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Effect of ZnO-PEDOT:PSS incorporation in epoxy based coating on corrosion behaviour in immersed condition

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Corrosion is a natural deterioration process that destructs metal surface. Metal of highly protected by passivation layer such as Stainless Steel 316L also undergoes pitting corrosion when continuously exposed to aggressive environment. To overcome this phenomenon, application of epoxy based coating with addition of zinc oxide- poly (3,4-ethylenedioxythiophene) doped with poly (styrene sulphonate) hybrid nanocomposite additive was introduced as paint/metal surface coating. The compatibility between these two materials as additive was studied by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy/Energy-Dispersive X-ray spectroscopy (FE-SEM/EDX) and Transmission Electron Microscopy (TEM) analysis. The effect of nanocomposite wt.% in epoxy based coating with immersion duration in real environment on corrosion protection performance was analyzed through potentiodynamic polarization analysis. The main finding showed that addition of hybrid nanocomposite had increased corrosion protection yet enhanced corrosion process when excess additives was loaded into epoxy coating. Addition of 2 wt.% ZnO-PEDOT:PSS was found significantly provided optimum corrosion protection to stainless steel 316L as the corrosion rate for 0 day, 15 days and 30 days of immersion duration is 0.0022 mm/yr, 0.0004 mm/yr and 0.0015 mm/yr; respectively.

Keywords: Organic-inorganic additives, Stainless steel 316L, p-n junction, Immersion test, Potentiodynamic polarization

I. INTRODUCTION

Corrosion is a natural electrochemical process that degrades metal surfaces when exposed to aggressive environment [1]-[2]. Severity of and

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its rates strongly related to factors such as pH, oxygen concentration, relative humidity, temperature and types of electrolyte [3]. In marine environment, continuous contact of highly aerated sea water and the erosive effects of spray, waves and tidal action makes metal expose to this zone has a very high corrosion rate. Thus, protecting metal that can withstand in such environment is important for long-term uses and to avoid any accidents due to corrode structure.

Stainless steel 316L is one of the most satisfactory alloys for marine application as it has minimum cost of material, good mechanical properties at elevated temperature, ease of fabrication and able to withstand corrosion at high water velocities [4]-[5]. Stainless steel provides excellent corrosion protection due its existing passive film containing chromium hydroxide, Cr_2O_3. However, the occurrence of localized corrosion such as pitting and crevice corrosion is formed when the protective oxide layer of the metal breakdown. Although this type of corrosion rate is very low, this type of stainless steel is no longer recommended for permanent contact with seawater [6]. In order to control this destructive process, corrosion control method such as coating application had being introduced. Instead of conversion coating which depends on chromium, Cr element, an eco-friendly approach is investigated by introducing organic material which are polymers into ZnO to protect the metals against corrosion.

Epoxy resin is widely being used for harsh environment application due to its strong mechanical properties, excellent insulating and chemical resistance as well as able to provide gloss and transparency of the coating. Addition of additives into epoxy based coating able to enhance desired properties of the coating. Additives comprise of electro active polymers are widely being explored due to its compromising protection against metal. Armelin *et al.* studied the potential of polyaniline (PANI), polypyrrole (PPy) and poly (3, 4-ethylenedioxythiophene)(PEDOT) as additives in epoxy paint to prevent corrosion [7]. In this work, it is reported that the PANI and PEDOT doped with polystyrene sulphonate (PSS) showed better anti-corrosive against metal [7]. Poly (3, 4-ethylenedioxythiophene), PEDOT one of the polythiophene derivatives have interesting properties to protect metals against corrosion. PEDOT is commonly an intrinsic conducting polymer and the presence of PSS ensures the dispersion and stability of PEDOT in the solvents [8]. Owing to PEDOT:PSS conjugated structure of a positively charged PEDOT and the saturated negatively charged PSS, this polymer electrolyte is able to exhibit high conductivity and stability in the oxidized state [8]. Increasing concentration of PEDOT:PSS has decreased the mechanical properties, increase the curing time and difficult to dissolve in epoxy paint. To control the arising problems, nanoparticles addition is introduced. According to previous works, nanoparticles addition was reported to assist the dispersion of conducting polymer in matrix, improves the mechanical properties and improves the corrosion protection [9]-[11]. Among nanoparticles, metal oxides such as ZnO, SiO_2 and TiO_2 exhibit some interesting properties in corrosion performance. Zinc oxide is physically and chemically stable, easier to be synthesized and fabricated in thin film form, able to protect against UV and bacteria, and has high oxidation and electron mobility. Besides, ZnO is n-type semiconductor that has a wide band gap and large excitation binding energy [12]-[13].

