

Corrosion Inhibition Properties of Sulfonated Polyaniline-Poly(Vinyl Alcohol) Composite on Mild Steel

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ABSTRACT: *In this work, we demonstrate water-based corrosion inhibition properties of engineered sulfonated polyaniline molecules on poly(vinyl alcohol), PANI-PVA, for mild steel. The corrosion-inhibition performances were evaluated using potentiodynamic polarization in a salty corrosive 3 % NaCl solution. The anti-corrosion coating based on these composite materials displays barrier properties against corrosion-causing agents and shows a corrosion protection efficiency of 84.39 %, compared with uncoated. The material showed a lower value of corrosion current (I_{corr}) which is $2.56 \mu A/cm^2$ and a positive shift in corrosion potential (E_{corr}), $-0.426 V$, in comparison with uncoated steel. Open Circuit Potential (OCP) Studies and electrochemical impedance (EIS) were also carried out to check the corrosion protection ability of the material. OCP studies, Nyquist plot, and Bode plots showed that the synthesized PANI-PVA possess a corrosion protection ability on mild steel against the corrosive species.*

KEYWORDS: *Poly (vinyl alcohol); polyaniline; Corrosion protective coating; Corrosion potential; Corrosion current.*

INTRODUCTION

Metal and metal alloys corrosion are causing immense economic loss, and casualties [1] and are a serious threat to the development of industry [2]. Corrosion is defined as the destruction or deterioration of a material due to a reaction to its environment. Metals and metal alloys are favored

thermodynamically to suffer from corrosion [3]. Because of the fact that corrosion cannot be completely eliminated, so, various strategies are adopted for its control. These strategies are mainly focused on slowing the kinetics and/or altering its mechanism. Some of them include

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applying various inhibitors [4], electroplating processes, cathodic protection, and depositing protective coatings. Among them, the most common and effective method for protecting metals and steel from corrosion is the application of organic coatings. Ordinary organic coatings are, however, not quite suitable for the heavy-duty corrosion environment due to the lack of hydrolytic stability at the substrate-coating interface. Therefore, the preparation of such coatings is needed that has high corrosion protection performance and a long service lifetime.

Conductive Polymer (CPs) based organic coatings have the ability to protect the steel against corrosion [2]. Among CPs, Polyaniline (PANI) is promising because of its easy synthesis, chemical stability [5], and relatively low cost [6]. Due to reversible transformation among its various oxidation states, there is the possibility of the formation of a dense metal oxide passive layer, particularly in the immersing state. PANI has the ability to act as a protective coating against corrosion due to the presence of amine and carbonyl groups in its backbone which act as a protective barrier against corrosive species [7]. Similarly, the reversible behavior of the polymer in the redox process enhances the formation of a uniform layer of oxide on the metal surface. This oxide layer decreases the level of corrosion and the metal corrosion potential is shifted towards positive values [8]. However, the effective use of PANI as a protective layer has been limited by its poor solubility in most common organic solvents and intractability [9]. To improve the processibility of PANI different approaches have been adopted by scientists to synthesize its copolymers [10], polymer composites [11], blends [12], PANI dispersions [13], and PANI nanostructures [14].

A number of conductive composites have been synthesized via chemical polymerization of aniline monomers in the presence of water-soluble polymers or anionic surfactants, metals and metal oxides, and carbon nanotubes, under different polymerization conditions [15]. Composite materials are more important due to their lightweight and enhanced corrosion resistance. These materials usually consist of a polymer matrix in which fibers and/or small filler particles are continuously dispersed [16].

Poly (Vinyl Alcohol) (PVA) is a water-soluble, highly transparent flexible, nontoxic, and commercially available polymer. Mirmohsini and G.G. Wallace reported good mechanical properties and increased conductivity of PANI

dispersion composite, synthesized *via* chemical polymerization in a media containing PVA [17]. M. Irimia-Vladu and J. W. Fergus prepared the emeraldine base PANI-PVA composite film. The composite materials were used for CO₂ sensing [18]. Y. Li *et al* reported a water soluble PANI-PVA composite for humidity sensing [19]. D.S. Patil *et al* have mentioned super capacitor character for PANI-PVA thin film, synthesized through chemical oxidation route and the stability was reported for more than 20,000 cycles in 1M aqueous H₂SO₄ solution [20]. M. Shahi *et al* synthesized PANI-PVA and PVA-PANI-AgNO₃ nanofibers and characterized them through various techniques [21]. PANI nanostructures were polymerized on swollen PVA gel by *in situ* polymerization and it is reported that the conductivity increases with the time of swelling of PVA gel [22]. PANI has also been electrodeposited in the presence of PVA from an aqueous sulfuric acid solution on the stainless steel surface and is regarded as protection of steel from general and pitting corrosion [23]. Most recently, PANI composite free-standing membranes were made by a solvent method in the presence of water-soluble PVA [24]. However to the best of our knowledge, after a thorough search of the literature, there is no work on corrosion protection based on PANI-PVA composite.

