Polyaniline-ZnO composites for Smart Corrosion Resistance Coatings

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Abstract

Polyaniline-ZnO composites coatings were prepared by in situ polymerization which shows tremendous resistance to corrosion and is much more than pure Polyaniline in the harsh environment. The studies of corrosion were carried out in the plates of steel coated with these compositions having 10 wt% Polyaniline made by different concentration of ZnO i.e. 0, 0.1, 0.2, 0.3 & 0.5 wt %. The electrochemical impedance spectroscopy was used during hot saline water (65 ^{o} C) exposure at conditions at periodic interval for the complete duration of 90h. It was observed that the open circuit potential (OCP) shifts with time from -0.42 V SCE to more anodic side (-0.2 V) SCE which is much greater than the bare steel (-0.5 V SCE). The ZnO particles proved to be important in the corrosion prevention and towards anodic side OCP shifts. These data interprets the 100 times progress in the resistance corrosion especially for Polyaniline containing 4.46 wt% ZnO. The excellent improvement of the performance of these composites coatings has been resulted with the redox behavior of Polyaniline, the enhancement in the barrier properties and the easy charge transport because of p-n junction and also the large surface area accessible for the liberation of dopant because of ZnO additive. The composites were characterized by Fourier Transform infrared (FTIR) X-ray diffraction (XRD) and Corrosion Resistant studies and their comparison was made with pure Polyaniline which completely satisfies the literature.

Key Words: Polyaniline, Composite, Corrosion Resistance

1. Introduction

Polyaniline the conducting polymer has been used in many applications including electrostatic dispersive (ESD) coatings and blends, transparent conductor, electromagnetic interference shielding (EMI) protection, sensors, electro chromic displays, electrostatic discharges etc. [1]. This polymer has been effectively used in materials which act as corrosion inhibitors [2-7]. Polyaniline is phenylene based polymer. It has –NH group chemically flexible in a polymer chain flanked on both side by a ring of phenylene. It can be shown as monomeric aniline molecule 1, 4-coupling product. The presence of –NH group is responsible for the deprotonation, protonation and many other physio-chemical properties of the Polyaniline. It is one of the detailed studied and known conducting polymers. In various oxidation states a compound exist which conductivity strongly lean on inorganic or organic acids with protonation. The common green protonated emeraldine has semi-conductive level of the order 100 S/cm conductivity, many magnitude orders lower than typical metals ($>10^4$ S/cm) but more than common polymers($< 10^{-9}$).Whereas, PANI protonated e.g. Polyaniline hydrochloride when treated with ammonium hydroxide converts to non-conducting blue emeraldine base [8]. It has been noticed that where bare steel surface is exposed to harsh environment the coatings of Polyaniline can cause corrosion prevention [9, 10]. The addition of fillers in Polyaniline it exhibits the combining properties of both the materials and causes the development in the properties for multifunctional devices. There are many reports on the composites of Polyaniline with the different oxides of the metals among them are ZnO, NiO, Fe_3O_4, TiO_2, MnO_2 etc. [11-15]. The properties of corrosion protection can be enhanced if the appropriate filler is used. It is anticipated that

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composite materials which posses the additives in conducting polymers improves the self healing effect and anticorrosion behavior. In materials of inorganic oxides the ZnO is semiconducting material that posses the property of large exciton binding energy (60meV) and wide band gap i.e. 3.37eV at room temperature [16, 17]. That is why it has been widely used in photo detectors, solar cells, emitting diodes and other electronic devices [18-20].

In this study the main focus is on the comparative study for smart corrosion resistant composites behavior .Pure Polyaniline was synthesized chemically and its comparison was made with Polyaniline-ZnO composites at 0, 0.1, 0.2, 0.3 & 0.5 wt % to analyze which composite composition shows better corrosion resistance properties. So, for this purpose Fourier Transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) and Corrosion Resistant Analysis were made.

2. Experimental

2.1 Materials

Aniline (ANI) was obtained from Aldrich Chemical Co. Ltd. and was distilled to attain purified Aniline. Hydrochloric acid, Zinc oxide particles (ZnO), Potassium Di Chromate ($K_2Cr_2O_7$) and Methanol were obtained from MERCK and these chemicals are used without any pretreatment.

2.2 Synthesis of Pure Polyaniline & Polyaniline-ZnO Composites.

Polyaniline-ZnO composite was prepared by adding 0, 0.1, 0.2, 0.3 &0.5 wt % of ZnO particles in 5ml of distilled aniline monomer and then this mixture was charged into the reaction vessel containing 90ml 1N HCl solution. Mixture was stirred by using magnetic stirrer in ice bath for 2hr and uniform solution was obtained. After 2hr add drop wise the mixture of pre-cooled 100ml 1N HCl solution and 2.5g of $K_2Cr_2O_7$ into these mixtures. The

mixture was allowed to react in ice bath for 5hr. Polyaniline- ZnO composites was obtained and then this resultant product was first washed with distilled water and then with Methanol to remove any impurities and un-reacted materials. All of these samples were dried in oven for 12hr. Table 1 depicts the Pure Polyaniline and Polyaniline-ZnO composites with different compositions.

2.3 Synthesis of PANI-ZnO dispersion formulations for the coating.

2g of PVB was mixed with 20ml of methanol. Mixture was stirred for 8hr by magnetic stirrer. The Polyaniline-ZnO 10wt % powder which has different composition was grinded and slurry with small amount of methanol was made. This slurry was than mixed with the solution of PVB for 12 hr and stirred continuously. The resultant dispersion is uniform mixture of Polyaniline-ZnO in the PVB solution. The coupons of stainless steel having corners of round edges (50mmx 10mmx 1mm) were washed with 5 N HCl solution; stainless steel coupons were dried and then sand grid blasting was made on these plates. The substrate was immersed in PVB-Polyaniline-ZnO dispersion for 40 second and then dried at room temperature for about 1 hr. The thicknesses of the samples ranges between 15-17µm.These samples were then subjected for measurement of properties of corrosion inhibition. The final composition coatings are mentioned in Table 2.

3. Characterization

3.1 Fourier Transform Infrared Technique (FTIR)

An infrared spectrum is obtained by FTIR which determine the functional groups. These functional groups are detected by the wavelength of the light absorbed. The measurements of infrared absorption spectrum determine the chemical bonds. The differences in the structure in molecules made during synthesis are investigated by it. The Spectra of FTIR samples were scanned by using IR-Prestige-21 (Shimadzu), its frequency ranges from 600 to 4000 cm^{-1}. The analysis of the samples was done by mixing Potassium Bromide (KBr) fine powder with small quantity of samples in it. This sample powder was mixed first with KBr and then with the compressor it converts to pellet form.