In this work, we report the preparation of epoxy based coating containing ZnO-PEDOT:PSS hybrid nanocomposite as additives and its corrosion protection ability to protect stainless steel 316L against corrosion as a function of immersion duration. The developed nanocomposite had been characterized by FTIR, XRD, FESEM/EDX and TEM analysis whereas the anti-corrosive performance was evaluated by potentiodynamic polarization analysis.

II. MATERIALS AND METHODS

A. Materials

The epoxy resin (Bisphenol A and butyl glycidyl ether) and its hardener (diethylentriamine) used in this research were obtained from PACE Technologies. It should be emphasized that the epoxy resin does not have any anti-corrosive pigments or additives. The weight ratio of epoxy resin to its hardener was 10:1. The additives, ZnO nanoparticles with mean diameter of $< 50nm$ and poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate), PEDOT:PSS (low conductivity grade with 2.8 wt.% dispersion in H_2O) were supplied from Sigma-Aldrich Corporation. The stainless steel 316L sheet was purchased from CG Tradeware (chemical composition: C0.03%, Mn2.00%, P0.045%, S0.03%, Si0.75%, Cr 16.00-18.00%, Mo 2.00-3.00%, Ni 10.00-14.00% and balances is Fe) and acetone was supplied from Merck. In this study, natural seawater with salinity of 35 ppt is used as electrolyte.

B. Methods

Coating Preparation

The additives of the coating, was prepared by mixing ZnO and PEDOT:PSS at ratio of 3:1 to increase the reaction surface contact before being dispersed into epoxy resin. This process was carried out for an hour at 200 rpm using magnetic stirrer. Then, ZnO-PEDOT:PSS hybrid nanocomposite was dispersed into epoxy resin matrix. This mixture was mixed at 1000 rpm for 2 hours. In order to improve the uniform dispersion hybrid nanocomposite and also to reduce trapped air in the matrix, the mixture was sonicated for 5 minutes. After sonication process, diethylentriamide was added to cross-link the epoxy component in the mixture.

Substrate Preparation

Stainless steel sheet was cut into 25 x 25 x 1.5 mm coupons. According to standard procedure which applied by using American Standard Testing Method (ASTM) G31-2004, the substrates were cleaned with 600-grit silicon carbide, SiC paper to remove native oxide layer by using polisher machine. Then, the substrates were rinsed with deionized water followed by acetone, air dried, and were used without any further storage. Then, dry substrates were coated with prepared coating using brush coating method and were dried in the oven at 60°C for 24 hours to speed up the drying process.

Nanocomposite and Coating Characterization

Combination of ZnO and PEDOT:PSS was analyzed by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR, Model: Thermo-Nicolet 380) with spectral resolution range from 400 to 4000 cm^{-1} in transmittance mode. Nanocomposite and formulated coating was also analyzed by X-ray Diffraction (XRD) to verify the compatibility between additives as nanocomposite and to detect any coating phase change when ZnO was added into epoxy based coating. XRD (Model: Rigaku-Miniflex II) with monochromatic Cu Kα radiation of λ=1.5406 Å was used for this analysis. The scan angle, 2Θ used was from 10° to 80° at scan rate of 2° min^{-1}. The surface morphology were observed using Field Emission Scanning Electron Microscopy (FESEM, Model: JEOL JSM-7600F) equipped with Energy-Dispersive X-ray spectroscopy (EDX) operated at 5 kV. Besides, Transmission Electron Misccroscopy (TEM, Model: Zeiss Libra 120 Plus) was used to study the interaction structure formed between ZnO and PEDOT:PSS as hybrid nanocomposite.

