Preparation of Polyaniline-based Conducting Composites and Performance Evaluation against Corrosion

Wondalem Misganaw, M.A. Azaz Ahmed[*]

Department of Chemical Engineering, College of Engineering, Defence University, Ethiopia.

Abstract: This work describes the preparation of conducting polymer composites and their use as corrosion protection coatings for aluminum and mild steel. Two doped forms of Polyaniline (PANI) (PANI- Dodecylbenzenesulfonic acid-DBSA and PANI-Graphite) were prepared. A new procedure for synthesis of Polyaniline has been developed by inverse emulsion process in order to make it readily soluble in Polyurethane (PU) paint which can then be directly applied on the substrate and dried easily within 20-30 minutes without evolution of toxic vapors. The two forms of PANI blended with PU were coated on aluminum and mild steel sheets. The corrosion protection performance of the coating was tested using salt spray and immersion techniques. Rate of corrosion was determined by measurement of change in metal weight after the exposure. To produce a good comparison, the corrosion study was performed on both polymer-coated and uncoated metal samples. It was found that PANI-PU coatings can provide considerable protection, as well as a physical barrier against corrosive environments (NaCl) in which the metal are exposed. The corrosion rate for the polymer-coated mild steel and aluminum sheets were significantly lower than the bare sheets. The PANI composites have been found to be promising materials for corrosion prevention

Keywords: Polyaniline, PANI-DBSA, PANI-Graphite, Conducting Polymer, Corrosion

1. Introduction

World is losing billions of dollars, as much as 2.5 trillion USD in 2013 alone [1] and India lost 40 billion (approx.. 2.4% of its GDP) [2] due to the deterioration of metals and alloys by a naturally occurring electrochemical process called corrosion in which materials tend to acquire a stable lowest energy state as against high energy metals and alloys [3]. It is nevertheless to say that preventing corrosion altogether by using whatever preventing methods available is not possible. However, a careful management and control practices can save 15 – 35% of economic losses [4]. When it comes to engineering alloys such as steel and aluminum which are the most widely used materials as they have considerable natural protection against corrosion due to the formation of an impervious oxide layer on their surface. But these materials also do not offer long-lasting protection against corrosion due to localized depletion of the oxide layer [5].

Both manufacturers and consumers use different preventive methods to overcome the corrosion of materials. Therefore, there is a requirement of scientific research either to prevent or minimize the corrosion [6, 7]. The presently available techniques are proper material selection and design of the equipment, surface coatings like paints and varnishes, corrosion inhibitors (chromates, silicates and organic amines), impressed current cathodic protection (ICCP) and sacrificial anodic protection (SAP) [8]. These preventive measures are not long lasting and eventually fail causing the delaminating [9, 10]. To prolong the protective barrier life-time, pretreatment coatings containing phosphates, chromates and oxides are applied before application of any organic coating [11]. Hexavalent chromium is one such important and widely used primer of chromate conversion coating (CCC) [12]. But unfortunately it is a known fact that chromium is a carcinogen and has detrimental environmental effects [13]

Conducting polymers are better replacements for chromate and zinc coatings as they provide passivation to stainless steel under high acidic conditions [14] and also cost effective [15]. Polyaniline (PANI) is one of the well-known highly tunable and environmentally friendly conducting polymers [16, 17]. It is easier to synthesize and has good electrical conductivity (4.4 Scm^{-1}). Polyaniline can be produced in bulk quantity as powder, films and fibers [18]. Polyaniline finds numerous applications in corrosion protection, batteries, sensors, electro-optic and electrochromic devices [19].

In polymerization process aniline molecules can be arranged in head-to-tail fashion at the *para* position of the aromatic ring while polymerizing to polyaniline in a linear octameric structure [20]. Considerable amount of flexibility is provided by –NH– groups and rigidity by phenyl rings to the polyaniline chain. Varying physicochemical properties of polyaniline can be attributed to the –NH– group which is due to the difference in the composition of amine and imine segments of polyaniline creates numerous oxidation states ranging from completely reduced leucoemeraldine to completely oxidized pernigraniline states, green protonated emeraldine being the most common form [18] which exhibits electrical conductivity. Redox methods can be utilized to interconvert PANI into its various forms [21].

The synthesis of PANI can be carried out either by the direct oxidation of aniline by chemical oxidants and or through electro oxidation on an inert electrode, Figure-1. PANI has a twofold use as corrosion inhibitor and as a protective coating [15] in corrosion prevention. PANI, in soluble form, is adsorbed on the metal surface by C=N functional group preventing anodic and cathodic reactions taking place on the metal surfaces of stainless steel, iron, mild steel, copper, aluminum and zinc [7]. PANI can be blended with epoxy resin and applied on the metal surface as a protective coating [7, 22]. Counter ions play crucial role PANI acrylic coatings toward the protective performance of the coatings [23]. Solubility of PANI in a variety of solvents makes it a good choice for corrosion prevention coatings as against other conducting polymers which are not soluble in any solvent.