3.2 X ray Diffraction Analysis (XRD)

The XRD wide range angle of the pure Polyaniline and Polyaniline-ZnO powders are shown in the Figure for the analysis by using X' PertPRO PANALYTICAL 40mA, 40kV between the Intensity (a.u) and Diffraction angle (2θ).

3.3 Corrosion Resistance

3.5% NaCl solution was used as an electrolyte for the impedance measurements, Tafel Plot and photovoltaic measurement. All the analysis were made by using electrochemical Analyzer. The SCE and Pt were used in this study as the reference and counter electrodes respectively. Three samples were analyzed for each composition to measure the results reproducibility. The data normalized for 1 cm^2 area, whereas for testing 2 cm^2 area was used. The Voltammograms were analyzed between +1 and-1 V (vs. SCE) at a scan rate of 60 mV/s, and for Tafel plots the scan rate was of 2 mV/s. After measuring the initial

readings all the coupons were dipped in the external bath for 4 hr. The bath contains hot 3.5% NaCl solution (65°C) and measures the accelerated testing. The coupons were dipped again in the electrochemical analyzer and the process was continued for 5days [21, 22].

Results & Discussion

3.1 Fourier Transform Infrared Technique (FTIR)

Figure shows that FTIR spectra of pure PANI, PANI-ZnO composites. The characteristic absorption peaks of pure PANI at 798.53 cm^{-1}, 1116.78cm^{-1},1384.89cm^{-1},1616.35cm^{-1}, 2369.3cm^{-1} and 3435.22cm^{-1} corresponds to the C=N imino quinone, C=C stretching mode of the benzenoid rings, the stretching mode of C-N, the stretching mode of N=Q=N where Q represents the quinoid ring and C-H bonding mode of aromatic rings [23-26]. The PANI-ZnO composite also shows the same characteristic peaks. However, the corresponding peaks of pure PANI at 798.53 cm^{-1} shifted to 794.67 cm^{-1},798.53 cm^{-1},808.17 cm^{-1} and 1116.78 cm^{-1}, 1384.89 cm^{-1} remains the same , 1616.35 cm^{-1} shifted to 1622.13 cm^{-1},1620.21 cm^{-1},1602.85 $cm^{-1}$and 1616.28 cm^{-1} whereas, 2341.58 cm^{-1}shifted to 2351.23 cm^{-1},2341.58 cm^{-1},2339.58 cm^{-1},2340.15 cm^{-1} and 3435.22 cm^{-1} shifted to 3437.15 cm^{-1},3433.29 cm^{-1},3437.15 cm^{-1} and 3429.43 cm^{-1} wave numbers in PANI-ZnO composites (0.1,0.2,0.3,0.5 wt % of ZnO). The shift may be ascribed to the formation of hydrogen bonding between ZnO and the NH group of PANI on the surface of the ZnO particles. Such kind of interaction in PANI and ZnO particles were also observed in the literature [26].

3.2 X ray Diffraction Analysis (XRD)

The analysis of XRD composite was made over the substrate of glass. The ZnO characteristic peaks are at 31.69, 33.5, 35.3, 47.81, 56.1, 61.2 and 65. Which corresponds to miller indices (100) (002) (101) (102) (110) (103) and (201) respectively. The average size of crystallite was calculated with Scherer formula with the help of determining the full width at half maxima of 101 peaks. At 27nm the average size was observed.

In Figure 2 the XRD characteristics of Polyaniline observed at $2\theta=19$ a broad peak. The ZnO powder in Figure 3 and the composite of Polyaniline-ZnO in Figure 4 shows the peak for ZnO crystalline wurtzite structure which gives that structure crystal of ZnO is not adapted because of the Polyaniline presence. All the peaks of Polyaniline-ZnO composites shift to slight higher values of 2θ.

The lattice parameter for ZnO at a=b=3.2269A was observed from peaks of XRD and Polyaniline-ZnO composite the peak were at a=b=3.2442A, c=5.2061 A. The lattice parameter change depicts that along horizontal plane the ZnO unit cell stretches and along c-axis the vertical direction suppresses. The vertical axis unit cell surface area is more as compared to the top & bottom combined surface area, it is the expected that more the molecular chains of Polyaniline get connected on the unit cell vertical surfaces then on the surfaces of top & bottom. The strong interaction because of ZnO particles attachment with molecular chains of Polyaniline as unit cell stretching in a-b plane & along c-axis plan suppression.

ZnO contains the structure i.e. hexagonal closed packed wurtzite crystal contains Zn and O atoms alternating planes. There is a parallel plane between (002) plane and the planes

which contains atoms of O and Zn. whereas at (100) the plane is at a 90 degree angle to (002) plane, intersecting alternating layers of Zn & O atoms. The size of crystallite in (002) and (100) planes can basically be measured as matrices of diameter (D) and length (L) respectively.

By the crystallite sizes ratio in (100) and (002) planes can estimate the crystal aspect ratio. The Scherer formula was used to calculate the ZnO and Polyaniline - ZnO composite crystallite sizes for the two peaks (100) and (002). For the ZnO in 100 plane the crystallite sizes decreases by 4.28% and with the addition 4.46 wt % of ZnO in the matrix of Polyaniline , however ZnO in (002) plane crystallite size increases by 14.6% in the composite of Polyaniline-ZnO. The crystal aspect ratio decreases by 16% for Polyaniline-ZnO composite when compared with the pure ZnO powder.

The results show the interaction between ZnO particles & molecular chains of Polyaniline because of the adsorption on the surface ZnO particles of Polyaniline molecular chains.

3.3 Corrosion Resistant

Figure 7 shows the Tafel plot of PVB coatings that contains 10wt % of different ratios of pure PANI and PANI-ZnO composites. The plots from the open circuit potentials (OCP) were obtained after different time intervals of the exposure to saline hot environment are shown in figure 4. The starting values of OCP of PVB is obtained on this side which is more cathodic and more positive (-0.42V SCE) as compared to bare steel (-0.6VSCE) [27] but after extended contact to environment which is more corrosive, the shift of OCP to more cathodic side. The coating which contains pure PANI shows the effect of self healing, however a little decrease in the OCP initially occurs and it shifts to the side after a while which is more anodic point.