Herein, we became enthralled to prepare PANI-PVA composite doped with DBSA through inverse emulsion polymerization to investigate the PVA-PANI composite and corrosion protection performance of the material. DBSA was used as a dopant and as a surfactant for the dispersion medium. We used the mixture of toluene and 2-butanol as a dispersion medium and water-dissolved percent PVA solution as a dispersed phase. The products obtained are dispersible and stable in most common organic solvents and a mixture of solvents like chloroform, 2:1 mixture of toluene and methanol, etc. The composite materials show good electrochemical behavior and high protection for mild steel substrate under saline conditions.

EXPERIMENTAL SECTION

Materials

Aniline was purchased from Acros Organic, distilled twice then and stored under cold. While Poly Vinyl Alcohol (PVA), benzyl peroxide (BPO), toluene, 2-propanol, and dodecylbenzene sulfonic acid (DBSA) were purchased from Merck and used as received.

Procedure

The experiment was initiated by taking 50 mL of toluene in a round bottom flask. 0.40 g of benzyl peroxide was added to it with constant stirring and dissolved completely. To the above solution, 10 ml of 2-propanol was added. The mixture was stabilized with 1.5 mL of dodecylbenzene sulfonic acid (DBSA), which act as a surfactant and dopant. Then 0.2 mL of aniline was added to this mixture. A milky white emulsion was obtained upon the addition of 10 mL of double distilled water. The reaction mixture turned green after 5 to 6 hours. The reaction was allowed to proceed for 24 hours under mechanical stirring at room temperature. After 24 hours the reaction mixture was poured into a separating funnel and washed with distilled water and then three times with acetone. The dark green polyaniline (PANI) salt obtained was dried at room temperature for 24 hrs. The same procedure was carried out for polyaniline-Polyvinyl alcohol (PANI-PVA) composite, but instead of distilled water, 5% solution of PVA in water (10 mL) was added to the mixture.

Preparation of mild steel electrode for corrosion study

The mild steel substrate was polished with abrasive paper followed by rinsing with ethanol and acetone mixture and finally distilled water. To coat the steel substrate with PANI or PANI-PVA composite, 0.2 g of sample was dispersed in 10 mL chloroform, and about 10 μ L of that solution was dropped cast on the surface and dried in the open air which forms a uniform layer.

Instrumentation

Ultraviolet-visible (UV-Vis) spectra were carried out in chloroform using a Shimadzu-1700 spectrophotometer. The sample interval was 0.5 nm and the spectrum was recorded in 200-800 nm range. Fourier transmission infrared spectrophotometer (FTIR)-8400, Shimadzu, Japan was used to record the FT-IR spectra of samples in 400-4000 cm^{-1} range. The morphology was examined through Scanning electron microscopy (SEM) JSM5910 (JEOL Japan) in solid powder form. X-ray diffraction patterns of the materials were recorded through JEOL JAPAN (JDX-3532) X-ray diffractometer using Cu K α radiations of wavelength 1.5405Å with a scan speed of 0.05 $^\circ$ /s. Thermal stability was checked using Thermo Gravimetric Analysis (TGA) at a heating temperature 10 $^\circ\text{C}/\text{min}$ under N_2 atmosphere by using Pyris Diamond Series TG/DTA

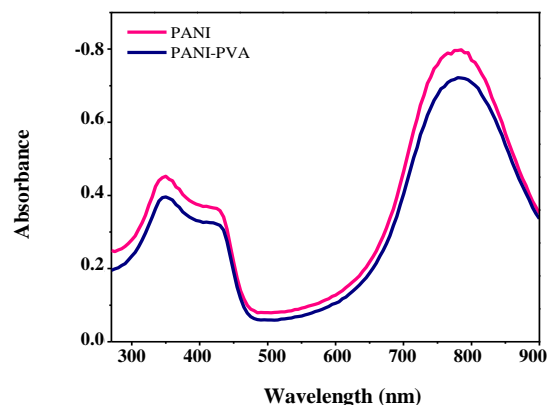


Fig. 1: UV-Visible spectra of PANI and PANI-PVA composite in chloroform

(Perkin Elmer, USA, rang 1300 $^\circ\text{C}$). Gamry reference 3000 ZRA potentiostat/galvanostat (USA) was used for the corrosion study. Samples were deposited on mild steel electrodes which act as working electrodes, while a saturated calomel electrode (SCE) was used as a reference electrode and platinum wire was used as the counter electrode. The mild steel electrode was composed of Carbon, (C 0.25 - 0.290 %), Copper (Cu 0.20 %), Iron (Fe 98.0 %), Manganese (Mn 1.03 %), Phosphorous (P 0.040 %), Silicon (Si 0.280 %) and Sulfur (S 0.050 %). Open circuit potential (OCP) study and electrochemical impedance (EIS) were also carried out in the same setup.