Electrochemical Characterization of Coatings

Samples coated with different loading wt.% of hybrid nanocomposite were immersed in real environment (Location: 5°32′17.7″N, 102°56′44.9″E), and were analysed after 15 days and 30 days of immersion duration. Electrochemical measurement for all samples were done using potentiostat/ galvanostat PGSTAT302N Metrohm Autolab B.V. equipped with Nova Software 1.10 was used connecting three-electrodes, the working electrode consisted of coated substrate, with an exposed area of 1.0 cm^2, the counter electrode and the reference electrode is glassy carbon and Silver/Silver Chloride (Ag/AgCl); respectively. By using potentiodynamic polarization analysis, all samples were measured using direct current (DC) optimize current of 1 mA. The potential range [-0.6, 0.3] was applied with the scan rate of 0.01 mV/s. The parameters that had been considered in this analysis are corrosion current density (i_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR).

III. RESULTS AND DISCUSSIONS

A. Nanocomposite and Coating Characterization

Fourier Transform Infrared Spectroscopy

Figure 1 shows Fourier Transform Infrared (FTIR) spectrum of electoactive polymer, PEDOT:PSS and ZnO. From the FTIR spectrum, two peaks of ZnO were identified at 432 cm^{-1} and 675 cm^{-1} which is due to Zn-O vibrational band and stretching vibrational band, respectively. These peaks are also reported by [14]-[15]. The spectrum for pure PEDOT:PSS was observed at 1122 cm^{-1} and can be attributed to stretching vibration of C-O-C bond from PEDOT structure [16]. The sulphonic acid group from PSS show peaks at 1002, 1031 and 1166 cm^{-1} stretching vibrations of SO_3- from PSS structure [17]-[18]. Apart from that, the presence of peaks at 1639 cm^{-1} and 3369 cm^{-1} are resulting from O-H bending vibrations and stretching vibration of H_2O from PSS structure in PEDOT:PSS [17]. Combination of these materials show shifting of ZnO peaks from 432 cm^{-1} to 414 cm^{-1} and from 675 cm^{-1} to 648 cm^{-1}.The -OH peak appearance at 3367 cm^{-1} and 1627 cm^{-1} in composite attributed to strong electronegative oxygen atom of -OH on ZnO surface which may form hydrogen bond with the sulphur cation, S^+ on thiophene ring of PEDOT thus weakening electrostatic interaction between PEDOT and PSS [19]. According to the patterns, transmittance intensity of 1002, 1031 and 1166 cm^{-1} peaks also reduces due to decrease stretch vibrations of SO_3- from PSS structure. These results indicate strong chemical interaction between ZnO and PEDOT:PSS in formation of hybrid nanocomposite.