This approach of shifting the OCP to potentials is more innovative than the original steel which rises with the rise in ZnO content in coatings of PANI-ZnO Composites. For the PANI-ZnO 4.46 % composite the OCP remains on the side which is more anodic than that of the other values even after 40hr of immersion in saline hot atmosphere. High value of OCP as compared to the bare substrate as well as plain PVB coated steel mentioned clearly shows the high resistance to corrosion by these composite coatings. It must also be observed that breath of the Tafel curve in PANI-ZnO 4.46% is more than that of the other composites. Such type of behavior of width in the Tafel plot shows that there is much more protection given against corrosion as it was shown by [22]

The Bode plot shows that PANI-ZnO 4.46% observes the more resistance than that of their coatings specifically at less frequency which is due to the ionic transportation in the composite. The increased values of frequency phase angle shows that the coatings have ZnO particles whereas, the coating of pure PANI shows the degradation sign. The value of low impedance frequencies were derived from the Bode Plot continuously remains enhanced for PANI-ZnO composite even after interaction with the corrosive atmosphere. This shows the obvious indication of the excellent protection from the corrosion. The figure 6 also indicates that in start the value of impedance decreases and then afterwards it comes back to high level, which depicts that there is a process of self healing in these composite coatings. Furthermore, this property of self protection tendency enhanced with the addition of ZnO particles.

In this study the accelerated conditions of testing are used which provides the equivalence to approximately 800hr at the ambient temperature which is obtained with the help of stated logarithmic relations of rate of corrosion of steel with the temperature and it gives nearly 10

x as constant of acceleration [28, 29]. Hence, the result shows that tremendous protection of corrosion attained in these composite coatings specifically when PANI-ZnO 4.46% composite is used even at low level loading (10wt %) as an additive.

Other than the data of electrochemical analysis the visual appearance of the composite coatings verifies that enhanced quality of these coatings after the strong testing of corrosion.

The protection from corrosion by an inorganic material filled composite is transport by many factors; effects of barrier which stops moisture and oxygen to reach the metal substrate, passivation layer formation and the reaction with the ions which are corrosive in nature[30-32] . In this study the properties of the barrier get better because of the addition of inorganic filler ZnO. The inorganic oxides enhance the properties of barrier for polymers by a 10 or more factor for diffusion of gases/solvent [33]. In the Bode plots the data of low frequency has been related with the process of diffusion [34] and as above mentioned it shows inorganic oxides direct to such progress.   Whereas, there is an additional cause for advancement of resistance in corrosion specifically when the total additive concentration in all the cases was at the same (10 wt. %).

The behavior of PANI in the protection from corrosion is because of redox nature. It is anticipated that PANI incarcerate the ions which are liberated while the reaction of corrosion with steel in NaCl presence, oxygen and water doped and the dopant ions liberated ultimately shows a passivating layer even at the initial stage of the process of corrosion at substrate. So, it operates as self healing composite coating with developed resistance of corrosion. Also the ions release by PANI was accelerated if the ZnO thin layer support is available and in the form of solid particles and its prevention of corrosion

becomes more effective. There are also chances that charge trap in composite of PANI-ZnO due to the reason that ZnO is n-type having the 3.13 eV band gap whereas, PANI is p-type having 2.1eV band gap [35] which increase the formation to potential barrier at the interface which across the layer stops the ease of charge transport. It is necessary in any electrochemical process that the transport of charge is done by metal across the composite for completion of circuit with the help of virtual electrodes.

The potential barriers which are internal may decrease the total passage of current, in this study I $_{corr}$ the current of corrosion will reduce because of the internal barriers.

The I_{corr} = Bare Steel is in the part of few microamperes [36]. On the other side this lessen by a factor of 100 i.e. I_{corr} of the order of 10 nano-amperes using present composite coatings. By using the equation I $_{corr}$ values and C_R corrosion rate was derived as, [22, 36]
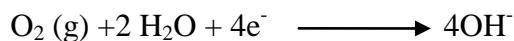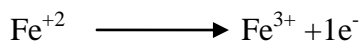
$$C_R = 0.129\, I_{corr}\, \frac{EW}{Ad}$$

Where, A is the Area, d is the Density and EW is the Equivalent weight.

In saline hot conditions, it is shown in figure 8 that the rate of corrosion increases in the start but taper off above 10-20 hr. whereas, there is a second part which is above 30 hr where rate of corrosion observed to be increased effectively. Such type of behavior may be shown due to the resin matrix failure; Polyaniline caused self healing and drastic failure above severe corrosion testing conditions. It can be observed that such variations can be fully minimized in the composite coatings containing Polyaniline-ZnO 4.46% which shows stable behavior even in severe conditions as compared to other composite coatings.

The formation of rust and corrosion on steel contains many steps and oxidation, reduction

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equations [36].

$$Fe \longrightarrow Fe^{+2} + 2e^-$$

$$Fe^{+2} \longrightarrow Fe^{3+} + 1e^-$$

$$O_2 (g) + 2 H_2O + 4e^- \longrightarrow 4OH^-$$

$$2Fe^{+2} (aq) + O_2 + 2H2O \longrightarrow 2 FeOOH + 2H^+$$
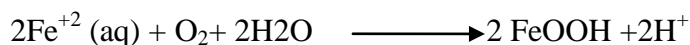
It is viewed a need for enough charge transport and oxidation ions for their dissolution of steel and formation of rust for creating corrosion. If any of the processes prevented the corrosion is stopped and coating proves to be effective for prevention of corrosion. In this study figure 9 shows the various levels of energy for the in contact materials. It is viewed that ZnO being n-type provide hole transport a hindrance across interface whereas the Polyaniline is p-type and gives a huge barrier for the transfer of electron. Because of the difference in energy gaps & valence bands the charge moves from Polyaniline to ZnO.