RESULTS AND DISCUSSION

UV-Visible Spectroscopic Analysis

Absorption spectroscopy is a very useful technique to identify the PANI and its base and salt forms. Absorption spectra of the PANI and PANI-PVA composites dissolved in chloroform are shown in Fig. 1.

In Fig. 1 electronic-absorption spectra of PANI and PANI-PVA samples indicate three bands in the range of 342-349, 424-429, and 779-800 nm. These bands indicate the conductive emeraldine salt structure and are in agreement with the literature [25]. The first band (342-349 nm) is assigned to $\pi \rightarrow \pi^*$ of the polymer backbone benzenoid rings, while the second (424-429 nm) and third (779-800 nm) peaks are attributed to the polaron $\rightarrow \pi^*$ transition of the quinoid ring and $\pi \rightarrow$ polaron (exciton) transition, respectively. The last two bands give information about the doping level and polaron formation, which indicate the protonation stage of the PANI Chain [26].

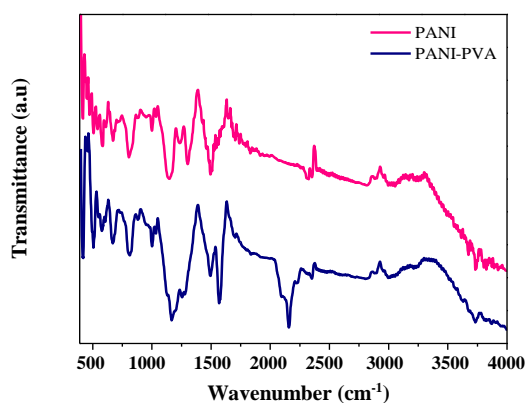


Fig. 2: FT-IR spectra of (a) PANI and (b) PANI-PVA composite.

PVA, itself has no specific absorption band in the particular wavelength region (250-900 nm) [27].

Fourier-Transmission Infrared Spectroscopy

FT-IR spectroscopy is a useful technique for the determination of structure. FT-IR spectra of PANI and PANI-PVA composite are shown in Fig. 2. The FT-IR analysis of pure PANI shows various peaks. The peaks around 1567 and 1504 cm^{-1} are due to the absorption of quinoid and benzenoid rings, respectively, which are accordingly to the previous results. The peak at 1304 cm^{-1} is attributed to the C-N stretching vibration of aromatic conjugation in the benzene ring [28]. The peaks at 1143 cm^{-1} and 811 cm^{-1} are assigned to the N-Q-N (Q denotes quinoid ring) [28] in-plane and out-of-plane bending, respectively. A band at 663 cm^{-1} is due to the ring C-C bending vibration [29]. The FT-IR spectra for PANI-PVA composite show almost a similar pattern as for pure PANI, however, there are two extra peaks observed at 2163 and 3469 cm^{-1} , that are assigned to C-H stretching and O-H stretching of the PVA, respectively [30]. The FT-IR spectrum comparison of the two samples suggests that the PVA had been adsorbed or doped with PANI matrix.

X-rays diffraction analysis

XRD technique is extensively used in material characterization. PANI salts usually show characteristic peaks at $2\theta = 20^\circ - 25^\circ$ [31]. The peaks around 20° and 25° are weak, however, their intensity and sharpness increase with the addition of PVA as shown in Fig. 3. The peak centered at $2\theta = 17^\circ$ and $2\theta = 10^\circ$ may be attributed to periodicity

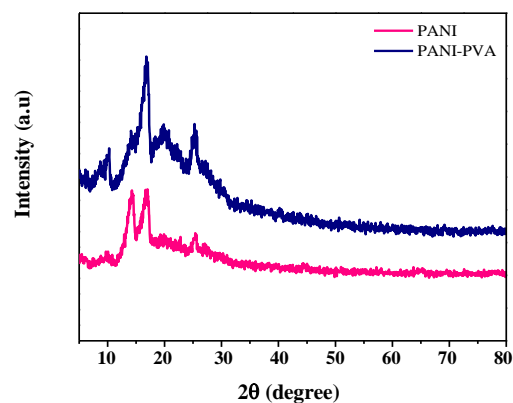


Fig. 3: XRD pattern of PANI and PANI-PVA composite.

parallel to the polymer chain, whereas the peaks at $2\theta = 25^\circ$ may be caused by the periodicity perpendicular to the polymer chain [32]. The crystallinity and orientation of conducting polymers have been of much interest because more highly ordered systems can show a metallic conductive state. Since the intensities and sharpness of the peaks significantly increased with the incorporation of PVA, thus it also confirms the formation of PANI-PVA composite. This also shows high crystallinity and hence increases conductivity.

