to the polymer coating. The improvements in the mechanical properties were attributed towards the dispersion hardening of Al$_2$O$_3$ nanoparticles in polymer coatings$^3$. In a research work epoxy coatings containing nanoparticles of SiO$_2$, Zn, Fe$_2$O$_3$ and halloysite were applied on steel substrates. Figure 1.2 and Figure 1.3 shows the beneficial role of the nano fillers as anti-corrosion pigments in epoxy coatings after immersion in corrosive solution for 28 days. Different protection mechanisms were proposed for mentioned oxides. Zn nanoparticles and Fe$_2$O$_3$ were worked as both an anodic-type inhibitor and a good nano-filler alongside good barrier in case of Fe$_2$O$_3$ to significantly inhibited corrosion of bare steel$^4$. The fillers can be divided on the basis of their protecting ability when corrosive solution enters in the coatings. The protecting abilities of the anti-corrosion fillers in coating can be best measured by using electrochemical techniques for example, the pore resistance represent the coating resistance, positive shift in open circuit potential indicates the formation of passive protective layer on the surface etc
1.3 Conducting polymers anti-corrosion pigments

The $\pi$-conjugation in the main chain of polymer represents the class of conducting polymers. The oxidation or reduction possibility of Cps through doping has made them the most distinctiveness materials. Along with many applications of conducting polymers, they are specifically used for corrosion protection. Conducting polymers can be blended or composite depend upon the matrix system. Besides developing the blends, the derivatives, and different forms of conducting polymers are also developed i.e. emerald base, or emerald salt form of

Figure 1.2 Temporal evolution of corrosion rate of epoxy-coated steel in (a) 0.3 wt. percent NaCl solution, and (b) 3 wt. percent NaCl solution, as a function of nanoparticles (Reprinted from Surface and Coating Technology, 204/3, S. Xianming, N. Tuan Anh, S.Zhiyong, L. Yajun, A. Recep, Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating, 241, Copyright (2016), with permission from Elsevier)
polyaniline. Polyaniline, polypyrrole, poly-o-anisidine and polythiophene and their derivatives have gained much attention for corrosion protection.

![Figure 1.3 Temporal evolution of polarization resistance of epoxy-coated steel in (a) 0.3 wt. percent NaCl solution, and (b) 3 wt. percent NaCl solution, as a function of nanoparticles. (Reprinted from Surface and Coating Technology, 204 /3, S. Xianming, N. Tuan Anh, S.Zhiyong, L. Yajun, A. Recep, Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating, 241, Copyright (2016), with permission from Elsevier)](image)

Generally, conducting polymers have poor mechanical properties which can improved by using blending approach with certain kind of polymer coatings like epoxy, polyurethane, polyimide, acrylic etc. In a recent report, different forms of polyaniline such as emeraldine salt and emeraldine base doped with different kind of dopants were incorporated in epoxy coatings. The EB form of Pani has demonstrated superior anticorrosive properties than ES also the behaviour was strongly dependent on the nature of dopant [29]. Conducting polymers have also
found application in marine coatings as an anti-fouling agent. In marines sulphonated polyaniline was reported as anti-corrosion pigments in coatings.

1.4 Protection mechanism

In general, the corrosion inhibition of metals can be attributed to interactions between electrons of inhibitor and empty orbital of metals which result in the formation of metal protective surface complexes. These protective films slow down the deterioration process of metals by suppressing either cathodic, anodic.

1.4.1 Inorganic pigments

Corrosion inhibitors can be classified as organic and inorganic. Inorganic corrosion inhibitors include sulfites, ferric salts, nitrates and calcium ions etc. The protection mechanisms offered by inorganic inhibitors are based on their type. For example, sulfites consume the dissolved oxygen in solutions to reduce oxygen availability to retard corrosion, ferric salts and nitrates foster passivity of metals in active-passive regions, and the calcium ions reinforce the protective films forms on metal surfaces. Inorganic pigments such as litharge, metallic lead, red lead, basic lead carbonate, hexavalent chromium compounds, and zinc oxide have been extensively used in polymer coatings for the enhancement of anti-corrosion, barrier, mechanical, electrical and optical, rheological and adhesion properties, and resistance against the environmental degradation. Certain metallic cations in solutions can also be used to retard corrosion of metals in different environments. Metallic cations affect the electrochemical process of corrosion. The metallic cations find applications in various processes; I) inhibiting hydrogen evolution by Cd$^{2+}$, Mn$^{2+}$, Ce$^{4+}$; II) corrosion inhibition of titanium and stainless steel in passive regions by Fe$^{3+}$ and Cu$^{2+}$ via fostering passivity of these metals by the action of these...
cations in the cathodic reactions\textsuperscript{16, 17, 18}; III) corrosion retarding properties of lead anode in sulphuric acid by \(\text{Co}^{2+}\) ions via increasing catalytic activity of surface oxides for oxygen evolution which in turn increases the current efficiency of the oxygen evolution reaction; and hence little current is available for counter anodic reaction\textsuperscript{19}, IV) corrosion inhibition of iron by reducing corrosion promoting species using \(\text{Sn}^{2+}\) ions in acid pickling process\textsuperscript{20}.

### 1.4.2 Organic pigments (Conducting Polymer)

Similarly, various protection mechanisms using conducting polymer have been proposed. Spinks et al. \[14\] presented a review paper in which the classification the Cps coatings were based on their protection mechanisms. The reported mechanisms were barrier protection, corrosion inhibitions, and anodic protection. Barrier mechanism deals with the disconnection of the metal surface from the corrosive environment such as coatings of surfaces with paints. In the case of corrosion inhibitions, the purpose of the applied coating is to slow down the rate of corrosion due to the formation of a monomolecular layer on the surface. During electro-polymerization of the Cps, this method is used for easy deposition of Cps, depending upon the material and electrolyte solution used \[14\]. Similarly, nano-polyaniline and poly-o-anisidine were synthesized using microemulsion polymerization and formulated using alkyd paint for coatings on mild steel. Water lose measurement showed the nano PANI/Alkyd coatings showed considerable protection against corrosion than the POA/alkyd coatings\textsuperscript{23}. In a similar work, nano-polyaniline blended with epoxy-esters system. Figure 1.4 showed the TEM image of nanopolyaniline which depicted spherical shape with a particle size less than 30 nm. This morphological characteristic is mainly dominated by the shape and size of micelles formed during polymerization.
In this work, they used Nyquist plots and showed the anticorrosion performance of EPE and n-PANI(DBSA)/EPE coatings. According to them, two stages of corrosion mechanism including "intact" (without corrosion reaction occurrence) and "defected" (with corrosion reaction occurrence) stages are recognizable from one-part semicircle and a two-part semicircle of the Nyquist plots, respectively as shown in Figure 1.5. For the intact stage, by comparing Figure 1.5a with Figure 1.5b it can be inferred that semicircle of n-PANI(DBSA)/EPE coating is incomplete relative to EPE coating system. This indicates that n-PANI(DBSA)/EPE has longer intact time.

Figure 1.4 TEM image of synthesized n-PANI(DBSA) particles via inverse microemulsion polymerization (Reprinted from Progress in organic coating, 75 /4, Reza Arefiniaa, Akbar Shojaei, HomiraShariatpanahi, JaberNeshati, Anticorrosion properties of smart coating based on polyaniline nanoparticles/epoxy-ester system, 504, Copyright (2016), with permission from Elsevier)

Figure 1.5b and Figure 1.5c EPE and n-PANI(DBSA)/EPE coatings comprised of two distinct parts which indicate the detected stage. In this stage, the first part (semi-circle) and the second part (non-circular) of the Nyquist plots are attributed to the impedance of
coating and corrosion phenomena, respectively. Therefore, according to the second part of the Nyquist plots, three different states including kinetic (semicircle), diffusion (straight line) or mixed kinetic diffusion (semicircle followed by a straight line) controlled mechanisms can be recognized during the immersion period\textsuperscript{24}. Similar results were confirmed by sing nano-polyaniline fibers with epoxy coatings\textsuperscript{25}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.5.png}
\caption{Nyquist plots for the (Left) EPE and (Right) n-PANI(DBSA)/EPE coating in 3.5 percent NaCl solution (a) intact stage defected stage under (b) kinetic and (c) mixed kinetic diffusion control mechanisms (Reprinted from Progress in organic coating, 75 /4, Reza Arefiniaa, Akbar Shojaei, HomiraShariatpanahi, JaberNeshati, Anticorrosion properties of smart coating based on polyaniline nanoparticles/epoxy-ester system, 505, Copyright (2016), with permission from Elsevier)}
\end{figure}
1.5 Inorganic anti-corrosion pigments to be used in Coating

Following are the different kinds of inorganic and organic pigments used in our research work. For inorganic pigments ferrites such as Ni\(_{(x)}\)Zn\(_{(1-x)}\)Fe\(_2\)O\(_4\) and Graphene whereas for organic pigments conducting polymers like Polyaniline and Poly ortho-anisidine were selected for anti-corrosion studies.

1.5.1 Nickel Zinc Ferrites and Nickel Ferrites

Spinel-based inorganic pigments (general formula AB\(_2\)X\(_4\)) have shown superior thermal and weather degradation resistance and are also environment benign\(^{13}\). The applications of these pigments have been proven in the fields of biomedical\(^{26}\), semiconductors\(^{27}\), smart materials\(^{28}\), magnetic and optical materials\(^{29}\). The spinel-based pigments can be produced by combination of two or more metallic cations in lattice structure of metallic oxide, according to the following reaction indicated by equation:

\[
MO + A_2O_3 \rightarrow MO.A_2O_3
\]

where, M and A can be metallic cations etc. MO.A\(_2\)O\(_3\) consists of an almost cubic, closely packed oxygen arrangement in which the cations reside on the tetra- and octahedral interstices\(^{30}\).

In spinal-based inorganic pigments, using ferrites can be used as anticorrosion pigments: ferrites retain their anticorrosion efficiency even exposing to higher temperatures and aggressive environment\(^{31}\). The inhibition action of the extracts depends on the solubility of pigments in a corrosive solvent, development of passive layer on metals separating metals from the corrosive media, thickness and nature of the passive layer, and the nature of electrolyte\(^{32}\).
1.5.2 Graphene

Graphene, a two-dimensional sp²-hybridized carbon sheet, is currently a widely studied material. This single-atom-thick sheet of C-atoms arrayed in a honeycomb pattern is the world’s thinnest and stiffest material which is also an excellent conductor of heat and electricity. Graphene is considered more promising than other nanostructured C-fillers such as 1-dimensional CNTs and 0-dimensional fullerenes in various applications. Due to its high electrical conductivity (6000 S/cm), Young’s modulus (~1TPa) and thermal conductivity (5000 W/(m.K)) along with very high surface area (theoretically 2600 m²/g), graphene has been vastly used in areas such as conducting polymer nanocomposites, field effect transistors, transparent conducting films, gas sensors, clean energy devices and diodes, etc.

Figure 1.6 Representation of graphene as the building block for graphite, CNTs and fullerenes (adapted from [37]).

(Reprinted (adapted) with permission from (Graphene/Polymer Nanocomposites, Hyunwoo Kim, Ahmed A. Abdala and Christopher W. Macosko, Macromolecules, 2010, 43 (16), pp 6515–6530). Copyright (2016) American Chemical Society.)
1.5.3 Polyaniline and Poly o-anisidine

Conducting polymers belong to special class of polymer due to conductivity, low cost, stability, non-toxic, easiness in synthesis and doping primacy. Besides developing the blends, the derivatives, and different forms i.e. EB, or ES in the case of Polyaniline are already developed. Polyaniline, Poly o-anisidine, Polypyrrole, and Polythiophene and their derivatives have gained much consideration. The interest in Polyaniline grew starting from the 1960s, owing to its remarkable electrical properties. Poly o-anisidine, and Polythiophene come under the class of poly heterocyclic.

1.6 Thesis organization

This thesis addresses the following objectives:

1. Selection and preparation of suitable nano-inorganic pigments such as ferrites, graphene and conducting polymers which have the ability to withstand aggressive environments.

2. Formulation of suitable coating using these pigments into coatings.

3. Evaluation of these anticorrosion pigments using electrochemical corrosion testing.

4. Understanding the corrosion protection mechanism of novel anticorrosion pigments.

This thesis is structured as follows:

**Chapter 1:** Introduction.

**Chapter 2:** This chapter deals with the solution properties of graphene oxide in corrosive media was studied in the presence of carbon steel. The purpose of this work was to understand the effect of graphene oxide on corrosion properties of steel. This chapter provides a detail on the effect of graphene oxide nanoplatelets on electrochemical properties of steel in saline media. The whole section of Chapter 2 was Reproduced from Ref. (Effect of graphene oxide nanoplatelets
on electrochemical properties of steel substrate in saline media, AU Chaudhry, V Mittal, B Mishra, Materials Chemistry and Physics, 163, 2015, 130-137.) with permission from Elsevier and a part Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

**Chapter 3:** This Chapter provides a detail on corrosion inhibition provided by unmodified graphene nanoplatelets in polymer coatings. The whole section of Chapter 3 was Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

**Chapter 4** This Chapter provides a comparison between unmodified graphene nanoplatelets and graphene produced by plasma modified graphene in polymer coatings on corrosion inhibition properties coatings. This Section of Chapter 4 will be submitted for publication in a peer-reviewed journal. This whole of the chapter is reproduced with minor changes. AU Chaudhry, Vikas Mittal, Brajendra Mishra and a part Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

**Chapter 5.** This Chapter provides a detail on corrosion inhibition properties by polyaniline modified graphene in polymer coatings. This Section of Chapter 5 will be submitted for publication in a peer-reviewed Journal of Reinforced Plastics and Composites. This whole of the chapter is also reproduced with minor changes. AU Chaudhry, Vikas Mitta, Brajendra Mishra and the minor Section of Chapter 5 was Reproduced from Ref. (Nano nickel ferrite (NiFe$_2$O$_4$) as
anti-corrosion pigment for API 5L X-80 steel: An electrochemical study in acidic and saline media, AU Chaudhry, V Mittal, B Mishra, Dyes and Pigments, 118 (98) 2015, 18-26,) with permission from Elsevier

**Chapter 6** This chapter provides a detail on corrosion inhibition provided by nickel zinc ferrites in solutions. The whole section of Chapter 6 was Reproduced from Ref. (Ni0.5Zn0.5Fe2O4 as a potential corrosion inhibitor for API 5L X80 steel in acidic environment, AU Chaudhry, R Bhola, V Mittal, B Mishra, Journal of Electrochemical Science 9 (2014) 4478 - 4492,) with permission from ESG and a part Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

**Chapter 7** This Chapter provides a detail on corrosion inhibition provided by nickel ferrites in corrosion solutions in the presence of carbon steel. The whole Section of Chapter 7 was Reproduced from Ref. (Nano nickel ferrite (NiFe2O4) as anti-corrosion pigment for API 5L X-80 steel: An electrochemical study in acidic and saline media, AU Chaudhry, V Mittal, B Mishra, Dyes and Pigments, 118 (98) 2015, 18-26,) with permission from Elsevier and A part of Chapter was Reproduced from Ref. (Evaluation of iron-nickel oxide nanopowder as corrosion inhibitor: Effect of metallic cations on carbon steel in aqueous NaCl, AU Chaudhry, V Mittal, B Mishra, Corrosion Science and Technology, 15 (1) 2016, 13-17) with permission from CST, and a part Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

**Chapter 8** This chapter provides a detail on corrosion inhibition properties by nickel zinc ferrites in polymer coatings. This section of Chapter 8 will be submitted for publication in a peer
reviewed journal (CORROSION). This whole of the chapter is reproduced with minor changes.

AU Chaudhry, Vikas Mitta, Brajendra Mishra and minor section of Chapter 8 was Reproduced from Ref. (\(\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\) as a potential corrosion inhibitor for API 5L X80 steel in acidic environment, AU Chaudhry, R Bhola, V Mittal, B Mishra, Int. J. Electrochem. Sci., 9 (2014) 4478 - 4492,) with permission from ESG and minor Section of Chapter 8 was Reproduced from Ref. (Nano nickel ferrite (\(\text{NiFe}_2\text{O}_4\)) as anti-corrosion pigment for API 5L X-80 steel: An electrochemical study in acidic and saline media, AU Chaudhry, V Mittal, B Mishra, Dyes and Pigments, 118 (98) 2015, 18-26,) with permission from Elsevier

Chapter 9. This chapter provides a detail on corrosion inhibition properties by poly orthoanisidine in polymer coatings. This section of Chapter 9 will be submitted for publication in a peer-reviewed journal by AU Chaudhry, Vikas Mitta, Brajendra Mishra and the minor section of Chapter 9 was Reproduced from Ref. (Inhibition and promotion of electrochemical reactions by graphene in organic coatings, AU Chaudhry, V Mittal, B Mishra, RSC Advances, 5 (98) 2015, 80365-80368,) with permission from the Royal Society of Chemistry

Chapter 10 This chapter deals with the conclusion and future recommendation

Chapter 11 Appendix A containing copyrights for the papers and figure reused in this thesis.
Papers were published in *Materials Chemistry and Physics* and *RSC Advances*

A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

There has been increased interest in using graphene oxide (GO) in various industrial applications such as working fluids, lubricants, oil and gas fields, heavy metal removal from water, anticorrosion paints and coatings etc. The electrochemical properties of steel were studied in the presence of suspended GO in saline media. GO suspension has been characterized using Transmission electron microscopy (TEM) and X-ray diffractometer (XRD). We measured the effect of the GO concentration (0–15 ppm) on electrochemical properties of steel using different techniques: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic (PD) methods. Results indicate that the suppression of corrosion is directly proportional to increasing GO concentrations in saline environments. Surface morphology of corroded samples was examined using Scanning Electron Microscopy (SEM). Identification of the elements at accumulated layer was estimated from peaks of energy dispersive x-ray spectroscopy (EDX) and XRD. Increased protection abilities with increasing GO concentration have been attributed to the domination of salt layer presence at the surface of steel which occurs via precipitation of sodium chloride. Surface analysis confirms that there is no direct effect of GO on the protection behavior of steel. The presence of GO in the solution can enhance the precipitation of NaCl due to the decreased solubility NaCl which further slows down the corrosion. The Pourbaix diagram shows that GO forms an anionic compound with sodium which may enhance the precipitation at working electrode.
2.1 Introduction

Graphene oxide (GO), two-dimensional hydrophilic oxygenated layered sheets attracted due to many factors such as very large surface area, in solution processing, good physical and mechanical properties. Further deoxygenation leads towards improvements in the aforementioned properties of GO. Dreyer et al. reported many types of functional groups at basal planes and including epoxy, hydroxyl, carboxylic and alcohols. Figure 2.1 represents Hummer’s method for synthesis of GO. This produces an intercalated structure of oxidized sheets of graphite with the aid of strong oxidizing agent and concentrated sulphuric acid. The anchored oxygenated GO to produce stable dispersion in many polar and non-polar solvents including water which is the most important and widely used medium for many industrial applications. The dispersing ability of GO in many solvents more specifically in water is because of the ignitable carboxylic acid at the edges act as hydrophilic whereas phenol hydroxyl, epoxide groups at basal planes act as a hydrophobic area. The properties such as large surface area and amphiphilic nature make GO suitable for various industrial applications. It includes the stabilization of multiphase systems like oil and water interface, enhanced oil recovery, stabilization of CO₂ foam, a surfactant for detergents and emulsifiers, dispersing agent, desalination and water purification, and for delivery purposes of nanoparticles in deep oil reservoirs.

Recently, Yoon et al. reported the stabilization of oil and water emulsions in 5 wt percent NaCl using GO at low concentration. This behavior of GO was attributed towards the presence of high charge density at the edges due to the presence of carboxylic anions. These anions slightly extend out into the water phase and stabilize the interface. It was also presented that GO adsorbs at the oil/water interface and promote the stabilization.
Corrosion is an electrochemical process having deterioration effect on the metal or alloy. For iron, corrosion produces porous and pervious film which is composed of different forms of iron oxide. It can be seen from Figure 2.2 that redox reactions are occurring on the surface. The presence of sodium and chloride ions acting as an electrolyte, where chloride ions accelerating the corrosion process by destroying any type of passivity which increases the active corrosion rate. In this case, the accelerating corrosion process involves the dissolution of iron oxide film and in addition sodium and chloride ions also enhance the transportation of electrons

In recent literature, anti-corrosion properties of graphene oxide and reduced graphene oxide (rGO) have also been reported for different metals. The main associated protection mechanism was a barrier to the corrosive media.

Figure 2.1 Graphene oxide synthesis and structure
Recently, polystyrene/graphene nanocomposites showed superior anti-corrosion properties with the incorporation of 2 wt. percent of modified reduced (r-GO) owing to excellent barrier properties.50

Similar results were shown for the composites of silane modified r-GO/polyvinyl butyral (PVB)51 and graphene/pernigraniline/PVB 52. With so many potential and possible solution based applications of GO, it is necessary to see the effect of GO on corrosion properties of metals in the presence of corrosive media such as saline solution. In this work solution based electrochemical testing of dispersed GO were observed using carbon steel as working electrode in 3.5 wt. percent NaCl solution containing a various concentration of GO.

![Figure 2.2 Schematic diagram of iron corrosion process, production, and consumption of electrons resulting corrosion products](image)

2.2 Materials and Methods

2.2.1 Materials

Nano-Graphene Oxide aqueous solution (concentration: 1g/L, pH: 2.90 diameters: 90 nm, +/-15 nm, thickness: about 1 nm, single layer ratio: >99 percent, Purity: >99 percent as provided by the supplier) was purchased from Graphene supermarket, USA and used as received. The industrial steel used in this study was cut from pipeline. API-5L X80 steel coupons (elemental
composition (wt. percent): C 0.07, Mn 1.36, Ti 0.008, S 0.003, P 0.004, Cr 0.45+Ni and remaining Fe), were machined to 10 × 10 × 4 mm dimensions and a tap and drill hole of 3- 48 tpi (threads per inch) was drilled to one long side of the coupon. Machined carbon steel is used as the working electrode and the exposed surface area was 3.4 cm². The specimens were surface finished using different grades of SiC grit papers up to 240 grit to ensure the same surface roughness, followed by cleaning and degreasing with industrial grade acetone and ethanol followed by drying in air. To evaluate the protection behavior of Nano-GO, solution was prepared in 3.5 wt. percent NaCl with varying concentration of GO i.e. 0-15 ppm. Table 2.1 shows the pH of GO solution with 3.5 wt. percent NaCl. The decreasing trend in the pH of the GO solution was due to the higher pH of the original solution.

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>0</th>
<th>3</th>
<th>9</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.80</td>
<td>5.7</td>
<td>5.4</td>
<td>5.38</td>
<td>5.35</td>
</tr>
</tbody>
</table>

### 2.2.2 Electrochemical Measurements

A three-electrode cell assembly consisting of steel coupon as the working electrode (WE), graphite as the counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode (RE) were used for the electrochemical measurement (Figure 2.3). Electrochemical testing was performed in a closed system under naturally aerated conditions using a Gamry 600 potentiostat/galvanostat/ZRA at room temperature. The sequence of electrochemical techniques is described below. Corrosion studies were carried out in 3.5 wt. percent NaCl containing a varying concentration of GO (0-15 ppm).
2.2.3 Open circuit Potential (OCP)

The open circuit potential of steel samples was recorded against SCE for five hours in solutions of 3.5 wt. percent NaCl with different concentrations of GO. After the completion of OCP; EIS, LPR, and PD were measured by closely following the ref. 55

2.2.4 Electrochemical impedance spectroscopy (EIS)

Impedance measurements were performed as a function of open circuit potential after five hours from the time of immersion. The frequency sweep was performed from $10^5$ to $10^{-2}$ Hz at 10 mV AC amplitude. To simulate the electrochemical interface, EIS data was analyzed with Echem analyst using circuit model having electrical equivalent parameters, where $R_c$ is the charge transfer resistance, $L$ is the inductor and CPE is the constant phase element. Accordingly, the impedance can be represented by the following equation

$$Z(CPE) = Y_o^{-1} [j\omega]^{-n}$$
Where $Y_o$ is the CPE constant, $\omega$ is the angular frequency (rad/s), $j = \sqrt{-1}$, and $n$ is another CPE constant that varies from 1 to 0 for pure capacitance and pure resistor, respectively. The Double layer capacitance $C_{dl}$ has been calculated using the following equation:

$$C_{dl} = Y_o \left[ j\omega^n \right]^{n-1}$$

where $\omega^n$ is the frequency found at the maximum of the imaginary part of the impedance, $Z''$.

Figure 2.4 A representative circuit model used to model the electrochemical impedance spectroscopy

### 2.2.5 Linear Polarization resistance (LPR)

For linear polarization resistance measurements, the electrodes were scanned from -0.02 to +0.02 V vs open circuit potential after 5 hours of immersion with a scan rate of 0.125 mV/s. The polarization resistance can be measured using slope of the polarization curve ($\Delta E / \Delta i$) at origin using seed values of 0.11 voltage/decades for Tafel constants, i.e. for $\beta_a$ and $\beta_c$.

### 2.2.6 Potentiodynamic polarization (PD)

The Potentiodynamic polarization measurements were performed at six hours of immersion by polarizing the working electrode from an initial potential of -500 mV up to a final potential of 500 mV compare to open circuit potential. A scan rate of 0.1667 mV/s was used for
the polarization sweep\textsuperscript{56, 57}. Corrosion current densities $i_{\text{corr}}$ were obtained by extrapolating anodic and cathodic linear segments of Tafel plot using Echem Analyst.

2.2.7 Surface characterization

Steel coupons were carefully disengaged from the cell assembly, dried and observed under the microscope. JEOL JSM-7000F, Field Emission Scanning Electron Microscopy (FE-SEM) was performed to evaluate surface morphology and for elemental composition of the corrosion products, energy dispersive spectroscopies (EDS) were examined at 5 kV under high vacuum at a working distance of 10 mm. X-ray diffraction (XRD) was also performed to differentiate between the various phases present in the corrosion products over the metal coupon. Philips PW 3040/60 spectrometer using Cu Kα radiation in the range of 10° to 100° with a scan rate of 0.050° was used and the peaks and planes were analyzed using X'Pert High Score software and compared with obtained data with JCPDS cards issued by ICDD.

2.2.8 GO characterization

Transmission electron microscopy (TEM) imaging was performed to characterize the GO. FEI Philips C200 TEM with a point-to-point resolution of 0.11 nm, at 200 kV was used. The samples were prepared by dispersing approximately 1 mg of GO in 10 mL of methanol and sonicating for one hour in a water bath at room temperature. One drop of the suspension was then deposited on a 400-mesh copper grid covered with a thin amorphous film to view under the microscope.
2.3 Results and Discussion

Figure 2.5a shows the few layers thick flakes of GO as produce by modified hummer method. Figure 2.5b depicts the x-ray diffraction pattern for GO, where the strong and sharp peak at $2\theta \sim 12^\circ$ corresponds to an interlayer distance of 7.6 Å (d002).

Figure 2.5 TEM micro-image a) and X-ray diffraction b) of GO
The OCP measurements were accomplished to measure the equilibrium or the corrosion potential of subjected carbon steel in the presence of GO suspension. Figure 2.6 showed the potential changes of working electrode in salt solution during five hours immersion with and without GO nano platelets. As compared to the blank solution, after five hours there is a negative shift in the corrosion potentials of the working electrodes and slightly move towards more negative with increased concentration of nano-sheets. The OCP of steel surface in blank solution was recorded approximately 713 mV$_{SCE}$ whereas in the presence of suspended GO, it falls between 715 mV and 745 mV. The result implies that presence of GO in solution has slight effect on the electrochemical potential of the steel. The trend was found same in all the concentrations except 15 ppm where it continues to fall and finished at 745 mV$_{SCE}$. The OCP of blank and another concentration was decreasing first and then slightly increasing having different ending potentials.