Hence, the above reactions shows that step 1 and 2 are prohibited by the existence of Polyaniline, while step 3 and 4 are hindered by ZnO. These can be attained in the form of low frequency impedance spectroscopy [37, 38]. It is necessary to state here that such results are in harmony with the previous data [39] on Polyaniline-ZnO where in the ZnO was used in high percentages i.e. greater than 68 % as anticipated from the proportions given in the paper, but also at low concentrations (less than 10%) the effectiveness of these additive when used. There were also reports in previous years about corrosion resistance enhancement of pure Polyaniline using composites of nano- clay [40, 41] and the main mechanism has been proposed as the oxygen diffusion barrier. Nevertheless, in those

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mentioned cases the E_{corr} ($\approx$ OCP) corrosion potential not shifted more to anodic region as in this case. The maximum reported case of E_{corr} range is of -0.52 to -0.4V (SCE) whereas, we attained -0.4V (SCE) which after first heat treatment increases. This type of large shift in OCP for Polyaniline-ZnO composites can be described on the internal potential barrier basis. The Technique of Kelvin Probe [42] indicates clearly the potential difference at different spots on pure Polyaniline integrated coatings. Therefore, it is considered that Polyaniline-ZnO would depict the similar differences.

Self healing is the most exciting findings in this study. The smart material Polyaniline can be assembled in such a way that on demand it can give inhibition of corrosion that at defects slows and stops [43]. In this study, Polyaniline-ZnO 4.46% reveals the fact that the composite coatings prevent corrosion. For the purpose of diffusion of chemicals which are external corrosive there is a physical barrier present because of these additives. Also the more area of surface present for dopant release because of Polyaniline-ZnO composite and finally because of hetero junction formation. Which cause potential barrier in transport of charge. All the above factors gives better results against corrosion then single component.

Conclusion.

The PANI-ZnO conducting Composites were prepared by the in situ polymerization method with PVB for coating. The addition of ZnO and the improvement in the composite has been brought out clearly. The novelty of these composite coatings falls in the generation of inhibiting corrosion by three mechanisms that operate concurrently, i.e. the redox behavior of PANI, enhancement in the barrier properties and the easy charge transport because of p-n junction when the coating is vulnerable to be damaged due to scribble or scratch. The additives can prevent catastrophic failure and can also provide healing effect even though if

the main resin destroyed. The coatings also provide gloss effect other than their use in prevention from corrosion; the shiny surface was obtained which is not easily obtained in conventional coating, prepared by commercial particle size additives. Such systems can be used for single coating or primer coat on steel where the color is not an issue.

References

[1] L. Alcacer, Conducting Polymers, Riedel, Dordrecht, Holland, 1987.

[2] A.J. Dominis, G.M. Spinks, G.G.Wallace, Prog. Org. Coat. 48 (2003) 43.

[3] P.J. Kinlen, J. Ding, D.C. Silverman, Corrosion 58 (2002) 490.

[4] N. Ahmad, A.G. MacDiarmid, Synth. Met. 78 (1996) 103.

[5] P.J. Kinlen, D.C. Silverman, C.R. Jeffreys, Synth. Met. 85 (1997) 1327.

[6] T. Schauer, A. Joos, L. Dulog, C.D. Eisenbach, Prog. Org. Coat. 33 (1998) 20.

[7] C.K. Tan, D.J. Blackwood, Corros. Sci. 45 (2003) 545.

[8] P. Zarras, J.D. Stenge-Smith, Y.Wei, Electroactive Polymers for Corrosion Control ACS Symposium Series 843,Washington, DC, 2003.

[9] G.G.Wallace, G.M. Spinks, L.A.P. Kane-Maguire, P.R. Teasdale, Conductive Electroactive Polymers: Intelligent Materials Systems, CRC Press, New York, 2003 (Chapter1).

[10] J. STEJSKAL Pure and Applied Chemistry 74 (2002) 857-867.

[11] A.G. Yavuz, A. Gök, Synth. Met. 157 (2007) 235.

[12] J. Zhang, H. Feng, W. Hao, T. Wang, Ceram. Int. 33 (2007) 785.

[13] J. Alam, U. Riaz, S. Ahmad, J. Magn. Magn. Mater. 314 (2007) 93.

[14] G. Song, J. Han, R. Guo, Synth. Met. 157 (2007) 170.

[15] A.H. Gemeay, R.G. El-Sharkawy, I.A. Mansour, A.B. Zaki, Appl. Catal., B 80 (2008) 106.

[16] Singla ML, Shafeeq M, Kumar M. Optical characterization of ZnO nanoparticles capped with various surfactants. J Lumin 2009;129:434–8.

16

[17] U. Ozgur, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, H. Morkoc, J. Appl. Phys. 98 (2005) 04130.

[18] N. Satio, H.Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K.Koumoto,Adv.Mater. 14 (2002) 418.

[19] M.H. Koch, P.Y. Timbrell, R.N. Lamb, Semicond. Sci. Technol. 10 (1995) 1523.

[20] S. Liang, H. Sheng, Y. Liu, Z. Hio, Y. Lu, H. Shen, J. Cryst. Growth 225 (2001) 110.

[21] R.C. Patil, S. Radhakrishnan, Prog. Org. Coat. 57 (2006) 332.

[22] R.G. Groseclose, C.M. Frey, F.L. Floyd, J. Coat. Technol. 56 (1984) 31

[23] Y. He, Appl. Surf. Sci. 249 (2005) 1.

[24] T.K. Sarma, A. Chattopadhyay, Langmuir 20 (2004) 4733.

[25] S.R.C. Vivekchand, K.C. Kam, G. Gundiah, A. Govindraj, A.K. Cheetham, C.N.R. Rao, J. Mater. Chem. 15 (2005) 4922.

[26] G.K. Paul, A. Bhaumik, A.S. Patra, S.K. Bera, Mater. Chem. Phys. 106 (2007) 360−363.

[27] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980.

[28] J.C. Li, M. Zhao, Q. Jiang, Mater. Corros. 53 (2002) 269.

[29] P. Bruke, A.I. Sphahani, B.S. Wright, Advances in CO2 Corrosion, vol. 2, NACE, Houston, TX, 1985, p. 1

[30] R.A. Dicky, F.L. Floyd, ACS Symposium Series 322, ACS, Washington, DC, 1986, p.1.

[3] A. Forsgren, P.A. Schweitzer, Corrosion Control Through Organic Coatings, CRC Press, Boca Raton, 2006.

[32] Z.W. Wicks, F.N. Jone, S.P. Pappas, Organic Coatings: Science and Technology, Wiley, New Jersey, 2007.

[33] Q. Sun, F.J. Schork, Y. Deng, Compos. Sci. Technol. 67 (2007) 1823

[34] B.R. Hinderliter, S.G. Croll, D.E. Tallman, Q. Su, G.P. Bierwagen, Electrochim. Acta 51 (2006) 4505.