Morphological study

The morphology of PANI-PVA composites was examined through Scanning Electron Microscopy (SEM). Fig. S1 shows the pure PANI and PANI-PVA composite SEM images. As, the morphology of PANI depends on the method of preparation, solvent, or medium [33]. Both the images show a somewhat compact morphology, however, it can be observed that pure PANI shows a more porous nature as compared to composite. This indicates the insertion of PVA content into the PANI matrix. The surface of the material is rough and tough. The products obtained can be used for many potential applications such as corrosion protection, supercapacitor, and membrane.

Thermo gravimetric analysis

The thermal stability of PANI is very important for its use in many practical applications. Thermo Gravimetric Analysis (TGA) gives the change in mass versus temperature curve that further provides information regarding thermal stability and composition of the initial sample, intermediates, and the residue.

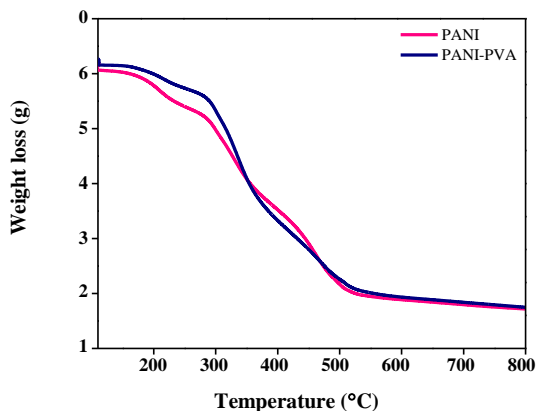


Fig. 4: TGA curve of PANI and PANI-PVA composite.

Thermograms of pure PANI and PANI-PVA are shown in Fig. 4. The curves of both samples present almost similar weight loss with respect to temperature. The initial weight loss, in the range 100-200 °C, is due to the moisture content and other volatile components associated with the sample. PANI is highly hygroscopic in nature and shows high moisture loss [34]. The second weight loss (40-50%) starting above 250 °C is assigned to the destruction of $\text{NH}^+ \dots \text{SO}_3^-$, comes from the interaction of DBSA with PANI chain and due to the degradation of DBSA [35]. The third weight loss started from 360-530 °C is attributed to the decomposition of the chemical structure of PANI backbone. The TGA analysis shows overall good stability. Thus, the material can be used under hard conditions of temperature for various applications.

Tafel polarization studies

The characteristic Tafel polarization curves of bare, PANI, and PANI-PVA coated mild steel in 3% NaCl is shown in Fig. 5. The swept potential range of the electrode was kept ± 250 mV vs OCP at 2 mV/s scan rate. The electrochemical corrosion parameters values, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) [36], cathodic Tafel slop (b_c), and anodic Tafel slop (b_a) are shown in Table 1. The corrosion protection efficiency (PE %) values were calculated by the following equation [31].

$$\% \text{ PE} = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (1)$$

Where i_{corr} and $i_{\text{corr(inh)}}$ stand for uncoated and coated corrosion current, respectively. It is clear from Fig. 5, that

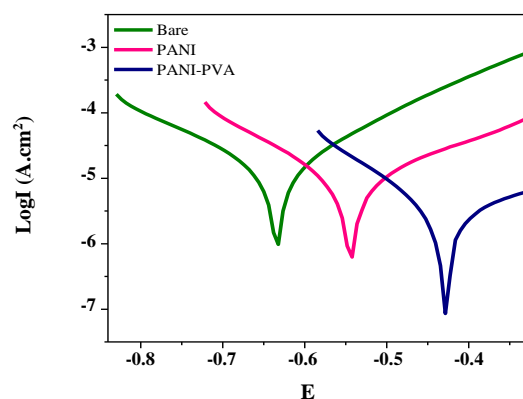


Fig. 5: Polarization behavior of bare, PANI, and PANI-PVA-coated mild steel in 3% NaCl Solution.