Figure 2.6 Open circuit potential with time of exposure to 3.5 wt. percent NaCl Blank and with different concentrations of GO
Further the slight shift in potential towards negative in case of higher concentration of GO could be due to the decrease in pH\(^{59}\). The behavior of electrochemical processes at electrical double layer such as charge transfer resistance and ions adsorption across the electrode/electrolyte interface can be in and Table 2.2. The figure and table depict the typical set of Nyquist plots and modeled EIS plots (Bode and Nyquist) with monophasic circuit model where charge transfer resistance was calculated from diameter of real part of semicircle. It can be seen that charge transfer resistance is increasing with the GO concentration in the solution. It can also be observed from Figure 2.7 that profile of the Nyquist plots remain similar as the concentration of GO increase which shows that there is no effect on the corrosion mechanism of carbon steel with the addition of GO. Further, the double layer capacitance also increases with the GO concentration and in some cases, it is more than the blank solution i.e. 9 and 12 ppm. Similarly, the value of \(n\) is also decreasing as the GO concentration is increasing, which is also a measure of the surface inhomogeneity; the lower is its value, the higher is the surface roughening of the metal/alloy\(^{60}\). Moreover, \(Y_o\) the value is also increasing with the increased concentration of GO, the higher \(Y_o\) value shows that more surface area is available for the electrochemical reaction\(^{61}\) due the presence of Cl\(^-\) ions which increases the film free area\(^{62}\). In case of Blank solution a porous corrosion product iron oxide is forming which increase the \(C_{dl}\) owing to dielectric effect as given by following equation:

\[
C = \frac{\varepsilon \varepsilon_0 r}{d}
\]

where \(d\) is charge separation distance, \(\varepsilon\) is relative dielectric constant, \(\varepsilon_0\) is permittivity of free space, \(A\) is surface area and \(C\) is capacitance\(^{63}\). The dissolution of this pervious layer is done by
Figure 2.7 Nyquist plots recorded after 5 h immersion in 3.5 wt. percent NaCl, Blank and with different concentrations of GO: 3 ppm, 9 ppm, 12 ppm, 15 ppm

chloride ions but as the addition of GO to the solution, act as an anionic surfactant which decreases the solubility of NaCl in solution\textsuperscript{64} and hence prompt the precipitation of salt on the working electrode. These precipitations create porous and inhomogeneous layers which allow the availability of the corrosive solution to the working electrode. However, this precipitation, appear to render more or less corrosion protection to the metal below by impeding the transportation of reactants and products among the solution and the metal\textsuperscript{63} which results in the increment of charge transfer resistance efficiency up to 70 percent. Further, there is no second arc seen in the Nyquist plots which shows that the layer forming on the surface is porous \textsuperscript{65,66}. Nyquist plots also showed inductance loop in intermediate and low-frequency domain which is mainly ascribed to the occurrence of an adsorbed intermediate on the surface due to chloride ion adsorption on the electrode surface\textsuperscript{62}. The total impedance at intermediate and low frequencies was calculated from charge transfer resistance and inductive element in series. The inductive behavior due to adsorption can be defined as \( L = R\tau \) where \( \tau \) represents the relaxation time for
adsorbed species at the working electrode\textsuperscript{67}. This can be manifested from Table 2.2 that inductance is increasing with a concentration of GO showing increased absorption of salt at the working surface.

Table 2.2 Electrochemical impedance spectroscopy and LPR parameters in 3.5 wt. percent after five hours immersion

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>$R_{ct}$ ($\Omega cm^2$) $\times 10^3$</th>
<th>$Y_o$ ($\Omega^{-1}s^n$) $\times 10^{-03}$</th>
<th>n</th>
<th>$C_{dl}$ ($F cm^2$) $\times 10^{-04}$</th>
<th>L ($H cm^2$) $\times 10^03$</th>
<th>$R_p$ ($\Omega$) (LPR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.27</td>
<td>0.72</td>
<td>0.800</td>
<td>6.57</td>
<td>2.9</td>
<td>373</td>
</tr>
<tr>
<td>3</td>
<td>1.50</td>
<td>0.68</td>
<td>0.776</td>
<td>5.86</td>
<td>5.2</td>
<td>439</td>
</tr>
<tr>
<td>9</td>
<td>1.86</td>
<td>1.28</td>
<td>0.773</td>
<td>9.77</td>
<td>8.2</td>
<td>515</td>
</tr>
<tr>
<td>12</td>
<td>2.41</td>
<td>1.50</td>
<td>0.711</td>
<td>9.97</td>
<td>9.8</td>
<td>592</td>
</tr>
<tr>
<td>15</td>
<td>3.27</td>
<td>1.20</td>
<td>0.727</td>
<td>7.63</td>
<td>18.5</td>
<td>915</td>
</tr>
</tbody>
</table>

Relative probable error 15 percent

Similar results were shown by Figure 2.8 and Table 2.2 where polarization resistance efficiency was increased up to 60 percent. These results are accordance with the EIS result and also indicate that precipitation on the WE slows down the easy transfer of corrosion products and reactant from the bulk solution to WE surface\textsuperscript{68}.

Corrosion kinetic parameters derived from polarization curve and Potentiodynamic polarization scans of blank and with GO varying concentration are shown in Figure 2.9 and Table 2.3. Corrosion current efficiency up to 56 percent can be observed in the case of 15 ppm of GO addition which also agrees with the polarization resistance experiments. There were no noticeable changes in the $E_{corr}$ (825±10) and anodic Tafel slopes (90±10 mV) found which indicate that presence of GO does not significantly affect these parameters. However, cathodic Tafel slopes are higher for a blank solution and has a difference of 40±5 mV/dec which shows the effect on cathodic reaction is suppressing in the presence of GO.
Figure 2.8 Linear polarization resistance after five hours immersion in 3.5 wt. percent NaCl, Blank and with different concentrations of GO: 3 ppm, 9 ppm, 12 ppm, and 15 ppm

Figure 2.9 Tafel plots recorded after 5 hours immersion in 3.5 wt. percent NaCl Blank and with different concentrations of GO: 3 ppm, 9 ppm, 12 ppm and 15 ppm
Table 2.3 Corrosion kinetics parameters of carbon steel in 3.5 wt. percent after five hours immersion

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>(E_{corr}) (mV)</th>
<th>(b_c) (mV dec(^{-1}))</th>
<th>(b_a) (mV dec(^{-1}))</th>
<th>(i_{corr}) ((\mu)A cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-825</td>
<td>-145</td>
<td>90</td>
<td>7.7</td>
</tr>
<tr>
<td>3</td>
<td>-828</td>
<td>-110</td>
<td>103</td>
<td>4.4</td>
</tr>
<tr>
<td>9</td>
<td>-816</td>
<td>-108</td>
<td>90</td>
<td>4.0</td>
</tr>
<tr>
<td>12</td>
<td>-846</td>
<td>-113</td>
<td>98</td>
<td>3.7</td>
</tr>
<tr>
<td>15</td>
<td>-828</td>
<td>-103</td>
<td>88</td>
<td>3.4</td>
</tr>
</tbody>
</table>

It can be further observed from Figure 2.10 that at higher applied potential in anodic region passive behavior was observed and dominant in case of 9 ppm, 12 ppm, and 15 ppm. This passivation behavior cannot attribute towards the presence of oxide films on the carbon steel surface as in the case of stainless steel due to the presence of chromium in the steel composition\(^{69}\).

In Figure 2.10 anodic part of polarization curves for 15, 12 and 9 ppm have been shown where a clear change in passivation behavior can be observed as the concentration of GO is increased. In the case of 15ppm the passive area was comprises over 70 mV whereas it was 60 mV for 12ppm and 40 mV for 9ppm which showed that with the increase of GO concentration the precipitation forming on the surface is more thick or compact impeding the mass transport. The reactions occurring at anodic and cathodic curves in 3.5 wt. percent NaCl are given as\(^{70}\).

\[
Fe \rightarrow Fe^{2+} + e^- \text{ (anodic – reactions)} \\
Fe^{2+} \rightarrow Fe^{3+} + e^- \\
2H^+ + 2e^- \rightarrow H_2 \text{ (cathodic – reaction)} \\
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (Neutral)}
\]
where the formation of a compact and thick layer of precipitates slow down the anodic and cathodic reactions as a results decrease in the corrosion current can be seen at higher applied potentials. Figure 2.11 and Figure 2.12 and show the morphology of the outermost corrosion products layer and their elemental composition where the surface morphology is becoming more compact as increasing GO concentration. This phenomenon indicates that presence of GO fosters the formation of NaCl layer on the surface which slows down the corrosion process. The element analysis for these layers for 9ppm, 12ppm and 15ppm of GO, also show that as the amount of added GO increasing NaCl layer is becoming richer and iron oxide are reducing.

X-ray diffraction pattern data Figure 2.13 for the mixed phases present on the corroded metal surface were characterized by comparing with JCPDS cards issued by ICDD \cite{71}. The surface pattern over the pure steel coupon was also examined. The characteristic peaks of iron carbide, $\alpha$-ferrite and iron carbide chromium observed in the case of carbon steel surface at a 20
~ 44° [(510) JCPDS 20-509], 2θ ~ 65° [(203) JCPDS 5-720] and 2θ ~ 45°[(110) JCPDS 6-696] respectively. These peaks were also observed in all the cases of corroded samples along with NaCl-Iron complex phase at 2θ ~ 27° [(111) JCPDS 11-123] and hydrated NaCl at 2θ ~ 31° [(200) JCPDS 29-1197]. No signals of free carbon were observed on the surface.

Further, Pourbaix diagram Figure 2.14 shows the possible phases at given pH as function of E (potential).

Figure 2.11 SEM micrograph of carbon steel surface after electrochemical testing in 3.5 wt. percent NaCl, Clean surface a) Blank b) and with different concentrations of GO: 3 c), 9 d), 12 e) and 15ppm f)
Figure 2.12 Energy dispersive x-ray spectroscopy of surface 9 a), 12 b) and 15ppm c)
Figure 2.13 X-ray diffraction pattern of corroded surfaces, Clean Surface, Blank and with different concentrations of GO: 3, 9, 12 and 15 ppm

From Table 2.1 (pH) and Figure 2.6 (OCP), it can be observed in the solution of NaCl and graphene oxide, the compound exists in anionic form near or at WE electrode having sodium at one end. This form of a compound having standard reaction Gibbs energy $\Delta G=-227.50$ kcal/mol facilitates the sodium chloride to accumulate on the surface of working electrode. As in the previous literature and Pourbaix diagrams, adsorption of metallic ions such as copper, zinc, lead, cadmium on graphene oxide was reported. It was also reported the formation of strong surface complexation of metal ions with the oxygen-containing groups on the surface of GO. The precipitation and agglomeration of GO were also observed after the absorbance $^72$ which was also seen in the case of nonpolarizable Na$^+$ ion $^73$. From the Pourbaix diagram of cadmium and copper, it was observed that formation of cationic compounds occurs as contrary sodium at same potential and pH. In the interaction of Cl$^-$ and nonpolarizable Na$^+$ at the surface of GO was described by Daniel et al $^73$. They found that the interaction is totally inverse i.e. Na+, ionic
interacts with the hydroxylated or oxidized graphene surface whereas \( \text{Cl}^- \) ions repels at the functionalized surface. We can expect that at the surface of WE, GO promoting the salt aggregation by sodium ion segregation close to an oxidized graphene. Further the direct WE.

Figure 2.14 Pourbaix Diagram of sodium chloride and carbon showing the stable phases at different pH vs Eh (potential)

surface-ion interaction via Colombian attraction also occurring at nanometer thick Helmholtz double layer which forms at the interface between working electrode interface and electrolyte. Recently reported by Park et al, that mixture of TiO_2 nanoparticles and graphene nanoplatelets forming composite clusters in suspension due to the electrostatic interaction between TiO_2 and graphene nanoplatelets and forming positively charged particles. TiO_2 were found to be attached to graphene platelets and co-depositing at the cathode in 3.5 wt. percent NaCl. They also found the interaction between the two types of particles through stability of the TiO_2-graphene colloidal suspension which was also found in GO/NaCl case\textsuperscript{74}. 

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2.4 Conclusion

Effect of Corrosion inhibition properties of GO in 3.5 wt. percent NaCl solution with varying concentrations of GO was studied. It can see that considerable decrement in corrosion rate in the presence of GO. The addition of GO has no direct consequence on corrosion inhibition properties of steel. The suppression of corrosion with the increasing amount of GO was due to the presence of salt layer at the working surface. GO helps to form a compact layer of NaCl to reduce the corrosion by impeding the corrosive ions to the surface. Further, studies are required to describe the mechanism of salt precipitation in the presence of GO. This study also shows that there is a need to take care while using of GO in a solution having NaCl for a different application.
CHAPTER-3  EFFECT OF GRAPHENE NANOPLATELETS CONCENTRATION ON ELECTROCHEMICAL REACTIONS IN ORGANIC COATINGS

A paper was published in RSC Advances
A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

Time-dependent electrochemical properties of graphene nanoplatelets (GP) and self-crosslinked polyvinyl butyral (PVB) composites are discussed. Electrochemical experiments in chloride medium revealed that GP offers short-term excellent protection from the physicochemical mechanisms operating within the barrier. For longer periods of time, corrosion promotion was discovered due to induced porosity and electrochemical mechanisms related to excellent electrical conductivity and higher position in the galvanic series. This research has helped to understand the misleading anti-corrosion properties associated with graphene-polymer composite coatings.

3.1 Introduction

The environmental constraints on using chromium (VI) based coatings promoted the development of non-hazardous organic and inorganic anticorrosion pigments incorporated in polymer coatings. Graphene sheets are one-atom-thick two-dimensional layers of sp²-bonded carbon having a variety of remarkable properties and can enhance properties of polymers such as electrical and thermal conductivity, gas impermeability and mechanical properties, etc.

Significant research has been conducted on the anti-corrosion properties of graphene in organic coatings which were due to its barrier nature towards corrosion promoting species. Recently, Yu et al. discussed the anti-corrosion properties of modified graphene incorporated in
polystyrene. The improved anti-corrosion properties of nanocomposites were due to the impartation of barrier property in polystyrene. Mayavan et al. also described the same phenomenon with composites of poly(sodium styrene sulfonate) and graphene. Similar mechanisms were explained and can be found in the literature such as graphene/epoxy, polyimide/graphene, polyurethane/graphene composites for anti-corrosion coatings. In the same manner, many studies have shown the single time barrier properties of stand-alone graphene films on the surface of aluminum, where excellent protection was shown after 0.5 hours of immersion in chloride environment. Likewise, Raman et al. measured the anti-corrosion properties of graphene film on copper after one hour of immersion.

However, to date, anti-corrosion properties of graphene-based polymer coatings were measured for a single point in time, which could mislead the long term protection. In this study, we measured time-dependent anti-corrosion properties of GP based PVB composite coating on carbon steel in 0.1M NaCl aqueous solution. Carbon steel samples were coated with thin film of self-crosslinked composites of PVB and GP. We used the electrochemical techniques and measured the corrosion properties after an immersion time of 1 and 26 h to differentiate between the corrosion barrier and corrosion promoting phenomena associated with graphene-based composites coatings.

3.2 Materials and Methods

Polyvinyl butyral (PVB) with trade name Butvar B-98 (molecular weight 40,000-70,000) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. PVB had 18-20 percent hydroxyl content and 80 percent butyral content. Graphene nano-powder was provided by
Graphene Supermarket, USA. The sample had particles with average thickness < 3nm (between 3-8 graphene monolayers) and lateral dimensions 2-8 µm.

Model coatings were prepared by dissolving PVB (Figure 3.1) 2000 ppm (0.2 wt. percent of methanol weight) and SDS 300 ppm (0.03 wt. percent of methanol weight) in 50 mL (39.6 g) methanol with continuous stirring for 24 h, followed by sonication in a sonicator bath. SDS was used as a dispersant and used in all coatings. Similarly, two different concentrations of GP powder i.e. 1000 ppm (0.1 wt. percent of methanol weight) and 2000 ppm (0.2 wt. percent of methanol weight) was subjected to sonication in 50 mL (39.6 g) methanol with 300 ppm (0.03 wt. percent of methanol weight) SDS for one hour. PVB was added to the GP dispersion and shaken for 72 hours to generate a uniform dispersion of GP in the PVB solution. Using dip coater (Figure 3.4), carbon steel substrates were coated with PVB-GP dispersion by immersion and withdraw speed of 50 and 200 mm/min respectively. Samples were immersed in the solution for one min. Three coats were applied for each sample in a similar manner with an interval of 20 minutes. Further, the samples were dried at room temperature for three days followed by baking in an air circulating oven at 175°C for 2 hours to generate final coating with a thickness in the range of 70±3 µm (Figure 3.12).

![Figure 3.1 Structure of Butvar B-98 (Bu: Butyral, Ac: Acetate, Al: Alcohol)](image-url)

Figure 3.1 Structure of Butvar B-98 (Bu: Butyral, Ac: Acetate, Al: Alcohol)
A flat cell assembly with working volume of 250 mL (Figure 3.2), consisting of carbon steel coupon as the working electrode (WE) with exposing area 2.6 cm², graphite plate as counter electrode (CE) having dimensions of 25 ×25×5 mm with exposing area 2.6 cm², and a silver/silver chloride electrode as reference electrode (RE), were used for the electrochemical measurements. Carbon steel panels were surface finished using different grades of SiC grit papers from 240 up to 600 grit, polished to a mirror finish followed by cleaning and degreasing with industrial grade acetone and drying in air. Before coating, specimen were treated with 2 percent nital for one minute and used immediately without any further treatment.

Electrochemical testing was performed in a closed system under naturally aerated conditions using a Gamry 600 potentiostat/galvanostat/ZRA at room temperature. The sequence of electrochemical techniques is described below. Corrosion studies were carried out in 0.1 M NaCl conditions.

The open circuit potential of steel samples was recorded against Ag/AgCl electrode as a reference electrode for one and 26 hours, in solutions of 0.1M NaCl (Figure 3.17). After the completion of each step, EIS was measured followed by final potentiodynamic measurements by closely following the ref 55.

Impedance measurements were performed vs. E_{OCP} at one and 26 hours from the time of immersion. The frequency sweep was performed from 10⁵ to 10⁻² Hz at 10 mV AC amplitude. The Bode plots were modeled with monophasic circuit model used to fit EIS data as resistor and capacitors as shown in Figure 3.3(a-b). For the description of a frequency independent phase shift between the applied AC potential and its corresponding current response, a constant phase element (CPE) is used, where impedance of the CPE is given by following equation:
\[ Z(CPE) = Y_o^{-1}[j\omega]^{-n} \]

where, \( Y_o \) is the constant of CPE, \( \omega \) is the angular frequency in rad s\(^{-1}\) and \( n \) is the exponential term which can vary between 1 for pure capacitance and 0 for a pure resistor\(^{85}\). \( n \) is a measure of surface inhomogeneity; the lower is its value, the higher is the surface roughening of the metal/alloy\(^{60}\).

This circuit model simulates the structure of a barrier coating over the electrode surface and also explains the surface inhomogeneity or roughness. At 1 and 26 hours, the alloy shows a one-time constant impedance response for all samples. This behavior can be easily noticed in the phase angle Bode curves as a single hump for dominant one-time constant phase. To simulate the electrochemical interface, EIS data was analyzed with Echem Analyst using circuit model having...
electrical equivalent parameters accordingly. The capacitance $C$ has been calculated using the following equation:

$$\frac{1}{C} = Y_0 [j\omega'']^{-n}$$

where $\omega''$ is the frequency found at the maximum of the imaginary part of the impedance, $Z''$. The resistance efficiency, $ER$ has been calculated as indicated by equation\textsuperscript{14}:

$$ER = \frac{R' - R}{R'}$$

where $R'$ and $R$ are the resistance value with and without GP respectively.

Figure 3.3 Circuit model after one hour a) and after 26-hours b) of immersion
The polarization measurements were performed at 26 hours of immersion by polarizing the working electrode from an initial potential of -0.3 mV up to a final potential of 0.3 mV as a function of open circuit potential (E_{OCP}). A scan rate of 0.5 mV/s was used for the polarization sweep. Corrosion current densities $i_{corr}$ were obtained by extrapolating anodic and cathodic linear segments of Tafel plot using Echem Analyst. The obtained current densities were used to calculate the efficiency of corrosion inhibition using the following Error! Reference source not found.:

$$CE = \left[ \frac{i_{corr} - i'_{corr}}{i_{corr}} \right]$$

where $i_{corr}$ and $i'_{corr}$ are the current densities without and with the GP.

Figure 3.4 Dip Coater for producing coatings on the carbon steel samples with uniform thickness
Transmission Electron Microscopy (TEM) imaging was performed to characterize the GP. FEI Philips C200 TEM with 200 kV was used. The samples were prepared by dispersing approximately 1 mg of GP in 10 mL of acetone and sonicating for 30 min in a water bath at room temperature. One drop of the suspension was then deposited on a 400-mesh copper grid covered with a thin amorphous film to view under the microscope.

JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) was used to evaluate coating morphology at different kV under high vacuum at a working distance of ten mm. Coated samples were cut from the corroded area and cross-sectional area of the coating was observed as shown in Figure 3.12.

X-ray diffraction (XRD) measurements were performed to confirm the GP by comparing it with graphite. Philips PW 3040/60 spectrometer using Cu Kα radiation in the range of 10° to 40° at scan rate 0.050° was used and the diffraction peaks were matched using X’PertHighScore software.

Thermo-Electron Nicolet 4700 FTIR spectrometer was used for measurements using ATR reflection mode. The IR spectra of PVB and composites films were taken using ZnSe crystal between 4000 and 600 cm\(^{-1}\).

A thermogravimetric analyzer (TGA) was used to record the thermal degradation properties of GP and PVB. Nitrogen was used as a carrier gas and the scans were obtained for different temperature using a heating rate of 20 °C/min.

TA Instruments Q20 differential scanning calorimeter (DSC) was used to measure the calorimetric properties of PVB under a nitrogen atmosphere. First scans were obtained from 25–
175°C using heating rate of 15 °C/min. Before second heating, the samples were also heated isothermally at 200 °C for 2 hours and scanned again from 25-175 °C to detect the variations in glass transition temperature (T_g) upon heating.

Raman spectra were taken using procedure earlier done \(^{86}\). Briefly, a small amount of GP powder was compressed between glass slides to acquire GnP layer. One of the glass slides was placed under the spectrometer objective with a magnification of ×50 and the spectra of these layers were recorded using Lab RAM HR. The charge-coupled device (CCD) exposure time was 20 s, and an average of 10 cycles was used to increase S/N ratio. Raman shifts were calibrated with the silicon reference peak at 520.7 cm\(^{-1}\). Raman mapping was conducted in Duoscan mode on an array size of 23 μm ×18 μm. Each spot size was 2 μm, and spectra were collected using an exposure time of 5 s and one Hertz.

### 3.3 Results and Discussion

Figure 3.5 and Table 3.1 show the infrared spectroscopy spectra and analysis of assigned peaks. The spectrum of heat-treated resin does not show any new peak indicating the absence of new bonds owing to cross-linking. These results are in agreement with the previous reports where heat treatment produced changes in PVB structure measured by hardening of sample \(^{87}\). Similarly, no new peak was observed in the case of PVB and GP composites.

The bulk conductivity of the GP sheet was found to be 5.78 × 10\(^{03}\) S/m which was measured using four probe methods and has good agreement with published literature \(^{88}\). The GP sheet was obtained by pressing powder GP in a sheet form on Teflon sheet using 10 lb\(_f\) for five min. The sheet bulk resistance was measured using four probe methods at different areas on GP sheet using 200 mV and 4.53 × 10\(^{-03}\) Ampere. The conductivity of the sheet shows that GP has
very high conductivity which can also change the conductivity of the coatings. Higher amount of graphene will produce polymer with higher conductivity which may affect the corrosion process happening on the surface. The conductivity of sheet was calculated according to following equations:

\[ \rho(\Omega.m) = R_s(sheetresistance, \frac{\Omega}{\square}) \times T_s(sheetthickness, m) \]

\[ \sigma (conductivity, \frac{S}{m}) = \frac{1}{\rho(\Omega.m)} \]

Figure 3.5 FT-IR spectrums of PVB, GP and PVB/GP nanocomposites
Table 3.1 FTIR analysis of PVB and cross-linked PVB

<table>
<thead>
<tr>
<th></th>
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</tr>
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<tr>
<td>3454</td>
<td>–OH asymmetric stretching of polyvinyl alcohol</td>
<td>3435</td>
<td>–OH asymmetric stretching of polyvinyl alcohol</td>
<td>3456</td>
<td>stretching and bending of the OH bond</td>
<td>2918</td>
<td>asymmetric –CH&lt;sub&gt;2&lt;/sub&gt; stretching</td>
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<tr>
<td>2939</td>
<td>asymmetric –CH&lt;sub&gt;2&lt;/sub&gt; stretching</td>
<td>2933</td>
<td>asymmetric –CH&lt;sub&gt;2&lt;/sub&gt; stretching</td>
<td>2881</td>
<td>C–H stretching vibration</td>
<td>2172</td>
<td>Acetal</td>
</tr>
<tr>
<td>2869</td>
<td>Symmetric –CH&lt;sub&gt;2&lt;/sub&gt; stretching</td>
<td>2870</td>
<td>Symmetric –CH&lt;sub&gt;2&lt;/sub&gt; stretching</td>
<td>2043</td>
<td>C=C stretching vibration</td>
<td>2083</td>
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</tr>
<tr>
<td>2740</td>
<td>O=C–H stretching (Aldehyde group)</td>
<td>1732</td>
<td>carbonyl stretching of the acetate</td>
<td>1633</td>
<td>Graphitic C=C π-bonds</td>
<td>2003</td>
<td>asymmetric C=C stretching vibration</td>
</tr>
<tr>
<td>1733</td>
<td>carbonyl stretching of the acetate</td>
<td>1433</td>
<td>–CH&lt;sub&gt;2&lt;/sub&gt; bending</td>
<td>1338-1203</td>
<td>C–H deformation vibration</td>
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<td>–CH&lt;sub&gt;2&lt;/sub&gt; bending</td>
<td>1379</td>
<td>C–H bending vibration</td>
<td></td>
<td></td>
<td>1377</td>
<td>C–H bending vibration</td>
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<td>1377-1337</td>
<td>C–H bending vibration</td>
<td>1342</td>
<td>C–H bending vibration</td>
<td></td>
<td></td>
<td>1013</td>
<td>C–O–C–O–C stretching vibrations of cyclic acetal groups</td>
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<td>C–O stretching vibration of acetate group</td>
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<td>1136-998</td>
<td>C–O–C–O–C stretching vibrations of cyclic acetal groups</td>
<td>1130-994</td>
<td>C–O–C–O–C stretching vibrations of cyclic acetal groups</td>
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</tbody>
</table>
Figure 3.13 shows characteristic low-resolution TEM images of graphene nanoplatelets (sheets) showing a flaky and transparent structure with wrinkles and folding on the surface \(^{89}\). Figure 3.6 shows the TGA thermogram of GP from 50 to 650°C under nitrogen. A very small weight loss in GP may be attributed to the adsorbed water molecules entrapped in graphene stacked galleries since GP has stacked structure as shown in XRD profile (Figure 3.7) \(^{90}\).

![Figure 3.6 Thermogravimetric curve for graphene nanoplatelets](image).

Figure 3.7 depicts XRD profile of graphite and GP. The characteristic peak at 2\(^\theta\)~26.5° represents the 002 plane in hexagonal graphite with an interlayer spacing of 0.334 nm. For XRD profile of GP, the sharp peak of graphite at 2\(^\theta\)~26.5° disappeared indicating the exfoliated graphene layers \(^{91}\).

Figure 3.8 shows the FE-SEM images of sandwich like the morphological structure of GP-PVB composites. The lateral dimension of graphene as provided and also confirmed by TEM (Figure 3.13) was about 2-8 microns. The thickness of the GP stacks in coatings was varying and
uniformly distributed. Most of the stacks found to be < 50 nm and except for few which were <100 nm indicating extensive exfoliation of graphene sheets\textsuperscript{92}. The monolayer stacks size range indicates that that graphene is more or less dispersed in PVB coatings but effective enough to act as barrier for corrosive solution owing to large lateral size.

Figure 3.7 XRD profile of graphite and GP

Figure 3.8 shows the FE-SEM images of sandwich like the morphological structure of GP-PVB composites. The lateral dimension of graphene as provided and also confirmed by TEM (Figure 3.13) was about 2-8 microns. The thickness of the GP stacks in coatings was varying and uniformly distributed. Most of the stacks found to be < 50 nm and except for few which were <100 nm indicating extensive exfoliation of graphene sheets\textsuperscript{92}. The monolayer stacks size range indicates that that graphene is more or less dispersed in PVB coatings but effective enough to act as a barrier for corrosive solution owing to large lateral size.
Figure 3.8 FE-SEM images of cross sections of coatings showing dispersion of GP in PVB for G-2 at 90 and 180 thousand X of magnification.

Figure 3.9 depicts common features of Raman spectrum for GP showing the presence of D band ~1330 (zone center phonons of $E_{2g}$ symmetry), G band ~1560(K-point phonons of $A_{1g}$ symmetry) and 2D band ~2650 cm$^{-1}$. D peaks correspond the breathing modes of sp$^2$ rings$^{93}$ and confirms the presence of defects in graphene. The much lower intensity of D peak as compared to G peak indicates the high quality of graphene. The lower intensity of 2D peak as compared to D peak indicates the presence of multiple graphene layers$^{94}$.