The main objective of the present investigation is to synthesize polyaniline conducting polymers and to check how effective they are as corrosion inhibitors. In this effort two such polyaniline composites namely, polyaniline- dodecylbenzenesulfonic acid (PANI-DBSA) and polyaniline-graphite (PANI-Graphite) have been synthesized on a laboratory scale. Performance of these polymer composite materials has been tested as corrosion inhibitors by methods such as salt spray test and simple immersion test.

2. Experimental

All the required reagents and materials were acquired from well-known manufacturers like Aldrich, Rankem, Loba Chemie and SRL laboratories. Double distilled water has been used throughout the research work.

2.1 Sample Preparation

2.1.1 Preparation of Polyaniline –DBSA

In this method, synthesis of polyaniline was carried out by Inverse emulsion using DBSA as a protonating agent. Benzoyl peroxide was added to toluene in a 100 ml round-bottomed flask. The mixture was kept under mechanical stirring. 2-propanol, DBSA and aniline were added to the above mixture. Water was added to this clear solution to form an inverted emulsion. Four different experiments have been done by the same procedure by varying the ingredients, Figure-1. The amount of each ingredient corresponding to each experiment is shown in Table-1.

Here aniline-DBSA salt and 2-propanol in water form dispersed phase whereas benzoyl peroxide and 2-propanol in toluene form continuous phase. The reaction mixture gradually turns green in 2.5 hours and the stirring was continued for 24 hours at room temperature. The solution was then filtered by vacuum through a Whatman filter paper. At the end of the reaction, organic phase containing the polymer was separated.

Table 1: *Amount ingredients used for the preparation of PANI-DBSA*

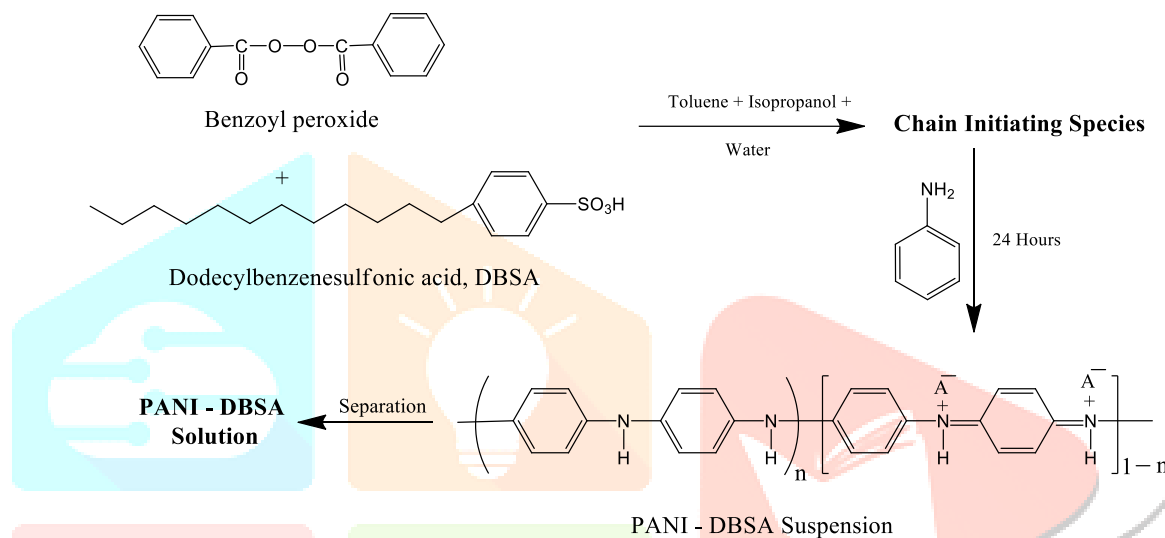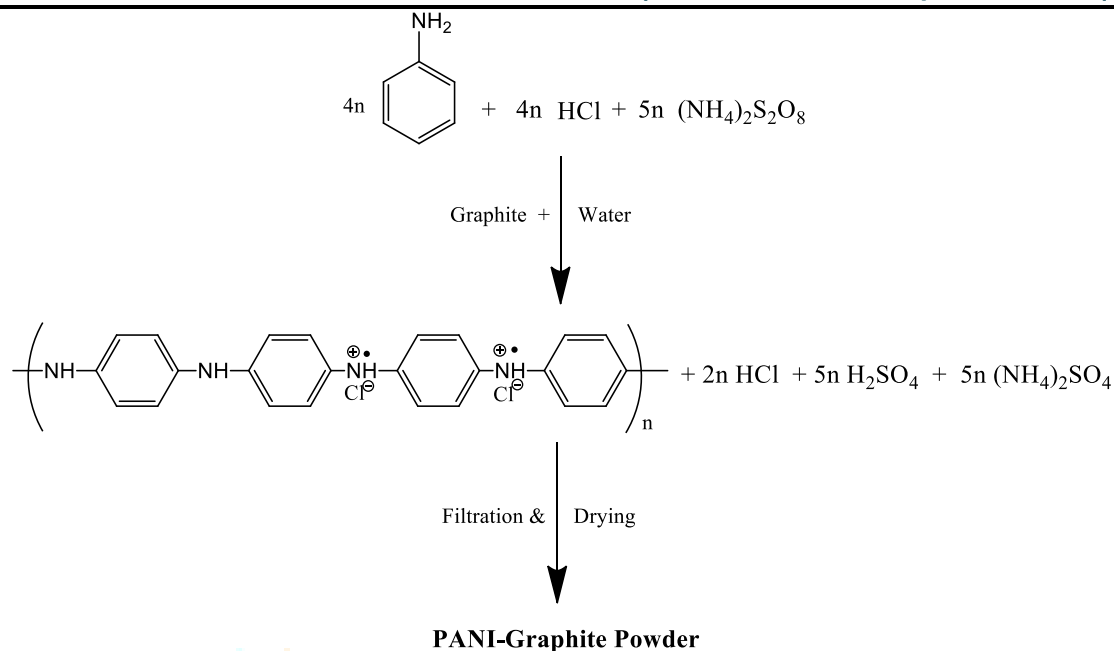| Reagent / Expt. No.	Aniline	Benzoyl peroxide (BPO)	Toluene	2-propanol	DBSA*	Distilled water
Expt-1	5.5 ml	24 g	100 ml	40 ml	34.48 g	50 ml
Expt-2	11.5 ml	24 g	50 ml	30 ml	34.48 g	50 ml
Expt-3	11.5 ml	24 g	50 ml	30 ml	17.24 g	50 ml
Expt-4	11.5ml	24 g	50 ml	20 ml	0 g	50 ml