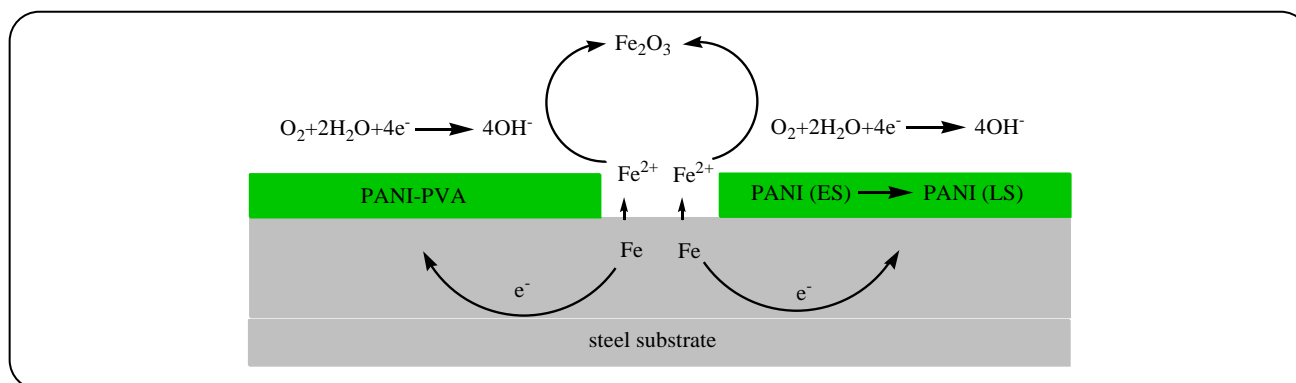
for PANI-PVA coated steel, a positive shift of 209 mV was observed in the corrosion potential. This positive shift in the corrosion potential of mild steel indicates that PANI-PVA offers higher resistance to corrosion in the saline environment [37]. From the data analysis, it is clear that I_{corr} value decreases significantly for PANI and PANI-PVA composite. The values of I_{corr} decrease from 16.4 (bare steel) to 8.256 $\mu\text{A}/\text{cm}^2$ for PANI-coated mild steel and to 2.56 $\mu\text{A}/\text{cm}^2$ for PANI-PVA-coated mild steel. Similarly, the corrosion rate of PANI-PVA-coated mild steel is lower than that of uncoated mild steel. The corrosion protection performance, calculated from the Tafel parameters using Equation (1), shows that PANI coated sample show 49.65 % efficiency against corrosion while that of PANI-PVA coated show 84.39 % protection. Since PANI is conductive in nature and it can passivate the surface through charge barriers. Further, in PANI-PVA due PVA cross-linking and hydrogen bonding phenomenon, the coating is more compact on the surface and hence offers greater protection as compared to PANI alone.

Corrosion mechanism

The protection mechanism of PANI-PVA against corrosion is illustrated in Fig. 6. The corrosion protection is mainly because of three factors: passive layer formation, barrier effects that can prevent moisture and oxygen to reach the metal surfaces, and adhesion. During the immersion of coated steel substrate in 3% NaCl solution, Fe oxidized to Fe^{+2} and then to Fe^{+3} . This is followed by the reduction of PANI emeraldine salt to PANI leucoemeraldine salt, accepting the electrons generated

Table 1: Electrochemical parameters of bare, PANI and PANI-PVA-coated mild steel in 3% NaCl solution

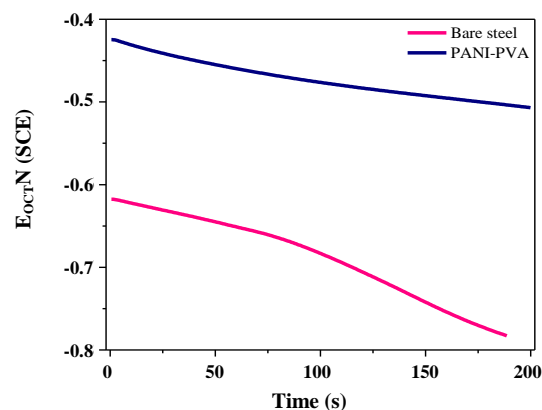
Sample	I_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (V vs SCE)	B_a (V/dec)	B_c (V/dec)	CR (mpy)	PE %
Bare	16.4	-0.635	0.1762	0.2008	7.46	—
PANI	8.256	-0.549	0.2027	0.1481	3.768	49.65
PANI-PVA	2.56	-0.426	0.2406	0.117	1.168	84.39

**Fig. 6: Schematic diagram of PANI-PVA coated mild steel corrosion protection mechanism [38].**

during the oxidation of iron. During this process, the electrons can also combine with the dissolved oxygen in the aqueous medium to form OH^- ions. These OH^- ions also react with Fe^{3+} ions to form Fe_2O_3 passive layer, which prevents the steel from further corrosion [13,38]. Due to these protective layers and strong adhesion, PANI-PVA-coating is capable to offer higher protection against corrosion, which is supported by the potentiodynamic polarization results. Since the FT-IR results reveal the interaction of PVA molecules with PANI chain, the corrosion inhibition role of PVA is due to cross-linking or hydrogen bonding phenomenon to make a compact coating layer on the metal surface. Thus, PVA plays a role along with PANI to protect the metal surface against corrosion.

Open Circuit Potential (OCP) studies

To further study the corrosion properties of PANI-PVA, OCP study was carried out. It is clear from Fig. 7 that the initial OCP values of the bare steel are -0.617 V vs SCE which abruptly decreased to -0.728 V after 200s. While for PANI-PVA it is -0.424 V vs SCE and it decreases to -0.506 V after 200 s. The results indicated that PANI-PVA is able to maintain more noble potential. Thus, this coating material is able to passivate the steel. This shift in OCP is due to the passivation of iron by PANI-PVA coating [28].