The scheme in Figure 3.10 describes general physicochemical and electrochemical mechanisms of corrosion protection and promotion respectively due to the incorporation of GP in organic coatings$^{95}$. The short-term protection is explained by a physicochemical mechanism which is generally associated with the obstruction of corrosive agents. This effect may be enhanced significantly by incorporating plate like reinforcements, thus, increasing the diffusion length for the corrosion agents to reach at the defects through microscopic pores. For reinforcement-free organic coating coatings, the basic mechanism is a separation of the metal surface from the environment.
Figure 3.9 Raman spectrums for Graphene nanoplatelets (GP)

Table 3.2 Electrochemical parameters obtained from OCP, EIS, and PD for different samples

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>T (h)</th>
<th>(^a)OCP (\text{mV})</th>
<th>(^b)R_{pore} (\Omega \cdot \text{cm}^2)</th>
<th>(^c)C (\text{F/cm}^2)</th>
<th>(^d)R_{ct} (\Omega \cdot \text{cm}^2)</th>
<th>(^e)C_{dl} (\text{F/cm}^2)</th>
<th>(^f)E_{corr} (\text{mV})</th>
<th>(^g)i_{corr} (\text{A/cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB</td>
<td>-525</td>
<td>1.17 (\times 10^3)</td>
<td>4.47 (\times 10^{-4})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G-1</td>
<td>-450</td>
<td>2.22 (\times 10^3)</td>
<td>4.11 (\times 10^{-4})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G-2</td>
<td>-460</td>
<td>3.98 (\times 10^3)</td>
<td>4.34 (\times 10^{-4})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PVB</td>
<td>-617</td>
<td>0.68 (\times 10^3)</td>
<td>4.84 (\times 10^{-4})</td>
<td>1.05 (\times 10^3)</td>
<td>1.07 (\times 10^{-4})</td>
<td>-663 (\times 10^{-6})</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>G-1</td>
<td>-607</td>
<td>0.62 (\times 10^3)</td>
<td>6.24 (\times 10^{-4})</td>
<td>0.82 (\times 10^3)</td>
<td>2.56 (\times 10^{-4})</td>
<td>-584 (\times 10^{-6})</td>
<td>8.0</td>
<td></td>
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<tr>
<td>G-2</td>
<td>-627</td>
<td>0.65 (\times 10^3)</td>
<td>9.36 (\times 10^{-4})</td>
<td>1.04 (\times 10^3)</td>
<td>3.63 (\times 10^{-4})</td>
<td>-615 (\times 10^{-6})</td>
<td>9.7</td>
<td></td>
</tr>
</tbody>
</table>

The permeability of organic coatings also depends on the nature of the binder matrix. In this study, we used crosslinked film \(^b\) of PVB coating in order to have enhanced barrier nature of binder. TGA (nitrogen) \(^a\).
demonstrates the thermal degradation of PVB resin over a temperature range of 20-800 °C. The weight lose of 9 percent up to 370°C can be observed due to the dehydration of copolymer. The degradation peak around 406°C indicates the major thermal degradation (89 percent) of PVB which continues to 460°C, liberating products such as butanol, C4- hydrocarbons followed by degradation of cyclic and cross-linked compounds. Error! Reference source not found.b depicts the SC thermograms of PVB before and after isothermal heating. First heating clearly indicates the presence of a sharp peak at 63°C indicating glass transition temperature (T_g). After isothermal heating at 200°C for two hrs, second heating indicates the disappearance of sharp peak and shows a small hump in the thermogram at 70 °C. This behavior was unlike to the previous reports where thermal treatment showed that T_g shifted to 170°C It was reported that the self-crosslinking of PVB was taking place owing to the interaction of -OH or acetate groups on adjacent PVB chains which may result reactions between functional groups leading the bridge bonds. The long term corrosion promotion effect was explained by the ‘active’ nature of GP in the coatings. As water molecules start to accumulate at the interface, which facilitates the corrosion under the coating, graphene nanoplatelets stimulate the electrochemical reaction due to the conductivity of electrons at the interface. This effect was also explained by the addition of carbon black to the zinc filled coating where carbon black was observed to promote the corrosion and acted as a perfect cathode for zinc. The addition of carbon black also improved electrical connections between the zinc particles promoting the galvanic effect. In addition, it was also reported that incorporating carbon increased the porosity of the organic coating and increased the absorbance of water, thus, promoting the corrosion. It was also reported that 1 g of reduced graphene (rG) sorbed 14 g of water.
To study the line of defense for each mechanism, thin coating was used i.e. 70 ±5 μm (Figure 3.12) having very low solid contents of binder (0.2 wt. /v percent) and GP (0.1 and 0.2 wt/v percent). PVB and GP were used in two different ratios i.e. PVB: GP was 2:1 and 1:1.

Figure 3.10 Scheme of corrosion protection phenomena in the absence a) and presence b) of GP in PVB (cross-sectional view) with electrochemical corrosion models for 26 h immersion in 0.1 NaCl

EIS is a powerful tool for explicating the behavior of coating resistance and water absorption. EIS was used to examine the characteristics of defects arising in PVB and
PVB/GP composites coatings presented by complex plane plots. The coating shows the porous structure and non-ideal capacitive behavior (Figure 3.10 and Table 3.2). The pore resistance of coating reduced with the addition of GP which indicates the increased ionic resistance to current flow between the bulk and interface\textsuperscript{103}. At the initial stage of immersion (1 h), G-2 coating exhibit quasi-ideal resistive behavior. The pore resistance of G-2 was observed to be very high as showed by half semicircle of Nyquist plot indicating the strict barrier nature of the coating, resulting in the hindrance of faradic reactions. As shown by Scheme in Figure 3.10, this barrier nature could be explained by the low diffusivity of corrosion reactants due to GP sheet-like structure (Figure 3.13)\textsuperscript{104}. The corrosive solution has to adopt longer diffusion and tortuous paths to reach at the metal surface which in results slow down the corrosion rate. In case the defects created by the incorporation filler due to the poor dispersion and agglomerations of fillers, this phenomena may cause severe results.

![Figure 3.11 TGA a) and DSC b) thermograms of PVB](image)

Figure 3.11 TGA a) and DSC b) thermograms of PVB
Figure 3.11(b) Continued.

Figure 3.12 Cross-sectional area showing metal-coating interface
The pore resistance of coatings was calculated by following equation\textsuperscript{83}

$$|Z| = \sqrt{Z_{\text{real}}^2 + Z_{\text{imaginary}}^2}$$

at lowest frequency, where $Z_{\text{imaginary}} \to 0$ giving $|Z| = Z_{\text{real}}$ in Bode plot. It is also evident from Bode plots of Figure 3.14a that the pore resistance of G-1 and G-2 was at least 50 percent and 70 percent respectively greater than that of PVB coated steel after one hour of immersion. With increasing exposure time i.e. 26 hours of immersion, it was taken into account that corrosive media had accumulated on the carbon steel surface through the coating. EIS data from Figure 3.14a and Table 3.2 shows the variations in the impedance model as a response to the intact area. The change in the EIS plots indicated that the model used for 1 h of immersion did not satisfy for longer period immersion. It can be noticed that coating capacitance of G-1 and G-2 was increased by 23 percent and 50 percent respectively. Similarly, interface capacitance of G-1 and G-2 had an increment of 58 percent and 71 percent respectively showing enhancement of corrosion. Although, there was not much difference in the coating and charge transfer resistance, but these parameters showed decreased value for G-1 and G-2. The presence of water in the pores can change the dielectric constant of the coating or interface and it can be determined by the capacitance\textsuperscript{103}. The increased capacitance values with increased exposure time for G-1 and G-2 indicated that presence of corrosive reactant and products in coatings and coating/metal interface changed the local effective dielectric constant and water uptake properties according to the following equations\textsuperscript{105}.

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \text{ and } \theta(\text{percent}) = \log\left(\frac{C_t}{C_0}\right) \cdot \frac{\log(\varepsilon_w)}{\log(\varepsilon_w)}$$
where \( d \) is charge separation distance, \( \varepsilon \) is relative dielectric constant, \( \varepsilon_0 \) is permittivity of free space, \( A \) is surface area and \( C \) is capacitance, \( \theta \) is percentage of water uptake \( C_t \) is the coating capacitance at 26 hours, \( C \) is initial coating capacitance at one hour, and \( \varepsilon_w \) is the relative permittivity of water taken as 80.1 at 20 °C where Relative permittivity is a dimension less value. It can see from Figure 3.15 that addition of GP enhanced the water uptake percentage to 9.5 percent for PVB to GP ratio of 2:1 and almost double with the 1:1 ratio of PVB to GP. These results have conformity with the previous work reported on coatings containing carbon black\(^{100}\). SEM images were taken at the cross-sectional area to study the morphological alterations of coatings at metal/coating interface. The corrosion effects can be confirmed in Figure 3.15 where larger defects could be observed for G-1 and G-2. The approximate defect size of coating for PVB and GP was around 5 \( \mu \)m and 10 \( \mu \)m respectively.

Figure 3.13 TEM of an aggregate consisting of a folded graphene nanoplatelets
The larger defects in the GP containing coatings indicates that water uptake properties of coatings were increasing which in turn produce accelerated coating deterioration.

Figure 3.14 EIS magnitude spectra of coated carbon steel after a) 1 h and b) 26 h immersion in 0.1 M NaCl
Figure 3.15 Cross-sectional area of coating showing coating/metal interface and water uptake θ(percent) after immersion of 26 h

Figure 3.16 and Table 3.2 show the anodic and cathodic polarization curves and corrosion kinetics parameters i.e. $i_{corr}$ and $E_{corr}$ for PVB and GP/PVB coated carbon steel obtained after immersion of 26 h in 0.1 M NaCl. The $i_{corr}$ (current density) represents the rate at which reduction and oxidation reactions become equal at $E_{corr}$ (Corrosion potential). The $i_{corr}$ value of PVB coated steel was nearly 50 percent lesser than G-1 or G-2 suggesting that the incorporated GP in PVB coating remarkably accelerated the corrosion processes at the interface after the destruction of barrier properties. The long-term reduction in protection behavior of GP/PVB can be attributed to the presence GP in the coating which acted as cathodic to the iron at the interface and increased the anodic process\(^9\). The electrical conductivity of GP had also a strong influence on the enhancement of corrosion process. The protection offered by organic coating is owing to the high electrical resistance of the interface thus preventing external flow between anodic and cathodic areas. It is believed that if the electrical resistance of the coating is maintained at a very high level, the electrochemical corrosion cannot occur. The presence of GP in coatings enhanced the electrical contact across the iron surface and maintained the charge transfer for the electrochemical reactions below the coating\(^9\) as shown in Figure 3.10. The
increased current density shows the enhanced flux of electrons throughout the electrochemical system in equilibrium. These findings were also supported by the optical micrographs of coated carbon steel (Figure 3.16). All of the samples were found to be corroded. Figure 3.16 also revealed that corrosion underneath the coating is more for G-2 and G-1 than PVB.

Figure 3.16 Potentiodynamic curve and Optical microscopy images (50X) a) PVB, b) G-1, c) G-2 after 26 h of immersion
Open Circuit potential was used to characterized the performance of coatings in the presence of corrosive solutions for different immersion of time. Shifts in OCP can be used to detect the defects in the coatings. The potential of the higher barrier nature of the coatings is shown by the slow decline of the profile. Whereas the fast decline of in the potential of the profile indicate presence of defects. So, open circuit potential of the coatings is a useful technique to characterize the coatings. Figure 3.17(a-b) shows variations in open circuit potential over a period of one and 26 hours. Both G-1 and G-2 found to be 80 mV noble after one hour due to the barrier properties of the coatings. During 1 hour of the immersion, all of the coatings have rapid and continuous decreasing trend toward negative direction indicating the adsorptions of corrosive media in the coatings. During 26 h of immersion, OCP curves for all coatings, clearly demonstrating the pronounced effect of charge transfer reactions and uniform corrosion for first and second half of the curves respectively. These results are in accordance with the EIS and PD.

XPS spectra for O1s (Figure 3.18 & Figure 3.19) show mixers of iron oxide compounds on the corroded surface. The XPS of the corroded samples were performed on the selected portion of the exposed area of working electrodes. The corrosion products mainly contained different forms of an iron oxide including Goethite (αFeOOH), Wüstite (FeO), hydrated iron oxide (Fe(OH)_3) and Hematite (αFe_2O_3) for all the cases. It can be concluded that presence of graphene does not affect the formation of corrosion products. The higher intensity of the XPS profiles in case of graphene containing coating indicates that presence of corrosion products have higher amounts on the metal surface.
Figure 3.17 Open circuit potential after one (a) and 26 hours (b) of immersion in 0.1M NaCl
Figure 3.18 Images of corroded sample after treated with methanol, XPS were recorded somewhere in the encircled area.

Figure 3.19 XPS spectra for O1s of corroded sample surface.
3.4 Conclusions

Electrochemical techniques such as OCP, EIS and PD were used to explain anti-corrosion properties associated with barrier behavior and corrosion promoting properties associated with the electrochemical reaction in organic coatings. Graphene shows excellent short-term anti-corrosion properties, but for longer periods of time, this effect becomes worse and corrosion promotion effect is observed.
A paper to be submitted in *Corrosion Science* and other paper was published in *RSC Advances*

A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

In this research, the electrochemical impedance spectroscopy (EIS) study was conducted on graphene/polyvinyl butyral nanocomposite (GP/PVB) coatings. Graphene (M-GP), used in this study was produced by Haydale’s plasma modification process involves different gasses or their mixers such as Argon, Fluorine, and Oxygen. The presence of porous bounded Warburg and Gerischer diffusion elements in the model circuits indicate that coatings behave as electrolyte diffusion limited or porous electrode that improves the mass transport resistance by trapping the electrolyte. Capacitive-Resistive behavior at intermediate to lower frequencies range in phase angles also confirms the blocking behavior towards corrosive species. Small-angle x-ray scattering (SAXS) study shows that coatings have surface fractal structure of intermediate roughness (larger size) for PVB to a smoother surface (smaller size) for composites indicating better dispersed M-GP in resin resulted in enhanced barrier properties.

### 4.1 Introduction

Recently, Haydale Ltd. introduced dry plasma process for functionalized graphene production as an alternative to graphene produced or functionalized from wet chemistry. Williams et. al patented and reported many advantages of GP produced from Haydale’ process such as improved exfoliation, enhanced dispersion and compatibility with host matrix owing to selective surface groups and undamaged crystalline structure\(^{108,109}\). The barrier nature of graphene owing to the layered structure can be used to slow down the penetration of corrosion
promoting species through organic coatings as reported earlier \(^ {110}\). Further, the barrier properties of composites depend on many factors such as; I) Nanoscale level dispersion and distribution of fillers, II) Interfacial compatibility of polymer and filler phases, III) polarity match between the filler surface and the polymer chains. The full advantage of nano-fillers can only be achieved by considering factors above that could lead to uniform transfer of chemical, physical and mechanical properties of filler to host polymer matrix \(^ {111, 112, 113, 114}\). This study deals with the comparison of barrier properties of nanocomposites prepared from Haydale’s graphene and thermally reduced graphene oxide (U-GP). We used four kinds of graphene i.e. RGP and Haydale’s processed graphene nanoplatelets produced using three types of process gasses i.e. fluorine (F-GP), oxygen (O-GP), and argon (A-GP).

### 4.2 Experimental Procedure

M-GP (commercial name HDPlas™) was used as purchased from graphene supermarket, USA with planer size 0.3-5 \(\mu\)m and platelets thickness < 50nm. U-GP (A-12, graphene supermarket, USA) thickness < 3 nm and planer size 2-8 \(\mu\)m were used for comparison. GP amount was kept constant i.e. 3 wt. percent of Resin (Butvar B-98) (5g Resin/50 ml methanol) for all the composites. EIS has performed on coated carbon steel panels at different times of immersion i.e. 1 and 12 hours in 4 w/v percent NaCl. Model coatings were prepared by bath sonication of GP for four hours in 50 ml methanol followed by 48 hours of mixing with PVB in a closely tight glass flask. Carbon steel samples were polished starting from 60 to 600 grit sand paper. Using dip coated, carbon steel substrates were coated with PVB-GP dispersion by immersion and withdraw speed of 50 and 200 mm/min respectively. Samples were immersed in the solution for one min. Two coats were applied to each sample in a similar manner with an interval of 15 min. Further, the samples were dried at room temperature for three days followed
by baking in an air circulating oven at 175°C for two hours to generate final coating with a thickness in the range of 270±3 μm. Four carbon steel samples were prepared for each PVB and composite coatings.

A flat cell assembly with working volume of 350 mL consisting of carbon steel coupon as the working electrode (WE) with expose area 2.6 cm², graphite plate as counter electrode (CE) having dimensions of 25 × 25×5 mm with expose area 2.6 cm², and a silver/silver chloride electrode as reference electrode (RE), were used for the electrochemical measurements. The open circuit potential of steel samples was recorded against Ag/AgCl electrode as a reference electrode for one and 12 hours. After the completion of each step, EIS was measured. Impedance measurements were performed vs. (E_OCP) after 1 and 12 hrs from the time of immersion. The frequency sweep was performed from 10⁵ to 10⁻² Hz at 10 mV AC amplitude

4.3 Results and Discussion

The microstructure of polymers can be analyzed using scattering methods, such as small angle x-ray scattering (SAXS)¹¹⁵. The structural features at various length scales (length scale ~ 2π/q) in polymers and nanocomposites are probed by the scattering vector (q). Also, the power-law delaying exponent (log(I) ~ log(q)⁻α) at lower q values explains the size of the scattering objects or fractals. In a report by Malekani et al.¹¹⁶, α was directly related to the fractal dimensions, D_f. Specifically, mass fractals exhibited an α ≤ 3 (a substance whose surface and mass are both characterized by the fractal properties). The α is directly related to the mass fractal dimensions, D_m. The surface fractals are formed for 3 ≤ α ≤ 4, and the surface fractal dimension, Ds, can be calculated as follows: α ≡ 6 - D_s where 3 < (6 - D_s) ≤ 4¹¹⁶,¹¹⁷.
SAXS patterns (Figure 4.1) from the free-standing thin films of PVB and its nanocomposites with various types of GP at 3 wt. percent loading were investigated. Neat PVB exhibited an $\alpha \sim 3.2$ (not shown here), which remained unchanged after the crosslinking reaction. An $\alpha > 3$, in this case, showed the presence of surface fractals, which might be associated with the crystallinity of PVB and its molecular architecture. The addition of GP, in all cases, increases the $\alpha$ value. Incorporating U-GP in PVB slightly increased $\alpha$, which further increased to 3.6 for both F-GP, and A-GP nanocomposites, and $\alpha = 3.5$ was observed for O-GP/PVB nanocomposites. Very close values of $\alpha$ in M-GP nanocomposite systems shows the nearly similar dispersion of M-GP in all cases. The surface fractal size $= 2\pi/\Delta q (R_{\text{squared}} \rightarrow 0.99)$ and Dimension $= 6 - \alpha$ was found as: PVB ($\sim 20.4$ nm, 2.8), U-GP ($\sim 17.4$ nm, 2.7), O-GP ($\sim 12$ nm, 2.5), F-GP ($\sim 10.8$, 2.4), A-GP ($\sim 10.7$, 2.4) indicates that graphene produced from Haydale’s process produced better dispersion in the resin. $D_s$ can be used to find the degree of roughness and irregularities where $D_s$ between $2 \leq D_s \leq 3$, the value of 2 and 3 indicate highly smooth and disordered surface respectively. A survey scan of GP was done using x-ray photoelectron spectroscopy (XPS), (Figure 4.4) showed different C/O atomic ratio as; U-GP, 62/1: A-GP, 10/1: O-GP, 11/1: and for F-GP, 14/1 and C/F is 133/1. These results show that Haydale’s graphene contain higher C/O ratio in the form of different groups such as epoxy, hydroxyl, carboxylic acids and alcohols which can result in the better dispersion. TEM (Figure 4.3) of M-GP shows clearly different morphological features from that of RGP. FT-IR (Table 4.2) does not hint any new peak in all the cases except some slight shifting of wave numbers of some peaks may be indicating interaction in M-GP composites.
Figure 4.5—Figure 4.6, Table 4.3 and Table 4.1 depict the phase angle, Nyquist, impedance spectra, extracted model parameters and errors of parameters respectively for coated carbon steel in 4 percent NaCl aqueous solution for different immersion time.

Figure 4.1 Small-angle X-ray Scattering spectrums of PVB and GP-PVB nanocomposites

Phase angle exhibits distinct behavior at a various range of frequency for PVB and composites coatings. The range of frequency corresponds to the various regions in the coating i.e. starting from coating surface to substrate surface. After 1 hours of immersion PVB coating, at higher frequency ~100 kHz show a mixed capacitive and resistive behavior (~-43°) indicating the barrier and diffusive nature of the coating. This behavior comprises over intermediate frequency range with a variation of theta around ~-45° ±-5° that changes to resistive behavior in
the low-frequency spectrum. At frequency, ~25 kHz the slight rises in the theta ~-37° indicating dominant resistive behavior. A little bump can be seen at 12.4 Hz corresponding theta ~-46° between two minima of theta i.e. ~-49° at 100 Hz and ~-48.8° at 2.5 Hz. This continuous
table 4.1 standard deviation for each value of EIS parameter

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<th>EIS parameters</th>
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<th>U-GP</th>
<th>O-GP</th>
<th>A-GP</th>
<th>F-GP</th>
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<td>Rpore</td>
<td>1.71E+02</td>
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Resistive; Ohm.cm², Y(admit.); S*s⁻¹/cm², An average of four readings.

resistive and capacitive behavior ranging from higher to intermediate frequency can be an indication of constrained diffusion of electrolyte through coating corresponding to porous bounded Warburg (PB-W) as mentioned in GamryEchemAnalyst™ manual. The major transition from mixed resistive-capacitive behavior to resistive behavior occurs at ~0.9 Hz corresponding to the metal/interface and metal characteristics. Some reports especially Zhang et al. used PB-W element to model the diffusion limited behavior in fuel cell containing meshes of steel 122, 123, 124. The addition of U-GP changed the phase angle behavior considerably. At frequency ~100 kHz, comparatively lower phase angle ~-68° showing high capacitive nature of coating followed by a dominant resistive owing to higher phase angle ~-30° at 800 Hz, which further changed to dominant capacitive behavior ~-57° at ~12.5 Hz. This trend indicates that a large amount of trapped electrolyte in the coating which further unable to respond to the AC
frequency at the intermediate frequency. This behavior can be modeled using Gerischer element\textsuperscript{125} used for modeling a porous electrode as mentioned in GamryEchemAnalyst\textsuperscript{TM} manual. Table 4.3 shows that addition of U-GP has not significantly improved the pore resistance and admittance of coating. The admittance value is very high as compared to PVB coating. However, there is a significant improvement in the $R_{cl}$ indicating that corrosive electrolyte is although already entered in the coating but unable to reach the interface. Upon adding graphene produced from Haydale’s process to PVB, the composite coating showed remarkable enhancement in anticorrosion properties owing to improved diffusion behavior indicating improved dispersion and interaction with the PVB resin.

![Figure 4.2 log Z vs Freq. after immersion in 4 percent NaCl](image)

Figure 4.2 log Z vs Freq. after immersion in 4 percent NaCl
Table 4.2 FTIR analysis of PVB and cross-linked PVB

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**3435**
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- OH asymmetric stretching of polyvinyl alcohol
- OH asymmetric stretching of polyvinyl alcohol
- OH asymmetric stretching of polyvinyl alcohol

**2933**
- CH2 asymmetric stretching
- CH2 asymmetric stretching
- CH2 asymmetric stretching
- CH2 asymmetric stretching

**2870**
- Symmetric C–CH2 stretching
- Symmetric C–CH2 stretching
- Symmetric C–CH2 stretching
- Symmetric C–CH2 stretching

**1732**
- Carbonyl stretching of the acetate
- C=C stretching
- CC stretching vibration
- CC stretching vibration

**1433**
- CH2 bending
- CH2 bending
- CH2 bending
- CH2 bending

**1379**
- C–H bending vibration
- CH2 bending
- CH2 bending
- CH2 bending
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Figure 4.3 TEM images of Graphene nanoplatelets

74
Figure 4.4 XPS Survey of graphene nanoplatelets
A-GP

O-GP

Figuer 4.4 Continued.
In case of nanocomposites produced from F-GP/PVB, at very high frequency ~100 kHz coating showed a very high capacitive behavior indicated by low phase angle i.e. ~-81° that indicates improved barrier properties and this behavior gradually change to capacitive-resistive behavior at frequency ~400 Hz. After that frequency independent behavior can be seen over a range of frequency i.e. from 400 Hz to 1.6 Hz with constant phase angle ~-45°±3° indicating a diffusion limited process followed by similar trend shown by all of other cases. This kind of impedance behavior enhances the RC by 28, 21 and 15 times for O-GP, A-GP, and F-GP respectively as compared to U-GP after 1 hours of immersion. After 12 hours of immersion, PVB coating showed an entirely different behavior i.e. at the higher frequency it depicts resistive behavior indicating lose of barrier properties whereas at intermediate and low-frequency range dominant capacitive hump can be seen indicating the appearance of larger blisters in the coatings126. Similar is the case for U-GP at intermediate and lower frequency, but it shows lesser capacitive behavior at a higher frequency as compared to 1 hr indicating reduced barrier and adhesion. For M-GP nanocomposites still it shows very higher capacitive behavior at higher frequency indicating the coating still retained barrier properties and in contact with the substrate. The capacitive behavior gradually changed to more resistive (~-33° for A-GP, ~-23°for F-GP and ~-17°for O-GP) as compared to 1-hour immersion and extends over a broad range of low frequencies. For O-GP, a little capacitive hump can be observed at very low frequency indicating appearing tiny blisters. Further, the continuous resistive behavior also indicates that delaminated area is small where the corrosion is taking place. Further, Figure 4.6 shows that Nyquist plots for M-GP have long diffusive tails at intermediate frequency indicating diffusion control processes in accordance with phase angle. Table 4.3 also indicates that compared to U-GP, M-GP
nanocomposites has very low admittance value determined from Gerischer element after 12 hours of immersion.

Figure 4.5 Phase angle behavior for PVB and GP-PVB nanocomposites coating on carbon steel recorded after a) 1 hour’s and 12 hours’ of immersion in 4 percent NaCl
Figure 4.6 Nyquist plots for PVB and GP-PVB nanocomposites coating on carbon steel recorded after a) 1 hour’s and b) 12 hours’ of immersion in 4 percent NaCl
Table 4.3: EIS parameters extracted using different circuit models

<table>
<thead>
<tr>
<th>Model Circuits</th>
<th>EIS parameters</th>
<th>PVB 1hr</th>
<th>U-GP 1hr</th>
<th>O-GP 1hr</th>
<th>Ar-GP 1hr</th>
<th>F-GP 1hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB 1hr</td>
<td>$R_{\text{pore}} \times 10^3$</td>
<td>2.93</td>
<td>2.75</td>
<td>26.9</td>
<td>87.4</td>
<td>49.0</td>
</tr>
<tr>
<td>M-GP 1hr</td>
<td>$R_{\text{cl}} \times 10^4$</td>
<td>2.67</td>
<td>21.6</td>
<td>618</td>
<td>456</td>
<td>326</td>
</tr>
<tr>
<td></td>
<td>$Y_{\text{admit}} \times 10^{-05}$</td>
<td>0.32$^W$</td>
<td>8.52$^G$</td>
<td>0.18$^G$</td>
<td>0.09$^G$</td>
<td>0.13$^G$</td>
</tr>
<tr>
<td>PVB 12hr</td>
<td>$R_{\text{pore}} \times 10^4$</td>
<td>1.01</td>
<td>1.28</td>
<td>1.36</td>
<td>1.52</td>
<td>4.40</td>
</tr>
<tr>
<td>M-GP 12hr</td>
<td>$R_{\text{cl}} \times 10^3$</td>
<td>4.51</td>
<td>12.6</td>
<td>10.4</td>
<td>24.6</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>$Y_{\text{admit}} \times 10^{-05}$</td>
<td>-</td>
<td>79.6</td>
<td>2.87</td>
<td>2.22</td>
<td>9.22</td>
</tr>
</tbody>
</table>

Resistance; Ohm.cm$^2$, $Y$(admit.); S*s$^{(1/2)}$/cm$^2$

Figure 4.7 Nyquist arcs corresponding to phase angle between -50° to -40° for M-GP nanocomposites coating on carbon steel recorded after 1 hour’s immersion in 4 percent NaCl.
Nyquist arcs (Figure 4.7) corresponding to phase angles (\(-50^\circ\) to \(-40^\circ\)) were plotted to show the range of mixed capacitive-resistive behavior in Nyquist plots. Coatings produced from nanocomposites of AR-GP and F-GP showed diffusion restricted behavior started relatively at higher frequency compare to O-GP coatings. These results are also confirmed by admittance value in Table 4.3, where O-GP coatings showed higher magnitudes of the admittance. The complex impedance \((Z(w))\) of constrained diffusion (Gerischer diffusion element) can be calculated by following equations\(^{127}\):

\[
\bar{Z}(w) = 1 / \left\{ Yo \sqrt{k + jw} \right\}
\]

where \(Yo\) is admittance, \(k\) is "rate constant" parameter, \(k\) (units: s\(^{-1}\)). Further the slopes of Nyquist arcs (\(~45^\circ\)) at higher to intermediate frequency also indicate the presence of perfectly constrained diffusion behavior of coatings. The slope angle (~\(^59^\circ\)) for O-GP coatings indicated deviation from constraint diffusion which is an indication of comparatively higher admittance value. The slope angle for O-GP coatings accounts the presence of higher amount of water in that particular region of the coating.