[35] J.P. Farges, OrganicConductors: Fundamentals andapplications,Marcel Dekker, New York, 1994 (Chapter 15)

[36] W.S. Tait, An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists, Pair O Docs Publications, Racine, Wisconsin, 1994, p. 57

[37] P.L. Bonora, F. Deflorian, L. Fedrizzi, Electrochim. Acta 41 (1996) 1073.

[38] J.N. Murray, Prog. Org. Coat. 31 (1997) 375.

[39] S. Sathiyanarayanan, S.S. Azim, G. Venkatachari, Electrochim. Acta 52 (2007) 2068

[40] J.K. Yeh, S.J. Liou, C.Y. Lai, P.C. Wu, T.Y. Tsai, Chem. Mater. 13 (2001) 1131.

[41] J.M. Yeh, C.L. Chen, Y.C. Chen, C.Y. Ma, K.R. Lee, Y. Wei, S. Li, Polymer 43 (2002) 2729.

[42] B. Wessling, J. Posdorfer, Electrochim. Acta 44 (1999) 2139.

[43] M. Kendig, M. Hon, L. Warren, Prog. Org. Coat. 47 (2003) 183.
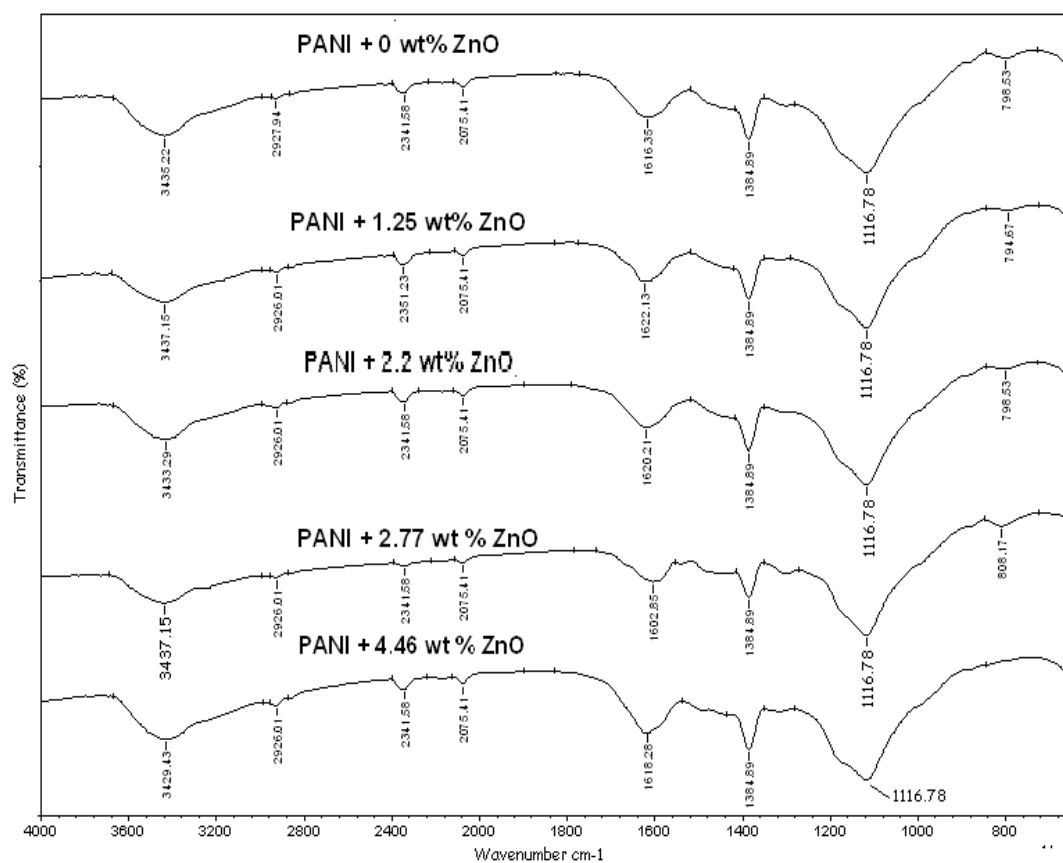
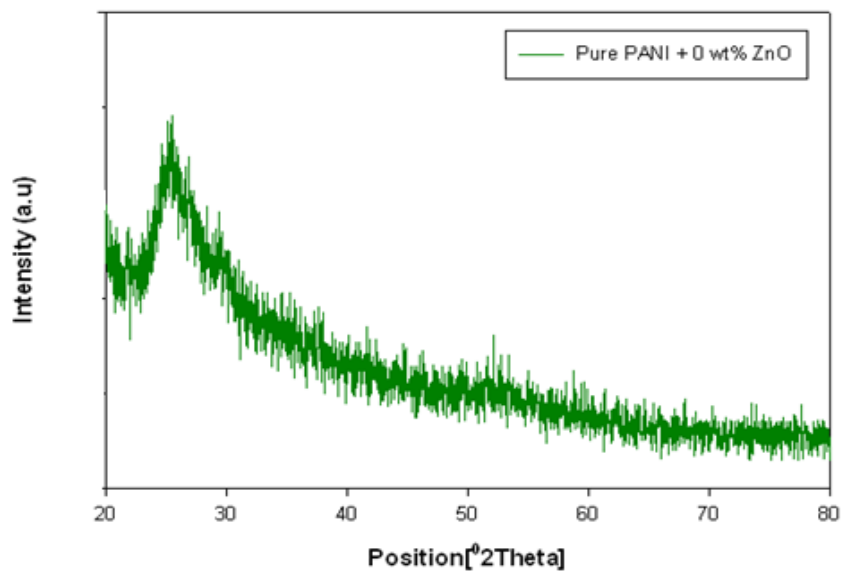**Figure1. FTIR Studies of Polyaniline & Polyaniline ZnO (10%) Composites**