**Fig. 7: OCP study of bare and coated steels in 3 % NaCl solution.**

EIS studies of PANI-PVA coated steel in 3 % NaCl

EIS was also carried out to check the protective nature of the coatings. Impedance plots (Bode plots, impedance versus frequency) of the bare steel and PANI-PVA coated steel are given in Fig. 8. The PANI-PVA coated steel show a better resistance value $4.57 \Omega/\text{cm}^2$ compared with bare steel. This is due to the resistance offered by PANI-PVA coating to the penetration of ions. Thus, PANI-PVA reduces the corrosion rate of steel [28]. These results are consistent with Tafel polarization and OCP Studies.

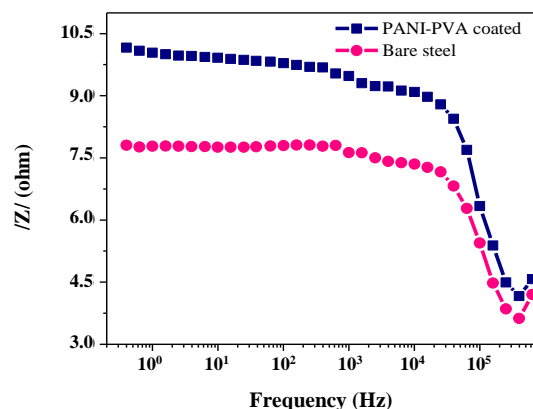


Fig. 8: Bode plots of bare steel and PANI-PVA coated steel.

Nyquist plot of PANI-PVA coated mild steel and equivalent circuits are given in Fig. 9. To simulate the EIS data, equivalent circuits were applied in which R_s refers to the solution resistance. While R_{ct} to the charge transfer resistance and R_{coat} to the resistance of the coating. A Constant Phase Element (CPE) was also used to replace an ideal capacitor. $C = CPE^n$, so CPE is equivalent to a capacitor when $n = 1$ [39]. The value of n ranges from -1 to 1 . It is equivalent to an ideal inductor for $n = -1$. When $n = 0$, it is an ideal resistor and for $n = 0.5$, it shows the diffusion characteristic. From equivalent circuits fitted model value of R_s is $0.811 \Omega/cm^2$, R_{coat} is $8.12 \Omega/cm^2$, R_{ct} is $0.988 \Omega/cm^2$. While CPE is $106.9 \times 10^{-9} S \cdot s^{\hat{a}}$, n is 0.989 . The higher value of R_{coat} indicates better barrier properties of PANI-PVA [40]. Thus, PANI-PVA can be used as a corrosion inhibitor for mild steel.

CONCLUSIONS

The Composite of PVA with PANI can successfully be synthesized through the inverse emulsion polymerization method. The successful formation of the composite was confirmed through various characterization techniques such as FT-IR, XRD, and SEM images. The synthesized composite shows corrosion protection efficiency up to 84.39% in comparison with uncoated steel. The value of corrosion current (I_{corr}) is $2.56 \mu A/cm^2$, shifted to a lower value, and there is also a positive shift in corrosion potential (E_{corr}), -0.426 V, versus SCE, when compared with uncoated steel. Open circuit potential (OCP) studies and electrochemical impedance (EIS) also supported the results obtained from Tafel polarization studies. Due to characteristics such as solubility in most common organic solvents, good electroactivity, high thermal stability, and

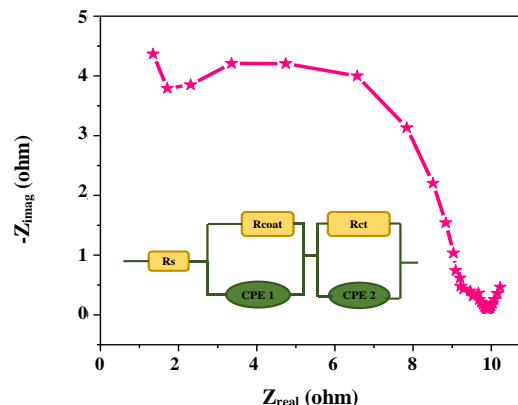


Fig. 9: Nyquist plot of PANI-PVA coated mild steel.

corrosion protection properties, PANI-PVA can be used as a protective layer to prevent corrosion.