### 4.4 Conclusion

PVB/GP produced from Haydale process nanocomposites showed remarkable anti-corrosion properties owing to better dispersion of M-GP. Although spectroscopic technique such as FT-IR does not confirm any new bond but still the presence of functional groups on GP surface (as indicated by XPS) which help for enhanced dispersion. Smaller fractals size for M-GP/PVB composites indicates that M-GP has better dispersion in PVB. The better dispersion resulted reduced interfacial defects and longer tortuous paths for a corrosive solution to reach the
metal surface. PVB coating itself showed diffusion restricted behavior that further enhanced in composites coatings. Further GP produced from Haydale process has superior properties as compared to U-GP.

4.5 Acknowledgments

Authors are grateful to Muhammad Z. Iqbal (Email: mziqbal12@gmail.com) from Chemical & Biological Engineering Department, Colorado school of mines, CO USA, for discussing, conducting, analyzing and writing the SAXS results. The use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (D.O.E.) Office of Science by Argonne National Laboratory was supported by the U.S. DOE under Contract No.DE-AC02-06CH11357.
CHAPTER-5 POLYANILINE-GRAPHENE COMPOSITE NANOPARTICLE PIGMENTS FOR ANTI-CORROSION COATINGS

A paper to be submitted in The Journal of Reinforced Plastics and Composites and other paper was published in RSC Advances

A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

Development of anti-corrosion coatings with the incorporation of polyaniline adsorbed graphene nanoparticle pigments (PANI/r-GO) in poly (vinyl butyral) (PVB) was successfully demonstrated in the current study. PANI/r-GO hybrids were generated by in-situ polymerization of aniline and hybrid composition was varied to evaluate the effect on the corrosion performance of the coatings. The diffraction studies of the hybrids exhibited slight broadness in the PANI diffraction peaks and did not reveal any diffraction peak corresponding to r-GO. Furthermore, crystallization of PANI was significantly affected in the presence of graphene platelets as the graphene platelets hindered the chain mobility and packing into the crystal structure, which also indicated that, the polymer was strongly adsorbed on the surface of the graphene platelets. Enhancement of thermal stability of the polymer with increasing graphene content further confirmed the physical interaction of polymer and graphene surface. Irrespective of the graphene content in the hybrids, the morphology of the graphene platelets altered due to uniform coverage on the surface with PANI. PVB coatings with PANI/40r-GO and PANI/50r-GO exhibited 52 percent and 58 percent higher corrosion protection efficiency respectively as compared to PVB coating without pigment, which was also confirmed optically. The coatings were also equally effective when immersed in the salt solution at 40 °C. The conductivity of the PANI/r-GO nanocomposites decreased as the amount of reduced graphene was increased probably due to a decrease in the degree of doping. Thus, due to synergistic combinations of factors like the tortuous path for the corrosive media in the presence of graphene platelets as well as the
formation of PANI/graphene, ‘Schottky barrier’ at interface leading to the depletion of electrons corrosion half-cell reactions could be slowed down. The PANI/r-GO nanoparticle pigments represent functional materials capable of enhancing the performance of corrosion protection coatings low weight fractions.

5.1 Introduction

Metallic corrosion is a result of an electrochemical phenomenon that involves the transfer of charge from one species to another, thus, leading to impairment of metal. Figure 5.1 depicts the corrosion phenomenon in the presence of sodium chloride aqueous media where chloride ions accelerate the corrosion process. In this case, the corrosion process proceeds by the dissolution of an iron oxide film with the aid of chloride ions as well as enhancement of the transportation of electrons by sodium and chloride ions. Among various methods developed to slow down the corrosion process, corrosion inhibitors and anti-corrosion pigments receive widespread use owing to cost effectiveness and easy application. These protective films slow down the deterioration process of metals by suppressing either cathodic, anodic or both types of corrosion processes.

Figure 5.1 Schematic of corrosion process of iron
The environmental constraints on using coatings incorporating chromium (VI) based corrosion inhibitors have driven the development of non-toxic organic and inorganic inhibitors and anti-corrosion pigments to be incorporated in polymer coatings. Organic inhibitors have polar groups such as sulfur, nitrogen, selenium, etc., which help them to chemisorb on metal surfaces resulting in the formation of protective surface complexes. Examples of such inhibitors are amine- and imidazoline derivatives, alkyl pyridines, and thioureas\textsuperscript{129}. On the other hand, inorganic corrosion inhibitors include sulfites, ferric salts, nitrates and calcium ions, with corrosion protection mechanisms based on the specific type of inorganic inhibitor \textsuperscript{6, 7, 8, 89}. For example, sulfites \textsuperscript{6, 130} consume the dissolved oxygen in solutions to reduce oxygen availability in order to retard corrosion; ferric salts and nitrates \textsuperscript{7} foster passivity of metals in active-passive regions and the calcium ions \textsuperscript{8} reinforce the protective films formed on metal surfaces. In addition, inorganic pigments such as litharge, metallic lead, red lead, basic lead carbonate, hexavalent chromium compounds and zinc oxide have been extensively used in polymer coatings for the enhancement of anti-corrosion \textsuperscript{131}, gas barrier \textsuperscript{10}, mechanical \textsuperscript{11}, electrical and optical \textsuperscript{132}, rheological and adhesion properties as well as environmental degradation resistance \textsuperscript{133}. Recent research studies have also reported about the potential of nano-inorganic particles as anti-corrosion pigments in polymer coatings \textsuperscript{134}. The nano-pigments exhibit advantages over conventional pigments due to improved barrier and anti-corrosion properties in polymer coatings \textsuperscript{2, 135} such as epoxy-clay \textsuperscript{136}, polyaniline/TiO\textsubscript{2} \textsuperscript{137}, poly(methyl methacrylate) (PMMA)/graphene \textsuperscript{138}, poly(vinyl carbazole) (PVK)/multiwall carbon nanotubes \textsuperscript{139} anti-corrosion coatings.

The development of free-standing single-layer graphene, which is the building block of all graphitic forms, has resulted in its extensive use as reinforcement for polymer materials \textsuperscript{140}. Graphene sheets are a one-atom-thick two-dimensional layer of sp\textsuperscript{2}-bonded carbon having a
variety of remarkable properties and can enhance properties of polymers such as electrical and thermal conductivity, gas impermeability and mechanical performance. Further, the role of conducting polymers, especially polyaniline (PANI), for corrosion protection of ferrous and non-ferrous metals has been vigorously studied. For this purpose, PANI has been reported to provide corrosion protection of metals either as a neat film or as resin blended coatings. Resin blending method is reported to be more convenient and acceptable method of coating on large structures as it leads to better mechanical properties of coatings. Huh et al. reported PANI and poly-o-ethoxyaniline blended coatings on pure iron, which resulted in better corrosion protection in 3 wt percent NaCl. Armelinet al. generated a comparison between corrosion inhibitor Zn₃(PO₄)₂ at 10 percent w/w and two forms of PANI (emeraldine base and emeraldine salt) mixed with epoxy at 0.3 percent w/w. Better behavior of emeraldine base at low concentration was attributed towards its ability to act as a barrier and to store charge due to oxidation and reduction in a reversible way as compared to emeraldine salt due to its fully oxidized state. In addition to resin blending, modification of inorganic pigments with PANI to achieve synergistic anti-corrosion effect has also been reported in literature. Kalendovaet al. proposed a method to combine the use of inorganic pigments and PANI so as to address the problems associated with resin blended coatings i.e. inefficient PANI distribution, lack of excellent polymer-polymer contact, poor substrate adhesion and change in volume of PANI due to redox reaction. Four pigments specularite (Fe₂O₃), goethite (FeO(OH)), talc (Mg₃(OH)₂(Si₄O₁₀)) and graphite were surface modified with PANI and subsequently blended with an epoxy binder. Better corrosion resistance was observed in all PANI coated pigments and PANI modified graphite exhibited excellent corrosion inhibition due to improvement in conductivity which promoted redox reactions between iron and PANI or oxygen and PANI. Sathiyaranayanananet al. modified TiO₂
and Fe$_2$O$_3$ with PANI and observed enhanced corrosion protection of steel as compared to pigments without polymer modification. The results were attributed towards the formation of the passive film along with the iron-phosphate salt film on the iron surface $^{147}$. Brodinova et al. used surface modified ferrites with contents of Zn, Mg and Ca cations. The results showed that modified ferrites were better in terms of corrosion protection than the non-modified versions. The corrosion protection mechanism was proposed to be a result of the formation of cation soaps which lowered the tendency of the binder to saponify on exposure to the hydroxyl ions formed during corrosion of the metal. The presence of PANI filled the pinholes present in the coating and also formed a better interconnection between inorganic pigments and resin $^{148}$. Similarly, Wu et al. reported hybrid coating of PANI-layered zinc nickel ferrites and organically modified silicate. The film was deposited via a spin coating on aluminum alloy. The anti-corrosion performance of the hybrid film was improved due to the denser configuration of organically modified silicate due to the incorporation of nickel zinc ferrites/PANI $^{149}$. Modification of graphene-based materials with PANI to generate anti-corrosion pigments is largely missing in literature and generation of such materials can result in anti-corrosion coatings with enhanced performance.

In the current study, PANI and nano-hybrids based on PANI-thermally reduced graphene (r-GO) were used as the anti-corrosion pigments incorporated in poly(vinyl butyral) (PVB) resin. The PANI/r-GO hybrids were generated with varying r-GO/aniline ratios during the hybrid generation, so as to relate the effect of graphene content to the coating performance. The coatings were applied on carbon steel panels and the corrosion performance of these pigments was investigated in 4 percent w/v sodium chloride (NaCl) solution.
5.2 Experimental

The following section deals with the materials purchased and methods adopted for this research.

5.2.1 Materials and Methods

PVB (M\textsubscript{W} 70,000-100,000) resin with broad molecular weight distribution, containing \(\sim 20\) percent vinyl alcohol and \(\sim 2\) percent vinyl acetate, was obtained as granules from Polysciences, Inc. (USA). Hydrochloric acid (38 percent) and NaCl were supplied by Merck, Germany, whereas aniline monomer was procured from Mallinckrodt, USA. Hexamethylenetetramine, ammonium persulfate (APS) and acetone were received from Sigma-Aldrich, Germany. Graphite powder (325 mesh) was supplied by Alfa Aesar GmbH and Co., Germany. Concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 95-98 percent), sodium nitrate (NaNO\textsubscript{3}) and potassium permanganate (KMnO\textsubscript{4}) were purchased respectively from S. D. Fine Chemicals India, Eurostar Scientific UK, and Fisher Scientific UAE. Carbon steel coupons (elemental composition: C 0.07 wt percent, Mn 1.36 wt percent, Ti 0.008 wt percent, S 0.003 wt percent, P 0.004 wt percent and rest Fe) were purchased locally and were machined to 30 x 16 x 5 mm dimensions.

5.2.2 Preparation of Graphite Oxide (GO) and r-GO

r-GO was prepared through thermal exfoliation of precursor graphite oxide \textsuperscript{42} using modified Hummer’s method \textsuperscript{150}. A short description for the preparation of graphite oxide and r-GO is as follows (Figure 5.2): graphite powder was added with concentrated H\textsubscript{2}SO\textsubscript{4}, followed by addition of NaNO\textsubscript{3} to the mixture. The mixture was stirred in an ice bath (5°C) and KMnO\textsubscript{4} was...
added to the mixture after 30 min. Gradually, the temperature was allowed to rise to 35°C and the mixture was stirred for 2 h under these conditions. Deionized water was subsequently added while allowing the temperature to increase to 100°C. After 15 min, the mixture was quenched and diluted by pouring it into deionized water. 30 percent H₂O₂ was slowly added to the dilute solution and the solution was filtered to remove the non-graphite oxide waste. The residues were re-dispersed in deionized water and were added with dilute HCl to remove the SO₄²⁻ ions. The cleaning and filtration were continued until no SO₄²⁻ and Cl⁻ ions could be observed in the filtrate. Afterward, the washed GO was dried under vacuum at 60°C for 24 h. r-GO was generated via thermal exfoliation of dried graphite oxide by placing 1 g GO in a long quartz tube with 25 mm internal diameter and sealed at one end. The sample was flushed with nitrogen, followed by insertion of the tube in a tube furnace preheated to 1050°C. The tube was held in the furnace for 30 s.

5.2.3 Preparation of Polyaniline and r-GO Composite Nanoparticles

Polyaniline modified r-GO was prepared using in-situ polymerization. To generate PANI/r-GO composites with different weight ratios, 0, 10, 20, 30, 40 and 50 mg of r-GO nanoparticles were added to a mixture of 1 ml of aniline and 90 ml of 1N HCl in a reaction vessel (Figure 5.3).
Figure 5.2 Schematic diagram of generation r-GO through Modified Hummer’s Method

The mixture was stirred in ice water bath (5 °C) for 1 h to obtain a uniform dispersion of r-GO. To the mixture, 100 ml pre-cooled 1N HCl solution containing 2.5 g APS was added dropwise. The reaction was allowed to proceed in the ice bath for 4 h. The resulting product was washed with distilled water for several times and at last washed with methanol in order to eliminate oligomers and other impurities. Subsequently, the sample was dried in a vacuum oven for 12 h. Based on the amount of r-GO, these hybrids were named as PANI/10r-GO, PANI/20r-GO, PANI/30r-GO, PANI/40r-GO and PANI/50r-GO.
Figure 5.3 Schematic diagram of generation of PANI/r-GO composite particles

5.2.4 Characterization of PANI/r-GO Composite Nanoparticle Pigments

Calorimetric properties of PANI and PANI/r-GO composite nanoparticle pigments were recorded on a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) (nitrogen atmosphere). The scans were obtained from 50 to 250°C at a heating rate of 5°C/min. Thermogravimetric measurements were analyzed using Netzsch thermogravimetric analysis (TGA) using American Society for Testing and Materials (ASTM) standard ASTM E1131. Using nitrogen gas, the scans were obtained from 50 to 600 °C at a heating rate of 20 °C/min. Transmission electron microscopy (TEM) of hybrid samples was performed using EM 912 Omega (Zeiss, Oberkochen BRD) electron microscope at 120 kV and 200 kV accelerating voltage. Thin flakes of PANI/r-GO platelets were supported on 100 mesh grids sputter coated with a 3 nm thick carbon layer. X-ray diffraction (XRD) analysis of the samples was performed
on Panalytical powder diffractometer (X’Pert PRO) using CuKα radiation ($\lambda = 1.5406 \text{ Å}$) in reflection mode. Zero-background holder was used to minimizing the noise. The samples were step-scanned from 10-40$^\circ$ 2Θ at room temperature using a step size of 0.02$^\circ$ 2Θ and a step time of 10 s $^{42,151}$.

### 5.2.5 Generation of PANI/r-GO/PVB Coatings

PVB was dissolved in methanol (20 ml) under stirring for 6 h, followed by sonication in a bath sonicator for 2 h. PANI/r-GO nanoparticles of different compositions were finely powdered with a small quantity of methanol to obtain a uniform slurry. The slurry was added and mixed in the PVB solution and sonicated for 24 h to achieve uniform dispersion of nanoparticles in the PVB solution $^{84}$. The amount of PANI/r-GO particles was fixed to 10 wt percent of the amount of dry PVB. For coating of the generated PANI/r-GO/PVB formulations, carbon steel coupons with rounded corners and edges were polished by emery paper, washed with acetone, dried and weighed with an accuracy of ±1 mg. The substrates were brush coated with the PANI/r-GO/PVB formulations and dried at room temperature for 30 min. Subsequently, the coating was baked in an air circulating oven at 60 °C for 6 h and coatings with a thickness in the range of 15-20 μm were obtained.

### 5.2.6 Corrosion Performance Analysis

The anti-corrosion properties of the coatings were studied by immersion test (NaCl 4 percent w/v) according to ASTM G31. The coated coupons were placed in a specially designed set up for 800 h at 25 °C. The function of this set-up was to maintain temperature, air flow, and water level so as to attain similar conditions throughout the experiment $^{146}$. After completing the immersion period, the samples were taken out of salt solution, cleaned and weighed again.
Cleaning of the samples was achieved by removing the coating using acetone as a solvent and subsequently removing the corrosion products by a solution of 3.5 g of hexamethylenetetramine in 500 ml of hydrochloric acid diluted to 1000 ml with distilled water. The samples were dipped for 10 min in the amine solution at room temperature. Weight loss method was used to evaluate (CR) corrosion rate, using the following equation:

\[
Corrosion rate, CR = \frac{87.6 \text{W}}{\text{DAT}}
\]

where CR is corrosion rate in mm/year, W is weight loss in mg, D is the substrate density, A is the exposed surface area and T is exposure time in the salt solution in hours. The area of the exposed surface of the coated substrate was 9.60 cm\(^2\), whereas the density of substrate was taken as 7.85 g/cm\(^3\). The corrosion protection efficiency (CE) of anti-corrosion pigment was calculated using following equation:

\[
CE = \left[ \frac{\text{CR} - \text{CR}'}{\text{CR}} \right]
\]

Where CR and CR’ are the corrosion rates without and with the anti-corrosion pigment respectively.

5.3 Results and Discussion

In the current study, PANI/r-GO hybrids with varying amount of graphene were incorporated in PVB matrix so as to achieve anti-corrosion coatings where both PANI and graphene synergistically contributed to the coating’s performance. Use of \textit{in-situ} polymerization was chosen to generate the hybrid nanoparticles as the growing PANI chains would be able to extensively adsorb on graphene surface without steric hindrance. In addition, organic
modification of graphene platelets with PANI was also expected to lead to nanoscale dispersion of graphene platelets in PVB matrix.

### 5.3.1 Characterization of PANI/r-GO Hybrid Nanoparticles

X-ray diffraction patterns of PANI, r-GO, and PANI/r-GO hybrids are shown in Figure 5.4. The characteristic broad diffraction peak for r-GO was observed at $2\theta^\circ\sim27$ and (002) plane, which can be attributed towards short-range order in piled stacks having an interlayer spacing 0.34 nm. During thermal reduction, i.e. removal of intercalated water molecules and the oxide groups of hydroxyl and carboxyl groups, graphite oxide restores its crystalline state by reinstating conjugated graphene network (sp$^2$carbon) having structural defects such as residual oxygen-containing functional groups etc.$^{152, 153}$ The crystalline nature of pure PANI was observed due the presence of sharp crystalline diffraction peaks at $2\theta\sim25.2^\circ$ (interlayer spacing 0.35 nm) along with other peaks at $2\theta = 15^\circ$ and $21.9^\circ$. In the hybrids, where PANI intercalation took place between r-GO interlayers, slight broadness could be observed in the PANI diffraction peaks. On the other hand, the r-GO peak was absent in the spectra of the PANI/r-GO hybrids.$^{155}$ It indicated that extent of PANI intercalation in the graphene interlayers was significant, which resulted in the delamination of the graphene platelets. Even for the hybrid with the highest amount of graphene, the diffractogram did not show any diffraction peak corresponding to pristine graphene. However, it has to be noted that the diffraction peaks of PANI and graphene overlap to some extent. Thus, microscopy analysis was also carried out to confirm the intercalation of PANI in the graphene interlayers.
Figure 5.4 X-ray diffractograms of graphene, PANI, and PANI/r-GO hybrids

Error! Reference source not found. shows the TEM micrographs of pristine r-GO, ANI/10r-GO, and PANI/30r-GO. The morphology of the graphene platelets altered completely with PANI intercalation in the interlayers. As is evident in Figure 4(b),

Figure 5.5 TEM micrographs of (a) pristine graphene, (b) PANI/10r-GO hybrid and (c) PANI/30rGO
PANI was observed to uniformly cover the surface of the platelets, which was also the reason for the absence of any graphene diffraction signal in the X-ray diffractograms. Even increasing the amount of graphene in the hybrid exhibited similar morphology as shown in Figure 4(c). PANI chains are expected to physically adsorb on the surface of graphene nanoparticles due to interactions of N atoms with functional groups on graphene surface as well as due to van der Waals forces between PANI chains and graphene surface. This is, thus, also expected to affect the polymer crystallinity as the PANI chains would adsorb on the surface of platelets simultaneously during their synthesis, which will hinder their effective crystallization.

DSC melting curves of pure PANI and PANI/r-GO hybrids are shown in Figure 5.6. As is evident, the addition of r-GO in polyaniline resulted in significant decline in peak melting temperature of the polymer (Table 5.1). Moreover, the decrease in the melting point was proportional to the amount of graphene in the hybrid. As compared to 178°C for the pure polymer, the peak melting point of the polymer in PANI/50r-GO hybrid was reduced to 111°C. It
indicated that the crystallization of the polymer was affected with increasing amount of r-GO and the graphene platelets hindered the chain mobility and packing into the crystal structure.

Table 5.1 Calorimetric properties of PANI and PANI/r-GO composite particles

<table>
<thead>
<tr>
<th>Polymer/Composite</th>
<th>Peak melting temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>178</td>
</tr>
<tr>
<td>PANI/10r-GO</td>
<td>132</td>
</tr>
<tr>
<td>PANI/20r-GO</td>
<td>118</td>
</tr>
<tr>
<td>PANI/30r-GO</td>
<td>118</td>
</tr>
<tr>
<td>PANI/40r-GO</td>
<td>115</td>
</tr>
<tr>
<td>PANI/50r-GO</td>
<td>111</td>
</tr>
</tbody>
</table>

Figure 5.6 DSC melting curves for PANI/r-GO hybrids with different content of r-GO
It further indicated that the polymer was strongly adsorbed on the surface of the graphene platelets and was not just present as intercalated material in the interlayers. If the polymer was not immobilized to the surface, the excess polymer away from the interface would have been able to crystallize normally and would not have resulted in significant reduction in the melting point (e.g. in PANI/10r-GO, where a large excess of PANI would be available). With increasing amount of graphene in the hybrid, more surface was available for the growing PANI chains to absorb, which resulted in the increased extent of adsorption and subsequently gradual decrease in the peak melting point and overall crystallinity. Figure also shows the TGA thermograms of the PANI/r-GO hybrids compared with pure PANI. Initial mass loss around 100 °C was attributed to the evaporation of water molecules absorbed or adsorbed on the surface. The extent of moisture in the samples was minimal as the samples were dried overnight under vacuum before TGA analysis. For pure PANI, the weight loss from 100-350 °C could be attributed to the deprotonation of the PANI, whereas, before 600 °C, major weight loss transition was related to the degradation and decomposition of PANI. The hybrids exhibited similar degradation pattern as pure PANI. However, the extent of weight loss was decreased as the amount of graphene was enhanced in the hybrids, indicating increased thermal stability, though the thermal performance of the composites was very similar beyond PANI/10r-GO hybrid.

This improves thermal stability is really important in the coatings used for oil and gas industry where the coatings have to perform at higher temperature. The addition of these particles in the coatings neither will nor degrades during exposure to high temperature for longer periods of time. The coatings like epoxy or urethane can be used at higher temperature whereas incorporation these anti-corrosion pigments will not destroy their thermal stability. Further the use of these pigments with inorganic pigment can produce enhanced effect.
5.3.2 Anti-corrosion Performance and Protection Mechanism

Table 5.2 shows the corrosion rate of the PVB coatings reinforced with PANI/r-GO pigments when immersed in aqueous solution of 4 percent w/v NaCl for 800 h. Under the test conditions used, pure PANI pigment in PVB did not provide any superior corrosion protection than pure PVB coating itself, though both improved the protection of bare metal substrate. The corrosion protection efficiency (CE) was observed to increase with increasing amount of r-GO in the coatings. These results can be attributed to the additional protection provided by r-GO, along with the intrinsic protection provided by PANI. For instance, coating with PANI/40r-GO was nearly 52 percent more effective than the PVB coating without pigment. Further increase in
graphene content in PANI/50r-GO exhibited a marginal increase in protection efficiency to 58 percent, which indicated that the CE may have reached a plateau.

Table 5.2 Weight loss and corrosion rate after 800 h immersion in 4 percent NaCl

<table>
<thead>
<tr>
<th>Material/Coating</th>
<th>Weight loss (mg)</th>
<th>Corrosion rate (mm/y)</th>
<th>CE (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank substrate</td>
<td>26.7</td>
<td>0.039</td>
<td>-</td>
</tr>
<tr>
<td>Pure PVB</td>
<td>16.4</td>
<td>0.024</td>
<td>-</td>
</tr>
<tr>
<td>PANI</td>
<td>16.2</td>
<td>0.024</td>
<td>-</td>
</tr>
<tr>
<td>PANI/10r-GO</td>
<td>15.6</td>
<td>0.023</td>
<td>4.8t</td>
</tr>
<tr>
<td>PANI/20r-GO</td>
<td>12.4</td>
<td>0.018</td>
<td>24</td>
</tr>
<tr>
<td>PANI/30r-GO</td>
<td>10.7</td>
<td>0.016</td>
<td>34.7</td>
</tr>
<tr>
<td>PANI/40r-GO</td>
<td>7.9</td>
<td>0.012</td>
<td>51.6</td>
</tr>
<tr>
<td>PANI/50r-GO</td>
<td>6.9</td>
<td>0.01</td>
<td>58.2</td>
</tr>
</tbody>
</table>

To further confirm these findings, optical microscopy was employed to gain insights into the change in the surface topography of the substrates after the corrosion test. Figure 5.8 shows the surface of the coated carbon steel substrates before corrosion testing. Similar to the CE results, the PANI/40r-GO and PANI/50r-GO incorporated coatings were very similar dispersion
of pure PANI in PVB was difficult due to the aggregation of \textit{in-situ} generated polymer in the form of solid lumps, thus, resulting in the larger size distribution of PANI particles in PVB coatings. On the other hand, PANI/r-GO hybrids were more susceptible to uniform dispersion in the PVB matrix and resulted in much smaller particle sizes in the formed coatings. Moreover, a higher concentration of graphene in the hybrids did not pose any hindrance to the dispersion of the PANI/r-GO hybrids. The substrates were uniformly coated with the generated formulations, however, due to the brush coating method used, some surface roughness could be observed in the coatings. Figure 5.9 shows the surface of the coatings after the corrosion test as well as removal of the coating. Substrates coated with pure PVB (Figure 5.9(a)) and pure PANI in PVB (Figure
5.9(b)) formulations exhibited extensive surface corrosion, confirming the findings depicted in Table 5.2. It indicated that the corrosion media could penetrate faster through the coatings, thus, initiating the corrosion process. The substrate coated with PANI/10r-GO (Figure 5.9(c)) in PVB exhibited improved anti-corrosion performance as the extent of surface corrosion was markedly reduced in comparison with Figure 5.9(a) and (b). Similar to the findings in Table 5.2, a further increase in the graphene content enhanced the performance further. PANI/20r-GO, PANI/30r-GO, and PANI/40r-GO coated substrates optically exhibited a high level of stability to the immersion conditions. The similar testing of the substrates was also carried out at a relatively higher temperature of 40°C and the results are demonstrated in Figure 5.10 after removal of the surface coating. As expected, pure PANI was
observed to extensively corrode on the surface Figure 5.10(a). Similar to room temperature testing conditions, coating incorporating PANI/10r-GO exhibited decreased the extent of corrosion, which was further reduced in the PANI/20r-GO system. Formulation with PANI/40r-GO did not exhibit any significant initiation of the corrosion process. It indicated that the generated PANI/r-GO-based pigments were also effective at a higher temperature. Interestingly, the conductivity of the coatings decreased as the amount of reduced graphene was increased. It has been reported earlier that the lower conductivity of PANI/graphene composites results probably due to decrease in the degree of doping in PANI and change in the morphology of the composites \(^{155,158}\). Similarly, Sun et al. \(^{132}\) have also reported graphene/pernigraniline composite (GPCs) coatings in PVB with reduced conductivity for the corrosion protection of copper. The GPCs were generated by in-situ polymerization-reduction/doping process and the authors concluded that pernigraniline modified graphene in PVB was able to provide effective corrosion protection

The proposed phenomenon of corrosion protection by pure PVB coating and PANI/r-GO incorporated coatings is compared pictorially in Figure 5.11. The corrosion protection by the coating is due to generation of disconnection between bare metal and corrosive environment, thus, impeding the transportation of corrosive material. However, as shown in Figure 5.11(a), in the case of pure resin coating, the presence of free volume and coating defects result in faster penetration of corrosive solution, thus, resulting in corrosion at the surface. Fundamentally, it is, formation and degradation of iron oxide film occurs in the presence of water and oxygen along with additional accelerated effect caused by sodium chloride. Figure 5.11(b) shows the mechanism of corrosion protection in the presence of PANI/r-GO pigments embedded in the PVB coatings. The protection behavior of PANI at the interface of metal/electrolyte has been
described earlier in the literature. In this phenomenon, the formation of metal oxide layer occurs with the aid of more noble emeraldine salt (ES) of PANI. This form of PANI further leads to lower energy state and reduces to different forms such as non-conducting leucoemeraldine base (LEB) and emeraldine base (EB). This cycle is continuous and LE form turns to ES via EB form by oxygen. This cycle can be continuous only if the barrier properties of applied coating are able to avoid the removal of H⁺ (maintained acidic pH) by the surroundings. This process slows the formation of rust at the iron surface by providing passive layers of different forms of PANI.