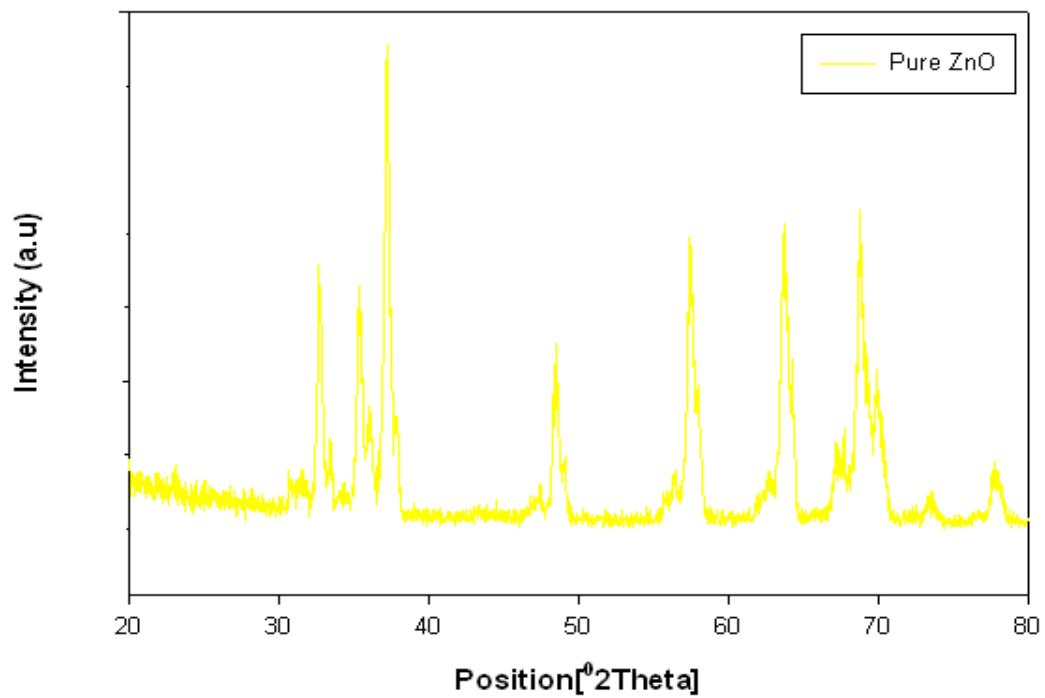**Figure 2. XRD Pattern of Polyaniline**
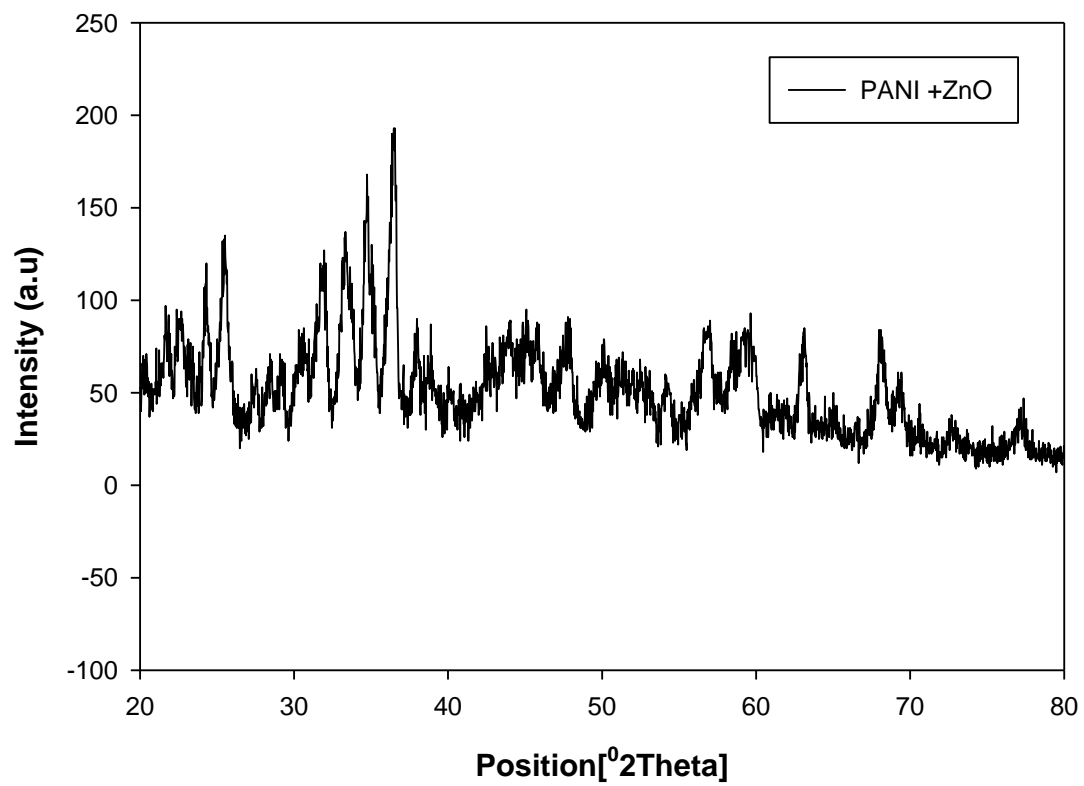