* Dodecylbenzenesulfonic acid

Figure 1: Scheme of Preparation of PANI - DBSA

2.1.2 Preparation of Polyaniline-Graphite

The method involves synthesis of polyaniline using graphite as a dopant. Graphite is known to increase conductivity; hence its percentage was varied gradually, and various types of compositions were prepared. A sample of dry graphite was dispersed by agitation overnight in 200 ml water and 200 ml of 1M HCl into a beaker containing 18ml of aniline. The solution was cooled to about 0°C. Then 22.8 g Ammonium persulfate, A.R. (APS) in 60ml of distilled water was prepared and added drop wise into the above mixture and kept at 0°C. The reaction mixture was allowed to stir overnight. The solution was then filtered by vacuum through a Whatman filter paper and washed with distilled water. The cake was then washed twice with 50 ml 1M HCl. The sample was then dried under vacuum. Five different samples were prepared using the same procedure by varying the amount of graphite, Figure-2, Table-2.

$$NH_2$$

$$4n \quad \bigcirc \quad + \quad 4n \quad HCl \quad + \quad 5n \quad (NH_4)_2S_2O_8$$

Graphite + Water

$$(-NH-\bigcirc-NH-\bigcirc-\overset{\oplus\bullet}{\underset{Cl^{\ominus}}{NH}}-\bigcirc-\overset{\oplus\bullet}{\underset{Cl^{\ominus}}{NH}}-\bigcirc-)_n + 2n \; HCl + 5n \; H_2SO_4 + 5n \; (NH_4)_2SO_4$$

Filtration & Drying

PANI-Graphite Powder

Figure 2: Scheme of Preparation of PANI - Graphite

Table 2: *Amount of graphite used for the preparation of PANI-Graphite*

Experiment	Amount of Graphite (grams)
Expt-5	8
Expt-6	4
Expt-7	2
Expt-8	1
Expt-9	0

2.1.3 Preparation of PANI-PU Mixture

The polyurethane (PU) paint comprises of two components, PU resin and hardener. For our experiment the PU resin used has been prepared by condensation polymerization of polyol i.e., polyethyleneglycol and acrylic acid and the hardener is hexamethylenedi-isocynate (HMDI). The thinner used was a mixture of xylene and butyl acetate. The ratio of resin: hardener is 4:1 volume wise and thinner used was between 1-3 ml. Each of the PANI samples was mixed with a sample of PU paint, R-1004 and all of them were found to be miscible. The percentage composition of PU with hardener used for painting of mild steel and aluminum sheets is listed in Table-3.