Figure 5.10 Surface of the substrates after corrosion testing at 40°C and coating removal; (a) PANI, (b) PANI/10r-GO, (c) PANI/20r-GO and (d) PANI/40r-GO. The width of the images equals 200 µm
However, as observed in the current study, pure PANI present in the PVB matrix was unable to significantly slow down the corrosion rate probably due to the lower extent of PANI-(a)

Figure 5.11 Comparison of corrosion protection mechanisms in the (a) absence and (b) of PANI/rGO pigment nanoparticles incorporated in PVB

(b)
metal interface formation. In addition, the process of corrosion protection could be specifically enhanced by the addition of r-GO, as it resulted in the tortuous path for the corrosive media, thus, delaying the corrosion process. This was also confirmed from the improving corrosion protection efficiency as the amount of graphene was enhanced in the coatings. Such barrier effect of graphene-based reinforcement is called a ‘passive’ role. Further, the ‘active’ behavior of such material was realized in the coatings by the formation of ‘Schottky barrier’ at the interface, thus, leading to the depletion of electrons, which slowed down the corrosion half-cell reactions. Composites of PANI acted like hetro-junction, where PANI behaves as p-type while r-GO being n-type, thus, hindering the anodic and cathodic reactions respectively. The decreased conductivity of composites also impedes the transport of electron from graphene to PANI.

Furthermore, due to the physical adsorption of PANI on the graphene surface, the effect of graphene incorporation was synergistically enhanced by the presence of PANI due to its better interface with the metal. It has also to be noted that with these coatings systems, the corrosion reaction was not completely eliminated, however, it was significantly slowed down, thus underlining the need for the functional coatings to achieve superior material performance.

5.4 Conclusions

In the current study, polyaniline/graphene composite nanoparticle pigments with different compositions were generated by in-situ polymerization of aniline in the presence of graphene nano-platelets. In the PANI/r-GO hybrids, PANI intercalation took place between r-GO interlayers, which resulted in slight broadness in the PANI diffraction peaks. Diffraction peak corresponding to r-GO was also absent in the spectra of the PANI/r-GO hybrids, irrespective of the hybrid composition. The morphology of the graphene platelets altered significantly with
PANI intercalation in the interlayers. The platelets were observed to be uniformly covered on the surface with PANI. The peak melting point of the polymer was observed to reduce as a function of graphene content in the hybrids (e.g. 111 °C for PANI/50r-GO hybrid as compared to 178 °C for pure polymer), which indicated that the crystallization of the polymer was affected and the graphene platelets hindered the chain mobility and packing into the crystal structure.

Significant reduction in the melting point also indicated that the polymer was strongly adsorbed on the surface of the graphene platelets. The hybrids exhibited similar degradation pattern as pure PANI, however, the extent of weight loss was decreased as the amount of graphene was enhanced in the hybrids, indicating increased thermal stability. The PVB coatings incorporating PANI/r-GO hybrids exhibited superior anti-corrosion performance, which was enhanced as the amount of graphene in the hybrid particles was increased. For instance, coatings with PANI/40r-GO and PANI/50r-GO were nearly 52 percent and 58 percent more effective than the PVB coating without pigment. The optical analysis of the substrates immersed in NaCl solution for 800 h also confirmed the superior performance of the PANI/r-GO reinforced coatings, which resulted due to the tortuous diffusion path for corrosion media in the presence of graphene platelets. The synergistic effect of PANI/r-GO hybrids was also expected to have resulted from the formation of ‘Schottky barrier’ at interface thus leading to the depletion of electrons, which slowed down the corrosion half-cell reactions. The resulting PANI/r-GO nanoparticles represent functional pigments for organic coatings to achieve effective corrosion protection of metals.
CHAPTER-6 Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ AS A POTENTIAL CORROSION INHIBITOR FOR API 5L X80 STEEL IN ACIDIC ENVIRONMENT

Papers were published in *International Journal of Electrochemical Science* and *RSC Advances*

A.U. Chaudhry, Rahul Bhola Vikas Mittal, Brajendra Mishra
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Corrosion inhibitors are widely used in acid solutions during pickling, cleaning/descaling of boilers and several other industrial applications. Mostly the organic compounds containing nitrogen, oxygen and sulphur are employed; however they are high toxic and environmentally non-friendly. In this study, the inhibition performance of nano-powder of ferrites of nickel, zinc and ferrous in varying concentrations of 1M sulphuric acid on the corrosion behavior of API 5L X80 steel has been investigated. The nano-powder has been characterized using TEM, FESEM, XRD and its corrosion behavior in 1M H$_2$SO$_4$ has been studied using various advanced electrochemical tools such as EIS and potentiodynamic polarization (PD). It has been found that under the given acidic conditions, ferrites act as efficient corrosion inhibitors of steel. The order of inhibition efficiencies of ferrite concentrations is $0.008 > 0.01 > 0.05 > 0.07 > 1$M sulphuric acid. This inhibition is considerable and can be of significant importance for the oil and gas industry.

6.1. Introduction

The addition of corrosion inhibitors to prevent acid induced corrosion is a common and established practice in several industrial systems (especially oil and gas industry). Acid pickling is a phenomenon in which strong acids such as hydrochloric, hydrofluoric, sulphuric, phosphoric and nitric acid are used to leach out impurities from various alloys of iron, copper and aluminum. Moreover, pickling corrodes the containing vessel and is not advantageous to the industrial
processes. To prevent such a corrosive attack to the containing environment, inhibitors are added to the acid solution. Mostly organic molecules are used\textsuperscript{160}, however, researchers have also used vitamins\textsuperscript{161} and other environmentally safe green organic compounds as inhibitors\textsuperscript{162}. It has also been reported by several researchers that the use of inorganic inhibitors in acidic environments could be even more detrimental, owing to the severe localized attack once the passive film over the metal is broken\textsuperscript{163, 164}.

Recent research has shown that spinel based inorganic pigments of the general formula \(AB_2O_4\) have not only distinctive thermal and weather degradation resistance, but are also more environment friendly\textsuperscript{26, 165}. These are produced by a combination of two or more cations in the lattice structure and their properties are primarily assumed through their lattice characteristics. These type of pigments not only enhance the mechanical strength of the binder but also decrease its permeability towards destructive species\textsuperscript{34}.

The general formula for \(\text{MeO.Fe}_2\text{O}_3\) consists of an almost cubic closely packed oxygen arrangement where the cations reside in the tetrahedral and octahedral interstices\textsuperscript{166}. The use of spinel based ferrites as pigments in coatings is advantageous owing to their greater anticorrosion efficacy at higher temperatures and aggressive environments\textsuperscript{13}.

Pigment extract method is a convenient way to know its anticorrosion efficacy on a metal surface and depends upon various factors such as the solubility of pigment in testing solvent, dissolved oxygen concentration, alkalinity of extracts, formation of passive layer, thickness and nature of passive layer, nature of electrolyte, solubility of corrosion products and many more\textsuperscript{167, 168}.\textsuperscript{168}
Pryor et al. [13] used this extract method to study the litharge, metallic lead, red lead, basic lead carbonate, zinc, and zinc oxide in detail. It was further observed that the litharge extracts showed complete corrosion inhibition owing to the formation of $\alpha$-$\text{Fe}_2\text{O}_3$. Similarly, Miszczyk and friends tested the Evan’s drop experiment of micronized nickel zinc ferrite extracts in distilled water on steel surface and showed different cathodic and anodic behavior. This phenomenon was referred to the formation of hydroxyl ion due to dissolved oxygen which further reacted with cations present in the extract solution.

These products precipitated on the surface and hindered the electrochemical reaction for the transport of ionic and non-ionic species on the metal surface shown by following equation.

$$yM^{2+} + (3 - y)\text{Fe}^{2+} + 6\text{OH}^- \rightarrow M_y\text{Fe}_{(3-y)}(\text{OH})_6$$

Brodinova et al. [35] also used surface modified ferrites with varying contents of zinc, magnesium and Ca cations. The results showed that modified ferrites were better in terms of corrosion protection than the non-modified versions. The corrosion protection mechanism was proposed to be a result of formation of cations soaps which lowered the tendency of the binder to saponify on exposure to the hydroxyl ions formed during corrosion of the metal. Similarly, Wu et al. [169] prepared hybrid coating of PANI layered zinc nickel ferrites and organically modified silicates. The film was deposited via a spin coating on aluminum alloy. The anticorrosion properties of the hybrid film was excellent owing to the denser configuration of organically modified silicate due to the incorporation of nickel zinc ferrites/PANI. In another work, Kalendova [166] used different types of spinel pigments containing Zn(II), Ca(II), Mg(II), Sr(II), Fe(III), Al(III), and Ti(IV) cations and studied the properties of their extracts. It was concluded that these ferrites showed varying corrosion inhibition owing to the alkaline nature, solubility of
the aqueous phases, and formation of metal soaps and high thermal stability of the spinels. Furthermore, metals cations also inhibit corrosion in acidic solutions. The charge induced change in the physical and electrical properties of the double layer at the electrolyte-electrode interface directly interferes with the surface adsorption over the metal and thereby prevents corrosion. Wahdan et al. \textsuperscript{170} showed that the maximum protective ability of Cu\textsuperscript{2+} in 1M sulphuric acid was observed at lower concentration. Several researchers also proposed Zn\textsuperscript{2+}, Cd\textsuperscript{2+} and Mn\textsuperscript{2+} to be efficient in acidic solution against corrosion owing to their ability to hinder the hydrogen evaluation reaction \textsuperscript{14, 15}. Nano-materials are unique because of their smaller size. The smaller particle has higher surface-to-volume ratio and thus more atoms tend to reside on the surface than inside the particle itself. The use of nano-particles for anticorrosion coatings has achieved significant attention and importance \textsuperscript{171}. Several researchers have shown nano particles to perform better and qualify them as a better alternative for anticorrosion coatings in composites and polymers \textsuperscript{172}.

In the present work, non-toxic, nano particle extracts of nickel zinc ferrites (Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}) in 1M Sulphuric acid were prepared and their inhibition effects were studied on the API 5L X80 steel.

6.2. Materials and Methods

6.2.1. Materials Preparation

Nano-powders of Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} (99.9 percent pure, American elements, CA USA) were used as supplied. The impurities details are Al <0.05, Ba <0.05, Ca <0.1, Cd < 0.001, Co <0.05, Cu <0.01, Mg <0.05, Pb<0.001, Si <0.01 in weight percent. API-5L X80 steel coupons having weight percent composition listed as; C 0.07, Mn 1.36, Ti 0.008, S 0.003, P 0.004, Fe Balanced,
were machined to 10 × 10 × 4 mm dimensions from a carbon steel pipeline. A tap and drill hole of 3-48 tpi was drilled to one long side of the coupon. The specimens were finished with different grades of SiC grit papers up to 2400 grit, polished to a mirror finish. The samples were then cleaned and degreased with industrial grade acetone, dried and weighed with an accuracy of ±1 mg.

The ferrite extracts were prepared according to the method explained by Zin et al.173 A stock solution of the extracts were prepared by solution leaching using 6 gm of each pigment in 1L of 1M H₂SO₄ stirred for 72 hours at room temperature. The solution was filtered using high suction and no residue was found on the filter paper suggesting its complete solubility in 1M H₂SO₄. In order to obtain solutions with different concentrations of nickel zinc ferrites, stock solution was further diluted with 1M H₂SO₄.

6.2.2. Pigment Characterization

Transmission electron microscopy (TEM) imaging was performed to characterize the nano powder. FEI Philips C200 TEM with point-to-point resolution of 0.11 nm, at 200 kV was used. The samples were prepared by dispersing approximately 1 mg of NZF in 10 mL of methanol and sonicating for 30 minutes in a water bath at room temperature. One drop of the suspension was then deposited on a 400-mesh copper grid covered with thin amorphous film to view under the microscope.

JEOL JSM-7000F, Field Emission Scanning Electron Microscopy (FE-SEM) was performed to evaluate particle morphology in the nano powder at 2kV under high vacuum at a working distance of 10 mm.
X-ray diffraction (XRD) measurements were performed to determine the crystalline nature of the nano particle. Philips PW 3040/60 spectrometer using Cu Kα radiation in range of 10° to 100° at scan rate 0.050° was used and the peaks and planes obtained were matched using X'PertHighScore software. Debye–Scherrer equation was further used to confirm the peaks obtained and has been given below:

\[ \tau = \frac{K\lambda}{\beta \cos\Theta} \]

where, \( \tau \) is the diameter, \( \beta \) (radian) is the half-intensity width of the relevant diffraction, \( \lambda \) is the x-ray wavelength, K is a dimensionless shape factor (in this case 0.9 was taken) and \( \Theta \) is the angle of diffraction (in this case is 35° corresponding to intense peak).

### 6.2.3. Electrochemical Measurements

A three-electrode cell assembly consisting of steel coupon as the working electrode (WE), platinum wire as the counter electrode (CE) and a saturated calomel electrode as the reference electrode (RE) was used for the electrochemical measurements. Electrochemical testing was performed in a closed system at room temperature under naturally aerated conditions using a Gamry 600 potentiostat/galvanostat/ZRA. The sequence of electrochemical techniques has been described below.

**Electrochemical impedance spectroscopy (EIS):** Impedance measurements were performed at the open circuit potential (OCP) at 2 and 5 hours of immersion. The frequency sweep was applied from \( 10^5 \) to \( 10^2 \) Hz with the AC amplitude of 10 mV.
Potentiodynamic polarization: Potentiodynamic polarization measurements were performed at 5 hours of immersion by polarizing the working electrode from an initial potential of -250 mV vs. OCP up to a final potential of 750 mV vs. OCP. A scan rate of 0.1667 mV/s was used for the polarization sweep.

6.2.4. Surface Characterization

Surface characterization of the working electrode was performed to carefully evaluate the corrosion products and the metal after the electrochemical attack. Steel coupons were carefully disengaged from the cell assembly, dried and observed under the microscope. The surface film was also gently removed from the coupons and observed under the microscope.

FEI Quanta 600i Environmental Scanning Electron Microscope (ESEM) with PGT Prism Energy Dispersive X-Ray Spectrometer (EDS), X-ray diffraction (XRD) and Bio-Rad Fourier transform infrared spectroscopy (FT-IR) were used to investigate the surface morphology and elemental composition of the corrosion products. For ESEM the samples were gold coated before use and observed at 20 kV and a working distance of 10 mm. XRD analysis was also performed to differentiate between the various phases present in the corrosion products over the metal coupon. Philips PW 3040/60 spectrometer using Cu Kα radiation in range of 10° to 100° with scan rate of 0.050° was used and the peaks and planes were analyzed using X’PertHighScore software. FTIR was performed in a range of 400-4000 cm⁻¹ at a scan rate of 100 scans/spectrum using the Perkin Elmer model Fourier Transform Infrared. Corroded steel samples were directly placed on the testing plate at room temperature.
6.3. Results and Discussion

The TEM images for the ferrites have been shown in Figure 6.1(a) and 1(b). The morphology of the nano particles resembles a sphere with a size ranging between 10 to 15 nm. FESEM images for the particles as shown in Figure 6.2, represent the powder in the form of agglomerates of sizes ranging between 1 to 10 μm. The aggregation of particles is due to the magnetic attraction between the particles. These aggregations of the particles can destroy the properties of coatings due to poor interaction with the coatings which creates defects in the coatings. These defects can provide easy passage for the corrosive solution to reach at the surface which further degrade the coating, promotes electrochemical reactions and blistering the coating. The careful synthesis of nanocomposites coating can reduce these defects.
Figure 6.1 (a-b) Transmission electron microscopy images of Nano-nickel zinc ferrite

Figure 6.2 FESEM of Nickel Zinc Ferrite showing agglomerated of nanoparticles
X-ray diffraction pattern obtained for nickel zinc ferrites has been shown in Figure 6.3 (JCPDS No.08-0234). The particle size as determined using Scherrer formula was found to be 12 nm which is in close range as calculated from TEM.

The analysis showed the presence of cubic spinal structure of the ferrites with a lattice parameter of 8.4Å° and corresponding planes of (111), (220), (311), (400), (422), (511), and (440), representing the ferrite lattice.

6.3.1. Electrochemical characterization

Figure 6.4 and Figure 6.6 presents the EIS Nyquist and Bode curves respectively for varying ferrite concentrations in 1M H₂SO₄. At both two and five hours of immersion, the alloy shows a
one time constant impedance response for all concentrations of ferrites. Analysis of phase angle are really helpful to understand the protecting action of corrosion inhibitor on steel. Phase angle helps to analyze the properties of film form on the metal surface during corrosion inhibition process. Phase angle can be divided with different range of frequency, i.e. at very high frequency the phase gives the behaviour of outermost layer of the film/coating. The intermediate frequency represents the properties of film/coatings where as the lowest frequency gives the metal properties. The reason to divide the regions of phase angle with frequency range, is that at very high frequency the ions are unable to respond to the applied AC frequency where as at very low frequency the ions have enough time to respond.

Figure 6.4: Impedance plots (Nyquist & Bode) for varying concentrations of Nickel Zinc Ferrite in 1M \( \text{H}_2\text{SO}_4 \) at two hours
Figure 6.4 Continued.

This behavior can be easily noticed in the phase angle Bode curves as a single hump for the one-time constant phase response. The inhibition efficiencies of the different ferries concentrations increase with time as noticed in Table 1. This indicates the stability of the protective ferrite film formed on the alloy surface.

Figure 6.5 represents the monophasic circuit model used to fit EIS data. This circuit model simulates the structure of a barrier coating over the electrode surface and is composed of $R_s$, the solution resistance and $R_{ct}$ and CPE, the resistance and capacitance of the barrier layer. CPE is known as constant phase element and shows a frequency independent behavior in the phase angle. CPE consists of two components known as capacitance and a constant. The constant defined the surface inhomogeneity of the working electrode.
The assumption of a simple $R_{ct} - C_{dl}$ is usually a poor approximation especially for systems showing depressed semicircle behavior. This behavior shows that the surface of the working electrode is changing with the time and corrosion reactions. For the description of a frequency independent phase shift between the applied AC potential and its corresponding current response, a constant phase element (CPE) is used, where impedance of the CPE is given by,

$$Z_{(CPE)} = [Q (jω)^n]^{-1}$$

where, $Q$ is the constant of CPE, $ω$ is the angular frequency in rad s$^{-1}$ and $n$ is the exponential term which can vary between 1 for pure capacitance and 0 for a pure resistor$^{14, 60, 176, 177}$. $n$ is a measure of the surface inhomogeneity; the lower is its value, the higher is the surface roughening of the metal/alloy$^{60}$. The value of $Q$ also shows the amount of area available for the corrosion process. The constant phase behavior also indicates that corrosion behavior of steel is changing with time which shows change in the surface of electrode. The frequency independent

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Figure 6.5: Circuit model used to fit the impedance plots
behavior usually observe at the intermediate frequency showing that ions are unable to response properly to the applied AC frequency.

Figure 6.6 Impedance plots (Nyquist & Bode) for varying concentrations of Nickel Zinc Ferrite in 1M $\text{H}_2\text{SO}_4$ at 5 hours
Table 6.1 Impedance parameters derived from circuit modeling at 2 hours of immersion

<table>
<thead>
<tr>
<th>Concentration of Nickel Zinc Ferrite (g/L)</th>
<th>Rs</th>
<th>Rct</th>
<th>IE percent</th>
<th>CPE</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0084</td>
<td>0.44</td>
<td>128.6</td>
<td>63.57</td>
<td>1.44 * 10^{-4}</td>
<td>0.956</td>
</tr>
<tr>
<td>0.016</td>
<td>0.82</td>
<td>63.75</td>
<td>26.52</td>
<td>1.92 * 10^{-4}</td>
<td>0.938</td>
</tr>
<tr>
<td>0.05</td>
<td>0.782</td>
<td>58.74</td>
<td>20.25</td>
<td>1.89 * 10^{-4}</td>
<td>0.942</td>
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<tr>
<td>0.07</td>
<td>0.297</td>
<td>53.23</td>
<td>12.00</td>
<td>1.63 * 10^{-4}</td>
<td>0.987</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$</td>
<td>0.298</td>
<td>46.84</td>
<td>-</td>
<td>1.81 * 10^{-4}</td>
<td>0.981</td>
</tr>
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</table>

At 5 hours of immersion

<table>
<thead>
<tr>
<th>Concentration of Nickel Zinc Ferrite (g/L)</th>
<th>Rs</th>
<th>Rct</th>
<th>IE percent</th>
<th>CPE</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0084</td>
<td>0.44</td>
<td>128.9</td>
<td>72.64</td>
<td>1.99 * 10^{-4}</td>
<td>0.959</td>
</tr>
<tr>
<td>0.016</td>
<td>0.839</td>
<td>57.52</td>
<td>38.69</td>
<td>3.16 * 10^{-4}</td>
<td>0.950</td>
</tr>
<tr>
<td>0.05</td>
<td>0.769</td>
<td>53.01</td>
<td>33.48</td>
<td>3.33 * 10^{-4}</td>
<td>0.955</td>
</tr>
<tr>
<td>0.07</td>
<td>0.235</td>
<td>41.66</td>
<td>15.36</td>
<td>2.89 * 10^{-4}</td>
<td>0.973</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$</td>
<td>0.931</td>
<td>35.26</td>
<td>-</td>
<td>4.65 * 10^{-4}</td>
<td>0.961</td>
</tr>
</tbody>
</table>

$R_s$, $R_{ct}$, and CPE values derived from the impedance plots have been tabulated in Table 6.1. $R_{ct}$ value is the lowest for pure acid, representing its low resistance to conduction of charge/electrons and thereby allowing easy flow of electrons over the metal surface resulting in oxidation of iron to the ferrous state (equation 5). According to the Butler-Volmer concept involving polarization with charge transfer kinetics, higher $R_{ct}$ restricts the movement of charges and prevents the various reactions occurring during the corrosion process. It increases from 46.8 Ω cm$^2$ for pure acid to 128.6 Ω cm$^2$ for the lowest concentration of ferrite.
Moreover, the $R_{ct}$ value is the highest for the lowest concentration of ferrite and decreases as the concentration of ferrite increases, suggesting greater corrosion inhibition effect at low ferrites concentrations. This result is economically relevant to industry and thus proposes ferrites as efficient corrosion inhibitors for industrial applications.

The potentiodynamic polarization curve for varying concentrations of ferrites in 1 M $\text{H}_2\text{SO}_4$ has been presented in Figure 6.7. The corrosion rate for the alloy in 1M $\text{H}_2\text{SO}_4$ is close to 244 mpy compared to 51 mpy at the lowest concentration of ferrites. The potentiodynamic data is in agreement with the corrosion parameters obtained from the impedance plots and has been shown in Table 6.2. This protection phenomena by ferrites ions in the solution indicates that cations from the ferrites adsorbs on the metal surface and form thin of protection. This phenomena converted in to galvanic at higher concentration.

![Figure 6.7 Potentiodynamic plots for varying concentrations of Nickel Zinc Ferrite in 1M $\text{H}_2\text{SO}_4$ at 5 hours](image)
Table 6.2 Potentiodynamic parameters obtained from polarization curves at 5 hours

<table>
<thead>
<tr>
<th>Concentration of Nickel Zinc Ferrite in 1M H$_2$SO$_4$ (g/L)</th>
<th>$I_{corr}$ (A/cm$^2$)</th>
<th>$E_{corr}$ (mV)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>$1.11 \times 10^{-3}$</td>
<td>-528.50</td>
<td>50.91</td>
</tr>
<tr>
<td>0.01</td>
<td>$3.19 \times 10^{-4}$</td>
<td>-442.2</td>
<td>161.7</td>
</tr>
<tr>
<td>0.05</td>
<td>$3.64 \times 10^{-4}$</td>
<td>-439.0</td>
<td>166.3</td>
</tr>
<tr>
<td>0.07</td>
<td>$4.01 \times 10^{-4}$</td>
<td>-432.1</td>
<td>183.4</td>
</tr>
<tr>
<td>1M</td>
<td>$5.31 \times 10^{-4}$</td>
<td>-458.6</td>
<td>244.0</td>
</tr>
</tbody>
</table>

The lower corrosion rate at the lowest ferrite concentration makes it suitable to be used in industrial application economically and efficiently. The different ferrites concentrations follow the corrosion inhibition efficiency as follows; 0.008 > 0.01 > 0.05 > 0.07 > 1M sulphuric acid, thus lesser the amount higher is the inhibition advantage.

6.3.2. Surface characterization

The inhibition of iron corrosion in the presence of sulphuric acid owing to the formation of ferrous sulfate (FeSO$_4$) has been proposed by several authors $^{178}$. The various reactions taking part in the surface phenomena are summarized below$^{179}$:

$$Fe \rightarrow Fe^{2+} + 2\bar{e} \text{(anodic)}$$

$$2H^+ + 2\bar{e} \rightarrow H_2 \text{(cathodic)}$$

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \text{(overall reaction)}$$
It was observed that each concentration revealed a peculiar image with the greatest surface damage over the pure acid and the least damage with minimal ferrite concentration in acid solution. The ferrites form a coherent and homogeneous layer on the metal surface and thus

![ESEM images of steel coupons for varying concentrations of nickel zinc ferrite in 1M H₂SO₄](image)

Figure 6.8 ESEM images of steel coupons for varying concentrations of nickel zinc ferrite in 1M H₂SO₄
inhibit corrosion. EDS analysis of the metal samples revealed two regions; lighter region and darker region. The lighter region corresponds to the surface rich in corrosion products comprising of sulfur and oxygen as shown in Figure 6.9a. The darker region represents the deeper areas with lesser concentrations of sulfur and oxygen compared to the lighter region. The presence of iron, sulfur and oxygen were found in general with a little amount of zinc and nickel in Figure 9b, present as various compounds in ferrite over the surface. The presence of zinc and nickel cations can be attributed to surface adsorption of ferrites over the metal surface [20, 33].

ESEM coupled with EDS was used to comprehend the surface morphology and elemental composition of the corrosion products over the metal coupons exposed to varying concentrations of ferrites and pure acid and has been shown in Figure 6.8a-e. Different regions on the surface i.e. dark and light regions were subjected to EDAX. Different composition of different elements were found on the surface.
Figure 6.9 Energy dispersive spectroscopy (EDS) of steel samples surface after testing in 0.01 g/L (a) Light Region (b) Dark Region

Figure 6.10 XRD pattern of corroded surface after immersion in 1M $\text{H}_2\text{SO}_4$
Figure 6.10 shows the X-ray diffraction pattern for the mixed phases present on the metal surface. X-ray diffraction was used to differentiate the various mixed phases by comparing obtained data with JCPDS cards issued by ICDD. The surface pattern over the pure steel coupon was also examined. The characteristic peaks of iron carbide and α-ferrite were observed in the case of carbon steel surface at a 2θ ~ 44° corresponding to (510) JCPDS 20-509 and a 2θ ~ 82° corresponding to the (211) JCPDS 6-696 respectively. These two peaks were also observed in all the cases of corroded samples. In case of 1M sulphuric acid not only the intrinsic carbon steel peaks but also the peaks for the mixed phases of hydrous iron sulfate and iron sulfide were observed corresponding to 2θ ~ 41.5°(612) and 2θ ~ 42.5°(31) respectively.