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REFERENCES

- [1] Shi S., Zhao Y., Zhang Z., Yu, L., [Corrosion Protection of a Novel SiO₂@PANI Coating for Q235 Carbon Steel](#), *Prog. Org. Coat.*, **132**: 227-234 (2019)
- [2] He P., Wang J., Lu F., Ma Q., Wang Z., [Synergistic Effect of Polyaniline Grafted Basalt Plates for Enhanced Corrosion Protective Performance of Epoxy Coatings](#), *Prog. Org. Coat.*, **110**: 1-9 (2017).
- [3] Deshpande P.P., Jadhav N.G., Gelling V.J., Sazou D., [Conducting Polymers for Corrosion Protection: A Review](#), *J. Coat. Technol. Res.*, **11**: 473-494 (2014).
- [4] Boshkova N., Tabakova N., Atanassova G. Boshkov N., [Electrochemical Obtaining and Corrosion Behavior of Zinc-Polyaniline \(Zn-PANI\) Hybrid Coatings](#), *Coatings*, **9**: 487 (2019).
- [5] Valiollahi M.H., Abbasian, M., Pakzad, M., [Synthesis and Characterization of Polyaniline-Polystyrene-Chitosan/Zinc Oxide Hybrid Nanocomposite](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **38**:55-64 (2019).
- [6] Moshayedi H.R., Rabiee, M., Rabiee, N., [Graphene Oxide/Polyaniline-Based Multi Nano Sensor for Simultaneous Detection of Carbon Dioxide, Methane, Ethanol and Ammonia Gases](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **39**: 55-64 (2020)
- [7] Jafari Y., Ghoreishi S.M., Shabani-Nooshabadi M., [Electrosynthesis, Characterization and Corrosion Inhibition Study of DBSA-Doped Polyaniline Coating on 310 Stainless Steel](#), *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**: 23-32 (2017).

- [8] Vera R., Verdugo P., Orellana M., Muñoz E., Corrosion of Aluminium in Copper–Aluminium Couples under a Marine Environment: Influence of Polyaniline Deposited onto Copper, *Corros. Sci.*, **52**: 3803-3810 (2010).
- [9] Gul H., Shah A.U.A., Gul S., Arjomandi J., Bilal S., Study on the Thermal Decomposition Kinetics and Calculation of Activation Energy of Degradation of Poly (o-toluidine) Using Thermogravimetric Analysis, *Iran. J. Chem. Chem. Eng.*, **37**: 193-204 (2018)
- [10] Srikanth A.P., Raman V., Tamilselvi S., Nanjundan S., Rajendran N., Electropolymerization and Corrosion Protection of Polyaniline and its Copolymer on Carbon Steel, *Anti-Corros. Methods Mater.*, **55**: 3-9 (2008).
- [11] Chang C.H., Huang T.C., Peng C.W., Yeh T.C., Lu H.I., Hung W.I., Weng C.J., Yang T.I., Yeh J.M., Novel Anticorrosion Coatings Prepared from Polyaniline/Graphene Composites, *Carbon*, **50**: 5044-5051 (2012).
- [12] Akbarinezhad E., Ebrahimi M., Faridi H.R., Corrosion Inhibition of Steel in Sodium Chloride Solution by Undoped Polyaniline Epoxy Blend Coating, *Prog. Org. Coat.*, **64**: 361-364 (2009).
- [13] Chen F., Liu P., Conducting Polyaniline Nanoparticles and their Dispersion for Waterborne Corrosion Protection Coatings, *ACS Appl. Mater. Interfaces*, **3**: 2694-2702 (2011).
- [14] Yang X., Li B., Wang H., Hou B., Anticorrosion Performance of Polyaniline Nanostructures on Mild Steel, *Prog. Org. Coat.*, **69**: 267-271 (2010).
- [15] Bhadra S., Khastgir D., Singha N.K., Lee J.H., Progress in Preparation, Processing and Applications of Polyaniline, *Prog. Polym. Sci.*, **34**: 783-810 (2009).
- [16] Kuilla T., Bhadra S., Yao D., Kim N.H., Bose S., Lee J.H., Recent Advances in Graphene Based Polymer Composites, *Prog. Polym. Sci.* **35**: 1350-1375 (2010).
- [17] Mirmohseni A., Wallace G.G., Preparation and Characterization of Processable Electroactive Polyaniline–Polyvinyl Alcohol Composite, *Polymer*, **44**: 3523-3528 (2003).
- [18] Irimia-Vladu M., Fergus J.W., Suitability of Emeraldine Base Polyaniline-PVA Composite Film for Carbon Dioxide Sensing, *Synth. Met.*, **156**: 1401-1407 (2006).
- [19] Li Y., Ying B., Hong L., Yang M., Water-Soluble Polyaniline and its Composite with Poly (vinyl Alcohol) for Humidity Sensing, *Synth. Met.*, **160**: 455-461 (2010).
- [20] Patil D.S., Shaikh J.S., Dalavi D.S., Kalagi S.S., Patil P.S., Chemical Synthesis of Highly Stable PVA/PANI Films for Supercapacitor Application, *Mater. Chem. Phys.*, **128**: 449-455 (2011).
- [21] Shahi M., Moghimi A., Naderizadeh B., Maddah B., Electrospun PVA–PANI and PVA–PANI–composite Nanofibers, *SCI IRAN*, **18**: 1327-1331 (2011).
- [22] Adhikari S., Banerji P., Polyaniline Composite by in Situ Polymerization on a Swollen PVA Gel, *Synth. Met.*, **159**: 2519-2524 (2009).
- [23] Hermas A.A., Salam M.A., Al-Juaid S.S., Qusti A.H., Abdelaal M.Y., Electrosynthesis and Protection Role of Polyaniline–Polyvinylalcohol Composite on Stainless Steel, *Prog. Org. Coat.*, **77**: 403-411 (2014).
- [24] Mihai I., Addiego F., Ruch D., Ball V., Composite and Free Standing PANI-PVA Membranes as Flexible and Stable Optical pH Sensors, *Sens. Actuators, B*, **192**: 769-775 (2014).
- [25] Shreepathi S., Holze R., Spectroelectrochemical Investigations of Soluble Polyaniline Synthesized Via New Inverse Emulsion Pathway, *Chem. Mater.*, **17**: 4078-4085 (2005).
- [26] Sun M., Sheng G.P., Mu Z.X., Liu X.W., Chen Y.Z., Wang H.L., Yu H.Q., Manipulating the Hydrogen Production From Acetate in a Microbial Electrolysis Cell–Microbial Fuel Cell-Coupled System, *J. Power Sources*, **191**: 338-343 (2009).
- [27] Gangopadhyay R., De A., Ghosh G., Polyaniline–Poly(Vinyl Alcohol) Conducting Composite: Material with Easy Processability and Novel Application Potential, *Synth. Met.*, **123**: 21-31 (2001).
- [28] Chen F., Liu, P., Conducting Polyaniline Nanoparticles and their Dispersion for Waterborne Corrosion Protection Coatings, *ACS Appl. Mater. Interfaces*, **3**: 2694-2702 (2011).
- [29] Naidu B.V., Sairam M., Raju K.V., Aminabhavi T.M., Pervaporation Separation of Water+ Isopropanol Mixtures Using Novel Nanocomposite Membranes of Poly (vinyl alcohol) and Polyaniline, *Journal of Membrane Science*, **260**: 142-155 (2005).