2.1.4 Preparation of metal sheets

Commercial grade mild steel and aluminum samples were prepared for corrosion test. In order to reproduce data, similar areas (15.24 x 15.24 cm²) and thickness (0.2 cm) of the aluminum metal and mild steel coupons were used and each sheet was coated with the formulations prepared in Table-3.

Table 3: *Preparation of PANI-PU mixture for paint formulation.*

Sample	Quantity	Amount of PU* Resin (mL)	Amount of HMDI** (Hardener) (mL)
Expt-1	100 mL	160	40
Expt-2	100 mL	160	40
Expt-3	100 mL	160	40
Expt-4	100 mL	160	40
Expt-5	20 g	160	40
Expt-6	20 g	160	40
Expt-7	20 g	160	40
Expt-8	20 g	160	40
Expt-9	20 g	160	40

* Polyurethane
** Hexamethylenediisocynate

2.2 Anti-Corrosion Performance Test

2.2.1 Salt spray test

Salt spray test (ASTM B117) is a popular, cheap, quick and standard test yields a corrosive attack on the sample under investigation thereby predicting the suitability of any protective coating. This test widely produces uniform data for metals and alloys used in the process industries and structural applications. Salt test is carried out inside a uniform temperature (35°C) and 97% humidity containing test chamber in which a continuous 5% NaCl salt solution was sprayed on the surfaces of the sample mild steel and aluminum sheets under investigation. The test materials each coated with different samples prepared with coating thickness of 45 microns were exposed to the same environment in the test chamber for an exposure time of 500 h and the change of weight of the material was estimated for a period of time. To produce a good comparison, the corrosion study was performed on both polymer-coated and bare metallic samples. Bare samples were used as a reference and the loss of weight of the material is measured for a period of time. To evaluate the corrosion resistance behavior equation-1 was used.

$$\text{Rate of corrosion, } \mathbf{CR} = \frac{KxW}{AxTxD} \quad \ldots \qquad \ldots \qquad \ldots \qquad (1)$$

Where; K is conversion constant (2.40x10⁶), W is the weight loss or weight difference in (g) before and after corrosion, T is the time (hours), A is the area of the coupon (cm²), and D is density of the metal (g/cm³). The results of the salt spray test have been presented in Table-4.

Table 4: *Anti-corrosion performance test results (Salt spray test)*

Sheet Code	Material	Coating Sample code	Corrosion rate (CR*, MDD**)
A	Aluminum	Expt-9	0.25
B	Aluminum	Expt-6	0.15
C	Aluminum	Expt-5	0.05
D	Aluminum	Expt-3	0.13
E	Aluminum	Expt-1	0.25
F	Aluminum	Blank	4.93
G	Mild Steel	Expt-2	1.45
H	Mild Steel	Expt-4	3.56
I	Mild Steel	Expt-7	2.75
J	Mild Steel	Expt-8	4.38
k	Mild Steel	Blank	105.45

* Corrosion Rate
** Milligrams per square decimeter per day

2.2.2 Immersion Test

To generate uniform corrosion data the metal sheets were exposed to different aggressive and corrosive conditions (e.g., NaCl) in a beaker. The rate of corrosions was calculated using the equation-1. 100 hours of exposure time and a concentration 1 M NaCl solution at room temperature has been fixed. The test results have been presented in Table-5.

2.2.3 Effect of Concentration of NaCl on the Corrosion Rate

To find out the effect of salt concentration on corrosion rates, mild steel and aluminum plates coated with Expt-2 samples were exposed to NaCl solutions with different concentrations. To produce a good comparison, the corrosion study was performed on both polymer-coated and bare plates. 100 hours of exposure time and a concentration 1 M NaCl solution at room temperature has been used.

Table 5: *The effect of NaCl concentration on corrosion rates in MDD**

Concentration of NaCl (M)	0.125	0.25	0.5	0.75	1.0	1.5	2.0
CR** for coated MS*** sheet	1.25	2.35	2.62	3.17	3.83	4.56	5.93
CR for blank MS sheet	124	143	175	201	228	210	156
CR for coated Al sheet	0.015	0.02	0.04	0.06	0.09	0.85	0.50
CR for blank Al sheet	12.35	18.80	20.60	25.25	35.00	34.45	30.00

* Milligrams per square decimeter per day
** Corrosion Rate
*** Mild Steel

2.2.4 *Effect of Solution temperature on corrosion rate*

Effect of solution temperature on the rate of corrosion of mild steel and aluminum plates coated with Expt-2 samples has been carried out. 100 hours of exposure time and a concentration 1 M NaCl solution at room temperature has been used.