These peaks were also observed in the XRD patterns for varying concentrations of ferrites in acid. In those cases where ferrite inhibitor was used, mixed phases such as nickel sulfide 2θ ~ 15.5°(002) JCPDS24-1021, 2θ ~19°(022), 2θ ~21.5°(040) JCPDS 24-1021, zinc sulfide 2θ ~ 29.5°(104), 2θ ~ 27°(100), 2θ ~ 34°(106) JCPDS 12-688 and iron sulfide 2θ ~ 25.5°(220) were observed.

The analysis confirms that adsorption of zinc and nickel occurs on the surface and react to form sulfides in the same manner as iron reacts to form sulfide or sulfate. This leads to the formation of a protective film and prevents corrosion in the presence of ferrite particles.

Figure 6.11 shows the FT-IR spectra for the different phases present over the metal surface. The characteristic band at ~1080 cm⁻¹ represents the formation of sulfates and is not observed over the steel sample. The characteristic peaks at ~1089 in pure sulphuric acid, 1088.8 in 0.07 g/L, 1090 in 0.05 g/L, 1086 in 0.01 g/L, and 1080 cm⁻¹ in 0.008 g/L represent sulfates in various acid concentrations. Small proportions of characteristic iron oxide peaks at ~1090 cm⁻¹ were also observed. The band at 1635 cm⁻¹ could be due to the presence of adsorbed water in
corroded samples while this band does not appear on the pure steel sample\textsuperscript{183}. Magnetite (Fe\textsubscript{2}O\textsubscript{3}) peaks were also observed at \(\sim 600 \text{ cm}^{-1}\) in few samples.

\textbf{Figure 6.11: FT-IR spectra for varying concentration of Nickel Zinc Ferrite in 1M sulphuric acid}

\textbf{6.4. Conclusions}

Anti-corrosion behavior of Nickel Zinc Ferrite is well recognized and could be of significant help in corrosion inhibition in various industrial processes. The API 5L X80 steel investigated in sulphuric acid with varying concentrations of ferrites exhibit a considerable decrease in corrosion rate compared to the one without ferrites.

The lowest concentration of ferrites exhibit higher corrosion inhibition compared to the others and hence it can be used in minimal quantities economically and efficiently. The use of such a small concentration of inhibitor as a filler in various polymeric materials may act as a starting point in developing self-healing and corrosion resistant protective coatings.
Papers were published in *Dyes & Pigments, Corrosion Science & Technology* and *RSC Advances*,

A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

There have been increased interests in using nanoparticle-based anticorrosion pigments in various industrial applications such as working fluids, lubricants, oil and gas fields, cooling water, anticorrosion coatings, etc. In this article, nano-nickel ferrite used as corrosion inhibitor pigment for carbon steel in 1M sulphuric acid and 3.5percent NaCl solutions. The pigment has been characterized using Transmission electron microscopy and X-ray diffraction. Effects of solutions having varying concentrations of the pigment on corrosion response are studied using electrochemical cell via open circuit potential, electrochemical impedance spectroscopy, linear polarization resistance and potentiodynamic methods. Results indicate that the corrosion inhibition is inversely proportional to increasing cations concentrations. Increased corrosion with increasing cations concentration has been attributed to the domination of galvanic corrosion of the steel which occurs via adsorption of metallic cations produced from nickel ferrite such as Ni$^{++}$ and Fe$^{++}$. Marked inhibition efficiency can be of significant importance for industries.

### 7.1 Introduction

Corrosion caused by exposure to metals to the acidic or saline environment has been one of the key problems. Acid pickling, a commonly used process which consists strong acids such as hydrochloric, hydrofluoric, sulfuric, phosphoric and nitric acids, to remove impurities from ferrous, copper and aluminum alloys, causes corrosion$^{164, 184}$. On the other hand, seawater comprising upper limit of 3.5 percent NaCl, serves cost effective on industrial scale$^{185}$. X-80
steel is considered as an economical resource to design and build long pipelines and vessels for submersed or underground applications due to the handling of acidic and saline media frequently. Severe environments such as acidic or saline, make X-80 steel more susceptible towards corrosion, limiting its practical applications for long periods of time\textsuperscript{129}.

Corrosion process is a result of an electrochemical phenomenon that occurs between metals and the environment. It involves the transfer of charge from one chemical species to another which results in impairment of metal as shown in Figure 7.1 for sodium chloride aqueous media where chloride ions accelerate the corrosion process. The accelerating corrosion process involves the dissolution of an iron oxide film with the aid of chloride ions and also sodium and chloride ions enhance the transportation of electrons. To slow down the corrosion process, many methods can be employed, and among those corrosion inhibitors have their plenteous importance owing their cost effectiveness and easiness of use. In general, the corrosion inhibition of metals can be attributed to interactions between free electrons of inhibitor and empty orbital of metals which result in the formation of metal protective surface complexes\textsuperscript{5}. These protective films slow down the deterioration process of metals by suppressing either cathodic, anodic or both the processes. Based on the final applications of metals, corrosion inhibitors, classified as organic and inorganic, can be used. Inorganic corrosion inhibitors include sulfites, ferric salts, nitrates and calcium ions etc. The protection mechanisms offered by inorganic inhibitors are based on their type. For example, sulfites\textsuperscript{6} consume the dissolved oxygen in solutions to reduce oxygen availability to retard corrosion, ferric salts and nitrates\textsuperscript{7} foster passivity of metals in active-passive regions, and the calcium ions\textsuperscript{8} reinforce the protective films forms on metal surfaces. On the other hand, the organic inhibitors have polar groups such as sulfur, nitrogen, selenium etc which help them to chemisorb on metal surfaces resulting formation of protective surface
complexes. Such inhibitors are amines- and imidazolines-derivatives, alkyl pyridines, thioureas, etc\textsuperscript{186}.

Inorganic pigments such as litharge, metallic lead, red lead, basic lead carbonate, hexavalent chromium compounds, and zinc oxide have been extensively used in polymer coatings for the enhancement of anti-corrosion\textsuperscript{9}, barrier\textsuperscript{10}, mechanical\textsuperscript{11}, electrical and optical\textsuperscript{12}, rheological and adhesion properties, and resistance against the environmental degradation\textsuperscript{13}. Certain metallic cations in solutions can also be used to retard corrosion of metals in different environments. Metallic cations affect the electrochemical process of corrosion. The metallic cations find applications in various processes; I) inhibiting hydrogen evolution by Cd\textsuperscript{+2}, Mn\textsuperscript{+2}, Ce\textsuperscript{+4}\textsuperscript{14, 15}; II) corrosion inhibition of titanium and stainless steel in passive regions by Fe\textsuperscript{+3} and Cu\textsuperscript{+2} via fostering passivity of these metals by the action of these cations in the cathodic reactions\textsuperscript{16, 17, 18}; III) corrosion retarding properties of lead anode in sulphuric acid by Co\textsuperscript{+2} ions via increasing catalytic activity of surface oxides for oxygen evolution which in turn increases the current efficiency of the oxygen evolution reaction; and hence little current is available for counter anodic reaction\textsuperscript{19}, IV) corrosion inhibition of iron by reducing corrosion promoting species using Sn\textsuperscript{+2} ions in acid pickling process\textsuperscript{20}.

![Schematic diagram of iron corrosion process, production, and consumption of electrons resulting corrosion products](image-url)
Spinel-based inorganic pigments (general formula $AB_2X_4$) have shown superior thermal and weather degradation resistance and are also environment benign\textsuperscript{13}. The applications of these pigments have been proven in the fields of biomedical\textsuperscript{26}, semiconductors\textsuperscript{27}, smart materials\textsuperscript{28}, magnetic and optical materials\textsuperscript{29}. The spinel-based pigments can be produced by combination of two or more metallic cations in lattice structure of metallic oxide, according to the following reaction indicated by the following equation:

$$MO + A_2O_3 \rightarrow MO_2A_3O_3$$

where, $M$ and $A$ can be Fe, Al, Sr, Ba, Mg, Mn, Ni, Zn, or Ca etc. $MO_2A_3O_3$ consists of an almost cubic, closely packed oxygen arrangement in which the cations reside on the tetra- and octahedral interstices\textsuperscript{30}. Magnetic ceramics or ferrites adopt inverse spinel crystal structure which is similar to the general spinal structure where the divalent cation likes to reside at octahedral positions whereas trivalent divided equally among octa- and tetrahedral position\textsuperscript{187}. For nickel ferrite, total 56 atoms crystallizes in an Oh7 cubic system having space group Fd.3m (227) where nickel cations found at octahedral position (16d), whereas ferrite cation found at octa-(16d) and tetrahedral (8a) positions with oxygen occupies 32e represented by Wyckoff notations\textsuperscript{28}.

In spinal-based inorganic pigments, using ferrites can be advantageous as anticorrosion pigments: ferrites retain their anticorrosion efficiency even exposing to higher temperatures and aggressive environment\textsuperscript{31}. The inhibition action of ferrites on metal substrates can be determined via extract method\textsuperscript{32}. In this method, pigment ions are obtained by dissolving the pigments in corrosive solution and anticorrosion properties such as passive layer formation, are evaluated by immersing the substrate metal in corrosive solution\textsuperscript{168}. The inhibition action of the extracts depends on the solubility of pigments in a corrosive solvent, development of passive layer on
metals separating metals from the corrosive media, thickness and nature of the passive layer, and the nature of electrolyte\textsuperscript{32}.

Recently, various kinds of ferrites have been reported as corrosion inhibiting pigments\textsuperscript{30,35,188}. The ferrite pigments not only enhance the mechanical strength of binder via a reaction that produces cationic soaps but also decrease binder’s permeability towards the destructive species\textsuperscript{34}. Brodinova et al.\textsuperscript{35} used ferrites with contents of zinc, magnesium and calcium cations for carbon steel. They showed the formation of cationic soaps from ferrites which lowered the tendency of the binder to sponify upon exposure to the hydroxyl ions which are formed during metal corrosion. Similarly, Wu et al.\textsuperscript{169} prepared hybrid coating of zinc-nickel ferrites and organically modified-silicate and showed the improved anticorrosion behavior of these coatings for aluminum alloy. This improved performance of the coatings was attributed to the denser configuration of organically modified silicate via nickel zinc ferrites. Also, Miszczyk and coworkers\textsuperscript{189} tested the Evan’s drop experiment of micronized nickel zinc ferrite extracts in distilled water on the steel surface, and studied the formation of cathodic and anodic regions on steel using atomic force microscopy. The formation of different regions on the metal substrate was attributed to the reaction of hydroxyl ion with cations present in the extracts.

In some recent reports, the use of nano-inorganic particles as anticorrosion pigments in polymer coatings has been reported. The nano-pigments contain advantages over customary pigments for their improved barrier and anticorrosion properties in polymer coatings such as epoxy-clay\textsuperscript{190}, polyaniline/TiO\textsubscript{2}\textsuperscript{191}, PMMA/graphene\textsuperscript{192}, PVK/Multiwall nano tube\textsuperscript{193}.

In this work, non-toxic nano-nickel ferrites (NiFe\textsubscript{2}O\textsubscript{4}) have been used as an anticorrosion pigment for API 5L X-80 line pipe steel. The nano-ferrites were extracted in 1M Sulphuric acid
and 3.5 percent NaCl, and their protection mechanism and corrosion retardant properties are reported. The effects of nano-ferrites concentration and metal immersion time on the electrochemical properties of X-80 line pipe steel are studied.

7.2 Materials and methods

7.2.1 Material preparations

Nano-powders of NiFe$_2$O$_4$ (99.9 percent (weight) pure with Al, Ba, Co, Mg <0.05 percent, Ca <0.1 percent, Cu, Si <0.01 percent and Pb<0.001 percent) with average particle size 100 nm, molecular weight 234.38 g/mol and density 5.368 g/cm$^3$ were purchased from American Elements, USA and used as received. API-5L X-80 steel coupons (elemental composition: C 0.07 (weight) percent, Mn 1.36 percent, Ti 0.008 percent, S 0.003 percent, P 0.004 percent and remaining iron), purchased locally, were machined to 10 × 10 × 4 mm dimensions.

Machined X-80 steel is used as the working electrode, prepared by jointing with a copper wire via conductive silver adhesive and the joints were embedded in epoxy resin so that the exposed surface area was 10 mm$^2$. The specimens were surface finished using different grades of SiC grit papers up to 2400 grit, polished to a mirror finish followed by cleaning and degreasing with industrial grade acetone followed by drying in air.

To evaluate the protection behavior of ferrite, extracts were prepared in 1M H$_2$SO$_4$ and 3.5 percent NaCl using the method reported in ref. 173. Briefly, stock solutions of the extracts were prepared by solution leaching method in which pigment (6g) was added to 1M H$_2$SO$_4$(1L) followed by stirring for seventy-two hours using magnetic stirrers at room temperature and vacuum filtered using high suction. Similarly, six grams of pigment was added to NaCl aqueous
solution by shaking on alternative days continuously for fifteen days (because of the low solubility of pigment in water in the absence of acid) followed by vacuum filtration to obtain the extracts. The stock solutions were further diluted to various initiation concentrations. The concentrations of each ion in extracts were determined using inductively coupled plasma molar mass spectrometry (ICP-MS) before performing electrochemical testing and the pH of the solution 1M H$_2$SO$_4$ and 3.5 percent NaCl were found 0.90 and 6.8 at 20° C respectively.

7.2.2 Pigment Characterization

Transmission electron microscopy (TEM, FEI Philips C200) with a point-to-point resolution of 0.11 nm, at 200 kV was used. The samples were prepared by dispersing approximately 1mg of nickel ferrites in 10 mL of methanol followed by both sonicating for thirty minutes at room temperature. One drop of the suspension was then deposited on a 400-mesh copper grid covered with thin amorphous lacy carbon.

X-ray diffraction (XRD, Philips PW 3040/60 spectrometer) was carried out using Cu Kα radiation in the range of 10° to 100° at a scan rate 0.05°/min, and the peaks and planes obtained were matched using X'PertHighScore XRD software. The Debye–Scherrer equation$^{194}$ was used to determine the particle size using equation;

$$
\tau = \frac{k \lambda}{\beta \cos \theta}
$$

where, $\tau$ is diameter of the particle, $\beta$ (radian) is the half-intensity width of the relevant diffraction, $\lambda$ is x-ray wavelength, $k$ is a dimensionless shape factor (0.9 in this case), and $\theta$ is the angle of diffraction of the most intense peak.
7.2.3 **Electrochemical Measurements**

A three-electrode cell assembly consisting of steel coupon (embedded in epoxy) as the working electrode (WE) as shown in Figure 7.2, graphite as the counter electrode (CE) and a saturated calomel electrode as reference electrode (RE) were used for the electrochemical measurements. Electrochemical testing was performed in a closed system under naturally aerated conditions using a Gamry 600 potentiostat/galvanostat/ZRA at room temperature. The sequence of electrochemical techniques is described below. Corrosion studies were carried out in 1M H$_2$SO$_4$ and 3.5 percent NaCl containing varying concentration of nickel ferrites pigment solution (0-200 ppm).

Open Circuit Potential (OCP): The open circuit potential of steel samples was recorded against SCE electrode as a reference electrode for four hours consisting of two steps, each comprised of two hours, in solutions of 1M H$_2$SO$_4$ and 3.5 percent NaCl with different concentrations of nickel ferrites. After the completion of each step, EIS and LPR were measured by closely following the ref. 55.

Electrochemical impedance spectroscopy (EIS): Impedance measurements were performed as a function of open circuit potential (vs. E$_{OCP}$) at two and five hours from the time of immersion. The frequency sweep was performed from $10^5$ to $10^{-2}$ Hz at 10 mV AC amplitude. The Bode plots were modeled with monophasic circuit model used to fit EIS data as resistor and capacitors as shown in Figure 7.3, where R$_{ct}$ was calculated using the diameter of semicircle and C$_{dl}$ was derived from CPE element.
The assumption of a simple $R_{ct} - C_{dl}$ is usually a poor approximation especially for systems showing depressed semicircle behavior. For the description of a frequency independent phase shift between the applied AC potential and its corresponding current response, a constant phase element (CPE) is used, where impedance of the CPE is given by,

$$Z(CPE) = Y_o^{-1} [j\omega]^{-n}$$

where, $Y_o$ is constant of CPE, $\omega$ is the angular frequency in rad s$^{-1}$ and $n$ is the exponential term which can vary between 1 for pure capacitance and 0 for a pure resistor$^{14, 60, 176, 177}$. $n$ is a measure of surface in homogeneity; the lower is its value, the higher is the surface roughening of the metal/alloy$^{60}$.

This circuit model simulates the structure of a barrier coating over the electrode surface and also explain the surface inhomogeneity or roughness. At two and five hours, the alloy shows a one-time constant impedance response for all concentrations of ferrites. This behavior can be easily noticed in the phase angle Bode curves as a single hump for one time constant phase.
response. To simulate the electrochemical interface, EIS data was analyzed with Echem Analyst using circuit model having electrical equivalent parameters accordingly.

Figure 7.3 A representative circuit model used to model the EIS

The Double layer capacitance $C_{dl}$ has been calculated using the following equation:

$$C_{dl} = Y_0 \left[ j \omega \right]^{n-1}$$

where $\omega^\prime$ is the frequency found at the maximum of the imaginary part of the impedance, $Z^\prime$.

The charge transfer efficiency, $ER_{ct}$ has been calculated as indicated by equation 514:

$$ER_{ct} = \frac{R_c' - R_c}{R_c}$$

where $R_c'$ and $R_c$ are the charge transfer values with and without corrosion inhibitors respectively.

Linear polarization resistance (LPR): For linear polarization resistance measurements, the electrodes were scanned from -0.02 to +0.02 V as a function of open circuit potential ($E_{OCP}$) at
two and five hours of immersion with a scan rate of 0.125 mV/s. The inhibition efficiency was
determined using the following Equation:

\[ ER_p = \frac{R_p - R'_p}{R_p} \]

Where \( R_p \) and \( R'_p \) are polarization resistance without and with corrosion inhibitors and the
polarization resistance can be measured using the slope of the polarization curve (\( \Delta E/\Delta i \)) at
origin using seed values of 0.12 voltage/decades for Tafel constants, i.e. for \( \beta_a \) and \( \beta_c \).

Potentiodynamic polarization (PD): The Potentiodynamic polarization measurements
were performed at six hours of immersion by polarizing the working electrode from an initial
potential of -250 mV up to a final potential of 750 mV as a function of open circuit potential
(\( E_{OCP} \)). A scan rate of 0.1667 mV/s was used for the polarization sweep. Corrosion current
densities \( i_{corr} \) were obtained by extrapolating anodic and cathodic linear segments of Tafel plot
using Echem Analyst. The obtained current densities were used to calculate the efficiency of
corrosion inhibition using the following Equation:

\[ CE = \left( \frac{i_{corr}' - i_{corr}}{i_{corr}} \right) \]

where \( i_{corr} \) and \( i'_{corr} \) are the current densities without and with the corrosion inhibitors.

**7.3 Results and discussion**

Transmission electron microscopy shows the images of the nano particles are shown by
Figure 7.4a with core-shell structure and also in agglomerate form. The exposes crystal planes
220 and 311 are surrounded by shell of crystal defects. The morphology of the nano particles resemble a sphere with a size ranging between 10-15 nm. X-ray diffraction pattern obtained for nickel ferrites has been shown in Figure 7.4b was indexed by (JCPDS No.10-0325). The particle size as determined using peak having highest intensity diffracted by planes (311) by Scherrer formula was found to be 12±1.2 nm which is in close range as calculated through TEM. The analysis showed the presence of a cubic spinel structure of the ferrites with a lattice parameter of 8.341 Å and corresponding planes of (111), (220), (311), (400), (422), (511), and (440), (533) representing.

Figure 7.4: TEM micro-image (a) Left, and XRD patterns of nano-nickel ferrite (b) Right

Open circuit potential is a basic and useful tool in which potential of the specimen is measured in the absence of applied current; it has abundant preliminary information for other electrochemical corrosion monitoring techniques. It describes the intrinsic reactivity of metal and oxidizing power of solution without adding any effect to the surface oxidation and reduction reactions. In an open circuit potential experiment, the working electrode potential changes with accumulation of species on the electrode having different equilibrium potential. With increasing concentration of ferrite, the potential has been observed shifting towards the positive potential.
under the acidic environment (Figure 7.5a) whereas, in the saline environment, the shift towards positive potential is not that sharp (Figure 7.5b) compared with those under acidic conditions within the studied time range (4 h). Blanks were also run in pure acidic and saline solutions to separate their contributions from the effects of ferrite on X-80 steel. In acidic environment at higher concentration i.e. 100 and 200 ppm the shift difference is continuously increasing towards electropositive direction and ended at -462 and -460 mV respectively even after four hours as compared to 0 and 50 ppm where the potential becomes stable after one hour and remains stable for rest of time and ended at -551 and -468 mV respectively.

Similarly, in 3.5 percent NaCl, as the concentration is increasing potential shift is moving towards positive but to a lesser extent as compared to acidic medium and after four hours of immersion the potentials of all testing samples in neutral media were Table in case of all concentration and ended at -694 mV (0 ppm), -665 mV (10 ppm) 653 mV (70 ppm) and 637 mV (200 ppm). These phenomena can be attributed towards the cathodic reduction of the metallic cation at the surface of testing samples as a consequence the potential has a shift towards an electropositive direction. These results may be indicates the adsorption of metallic cation having inert anodic behavior as compared to testing specimens as indicated by the Nernst equation i.e. increased the activity of species in this case Ni$^{++}$ or Fe$^{++}$ and H$^{+}$ at the working electrode surface. These results also indicates that in acidic environments adsorption of metallic cations on working electrode are more active than in neutral environment i.e. after four hours of immersion the difference in the potential between the 0 and 200 ppm for acidic environments is 91mV and for NaCl is 57 mV. Linear polarization resistance (LPR) becomes a widely recognized method among electrochemical corrosion monitoring techniques to measure instantaneous important corrosion parameter such as resistance to the polarization by perturbing electrochemical potential
and measuring current generated between charged electrodes\[^{129}\]. From Table 7.1 that in 1M H\(_2\)SO\(_4\), with a concentration of 50 ppm, \(R_p\) increases from 10 to 29 \(\Omega cm^2\) and from 8 to 27 \(\Omega cm^2\) after two and five hours immersion respectively which showed efficiencies of 66 and 70 percent respectively (Table 7.1).

Figure 7.5 Open circuit potential with time of exposure to 1M H\(_2\)SO\(_4\) (a) Left and 3.5 percent NaCl (b) Right, blank and with different concentrations of NiFe\(_2\)O\(_4\): 50, 100 and 200 ppm

These results showed the long term corrosion inhabitation ability by metallic ions produced by nickel ferrite which slows down the easy occurrence of corrosion reaction between bulk solution and working electrode surface.

Table 7.1 Linear polarization parameters in 1M H\(_2\)SO\(_4\) and 3.5 percent NaCl after two and five hours immersion

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Concentration (ppm)</th>
<th>(R_p) ((\Omega cm^2))</th>
<th>(E_{Rp}) (percent)</th>
<th>(R_p) ((\Omega cm^2))</th>
<th>(E_{Rp}) (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1M H(_2)SO(_4)</td>
<td>3.5 percent NaCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Blank</td>
<td>10</td>
<td>-</td>
<td>1110</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>29</td>
<td>66</td>
<td>2722</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>23</td>
<td>57</td>
<td>1433</td>
<td>23</td>
</tr>
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<td></td>
<td>200</td>
<td>20</td>
<td>50</td>
<td>770</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Blank</td>
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<td>-</td>
<td>1056</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>27</td>
<td>70</td>
<td>2488</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>18</td>
<td>56</td>
<td>1145</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>15</td>
<td>47</td>
<td>470</td>
<td>-</td>
</tr>
</tbody>
</table>
This effectiveness is decreasing with the increasing amount of inhibitor. Similarly in saline environment, Rp increases from 1110 to $2722 \, \Omega cm^2$ having concentration 50 ppm and efficiency is 59 which decrease rapidly with the increasing amount of inhibitor and at 200 ppm, the Rp dropped down from 1110 to $770 \, \Omega cm^2$ (Table 7.1). These results could be attributed due to presence of metallic cations having higher position in electrochemical series i.e. Ni$^{++}$ and Fe$^{++}$ which not only protect the metal for further corrosion but can also setting up many galvanic cells on the surface$^{197}$. It can also be concluded from these results that protecting ability of these ferrites is lower in neutral media than acidic environments.

EIS is a powerful tool for explaining the behavior of electrochemical processes such as corrosion and adsorption occur at electrode/electrolyte interfaces. In general it can be seen that the real part of semicircle i.e. diameter of Nyquist curves decreases from time period of two hours to five hours (Figure 7.6), but the efficiency of R$_{ct}$ is increased after five hours immersion which implies that the resultant ferrite cations surface film over the electrode surface has greater influence on corrosion inhibition. R$_{ct}$ value is the lowest for pure acid, representing the highest corrosion rate in acid compared to other concentrations with varying ferrites because in case of blank solution porous corrosion products of oxides and sulphates are continuously forming which decreases charge transfer resistance efficiency. It increases from $12.40 \, \Omega cm^2$ for pure acid to $35.20 \, \Omega cm^2$ (Figure 7.6 and Table 7.2) for the lowest concentration of ferrite. Moreover, the R$_{ct}$ value is the highest for the lowest concentration of ferrite and decreases as the concentration of ferrite increases, suggesting higher corrosion inhibition in acid concentrations with lower ferrite addition.
Figure 7.6 Nyquist plots recorded after two hours (a) Left and five hours (b) Right immersion in 1M H$_2$SO$_4$, Blank and with different concentrations of NiFe$_2$O$_4$: 50, 100 and 200ppm

Table 7.2 Electrochemical Impedance Spectroscopy parameters in 1M H$_2$SO$_4$ after two and five hours immersion

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Concentration (ppm)</th>
<th>$R_{ct}$ (Ωcm$^2$)</th>
<th>$Y_0$ (Ω$^{-1}s^n$) $\times 10^{-6}$</th>
<th>n</th>
<th>$C_{dl}$ (Fcm$^2$) $\times 10^{-04}$</th>
<th>$ER_{ct}$ (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Blank</td>
<td>12.40</td>
<td>964.1</td>
<td>0.94</td>
<td>8.24</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>35.20</td>
<td>259.2</td>
<td>0.97</td>
<td>2.39</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>28.34</td>
<td>294.9</td>
<td>0.95</td>
<td>2.54</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>24.83</td>
<td>376.3</td>
<td>0.94</td>
<td>3.19</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
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<td>10</td>
<td>1677</td>
<td>0.96</td>
<td>15.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>32.51</td>
<td>431.7</td>
<td>0.99</td>
<td>4.22</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>21.26</td>
<td>553.1</td>
<td>0.97</td>
<td>5.13</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>18.81</td>
<td>657.3e</td>
<td>0.97</td>
<td>6.05</td>
<td>47</td>
</tr>
</tbody>
</table>

Electrical equivalent circuit parameters and nanometer thick Helmoholtz double layer which forms at the interface between working electrod interface and electrolyte as shown by Figure 7.7 where it can be seen that metallic cation adsorbed at inner helmoholtz plane $^{198}$.

The $C_{dl}$ values also follows a similar trend as the $R_{ct}$ i.e. it decreases first at lowest concentration and then just increases a bit as the concentration increases due to the change in local dielectric constant as given by Equation
\[ C_{dl} = \frac{\varepsilon \varepsilon_0 r}{d} \]

where \(d\) is the deposited layer thickness, \(\varepsilon\) the relative dielectric constant of deposition, the permittivity of free space \((8.9 \times 10^{-14} \text{ F/cm})\), \(r\) is the deposited layer surface and \(C_{dl}\) deposition layer capacitance\(^{199}\). Bode plot analysis for 1M H\(_2\)SO\(_4\) after two and five hours immersion (see Table 2) where after 5 hours of immersion where every value of \(C_{dl}\) was doubled due to increase in the thickness of the interfacial layer as indication of presence of oxides and sulphates at solution/metal interface. It can also be seen a little inductive loop at lower frequency from the Nyquist plots which also indicates the adsorption of cations species on the corroding surface\(^{200}\). Similarly, the value of \(n\) also showed increased trend as the ferrites concentration decreasing and lowest in case of blank, which is also measure of surface inhomogeneity; the lower is its value, the higher is the surface roughening of the metal/alloy\(^{60}\). Moreover, \(Y_o\) value also decreases with the decreasing amount of ferrites, this decreasing trend of \(Y_o\) value shows that reduction in surface area available for the electrochemical reaction\(^{61}\).