Figure 3 . XRD Pattern of ZnO

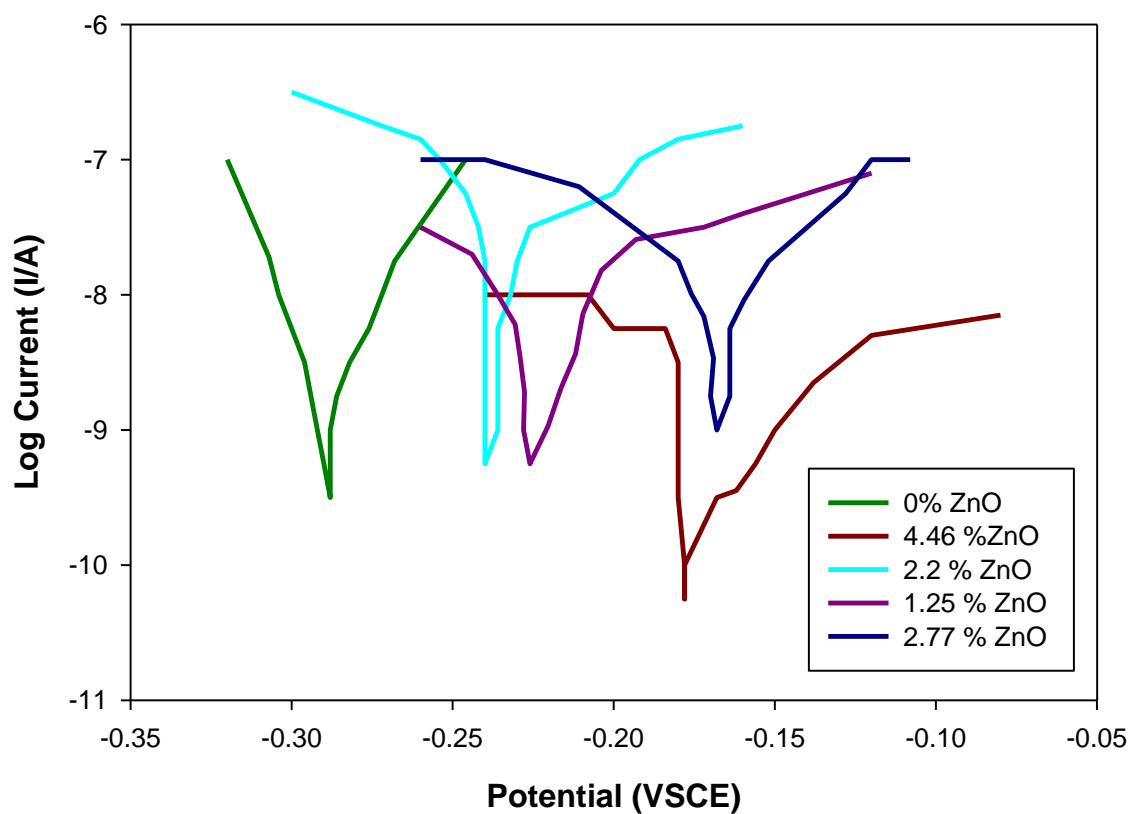**Figure 4. XRD Pattern of Polyaniline-ZnO (10 %) composite**

Figure 5. Tafel plots of PVB-Polyaniline-ZnO coatings recorded in NaCl 3.5 % solution. The different concentrations of ZnO are indicated with different colors.
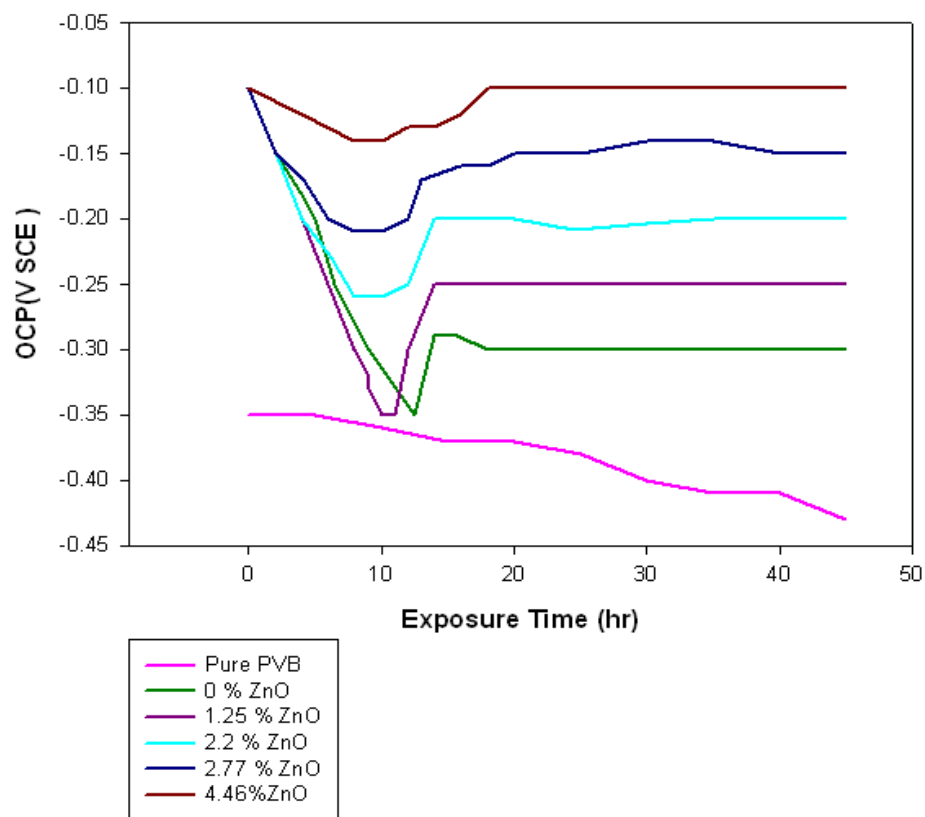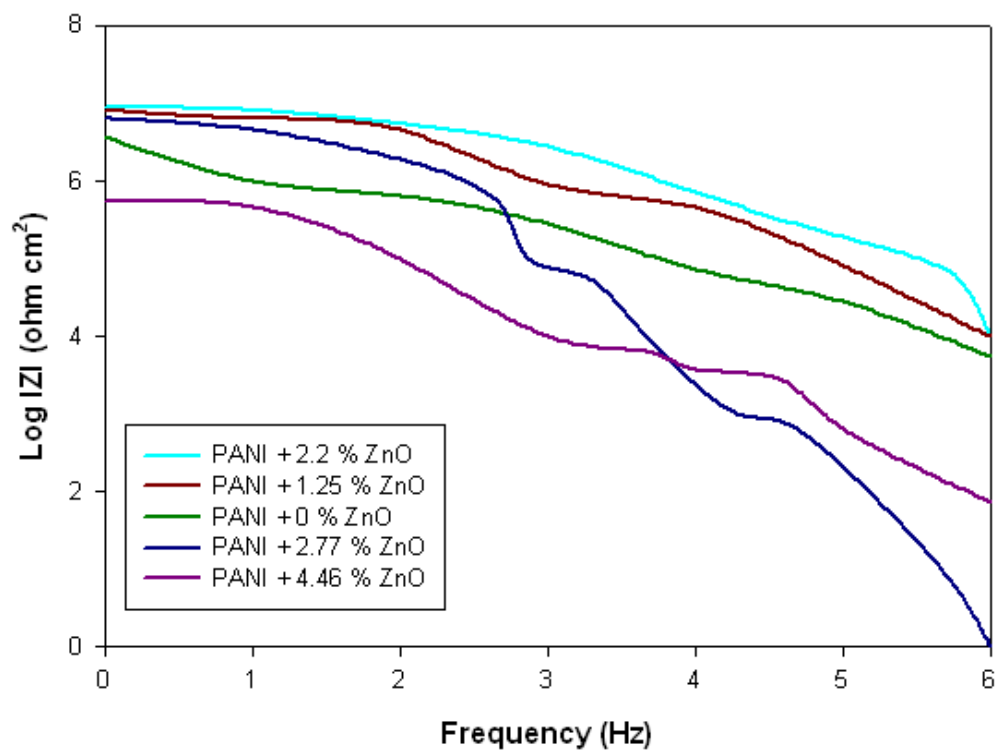
Figure 6. Corrosion resistance of the coatings indicated as shift in the OCP with time of exposure to hot saline conditions (a) PVB alone (b) PVB+ 10wt% of Polyaniline + 1.25 wt % ZnO (c) PVB+ 10wt% of Polyaniline + 2.2 wt % ZnO (d) PVB+ 10wt% of Polyaniline + 2.77 wt % ZnO (e) PVB+ 10wt% of Polyaniline + 4.46 wt % ZnO.