Table 6: *The effect of solution (electrolyte) temperature on corrosion rates in MDD[*]*

Test solution temperature (°C)	**20**	**40**	**60**	**80**	**100**
CR[**] for coated MS[***] sheet	3.50	10.15	27.35	20.40	15.90
CR for blank MS sheet	180.25	270.65	315.67	260.95	140.30
CR for coated Al sheet	0.28	2.20	2.80	4.10	3.75
CR for blank Al sheet	32.50	80.75	95.15	80.35	78.45

[*] Milligrams per square decimeter per day
[**] Corrosion Rate
[***] Mild Steel

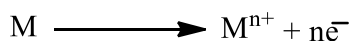**Table 7:** *Anti- corrosion performance test results (Immersion test)*

Sheet Code	Material	Coating Sample code	Corrosion rate (CR[*], MDD[**])
A	Aluminum	Expt-9	0.12
B	Aluminum	Expt-6	0.20
C	Aluminum	Expt-5	0.11
D	Aluminum	Expt-3	0.13
E	Aluminum	Expt-1	0.45
F	Aluminum	Blank	5.27
G	Mild Steel	Expt-2	1.45
H	Mild Steel	Expt-4	3.56
I	Mild Steel	Expt-7	2.75
J	Mild Steel	Expt-8	4.38
K	Mild Steel	Blank	125.25

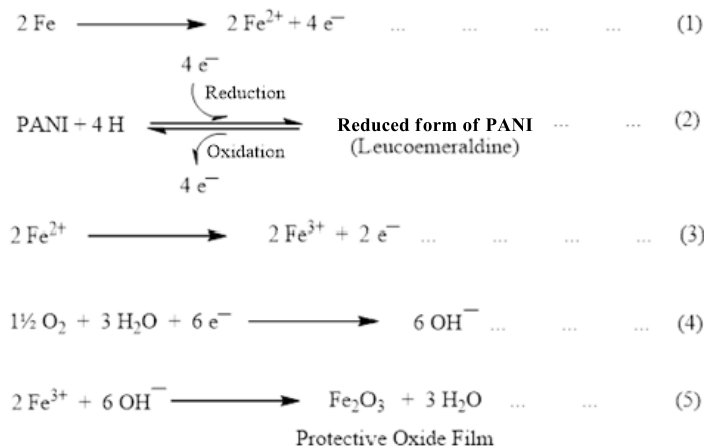[*] Corrosion Rate
[**] Milligrams per square decimeter per day

3. Discussion

Corrosion monitoring was performed by salt spray and simple immersion tests followed by the determination of the change in metal weight after the exposures. In a normal corrosion reaction, metal surface which is devoid of atmospheric oxygen due to dirt, dust, water etc. releases electrons and the surrounding areas of metal surface, where oxygen concentration is more, accept these electrons in presence of moisture and produce hydroxyl ions by redox reactions. Further, these hydroxyl ions react with base metal cations and converted into their oxides called rust as shown in the reaction (1).

$$M \longrightarrow M^{n+} + n\bar{e}$$

$$O_2 + 2H_2O + 4\bar{e} \longrightarrow 4OH^- + \text{Base Metal Cation} \longrightarrow \text{Metal Oxide (Rust)} \quad \ldots \quad \ldots \quad \ldots (1)$$

Polyaniline coating alters the electrochemistry of the metal surface by stabilizing the electric potential of the metal by making a protective passive film [24]. Metal dissolution is minimized by the polymer charge thereby stabilizing the electric potential of the base metal [25]. Several mechanisms [26, 27] are available to explain the functioning of PANI from barrier effect to maintaining a passive oxide layer on the metal surface. However, none of the mechanisms explain satisfactorily. In one such mechanism, PANI oxidizes the

metallic iron to Fe^{2+} then to Fe_2O_3. In the process first PANI gets reduced to leucoemeraldine and by gaining oxygen again oxidizes to emeraldine salt [22, 25] Figure-3. Metal passivation (formation of a thin, compact, adherent, and passive layer of Fe_2O_3 at the interface) may be due to the redox catalytic effect of PANI.

$$2\,Fe \longrightarrow 2\,Fe^{2+} + 4\,e^- \qquad \dots \qquad \dots \qquad \dots \qquad \dots \qquad (1)$$

$$PANI + 4\,H \underset{\substack{4\,e^- \\ Oxidation}}{\overset{\substack{4\,e^- \\ Reduction}}{\rightleftharpoons}} \textbf{Reduced form of PANI} \qquad \dots \qquad \dots \qquad (2)$$
$$\text{(Leucoemeraldine)}$$

$$2\,Fe^{2+} \longrightarrow 2\,Fe^{3+} + 2\,e^- \qquad \dots \qquad \dots \qquad \dots \qquad (3)$$

$$1\tfrac{1}{2}\,O_2 + 3\,H_2O + 6\,e^- \longrightarrow 6\,OH^- \qquad \dots \qquad \dots \qquad \dots \qquad (4)$$

$$2\,Fe^{3+} + 6\,OH^- \longrightarrow Fe_2O_3 + 3\,H_2O \qquad \dots \qquad \dots \qquad (5)$$
$$\text{Protective Oxide Film}$$