- [30] Yu X., Fan H., Wang H., Zhao N., Zhang X., Xu J., Self-Assembly of Flower-Like Polyaniline–Polyvinyl Alcohol Multidimensional Architectures From 2D Petals, *Mater. Lett.*, **65**: 2812-2815 (2011).
- [31] Palaniappan S., John A. A., A Novel Polyaniline–Fluoroboric Acid–Dodecylhydrogensulfate Salt: Versatile Reusable Polymer Based Solid Acid Catalyst for Organic Transformations, *J. Mol. Catal. A Chem.*, **233**: 9-15 (2005).
- [32] Palaniappan S., Devi S.L., Thermal Stability and Structure of Electroactive Polyaniline–Fluoroboric Acid–Dodecylhydrogensulfate Salt, *Polym. Degrad. Stab.*, **91**: 2415-2422 (2006).
- [33] Sinha S., Bhadra S., Khastgir D., Effect of Dopant Type on the Properties of Polyaniline, *J. Appl. Polym. Sci.*, **112**: 3135-3140 (2009).
- [34] Bhadra S., Chattopadhyay S., Singha N.K., Khastgir D., Improvement of Conductivity of Electrochemically Synthesized Polyaniline, *J. Appl. Polym. Sci.*, **108**: 57-64 (2008).
- [35] Babazadeh M., Aqueous Dispersions of DBSA-doped Polyaniline: One-pot Preparation, Characterization, And Properties Study, *J. Appl. Polym. Sci.*, **113**: 3980-3984 (2009).
- [36] Bilal S., Gul H., Gul S., Shah A.H.A., One Pot Synthesis of Highly Thermally Stable Poly (2-Methylaniline) for Corrosion Protection of Stainless Steel, *Iran. J. Sci. Technol. A*, **42**: 1915-1922 (2018).
- [37] Mobin M., Tanveer N., Corrosion Performance of Chemically Synthesized poly(aniline-co-o-toluidine) Copolymer Coating on Mild Steel, *J. Coat. Technol. Res.*, **9**: 27-38 (2012).
- [38] Bilal S., Gul S., Holze, R., Shah A.H.A, An Impressive Emulsion Polymerization Route for the Synthesis of Highly Soluble and Conducting Polyaniline Salts, *Synth. Met.*, **206**: 131-144 (2015).
- [39] Gul H., Shah A.U.H.A., Krewer U., Bilal, S., Study on Direct Synthesis of Energy Efficient Multifunctional Polyaniline–Graphene Oxide Nanocomposite and Its Application in Aqueous Symmetric Supercapacitor Devices, *Nanomaterials*, **10**: 118 (2020).
- [40] Lei Y., Qiu Z., Liu J., Li D., Tan N., Liu T., Zhang Y., Chang X., Gu Y., Yin, Y., Effect of Conducting Polyaniline/Graphene Nanosheet Content on the Corrosion Behavior of Zinc-Rich Epoxy Primers in 3.5% NaCl Solution, *Polymers*, **11**: 850 (2019).