Similar results were observed for 3.5 percent NaCl (Figure 7.8 and Table 7.3), but as contrary to acidic environment the efficiency of protection decreases very rapidly as the corrosion inhibitor concentration increases and even at 200 ppm in both immersion times there is no efficiency of protection. In case of NaCl corrosion results the production of porous pervious film composed of different form of iron oxide as shown in the presence of sodium and chloride ions acting as electrolyte, where chloride ions accelerating the corrosion process by destroying any type of passivity and increasing the active corrosion rate. The accelerating corrosion process involves the dissolution of iron oxide film with the aid of chloride ions and also sodium and chloride ions enhance the transportation of electrons\(^{49}\).
Usually, in the neutral solution containing sodium chloride, iron develops different kind of surface oxides owing to the anodic dissolution that partially protects it against the severe attack of chloride anions. The higher frequency (HF) region of Nyquist’s plot for blank solution shows a slight flattening corresponding to peripheral layer resistance indicating porous and pervious layer deposits having relatively lower capacitance value. Intermediate (IF) and low-frequency region (LF) show a mixed i.e. dominant capacitive and recessive mass transport restricted behavior corresponding to charge transfer resistance. The higher value of double layer capacitance ($C_{dl}$) can be attributed towards the higher degree of surface area available for
Figure 7.8 Nyquist plots recorded after two hours (a) Left and five hours(b) Right immersion in 3.5 percent NaCl, Blank and with different concentrations of NiFe$_2$O$_4$: 50, 100 and 200 ppm

Table 7.3 Electrochemical impedance spectroscopy parameters in 3.5 percent NaCl after two and five hours immersion

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Concentration (ppm)</th>
<th>$R_{ct}$ (Ωcm$^2$)</th>
<th>$Y_0$ ($\Omega^{-1} s^n$) $\times 10^{-6}$</th>
<th>$n$</th>
<th>$C_{dl}$ (Fcm$^2$) $\times 10^{-04}$</th>
<th>$E_{Rct}$ (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Blank</td>
<td>690</td>
<td>6.75</td>
<td>0.55</td>
<td>5.36e-02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1850</td>
<td>0.47</td>
<td>0.75</td>
<td>6.74e-04</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>870</td>
<td>4.36</td>
<td>0.54</td>
<td>3.63e-02</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>500</td>
<td>5.93</td>
<td>0.53</td>
<td>4.62e-02</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Blank</td>
<td>750</td>
<td>6.00</td>
<td>0.55</td>
<td>3.87e-02</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2100</td>
<td>1.64</td>
<td>0.61</td>
<td>4.41e-03</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>800</td>
<td>4.37</td>
<td>0.56</td>
<td>3.00e-02</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>730</td>
<td>4.32</td>
<td>0.57</td>
<td>9.53e-03</td>
<td>-</td>
</tr>
</tbody>
</table>

corrosion as indicated by the higher value of CPE constant ($Y_0$) owing to the distribution of reaction rate with the location on the electrode surface $^{201}$. Using Evan’s drop experiment, Miszczyk et al. showed that nickel zinc ferrites (NZF) have the ability to create precipitate even at low solubility as shown by low conductivity. They showed that drop containing aq. sol. of NZF develop the local anodic site at the center and a cathodic site near the edge of drop and $^{202,203}$ The mechanism of forming these sites was explained by Evan $^{204}$. By the alkaline nature of aq. sol. and in the presence of metallic cations M, the proposed reaction occurring at the steel surface was given by Miszczyk et al. is as follow $^{203}$
\[yM^{2+} + (3 - y)Fe^{2+} + 6OH^- \rightarrow M_{y}Fe_{(3-y)}(OH)_6\]

From Pourbaix diagram of iron, the stable phase at pH above 7 can be found as Fe(OH)$_2$ which may co-deposit with the metal cation. Along with the above reaction, Zhao et al. have also explained the corrosion inhibition process at a low concentration of metallic cations. Adsorption of metallic cations having higher electrode potential (E$_{O2/H2O}$ > E$_{M^{i+/M}}$ > E$_{Fe^{2+/Fe}}$) can lead the following oxidizing-reducing reaction.

The above reaction can produce electrodeposition of metallic ion on the iron surface forming a protecting film. Further, from the Pourbaix diagram of nickel, Ni was found as a stable phase above pH of 7. This process can be observed better at Nyquist plot where a long inductive loop can be seen at medium to low frequency. Induction loop at intermediate and lower frequency indicate the relaxation of adsorbed intermediates that may result in the corrosive attack of exposed area. Along with the above explanations about inductive behavior, Zhao et al. also explained that at higher concentration of metallic cations, a part of a thicker film formed due to adsorption of cations may fall into solution, which can result in the development of galvanic cell between exposed surface and adsorbed metallic cations.

The potentiodynamic polarization curve for varying concentrations of ferrites after six hours immersion in 1M H$_2$SO$_4$ and 3.5 percent NaCl.

Table 7.4 and Figure 7.9 and corrosion kinetics parameter were calculated. The $i_{corr}$ for the alloy in 1M H$_2$SO$_4$ is close to 1200 ($\mu$Acm$^{-2}$) compared to the 545 ($\mu$Acm$^{-2}$) (54 percent efficiency) at the lowest concentration of ferrite in acid and it increases with increase of inhibitor concentration whereas efficiency decrease. Similar, trend can be seen for ferrite solution with 3.5
percent NaCl i.e. $i_{corr}$ decreases from 3.1 ($\mu A cm^{-2}$) in pure 3.5 percent NaCl to 1.3 ($\mu A cm^{-2}$) in case of 50 ppm. The potentiodynamic data is in agreement with the corrosion parameters obtained from the impedance plots. The fact that exchange current density is lower in case of 3.5 percent NaCl than 1M $H_2SO_4$ is due to the dependence of exchange current density on activation energy of forward and backward reactions occurring on the surface of working electrode i.e. theoretically more $H^+$ ions are available for cathodic reactions (pH=0.90) as compare to saline solution (pH=6.8) which increase the rate of reaction at the surface.

![Tafel plots recorded after six hours immersion in 1M $H_2SO_4$ (a) Left, and 3.5 percent NaCl (b) Right. Blank and with different concentrations of NiFe$_2$O$_4$: 50, 100 and 200 ppm](image)

It can be seen from the results that $i_{corr}$ increases owing to the cationic reduction, and as a consequence the potential shifts towards positive direction (see Table 4) in case of 1M $H_2SO_4$, resulting from the deposition of cationic metallic ions. The inhibition effect can be attributed towards the phenomena of adsorption or electrodeposition reaction of metallic cations on the anodic surface showed by Equation

$$M^n + ne^- \rightarrow M^{n-1}$$
where M could be Ni$^{++}$ and Fe$^{++}$ where n is the number of electrons contributing in the electrochemical reaction. Further the higher concentration of cations could develop galvanic cells on the surface of anode which in turn increase the corrosion. The hydrogen evolution reactions in acidic and neutral environments are given Equations as:

$$2H^+ + 2e^- \rightarrow H_2 (Acidic)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- (Neutral)$$

$$O_2 + 4e^- + 2H^+ \rightarrow 2H_2O (Acid / Oxygen)$$

The addition of inhibitor having metallic cations can also effect the hydrogen evolution reaction by moving the potential towards positive direction due to inhibition of hydrogen reaction which results in raising its over voltage.\textsuperscript{207} Then the under potential deposition of metallic cations on working electrode which results in corrosion inhibition could be explained by the concept that hydrogen evolution reaction has more positive potential range than the equilibrium potential for the electrodeposition of these metallic cations\textsuperscript{15}.

Table 7.4 Corrosion kinetic parameters recorded after six hours immersion in 1M H$_2$SO$_4$ and 3.5 percent NaCl solution, blank and with different concentrations of NiFe$_2$O$_4$: 50, 100 and 200ppm

<table>
<thead>
<tr>
<th>Solution type</th>
<th>Concentration (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$b_c$ (mVdec$^{-1}$)</th>
<th>$b_a$ (mVdec$^{-1}$)</th>
<th>$i_{corr}$ ($\mu A cm^{-2}$)</th>
<th>CE (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-500</td>
<td>95</td>
<td>29</td>
<td>1200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-413</td>
<td>118</td>
<td>50</td>
<td>545</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-409</td>
<td>105</td>
<td>48</td>
<td>950</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>-407</td>
<td>106</td>
<td>45</td>
<td>1100</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>-730</td>
<td>150</td>
<td>80</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.5 percent NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-660</td>
<td>152</td>
<td>63</td>
<td>1.3</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-686</td>
<td>128</td>
<td>75</td>
<td>1.6</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>-700</td>
<td>161</td>
<td>70</td>
<td>2.8</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
There were no noticeable changes in the cathodic and anodic Tafel (±10 mV) slopes for 1M H$_2$SO$_4$ and 3.5 percent NaCl respectively for most of the concentration which indicate that presence of cations do not significantly affect these parameters$^{14}$.

The examination of Pourbaix potential-pH diagram (Figure 7.10)$^{208}$ reveals that near pH 0.90 and in the presence of sulphuric acid, the inhibition was most probably as a result of competitive adsorption of Ni$^{2+}$ and Fe$^{2+}$ with H$^+$ ions on the cathodic sites of working electrode surface. Further the reaction of these metallic ions with sulphur forming iron complexes and
nickel hydride will be formed at measured Eh and pH. Whereas at pH 7 the dominant reaction product is metallic nickel hydride hindering the corrosion inhibition.

It can be concluded from these results that a balance quantity of corrosion inhibitor containing metallic cations need to be used to protect the subjected metal. Further spectroscopic studies are needed to confirm the types and nature of adsorbed metallic ions and corrosion on subjected metal.

7.4 Conclusions

Corrosion inhibition properties of ferrites in 1M sulphuric acid and 3.5 percent NaCl solution with varying concentrations of ferrites were studied and proved effective. It can be seen that considerable decrement in corrosion rate in the presence of ferrites. The effectiveness of smaller amount of inhibitors as a pigment filler in various polymeric matrices may act as a starting point in formulating corrosion resistant protective coatings. The lower corrosion rate at the lowest ferrite concentration makes it suitable for industrial application i.e. economically and efficiently. The various concentrations of ferrites pigments follow the corrosion inhibition efficiency as follows; 50>100>200 ppm > pure in 1M sulphuric acid and 3.5 percent NaCl, thus lesser the amount higher is the inhibition advantage and the inhibition efficiency is more in 1M sulphuric acid than NaCl solution. The protection behavior of pigment was owing to the adsorption of metallic cation on the working electrodes surface having higher position in galvanic series. Further, incorporation of these nano particles pigments in various polymer matrixes for control release anti-corrosion coatings which could have effective role in various application. Moreover, the effects of these metallic cations on corrosion phenomena cannot be ignored in industrial processes.
A paper to be submitted in *CORROSION* and other paper was published in *International Journal of Electrochemical Science* and *Dyes & Pigments*

Inorganic oxide addition can be synergistically beneficial in organic coatings, if it can impart anti-corrosion properties and also as an additive to enhance physical and/or chemical properties. The aim of this study was to evaluate the anti-corrosion benefits of nano nickel zinc ferrite (NZF) in the polymer film. The time-dependent anti-corrosion ability of NZF (0.12 percent -1.0 percent w/w, NZF/binder), applied on API 5L X-80 carbon steel were characterized by electrochemical techniques (EC) such as open circuit potential, electrochemical impedance spectroscopy, linear polarization resistance and potentiodynamic. Characterization of corrosion layer was done by removing coatings after 216 hrs of immersion in 3.5 percent w/v NaCl. Optical microscopy, Field Emission Scanning Electron Microscopy, and X-ray diffraction techniques were used to characterize the corroded surface. Corrosion measurements confirm the electrochemical activity by metallic cations on the surface during corrosion process which results in improvement of anti-corrosion properties of steel. Moreover, surface techniques show compact corrosion layer coatings and presence of different metallic oxide phases for nanocomposite coatings.

8.1 Introduction

Corrosion leads the degradation of metals due to environmental interactions. The deterioration of metals occurs over time through electrochemical reactions at the metallic surface. Composites of polymer and inorganic anticorrosion pigments are widely applied to metallic surfaces as coatings and films. Hybrid coatings have synergistic effects on the anti-corrosion
properties of substrates in various manners. In the undegraded mode, I) coating provide a 
physical barrier to the transport of corrosive species, II) resistance to the electron transfer to 
avoid electrochemical activity. During degradation III) sparingly soluble inorganic parts leached 
by the electrolyte and reached coating defects or interface to hindered or replace the 
electrochemical reaction. Furthermore, the interaction between inhibitor ions, corroded metals 
corrosion products results in the formation of metal protective surface complexes which 
suppresses either cathodic, anodic or both the processes. Moreover, physical or chemical 
properties enhancement to the polymer coatings or films by inorganic pigments is also reported 
such as barrier, mechanical, electrical and optical, rheological and adhesion properties, 
and resistance against the environmental degradation.

Chromate pigments belong to a group of highly toxic pigments. The environmental 
restraints have diverted the research towards new inorganic anticorrosion pigments for polymer 
coatings. Metal oxides containing cations such as Cd\(^{2+}\), Mn\(^{2+}\), Ce\(^{4+}\), Fe\(^{3+}\), Cu\(^{+}\) and Co\(^{2+}\) ions are useful incorporation in organic coatings for anti-corrosion properties. Spinel based metal 
oxides with the general formula of AB\(_2\)O\(_4\) have distinctive properties of thermal and weather 
degradation resistance. A large number of research articles have been reported about anti-
corrosion properties of spinel based metal oxides. Kalendová et al. reported many anti-corrosion 
pigments based on spinel structure such as Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\), surface modified ZnFe\(_2\)O\(_4\), 
CaFe\(_2\)O\(_4\). Similarly, Mittal et al. modified micronized nickel zinc ferrites, zinc and nickel 
ferrites with polyaniline and incorporated in acrylic primer. Salt spray exposure of 400 hours 
showed better performance of modified nickel zinc ferrites. The protection mechanism of 
ferrites in organic coatings was explained due to many factors; I) formation of alkaline media at 
the coating interface, II) formation of soaps in some binders (alkyls, epoxy esters), III)
formation of anodic and cathodic sites on the surface through precipitation and IV) generally, enhancement in pore resistance through morphology of the particles. The nano-pigments contain advantages over conventional pigments for their improved barrier and anticorrosion properties in polymer coatings such as epoxy-clay\textsuperscript{136}, polyaniline/TiO\textsubscript{2}\textsuperscript{137}, MA/graphene\textsuperscript{138}, PVK/Multiwall nano tube\textsuperscript{139}. The inhibition action of the extracts depends on the solubility of pigments, development of passive layer metal surface, and the nature of electrolyte. Recently, Chaudhry et al. investigated the anti-corrosives properties of extracts of nano nickel ferrites (NiFe\textsubscript{2}O\textsubscript{4}) acid and saline media. The improved anti-corrosive properties of API 5L X-80 steel were found at a lower concentration of ferrites owing to the adsorption of metallic cations on the corroding surface leading the formation of surface complexes\textsuperscript{214, 217}.

In literature nano, NZF has been reported for numerous application such as thin films for microwave heating\textsuperscript{218}, smart multiferroic devices\textsuperscript{219}, microwave absorbers coatings\textsuperscript{220}, biological and biomedical purposes\textsuperscript{221}, semiconductors\textsuperscript{222}, and Lithium storage\textsuperscript{223}. These applications of nickel zinc ferrites are owing to the exhibition of excellent commanded properties such as superparamagnetic behavior, high electrical resistivity, low anisotropy, high capacity retention, high reversible specific capacity, and high magnetic permeability\textsuperscript{218, 219, 220, 221, 222, 223}.

In this work, we evaluated the anticorrosion properties of nano nickel zinc ferrites (Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}) in 3.5 percent w/v NaCl at ambient temperature. Carbon Steel was coated with un-crosslinked rubber as a binder with various concentration of NZF and immersed in saline media.
8.2 Materials and Methods

Chlorinated rubber (rubber, Pergut S 130) having chlorine content weight > 64.5 percent was supplied in powder form by Bayer materials science and used as obtained. Nearly spherical nano-powders of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (True Density; 2.81 g/cm$^3$, Bulk density~ 0.80 g/cm$^3$, Average particle size (APS) 10-30 nm, 99.9 percent pure, American elements, CA USA) were used as supplied. The impurities details are Al < 0.05, Ba < 0.05, Cd < 0.001, Co < 0.05, Cu < 0.01, Mg < 0.05, Pb < 0.001, API-5L X80 steel coupons having weight percent composition listed as; C 0.07, Mn 1.36, Ti 0.008, S 0.003, P 0.004, Fe Balanced.

8.3 Anti-corrosion properties of coating

Model primers were prepared by rubber 30 w/v percent in toluene with continuous shaking for 24 hours. Similarly, four different concentrations of NZF powder i.e. 0.1, 0.25, 0.5 and 1.0 w/w percent (rubber/powder) were subjected to bath sonication in toluene for 8 hours. Rubber was added quickly to the dispersive NZF solution and shake for 48 hours yielded a uniform dispersion of NZF in the rubbersolution$^{224}$. Magnetic stirring was avoided in this case due to magnetic nature of powder particles. Machined API 5L X-80 steel with dimensions 10 × 10 × 4 mm was used as the working electrode having a tap and drill hole of 3- 48 tpi drilled to one side of the coupon. Using dip coater, carbon steel substrates were coated with rubber-NZF dispersion at immersion and withdraw speed of 50 and 5 mm/minute respectively. Further, the samples were dried at room temperature for 3 days followed by drying in air circulating oven at 40 °C for 24 hours to give final dry coating film with at thickness in the range of 240–260 µm using a digital micrometer. To avoid water penetration from the sides of coated samples, edges
were sealed by commercially available nitrocellulose adhesive before subjected to electrochemical measurements (Figure 8.1a).
8.4 Electrochemical Measurements

A three-electrode cell assembly (Figure 8.1b) consisting of coated steel as the working electrode (WE), a graphite rod as the counter electrode (CE) and for reproducibility a saturated calomel electrode (SCE) as reference electrode (RE), were used for the electrochemical measurements. We used uncrosslinked rubber and a large volume of water (600 mL) available to the incorporated pigments to see the immediate effect of inhibition. Electrochemical testing was performed in a closed system under naturally aerated conditions using a Gamry 600 potentiostate room temperature. The sequence of electrochemical techniques is described as:

Open Circuit Potential (OCP): To obtain information on the protection mechanism of the ferrites in coatings, coated samples were subjected to OCP for 216 hours in 3.5 percent w/v of aqueous NaCl. OCP readings were taken after an interval of 24 hours over the period of 216 hours of immersion.

Electrochemical Impedance Spectroscopy (EIS): Impedance measurements were performed vs. $E_{OCP}$ after an interval of 24 hours over the period of 216 hours of immersion. The frequency sweep was performed from $10^{05}$ to $10^{02}$ Hz by applying small-amplitude perturbation of 10 mV AC amplitude. To simulate the coating and coating/metal interface, EIS data was analyzed with Echem Analyst using circuit model having equivalent electrical parameters shown in Figure 8.2. Accordingly, the impedance of capacitor can be represented by the following equation:

$$Z(CPE) = Y_o^{-1}[j\omega]^n$$
Figure 8.2 Circuit model used to model the EIS for carbon steel immersed in 3.5 percent w/v NaCl

Where $Y_o$ is the CPE amplitude ($\text{ohm}^{-1}$), $\omega$ is the angular frequency (rad/s), $j = \sqrt{-1}$, and $n$ is another CPE constant, where $n = \alpha \pi / 2$, $\alpha$ is the constant phase angle of the CPE (rad), also $n$ varies from 1 to 0 for pure capacitance and pure resistor, respectively. The coating or double layer capacitance $C_{dl}$ or $C_{cc}$ can be calculated using the following general mathematical equation:

$$C_{cc} or C_{dl} = Y_{cc} or Y_{dl} [j\omega]^n (1 - n_{cc} or n_{dl})$$

Where $\omega''$ is the frequency found at the maximum of the imaginary part of the impedance, $Z''$. $R_{ct}$, $R_p$ and $R_u$ represent the charge transfer resistance, coating resistance, and electrolyte resistance respectively$^{14}$. The following equation can be used to describe the diffusional impedance for the diffusion layer of infinite thickness as represented by diffusion circuit element, $W$ in Figure 8.2:

$$Z(W) = \frac{1}{Y_o \sqrt{j\omega}}$$

Where $Y_o$ represents the magnitude of the admittance ($\text{S} \cdot \text{s}^{1/2}$).
Linear Polarization Resistance (LPR): The WE was scanned for LPR after an interval of 24 hours over the period of 216 hours of immersion from -0.02 to +0.02 V vs. E_{OCP} with a scan rate of 0.125 mV/s. The polarization resistance was measured using the slope of the polarization curve $\Delta E/\Delta i$ at origin using seed values of 0.11 voltage/decades for Tafel constants, ($\beta_\alpha, \beta_c$).

Potentiodynamic Polarization (PD): PD measurements were performed after an interval of 24 hours over the period of 216 hours of immersion from -500 mV up to a final potential of 500 mV vs. E_{OCP}. A scan rate of 0.5 mV/s was used for the polarization sweep. Corrosion current densities $i_{corr}$, were obtained by extrapolating anodic and cathodic linear segments of Tafel plot using Echem Analyst.

### 8.5 Surface analysis of corroded carbon steel

Steel coupons were carefully disengaged from the cell assembly and dried. After removing the coatings, the macroscopic features of the surface were also observed under an optical microscope at a magnification of 20X. JEOL JSM-7000F, Field Emission Scanning Electron Microscopy (FE-SEM) was performed to evaluate surface morphology at 5kV to 20 kV under high vacuum at a working distance of 10mm. For X-ray diffraction (XRD), Philips PW 3040/60 spectrometer with scan range 10° to 100° and scan rate of 0.050° was used to differentiate the various phases present in the corrosion products over the metal surface. The peaks and planes were analyzed using X'Pert High Scores of tware and compared with JCPDS cards issued by ICDD.
8.6 Results and discussions

The results and discussions are as follows.

8.6.1 Pigment Characterization

The TEM, FE-SEM and XRD analysis for the NZF nanoparticles have been described in our previous work. As a short description, TEM confirms the spherical nature of particles with average particle size less than 20 nm, whereas SEM images show the extensive interaction between particles due to a magnetic character with an agglomerate size between 1 to 10 μm. The cubic spinal structure and particle size of 12 nm with a lattice parameter of 8.4 Å were confirmed from the analysis of diffraction pattern.217

8.6.2 Coating characterization:

Figure 8.3 describes the general theoretical picture and proposed corrosion inhibition mechanism by physicochemical and electrochemical processes upon addition of NZF in the rubber layer. The physicochemical phenomenon starts with the reinforcement of binder with incorporated nanoparticles, which increases the diffusion length for ingressive corrosive media. In reported literature the barrier actions of spherical particles are lower than those fillers having plate-like or lamella structure due to higher surface area.227 This effect can be reduced by using nano size particles having larger surface area available for barrier action. Further, the penetration of corrosive aqueous solution in coating dissolves the sparingly soluble pigments and takes the leached metallic cations to the coating/metal interface, which interacts with the electrochemical processes occurring there. The leached ions make surface complexes or precipitate at the metal surface to slow down the corrosion.
8.6.3 Open circuit potential

The OCP of CS coated with rubber and nanocomposites (Figure 8.4) immersed in 3.5 percent w/v NaCl over a period of 216 hours immersion which can be divided into three main regions such as 0-70 hrs, 70-115 hrs, and 115-216 hrs. In the first region, a rapid drop in potential from higher to relatively lower value for nanocomposite coatings, due to the infiltration of corrosive media through coatings microscopic pores and defects. The drop in potential is more for a higher concentration of particles showing the presence of more defects owing to magnetic particles interaction and agglomerations.

Figure 8.3 Schematic depiction of anti-corrosion mechanism of nickel zinc ferrites when incorporated in rubber
Figure 8.4 Open circuit potential of CS coated with rubber and nano-composites over a period of 216 hours immersion in 3.5 percent w/v NaCl

The reinforcement of particles for barrier properties first increased with the particle concentration and becoming lower with the increasing amount of NZF in coatings. This may be due to the increased interaction of nanoparticles\textsuperscript{112} with each other with increasing concentration, which causes defects and decreases pore resistance by developing ionic conduction pathways. The increased amount of filler also affects the corrosion process occurring at the metal surface especially for 1.0 percent NZF where it has a rise during 115-216 hours. During 115-216 hours, the potentials of rubber and composites coatings remain constant except 0.1 percent where it increased slightly towards positive. The optimum around 0.25 wt. percent of NZF shows a balance between pore resistance and reactions at the metal surface.

8.6.4 Electrochemical Spectroscopy impedance

To understand and analyze the electrochemical process in the coating and at the interface, Figure 8.2 shows the most probable equivalent electrical circuit used for the simulation of degrading coatings and coating/metal interface. The circuit was constructed by a series
combination of coating with double layer parameters. The reason to introduce Warburg impedance in parallel with pore resistance was due to the rapid degradation of coating leads to the corrosion progression and formation of corrosion product at the surface which acted as diffusion layer for corrosives products. In common practice Warburg impedance is associated with charge transfer resistance (Rct) and double layer capacitance (Cdl). In the presence of uncrosslinked rubber coatings containing permeable defects, rapid progression of corrosion may occur by immediate penetration of corrosive media through the coating. It was reported uncrosslinked rubber has the highest rate of increase in capacitance than other commercially available resins. As a consequence, the emergence of the electrical double layer at the metal/coating interface occurs. This process may lead the quick growth of corrosion products during early stage of immersion at coating pores and coatings/metal interface which act as diffusion layer for corrosive species. This behavior can be observed in Nyquist plot (not shown here) where incomplete semicircle was seen at higher frequency owing to the reduced the magnitude of relaxation time enough that it would not appear at applied frequency. The Nyquist plots also showed a long diffusional loop from intermediate to lower frequency. Further, it was also reported that incomplete semicircle at a higher frequency can be attributed towards the penetration of electrolyte solution through coating. For a deep insight into the electrochemical process, the employed circuit contained Warburg component (W) which explains the limited dissolved oxygen diffusion towards the cathodic areas along with two constant phase elements and resistors in series. Impedance spectra, which were obtained from rubber and composites coatings after 24 hours and 216 hours during exposure to 3.5 percent w/v NaCl solutions, are presented as selected Bode plots (Figure 8.5(a-d)).
The coating impedance increased from magnitude of 37.3 kΩ.cm² to 80.9 kΩ.cm² with incorporation of 1.0 percent NZF indicating barrier effect of pigments. This affect also proves good interaction and compatibility of pigment with chlorinated rubber owing to polar groups in side chains\textsuperscript{111}. With increasing exposure time i.e. 216 hours of immersion (Figure 8.5b) pore resistance of 1.0 percent and 0.5 percent coating decreased rapidly as compare to lower
concentrations. This phenomenon indicates that higher concentration of pigments can create more defects and conduction paths for corrosive media.

As can be seen (Figure 8.5a) after 24 hours of immersion, composites coating showed higher values of impedance at low frequency indicating the reinforcement effect owing to the presence of inorganic phase in rubber. Where as phase angle showed higher capacitive behaviour for nanocomposites coatings at high frequency i.e. ~58° for 0.12 percent and 0.25 percent, and ~67° for 0.5 percent and 1.0 percent compare to ~28° for rubber coating. This behaviour indicates that addition of filler has enhanced the Rpor resistance which is a bulk feature of the coating. At intermediate to lower frequency the phase angles for all the cases have sharp and continuous reduction and ended at ~17° for rubber coating and ~9° for nanocomposite coating indicating highly diffusive nature of the coating. This phenomenon results the rapid penetration of water through the pores in the bulk of the coating. After 216 hours of immersion rubber coating has lost its barrier properties completely as indicated by phase angle of ~10° whereas the nanocomposites coatings still retained barrier properties owing to higher value of phase angle i.e. ~21° to ~26°. The phase angle at very low frequency (a feature of metal surface) ~30° value for rubber coating indicated the presence of large amount of blisters in the oxide layer indicated the porous nature. Whereas for nano-composites coatings have comparatively lower phase angle values at low frequency i.e. ~21° to ~15° indicating that oxide layers have adsorbed lesser amount of water.