Figure 7. Bode plots for PVB+ Polyaniline + ZnO at room temperature in NaCl 3.5%. The curves for 0, 2.2, 1.25, 2.77 and 4.46 wt % ZnO shown with different colors.
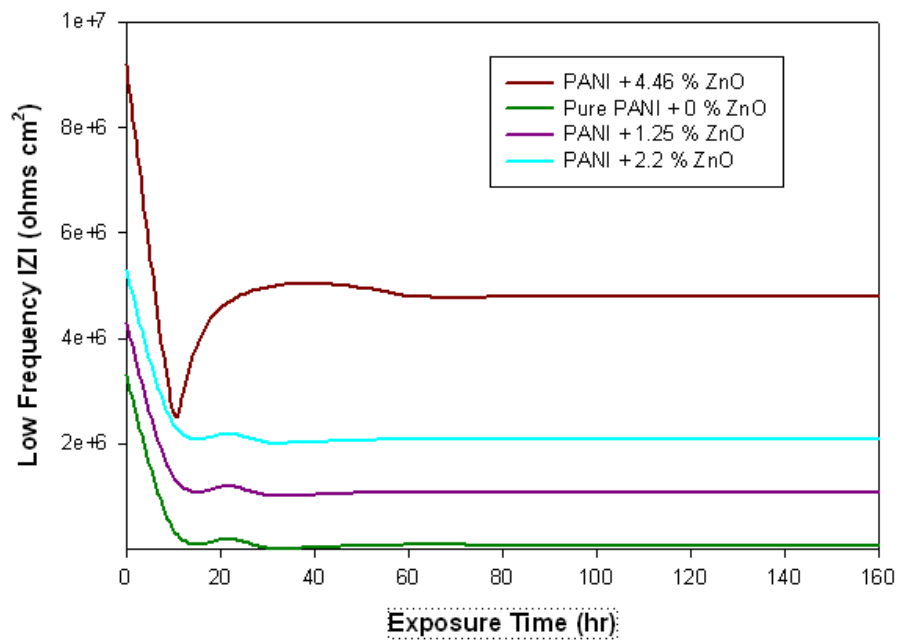
Figure 8. Low frequency impedance of PVB + Polyaniline + ZnO coatings after exposure to hot 65 ^{o} C saline conditions. Curves with different concentrations of ZnO 0, 1.25, 2.2 and 4.46 wt % are indicated with different colors.
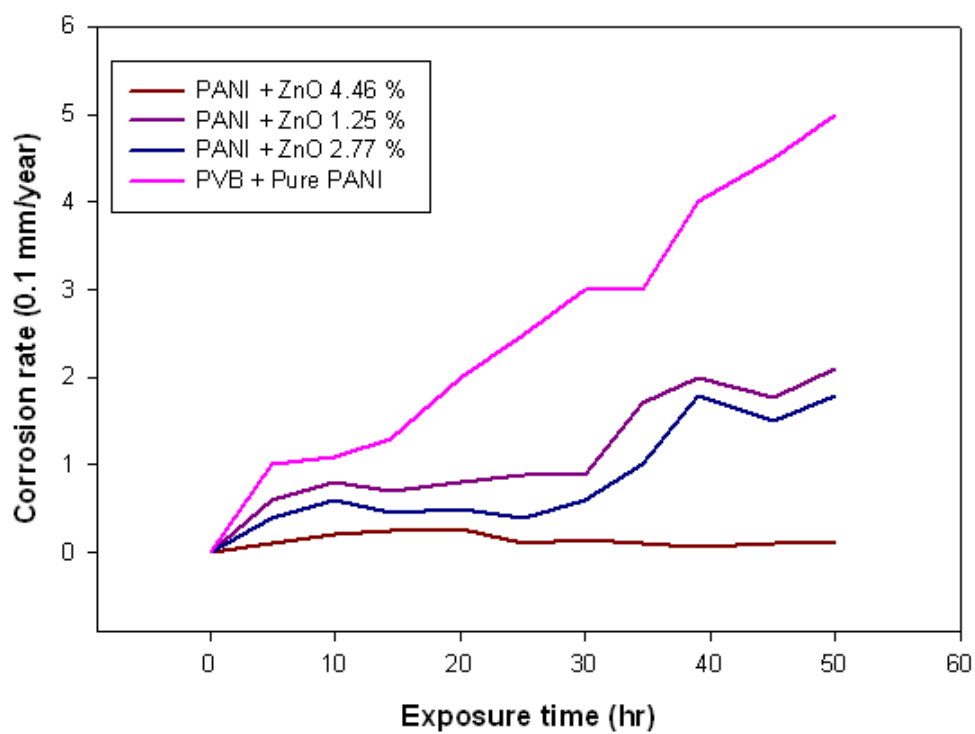
Figure9. Corrosion rate w.r.t. prolonged exposure of coatings to hot saline conditions.

Table 1: Synthesis of Polyaniline-ZnO composites with different composition

Samples	Aniline wt (g)	ZnO wt (g)	Composite yield (g)	ZnO % in Product
P1	1	0.0	0.61	0.0
P2	1	0.1	0.8	12.5
P3	1	0.2	0.88	22
P4	1	0.3	1.15	27.7
P5	1	0.5	1.23	44.6

Table 2: Composition of coatings made from 10wt% of above Polyaniline-ZnO

Samples	Polyaniline wt %	ZnO wt%	PVB
P1	0.11	0	100
P2	9.2	1.25	90
P3	8.5	2.2	90
P4	8.9	2.77	90
P5	7.5	4.46	90