Figure 1: Corrosion Protection Mechanism by PANI

It was found that PANI-PU coatings can provide good protection against corrosive environments in which the metals are exposed. The corrosion rate for the polymer coated steel and aluminum sheets was significantly lower than the bare metal sheets (~10 times) (Table-5). The corrosion rate is then reported as milligrams per square decimeter per day (MDD) throughout the text, in accordance with ASTM.

It is visibly clear from the results obtained (Table-3 and Table-4) that the highest corrosion inhibition was observed when high ratio of DBSA and graphite to aniline was used for the preparation of the PANI composite. The difference in their composition and then density of PANI composite coatings might be the reason for these observations.

The trend, in case of increasing concentration of salt solution, is obvious from the results obtained that the corrosion rates increase as concentration of the salt solution increases until the salt concentration reaches 1 M. The stripping of protective coating happens at higher chloride ion concentration leading to higher rates of corrosion which also include the increase of rate of cathode migration [28]. As the salt concentration increases beyond 1 M, the rate of corrosion decreases steadily except the coated MS sheet (Table-5; Figure-4). High corrosion rates observed above 1 M salt solution in case of coated MS sheet may be due to the accumulation of high chloride concentration underneath the coated film results in anodic polarization [29, 30].
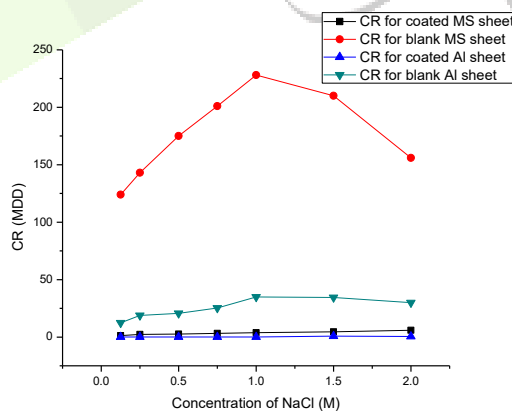

Figure 4: Effect of NaCl concentration on Corrosion Rates

Apart from the above parameters there are also significant environmental effects on the rates of corrosion such as O_2 concentration in electrolyte as well as in atmosphere, pH of the electrolyte and the temperature. Results on the effect of solution (electrolyte) temperature on corrosion rate (Table-6; Figure-5) prove that the high corrosion stability is due to the coatings of PANI composite on steel and aluminum plates. Rate of corrosion reaches a maximum at 60ºC, and then drops again for both coated and uncoated metallic plates. This can be due to a decrease in concentration of oxygen in the water at elevated temperatures. The increased rate of chemical

reaction achieved with increased temperature is balanced by a decreased cathodic depolarization reaction owing to the inverse solubility of oxygen in the solution.
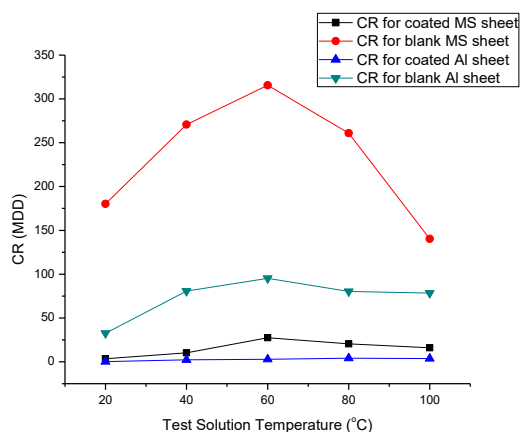
Figure 5: Effect of Temperature on Corrosion Rates

4. Conclusion

Conducting polymers are versatile, promising and latest corrosion resistant materials. There are different methods of synthesis are available based on their processing, stability, and ease of blending. A new concept in the synthesizing process has been used in the present investigation i.e. the substituted anilines were used for polymerization which improves its solubility. Though a number of oxidizing agents are available for such polymerization, in the present investigation only two, viz. Ammoniumpersulphate (APS) and Benzoylperoxide have been used. Benzoylperoxide has certain advantages over APS as its solubility in many organic solvents, less chances of over-oxidation and easiness to remove byproducts. The corrosion protection performance of the coating was tested using salt spray tests and immersion tests followed by the determination of change in weight of metallic samples. The results obtained showed that PANI-PU coatings can provide considerable protection, as well as a physical barrier against corrosive environments (e.g., NaCl) in which the metal are exposed. The corrosion rate for the polymer-coated mild steel and aluminum sheets were significantly lower than the bare sheets (~10 times).