In order to evaluate the coating performance, the profile of evolution of individual circuit parameters (Rpo, Rd, Cdl, Admitt.) with time are shown in Figure 8.6(a-b) and Figure 8.7(a-b). Pore resistance or resistivity of the coating indicates the ionically conducting paths or macrocapillaries across the coating through which sorption and transportation of uncharged
species i.e. oxygen and water occur. Pore resistance is first and very important step towards the suppression of corrosion as the main function of coatings is to provide barrier to the electrolyte penetration. Figure 8.6a shows the variation over time during exposure to 3.5wt percent NaCl for rubber and nanocomposites coatings with different concentration of NZF. After 24 hours, it can be seen that at higher concentration of NZF, Rpor is very high for 0.5 percent (~94 kΩ.cm²) and 1.0 percent (~81 kΩ.cm²) compare to rubber coating (~37 kΩ.cm²). It drops rapidly reaching a plateau after 150 hours and ended up at ~8.6 kΩ.cm² (0.5 percent) and ~5.4 kΩ.cm² (1 percent), and ~2.9 kΩ.cm² (Rubber). The rapid drop of Rpor can be attributed to the penetration of electrolyte in the external portion of coating through capillaries as defects. The linear drop in the Rpore can be attributed towards the diffusion of electrolyte through polymer which is improving for all the cases of NZF up to the end of measurements. The uniformity of plateau after 180 hrs to 216 hrs shows uniform corrosion owing to continuous contact of metal surface with corrosive solution. Charge transfer resistance (Rct, Figure 8.6b) describes the characteristics of metal-electrolyte interface; it shows that electrolyte has reached at the metal surface leading the surface reactions. In coating system, some part for the Rct depends on the Rpor of the coating, higher the compactness (Rpor) higher will be Rct and that can be called inherited Rct. Further the ability of metal to give off charge is also effect the magnitude of Rct. As the electrolyte penetrates through coating and reaches surface, it leaches the ions from incorporated pigments. At metal surface, these ions interfere with the corrosion process. In literature different mechanisms of protection by metallic cations are reported; I) inhibition of hydrogen evolution process by Cd²⁺, Mn²⁺, Ce⁴⁺; II) corrosion inhibition of titanium and stainless steel Fe³⁺ and Cu²⁺ via promoting passivity of these metals; III) corrosion retarding lead anode in sulphuric acid by Co²⁺ ions via increasing catalytic activity of surface
oxides for oxygen evolution which in turn increases the current efficiency of the oxygen evolution reaction; and hence little current is available for counter anodic reaction\textsuperscript{14, 19, IV}) corrosion inhibition of iron by reducing corrosion promoting species using Sn\textsuperscript{+2} ions in acid pickling process\textsuperscript{14, 234}. Analysis of Rct could be the best option to verify the inhibition process at metal surface coated with incorporated. Owing to higher Rpor, Figure 8.6b shows that Rct is higher for the cases of composite coating. As contrary to Rpor, where it was rapid and linearly changes with time, Rct increases first for all the composite coatings up to ~125 hrs and then linear decreases for 0.1 percent and 0.25 percent where it ended up at ~10.5 k\textOmega.cm\textsuperscript{2} and ~22 k\textOmega.cm\textsuperscript{2} respectively where as Rct of rubber coating is decaying lineary and became ~7 k\textOmega.cm\textsuperscript{2} after 216 hrs.

For coatings containing 0.5 percent and 1.0 percent NZF, showed increment after 125 hrs and reached at maximum i.e. (0.5 percent) ~123 k\textOmega.cm\textsuperscript{2} and (1.0 percent) ~219 k\textOmega.cm\textsuperscript{2} after ~175 hrs and ended up at (0.5 percent) 17 k\textOmega.cm\textsuperscript{2} and (1 percent) 18 k\textOmega.cm\textsuperscript{2}. These results show that ions leached from NZF during penetration of electrolytes, interfered at the surface and affect the Rct. Further it can be seen that although Rpor decrease rapidly at higher concentration but Rct was also achieve its maximum in these two cases. It was reported that time dependent impedance parameters show quite scatter which is a common behavior in long EIS studies\textsuperscript{235}. The scattering of data shows that the formation and breaking of passive layer at the surface owing to potentiodynamic measurement after each EIS measurement. This scattering can be seen more in case of 0.5 percent and 1.0 percent. The formation and breaking behavior of the passive layer on the surface and underneath the coatings indicates the effectiveness of the inhibitor used in the coatings
Figure 8.6 Evolution of parameters derived from EIS measured in 3.5 percent w/v NaCl, a) Pore resistance and b) Charge Transfer resistance

Double layer capacitance (Cdl) characterizes the electrochemical reactions occur at the metal/electrolyte interface after penetration of corrosive solution through coating. It can be
observed that the presence of corrosive reactant and products at coating/metal interface changes the local effective dielectric constant according to following equations \(^{110}\).

\[
C = \frac{εε_oA}{d}
\]

Where \(d\) is the charge separation distance, \(ε\) the relative local dielectric constant of oxides, \(ε_o\) the permittivity of free space \((8.9 \times 10^{-14} \text{ F/cm})\), \(A\) is area of the electrode, \(C\) is the capacitance of a conventional capacitor. Figure 8.7a shows the evolution of \(C_{dl}\) with time for rubber and composites coatings. \(C_{dl}\) is also related to the delimitating area, where electrolyte has reached and actually electrochemical activity has started which increases the \(C_{dl}\). Form Figure 8.7a, it can be seen that up to ~ 100 hrs, rubber coated steel depicts higher \(C_{dl}\) as compare to all other cases. After that \(C_{dl}\) curve for nanocomposites coating starts meeting with the \(C_{dl}\) of rubber coating indicating presence of materials having higher local dielectric constant value. It can be assume that higher value of \(C_{dl}\) for composites coatings is due to the formation of thicker oxide layer. Warburg admittance value is very much effective for analyzing the barrier effect and diffusion limited behavior provided by the interface film. Limitation on oxygen diffusion through corrosion products layer can affect the rate of corrosion especially where oxygen is a main reactant in the cathodic corrosion reaction. According to the admittance (\(Yo\)) values presented in Figure 8.7b, it can be seen that, rubber coatings has constant and linear increase with time whereas after 24 hour all of the composite coating showed slightly increased \(Yo\) values. After 50 hours of immersion time generally the \(Yo\) value of composites coatings is decreasing. This can be the result of lower diffusion of reactant species through the porosities in corrosion product layer formed at the surface just after the coating \(^{236}\). This can also be inferred that with the passage of time corrosion layered was getting compact and thicker instead owing to the
precipitation of oxides under the pores of coating. Miszczzyk et al reported that during corrosion of iron presence of any metallic ions can interfere with the corrosion product according to following equation

\[ yM^{2+} + (3-y)Fe^{2+} + 6OH^- \rightarrow M_yFe_{(3-y)}(OH)_6 \]
Miszczyket al had also conducted the Evan’s drop experiments using extracts of NZF on the surface of steel and using AFM they observed that precipitation from droplets formed anodic and cathodic regions on surface.

### 8.6.5 Linear polarization resistance

Figure 8 shows the evolution of instantaneous polarization resistance ($R_{LPR}$) with immersion time. It seems that LPR results have general agreement with EIS. Generally, the $R_{LPR}$ values of steel coated with composites coatings were higher comparable to rubber coatings.

![Polarization Resistance](image)

**Figure 8.8 Evolution of polarization resistance ($R_p$) derived from LPR measured in 3.5 percent w/v NaCl solution for rubber and nano-composite coating**

### 8.6.6 Potentiodynamic

Evolution of polarization parameters vs. time such as corrosion current ($i_{corr}$) obtained from Tafel Plots is shown in Figure 8.10. At beginning such as up to 90 hours of immersion $i_{corr}$
has adequately similar trend for all the cases. After that it was continuously increasing for rubber and has suppressive behavior for nanocomposites coatings indicating the formation of passive corrosion products on the surface. This phenomenon can also be observed in Tafel plots (Figure 8.9 (a-b)) showing anodic arcs profile towards lesser current density after 24 hrs of immersion. This process is more pronounced after 216 hours and can be seen in both cathodic and anodic arcs indicating suppression of polarization. Following possible anodic and cathodic reactions may occur in saline media:

\[ Fe \rightarrow Fe^{2+} + 2e^{\text{Anodic}} \]
\[ Fe^{2+} \rightarrow Fe^{3+} + 2e^{-} \]
\[ 2H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-} (\text{neutral media - Cathodic}) \]

Similarly, in the presence sodium chloride solution with dissolved oxygen the possible mechanisms of iron dissolution were explained 238, 239:

\[ Fe + H_2O \rightarrow Fe(OH)_{ads} + H^+ (NaCl - Neutral) \]
\[ Fe + Cl^- \rightarrow Fe(Cl^-)_{ads} \]
\[ Fe(OH)_{ads} + Fe(OH)_{ads} \rightarrow Fe + FeOH^+ + (Cl^-) + 2e^- \]
\[ FeOH^+ + H^+ \rightarrow Fe_{aq}^{+2} + H_2O \]
\[ Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 (deposit) \]
\[ 3Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_3O_3 + 3H_2O (Excess - O_2) \]
\[ Fe + 2Cl^- \rightarrow FeCl_2 + 2e^- (Excess - Cl^-) \]
\[ FeCl_2 + Cl^- \rightarrow FeCl_3 + e^- \]
During above mentioned complex processes and presence of metal cation in the leached solution, metal cation (M$^{++}$) complexes can be form and precipitate on the iron surface. These precipitate forms the passive layer on the surface of the iron which further slows down the corrosion.

Figure 8.9 Potentiodynamic polarization curves measured in 3.5 percent w/v NaCl solution for coated steel after immersion of a) 24 hours and b) 216 hours

Figure 8.10 Evolution of parameter derived from potentiodynamic polarization curves measured in 3.5 percent w/v NaCl solution for coated steel, corrosion current density vs. time

Figure 8.10 Evolution of parameter derived from potentiodynamic polarization curves measured in 3.5 percent w/v NaCl solution for coated steel, corrosion current density vs. time
8.7 Surface characterization

Surface characterization of corroded samples was done after carefully removing the coating using two following techniques.

8.7.1 Optical Microscopy

Optical microscopy (Figure 8.11 (a-e)) was used to study the corroded surface after removing coatings. At 20X, images show significant morphological difference on the surface film. This can be attributed to the different composition of NZF in the coating. As compare to rubber coating, all other cases shows thick and compact corrosion layers on the surface.

Left to right: (a-c)

Left to right: (d-e)

Figure 8.11 Optical micrographs (20X) showing morphology of corrosion product layers of a) rubber, b) 0.1, c) 0.25, d) 0.50, e) 0.1 after immersion of 216 hrs in 3.5 percent NaCl
8.7.2 **Field Emission scanning electron microscopy (FE-SEM)**

Figure 8.12 showed the FE-SEM surface morphology of steel surface after removing coatings and immersing in 3.5 percent w/v NaCl solution for 216 hrs. It can be seen in Figure 8.12 that rubber coating showed porous and less compact steel surface whereas in other cases significant changes in the surface morphology can be observed. Although it can be seen that large cracks are formed on the surface of all other cases but the nanocomposites coated steel’s surfaces show compactness in corrosion products which can slows down the corrosion processes. These results indicate that metallic cations precipitations create dense and homogeneous layers which impede the transportation of reactants and products towards the metal surface. These compact layers also hindered the charge transfer required for corrosion process which can be observed in Figure 8.6b where improvements in the charge transfer were seen [29,30].

![FE-SEM images showing morphology of corrosion product layers](image)

Left to right: (a)-(c)

Left to right: (d)-(e)

Figure 8.12 FE-SEM showing morphology of corrosion product layers after removing coating a) rubber, b) 0.1 percent, c) 0.25 percent, d) 0.50 percent, e) 1.0 percent after immersion of 216 hrs in 3.5 wt. percent aqueous NaCl
X-ray diffraction pattern data (Figure 8.13) for the mixed phases present on the corroded metal surface were characterized by comparing with JCPDS cards. Surface pattern over the rubber coated coupon was also examined. The characteristic peaks of iron carbide and α-ferrite at $2\theta \approx 44^\circ$ [(510) JCPDS 20-509], and $2\theta \approx 82^\circ$ [(211) JCPDS 6-696] respectively. Other common peaks were included, Maghemite; $2\theta \approx 26^\circ$ [(211) JCPDS 19-615], Chlorine-Iron oxide complex phase; $2\theta \approx 59^\circ$ [(113) JCPDS 13-088] and $2\theta \approx 48^\circ$ [(200) JCPDS 24-10055], iron oxide-hydroxide; $2\theta \approx 53^\circ$, $64^\circ$ [(211) and (301) JCPDS 26-792], Hematite; $2\theta \approx 78^\circ$, $83^\circ$ [(306), (210) JCPDS 13-053]. The additional peaks appeared in 0.5 percent and 1.0 percent were included, zinc hydroxide; $2\theta \approx 31^\circ$, $35^\circ$, $42^\circ$ [(220), (224), (424) JCPDS 20-1435], nickel oxide at $2\theta \approx 63^\circ$, $76^\circ$, [(103), (200) JCPDS 22-1189] and nickel hydroxide at $2\theta \approx 66^\circ$, [(310), JCPDS 13-0229].

Figure 8.13 X-ray diffraction patterns of corroded steel surfaces, after removing coatings and immersion for 216 hrs in 3.5 percent NaCl
8.8 Conclusion

We explored the anti-corrosion properties and protection mechanism imparted by NZF in coating for carbon steel using electrochemical techniques. The formation of corrosion products layer were characterized by spectroscopic techniques. Incorporated NZF in coatings formed a thick and compact corrosion products layer which was able to slow down the corrosion process. X-ray diffraction confirms different phases including oxides of nickel and zinc. The suggested protection mechanism was explained by the leaching and precipitation of metallic ion on the corroded surface which in turn slowed down the corrosion activity. Further, improvement in barrier properties of rubber based coatings was confirmed by the enhanced pore resistance. This work indicates that along with wide range applications of NZF, anti-corrosion properties can be taken as an addition.
CHAPTER-9 EFFECT OF POLY ORTHO-ANISIDINE DOPED WITH DIFFERENT POLYOXOMETALATE ON ANTI-CORROSION PROPERTIES OF COATING

A paper to be submitted in CORROSION and other paper was published in RSC Advances
A.U. Chaudhry, Vikas Mittal, Brajendra Mishra

This study deals with the evaluation of self-healing ability of conducting polymer corresponding to a corrosion process. Poly ortho-anisidine (poa) was doped with Phosphomolybdic acid (PMA) and Tungstosilicic acid (TSA) and incorporated in polyvinyl butyral (PVB) coatings. The self-healing abilities of coatings were evaluated using open circuit potential (OCP) in 0.1 M NaCl solution for 45 hours of immersion. The coatings containing doped PoA showed increased positive potential of OCP after 45 hours of immersion as compare to blank PVB which showed a constant profile of OCP over the time indicating uniform corrosion under the coating. Thermogravimetric analysis (TGA) showed that PoA doped with TSA is more stable and more effective in the coating. High resolution Transmission Electron microscopy (HR-TEM) and Energy dispersive x-ray spectroscopy (EDX) confirms the doping of PoA.

9.1 Introduction

Anti-corrosion fillers for coating can be categorized depending on the protection mechanisms offered by these fillers when incorporated in the coatings. Figure 9.1 shows a general scheme for the classification of fillers. The barrier fillers provide tortuous path for the corrosive solution owing to their palate like shape. The examples of barrier fillers are graphene, layered silicates etc. The next class comes under the electrochemical fillers such as chromates, metallic oxides, zinc (cathodic protection) and other oxides continuing different cations. Usually
corrosive solution leaches the ions from these fillers and takes it to the corroding surface where these ions interfere with the corrosion process and form corrosion product layer or provide cathodic protection. The third class deals with self-healing where fillers like intrinsically conducting polymer doped with higher molecular weight molecule which further releases as a correspondence to a cathodic reaction. This dopant reacts with the metal cation and forms a complex and slows down the corrosion process. Among these three main classes, fillers can be categorized into mixed types like barrier fillers can be make self-healing or electrochemical fillers by modification of platelike fillers with conducting polymers. Similarly, electrochemical fillers can also be barrier owing to their plate like or spherical shape.

Polymers that are Intrinsically conducting (ICPs) like polypyrrole, poly ortho-anisidine and polyaniline have redox abilities which can be used to inhibit the corrosion process. As a response to an anodic reaction there is always a corresponding reaction which is a cathodic reaction. Further, if ICP responses to anodic process and liberates it’s dopant as a consequence the dopant makes a complex with metallic cation on the surface which further slows down the corrosion process. This process can be referred as self-healing process and can be seen in Figure 9.2. Figure 9.3 depicts that reduction potential of Polyaniline, which is a type of ICP is below the oxygen reduction. In this manner if a corresponding cathodic reaction takes place polyaniline be will reduced and liberate it counter ion. The counter ion may interact with the cation form the metal and forms a complex which can further slowdown the corrosion process. In some cases, these doped conducting polymers can be formed passive layer near to the surface.
Figure 9.1 Types of fillers depending on protection action

Figure 9.2 Self-healing mechanism provided by intrinsically conducting polymer
(Reprinted from N.Y. Abu-Thabit, A.S.H. Makhoul, Recent advances in polyaniline (PANI)-based organic coatings for corrosion protection, in Handbook of Smart Coatings for Materials Protection, 459-486, Copyright (2016), with permission from Elsevier)
This phenomenon may be called as intelligent response of a corrosion process. In literature the reduction potential (vs. SHE at 7 pH) of some of the ICP is as; Polypyrrole (-0.8-0.3), Polyaniline (-0.4-1.0) and Polythiophene (0.8-1.2)\textsuperscript{240}. These reduction potential are below the reduction potential of oxygen which can be useful for ICP reduction. The use of dopant may affect the performance of dopant such the molecular size, nature, etc. Heteropolyacids having general formula $[XM_{12}O_{40}]^{n-}$ with high electro-activity compared with conventional acidic dopants\textsuperscript{242}. Molybdenum and tungsten heteropolyanions have been reported to be used as many catalysis systems. The use of these heteropolyanions can be beneficial along with ICP during the corrosion process. The presence of Molybdenum and tungsten in the main formula may act as corrosion inhibitor upon their release during the cathodic process. In this work, poly orthoanisidine was doped with Phosphomolybdic acid (PMA) and Tungstosilicic acid (TSA) using oxidative polymerization. The anti-corrosion ability of PoA was evaluated in PVB coatings on carbon steel in 0.1 M NaCl over 45 hours of immersion.

9.2 Experimental Procedure

The synthesis procedure for doped PoA was adopted from earlier references\textsuperscript{242}. Briefly, 4.1 g of o-anisidine were added to a solution 19.20g Phosphomolybdic acid hydrate and separately 30 gram of Tungstosilicic acid hydrate in 15 mL (initially) acetonitrile and mixed for six hours. Then 6.28 gram of ammonium persulfate dissolved in 15 ml of water was added dropwise to the reaction mixture in 4 hours 0.7 ml/ min. The synthesis was carried out at room temperature for 24 hours and after that, the contents of the reaction flask were poured into 500 mL of acetone and for TSA 500 mL of methanol, filtered washed thoroughly with water and acetone/methanol until the filtrate was colorless. Then the product was dried to constant mass.
Figure 9.3 Pourbaix diagram for steel showing stable phases for Polyaniline and steel (Reprinted from Progress in organic coating, 48/1, Anton J. Dominis, Geoffrey M. Spinks*, Gordon G. Wallace, Comparison of polyaniline primers prepared with different dopants for corrosion protection of steel, 48, Copyright (2016), with permission from Elsevier)

Doped PoA amount was kept constant i.e. 5 wt. percent of Resin (Butvar B-98) (5g Resin/50 ml methanol) for all the composites. OCP was performed on coated carbon steel panels over 45 hours of immersion in 0.1 M NaCl. Model coatings were prepared by bath sonication of PoA for 48 hours in 50 ml methanol followed by 48 hours of mixing with PVB in a closely tight glass flask. Carbon steel samples were polished with 240 grit sand paper. Using dip coater, carbon steel substrates were coated with PVB-PoA dispersion by immersion and withdraw speed of 50 and 200 mm/min respectively. Samples were immersed in the solution for one minute.
Three coats were applied for each sample in a similar manner with an interval of 15 min. Further, the samples were dried at room temperature for three days followed by baking in an air circulating oven at 175°C for two hours to generate final coating with a thickness in the range of 300±3 μm. Two carbon steel samples were prepared for each PVB and composite coatings.

A flat cell assembly with working volume of 350 mL consisting of carbon steel coupon as the working electrode (WE) with expose area 2.6 cm², graphite plate as counter electrode (CE) having dimensions of 25 ×25×5 mm with expose area 2.6 cm², and a silver/silver chloride electrode as reference electrode (RE), were used for the electrochemical measurements. The open circuit potential of steel samples was recorded against Ag/AgCl electrode as reference electrode.

9.3 Results and Discussion

Figure 9.4 shows the High-Resolution Transmission Electron Microscopy (HR-TEM), SEM and (Energy dispersive x-ray spectroscopy) EDAX for each of the technique for PoA doped with a Phosphomolybdic acid. EDAX analysis confirms the presence of a dopant in the PoA chains, whereas SEM shows that PoA has morphology similar to spherical particles. HR-TEM shows the presence of crystals planes which may be due to the presence of dopant on the surface. Similar morphology and EDAX analysis were shown by the PoA doped with Tungstosilicic acid (Figure 9.5). The chain-like structure can also be observed from the HR-TEM images which indicate that PoA presents as agglomerates of chains. From the EDAX analysis, we can see that PoA is doped heavily with the hetopolyacids.

Figure 9.6 shows the thermal stability (Thermogravimetric analysis, TGA) of doped PoA. It can be seen that Tungstosilicic acid doped PoA higher thermal stability as compared to...
Phosphomolybdic acid. The loss of adsorbed water and residual solvents (3-4 percent) up to \( \approx 220^\circ C \) (before quick decomposition) can be seen in both of the cases. In the case of TSA doped PoA, it shows remarkable stability and mass loss of 6-7 percent can be observed as compared to PMA doped PoA where 14-15 percent mass loss occurred after 600^\circ C. The lower mass loss for TSA doped PoA indicates that presence of higher amount of dopant in the PoA remaining after the thermal decomposition. The process of weight loss can be divided into following steps: 1) water loss, 2) decomposition of PoA, 3) decomposition of anions\(^{242}\).

![Figure 9.4 Left HR-TEM-EDAX and Right SEM-EDAX for Poly ortho-anisidine doped with Phosphomolybdic acid](image)

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Figure 9.4 Left HR-TEM-EDAX and Right SEM-EDAX for Poly ortho-anisidine doped with Phosphomolybdic acid
Figure 9.7 shows the DSC curves for doped PoA; it can be seen that melting and heat of enthalpy of PMA-doped PoA (100°C, 28 cal/g) higher than the TSA doped PoA (86°C, 20 cal/g). This phenomenon indicates that PMA-doped PoA has more ordered structure which shifts the melting temperature towards a higher degree.

![Image of HR-TEM-EDAX and SEM-EDAX](image)

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Figure 9.5 Left HR-TEM-EDAX and Right SEM-EDAX for Poly ortho-anisidine doped with Tungstosilicic acid

Figure 9.8 depicts OCP of PVB and ICP incorporated PVB coating on carbon steel after immersion over 45 hours whereas Figure 9.9 showed that OCP of polypyrrole doped with heteropolyanions of PMo$_{12}$O$_{40}$$^{3-243}$ It can be seen that Blank PVB is showing a uniform corrosion
and no sign of the positive shift. In the case of PVB containing doped PoA has a little dip after
12 hours. After that, there is a continuous positive shift in the OCP and ended at +340\text{mv} for
TSA-PoA and +270 \text{ mV} for PMA-PoA as compare to blank PVB where it ended at -60 \text{ mV}.
These results are in agreement with the previous result where Damian et al. used Pyy-PMA and
showed a positive shift of 230 \text{ mV} after 45 hours of immersion\textsuperscript{243}. The protection action of
released ion was described according to the following equation

\[
\text{PMo}_{12}\text{O}_{40}^3^- + 12\text{H}_2\text{O} = 12\text{MoO}_4^{2-} + \text{HPO}_4^{2-} + 23\text{H}^+
\]

The above describes that higher molecular weight compound decomposes into a smaller
compound which further help to passivate the iron owing to their catalytic ability and oxidative
capability of PoA. During iron dissolution presence of dopant can helps the iron-dopant salt
formation which forms the passive oxide layer.

![Figure 9.6 TGA profile for Doped Poly ortho-anisidine](image)

Similarly, TSA can be decomposed into smaller molecule according to the following equation
SiW_{12}O_{40}^{3-} + 12H_2O = 12WO_4^{2-} + HSiO_4^{2-} + 23H^+

Figure 9.7 DSC profile for Doped Poly ortho-anisidine

Figure 9.8 open circuit potential measured for PVB and PoA/PVB coatings on carbon steel after immersion in 0.1 M NaCl for 45 hours
This higher level of dopant presence at the interface during corrosion process can keep the steel in the passivation state for over 45 hours. The slight and quick drop in the OCP after 12 hours of immersion can be due to the penetration of corrosive solution at the interface. After that, the coatings kept the steel in the passive domain over 45 hours and ended higher than the PVB coating.

Figure 9.9 Open circuit potential (OCP) for steel coated with bi-layered PPy in which an artificial defect was formed after six hours of immersion in 3.5 percent NaCl solution (This figure was Reproduced from Ref. (Self-healing ion-permselective conducting polymer coating, Damian Kowalski, Mikito Ueda and Toshiaki Ohtsuka, Journal of Materials Chemistry, 20, 2010, 7630–76338,) with permission from the Royal Society of Chemistry)

9.4 Acknowledgements

This collaborative work was done during student internship, Fall 2014 at The Petroleum institute Abu Dhabi. The author is indebted to The Petroleum Institute Abu Dhabi for financial support. We also thank Dr. Vikas Mittal of Chemical Engineering Department, The Petroleum Institute, Abu Dhabi for providing us the opportunity.
This research work deals with the investigation of new possible anti-corrosion fillers for polymer coatings that can be used as a replacement of chromates and other hazardous pigments. We select three kinds of fillers depending on their protection mechanism i.e. barrier, electrochemical and self-healing. The protection mechanism of any anti-corrosion pigment start with the solution as the water penetrates and leaches the ions from it. These leached ions react at the metal surface and slow down the corrosion process. The first kind of filler used in this research was graphene. To start with the solution properties graphene oxide was used and found no direct effect of graphene oxide on the corrosion properties of steel. During the second step, the effect of unmodified graphene concentration in polymer coatings was observed. Graphene increases the anti-corrosion abilities of coatings when use at higher concentration but for the shorter periods of time. Further, we also studied the effect of the modified graphene nanoplatelets, which showed that modified graphene nanoplatelets showed improved different which results in the better anticorrosion properties of polymer coatings. To impart the electrochemical properties to the graphene, the modification was done using polyaniline. Polyaniline has been proven as corrosion inhibition owing to its redox properties. The long time immersion showed that polyaniline –modified graphene showed enhanced anti-corrosion properties in coatings owing to synergist effect shown by imparted pigment.

The second part of the research deals with the electrochemical anti-corrosion fillers in coatings. Here we selected nickel and nickel zinc ferrites, owing to the presence of different cations in the main formula. The solution properties of these pigments were tested and proved effective which further gave us a clue for the incorporation in coatings. Nickel Zinc Ferrites were added to the coatings applied on carbon steel which further immersed in sodium chloride
solution for 216 hours. The results showed that incorporated pigments form thick corrosion products layer which further slows down the corrosion.

The third research work deals with the self-healing ability of polymer when incorporated. During this research conducting polymer doped with higher molecular weight. In this case, Poly ortho-anisidine doped with heteropolyanions was incorporated in polyvinyl butyral. After immersion in 0.1 M NaCl for 45 hours, the coating remains in the protection domain whereas PVB coatings showed that potential was in negative domain.

For future recommendation, there is a need to overcome the disadvantage of graphene in polymer coating for longer periods of time, because graphene has major drawbacks like higher position in galvanic series, excellent electrical conductivity, and poor dispersion properties.

These fillers should be used in epoxy and urethane industrial coatings for practical applications. Along with this the mechanical properties of coatings must be determined for coatings that will be using for wear resistance
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