In conclusion, polyaniline coatings on active metals like iron provide anodic protection, act as electronic, chemical, and physical barriers to inhibit anodic reaction, and maintain high resistance to ionic flow, thereby blocking the metal dissolution and providing excellent corrosion protection.

References

[1] A. R. Prasad, K.K. Anupama, Abraham Joseph, "Corrosion Inhibition in Oil and Gas Industry: Economic Considerations", *Corrosion Inhibitors in the Oil and Gas Industry*, pp.135-150, April, 2020. DOI: 10.1002/9783527822140.ch5. https://www.researchgate.net/publication/339281629.

[2] R. Bhaskaran, Lalit Bhalla, Afzalur Rahman, Suruchi Juneja, "An Analysis of the Updated Cost of Corrosion in India", *Materials performance* 53(8), pp. 56-65, August 2014. https://www.researchgate.net/publication/286901886

[3] "Corrosion: Understanding the Basics", (#06691G), *ASM International*, pp. 1 – 21, 2000. www.asminternational.org.

[4] "Economic Impact: Assessment of the Global Cost of Corrosion". http://impact.nace.org/economic-impact.aspx

[5] G. S. Frankel, "Pitting Corrosion of Metals-A Review of the Critical Factors", *Journal of the Electrochemical Society*, Vol. 145, No. 6, pp. 2186-2198, 1998. DOI: 10.1149/1.1838615

[6] Günter Schmitt, "Global Needs for Knowledge Dissemination, Research, and Development in Materials Deterioration and Corrosion Control", *WCO*, May, 2009. https://www.researchgate.net/publication/237603255

[7] D. E. Tallman, G. Spinks, A. Dominis, G. G. Wallace, "Critical Factors in Localized Corrosion", *J. Solid State Electrochem.* 6, pp.73–84, 2002. https://link.springer.com/article/10.1007/s100080100212

[8] H.E. Townsend, R.G. Hart, "Composition of chromate passivation films on aluminum-zinc alloy coated sheet steel", *J. Electrochem. Soc.* 131, 6, pp. 1345–1348, 1984. DOI: 10.1149/1.2115817

[9] E.G. Fernandes, "Coatings and corrosion-even the best fail", *Ind. Eng. Chem. Prod. Res. Dev.* 24, 1985. https://www.researchgate.net/publication/231298367

[10] G.S. Frankel, "Pitting corrosion of metals a review of the critical factors", *J. Electrochem. Soc.* 145, 6, 1998. DOI: 10.1149/1.1838615. https://www.researchgate.net/publication/338014455

[11] T.W. Cape, "Phosphate conversion coatings", In: J.R. Davis, Editor, *ASM Handbook, Corrosion* Vol. 13, ASM International, Library of Congress, USA, pp. 383–388, 1987. https://www.academia.edu/29405156

[12] K.A. Korinek, "Chromate conversion coatings", In: J.R. Davis, Editor, *ASM Handbook, Corrosion* Vol. 13, ASM International, Library of Congress, USA, pp. 389–398, 1987. https://www.asminternational.org/search/-/journal_content/56/10192/06508G/PUBLICATION

[13] J. Blasiak, J. Kowalik, "A comparison of the in vitro genotoxicity of tri-and hexavalent chromium", *Mutat. Res.* 469, pp. 135–145, 2000. https://europepmc.org/article/med/10946250 DOI: 10.1016/s1383-5718(00)00065-6

[14] P.Zarras, N.Anderson, C.Webber, D.J.Irvin, J.A.Irvin, A.Guenthner, J.D.Stenger-Smith, "Progress in using conductive polymers as corrosion-inhibiting coatings panel", *Radiation Physics and Chemistry*, Vol. 68, Issues 3–4, pp. 387-394, October–November 2003. https://doi.org/10.1016/S0969-806X(03)00189-0

[15] M. Kraljic, K.Z. Mandic, L.J. Duic, "Inhibition of Steel Corrosion by Polyaniline Coatings", *Corros. Sci.,* 45, 1, pp. 181-198, 2003. doi:10.1016/s0010-938x(02)00083-5

[16] A. J.Dominis, M. Geoffrey, Spinks, G. G.Wallace, "Comparison of polyaniline primers prepared with different dopants for corrosion protection of steel", *Progress in Organic Coating,* Vol. 48, Issue 1, pp. 43-49, November 2003. https://doi.org/10.1016/S0300-9440(03)00111-5

[17]   Gouri Smitha Akundy, Ramakrishnan Rajagopalan, Jude O. Iroh, "Electrochemical deposition of polyaniline–polypyrrole composite coatings on aluminum", *Journal of Applied Polymer Science*, Vol. 83, Issue9, pp. 1970-1977, February 2002. https://onlinelibrary.wiley.com/. https://doi.org/10.1002/app.10123

[18] J. Stejskal, I. Sapurina, "Polyaniline -A Conducting Polymer", *Materials Syntheses,* pp. 199-207, 2005. https://link.springer.com/chapter/10.1007/978-3-211-75125-1_26

[19] Subrahmanya Shreepathi, Hung Van Hoang, Rudolf Holze, "Corrosion Protection Performance and Spectroscopic Investigations of Soluble Conducting Polyaniline-Dodecylbenzenesulfonate Synthesized via Inverse Emulsion Procedure", *Journal of the Electrochemical Society*, 154(2), January 2007. https://www.researchgate.net/publication/28669445, DOI: 10.1149/1.2398815

[20] Yan Sun, G. Alan, Mac Diarmid, A. J. Epstein, "Polyaniline: synthesis and characterization of pernigraniline base", *J. Chem. Soc., Chem. Commun.,* pp. 529-53, 1990. https://doi.org/10.1039/C39900000529

[21] B. Wessling, J. Posdorfer, "Corrosion prevention with an organic metal (polyaniline): corrosion test results", *Electrochim. Acta* 44, pp. 2139–2147, 1999. https://kundoc.com/pdf-corrosion-prevention-with-an-organic-metal-polyaniline-corrosion-test-results-.html

[22] Einar Bardal, "Corrosion and Protection (Engineering Materials and Processes)", *Springer-Verlag London Limited*, 2004. https://www.academia.edu/14713272

[23] José E Pereira Da Silva, Susana I. Córdoba de Torresi , Roberto M. Torresi, "Polyaniline acrylic coatings for corrosion inhibition: The role played by counter-ions", *Corrosion Science*, 47(3), pp. 811-822, March 2005. https://www.researchgate.net/publication/235586833 DOI: 10.1016/j.corsci.2004.07.014

[24] K. Saravanan, S. Sathiyanarayanan, S. Muralidharan, S. Syed Azim, G. Venkatachari, "Performance evaluation of polyaniline pigmented epoxy coating for corrosion protection of steel in concrete environment*", Progress in Organic Coatings*, 59, pp. 160–167, 2007. https://www.sciencedirect.com/science/article/pii/S030094400700080X. https://doi.org/10.1016/j.porgcoat.2007.03.002

[25] Gvozdenovic Milica, Jasmina Stevanović, Daliborka Jambrec, Branimir N. Grgur, "Application of polyaniline in corrosion protection of metals", *ZAŠTITA MATERIJALA*, 53, 2012. https://www.researchgate.net/publication/329755941

[26] Y.Chen, X.H.Wang, J.Li, J.L.Lu, F.S.Wang, "Long-term anticorrosion behaviour of polyaniline on mild Steel", *Corrosion Science*. Vol. 49, Issue 7, pp. 3052-3063, July 2007. https://doi.org/10.1016/j.corsci.2006.11.007

[27] A. Cook, A. Gabriel, N. Laycock, "On the Mechanism of Corrosion Protection of Mild Steel with Polyaniline" , *J. Electrochem. Soc., B* 151 (9), p. 529, 2004. https://iopscience.iop.org/article/10.1149/1.1782077/meta

[28] Yanyu Cui, Yongxiang Qin, Dilinuer Dilimulati, Yujun Wang, "The Effect of Chlorine Ion on Metal Corrosion Behavior under the Scratch Defect of Coating", *International Journal of Corrosion,* Vol. 2019. https://www.hindawi.com/journals/ijc/2019/7982893/. https://doi.org/10.1155/2019/7982893

[29] Zhipeng Zeng, R.S. Lillard, Hongbo Cong, "Effect of Salt Concentration on the Corrosion Behavior of Carbon Steel in CO_2 Environment", *ResearchGate*, *Corrosion Science Section*, Vol. 72 (6) pp. 805 – 823, 2016. https://www.researchgate.net/publication/304717649

[30] Wen Zhou, Wei Lan, Xianlong Cao, Hongda Deng, Yongbo Yan, Xianglong Hou, "Effect of a High Concentration of Chloride Ions on the Corrosion Behaviour of X80 Pipeline Steel in 0.5 mol L^{-1} $NaHCO_3$ Solutions", *Int. J. Electrochem. Sci.,* 13, pp. 1283 – 1292, 2018. doi: 10.20964/2018.02.03