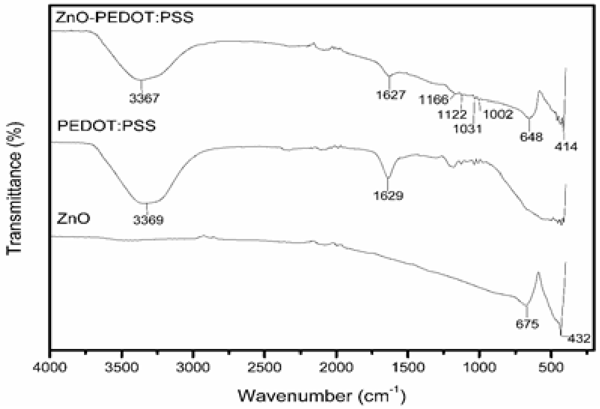

Figure 1. FTIR spectrum of ZnO, PEDOT:PSS and ZnO-PEDOT:PSS

X-ray Diffraction

X-ray Diffraction (XRD) analysis was carried out to confirm the interaction by changes in intensity or phase state of nanocomposite and coating. ZnO is the only crystalline material that had been added into coating formulation. The purpose of ZnO addition is to improve the mechanical properties of the coating as well as to enhance the corrosion protection. However, any changes on coating phase will affect the corrosion performance of the developed coating. Therefore, XRD analysis was crucial to ensure the coating barrier protection properties were retained. The XRD pattern of ZnO is shown in Figure 2. The diffraction patterns show hexagonal structure of ZnO matched with PDF no. 89-1397. Combination of PEDOT:PSS and ZnO reduces the intensity of ZnO detection hence confirms the formation of organic-inorganic nanocomposite. As nanocomposite was added into epoxy, only amorphous peak at $2\Theta=19^\circ$ is detected, No diffraction pattern of ZnO and the presence single amorphous peak were observed due to abundance of epoxy contents. The amorphous peak also shows insignificant low content (less than 2 wt.%) of ZnO in the coating to alter the coating phase [20]-[21]. XRD analyzes verify formation organic-inorganic hybrid nancomposite and amorphous state of coating.

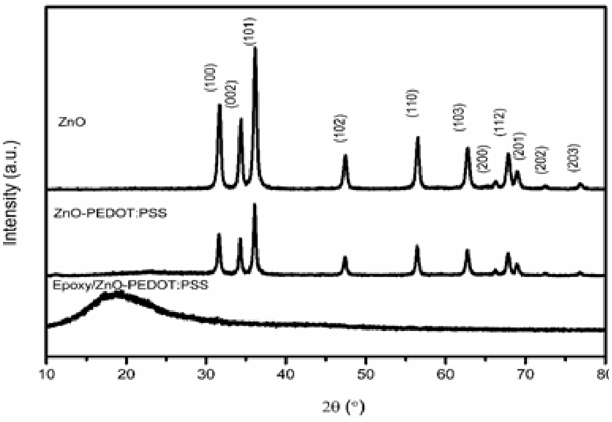

Figure 2. XRD patterns of ZnO, ZnO-PEDOT:PSS and epoxy/ZnO-PEDOT:PSS

Morphology of Nanocomposite

Morphology of nanocomposite was characterized by FESEM and TEM. Figure 3 ZnO nanoparticle tends to agglomerate due to strong van der Waals forces between each particle. This figure also depicts that the average size ZnO obtained is 21 nm. Addition of PEDOT:PSS with ZnO reveals a formation of dense globular cluster structure as shown in Figure 4 and Figure 5. An increase in average size of ZnO to 70 nm indicates that ZnO nanoparticles surfaces were covered with PEDOT:PSS. From Figure 6 and Figure 7, TEM images also showed that hexagonal ZnO and PEDOT:PSS exhibited different contrast where the darker part with an average size of <50 nm correspond to ZnO. Majority of ZnO is totally covered with PEDOT:PSS thus confirms the formation of core-shell structure between ZnO-PEDOT:PSS. Formation of this structure confirms the formation of p-n junction between ZnO and PEDOT:PSS as its parallel with FTIR and XRD analysis.

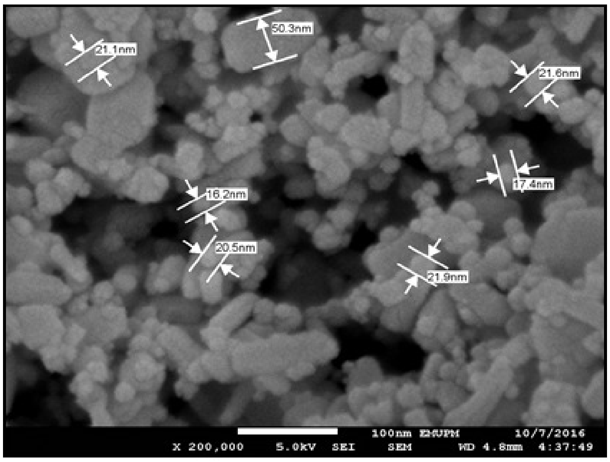

Figure 3. FESEM image of ZnO at x200k magnification

The elementary analysis of nanocomposite is presented in Figure 8 and Table 1. Table 1 shows the presence of elements, carbon and sulphur from PEDOT structure whereas oxygen el-

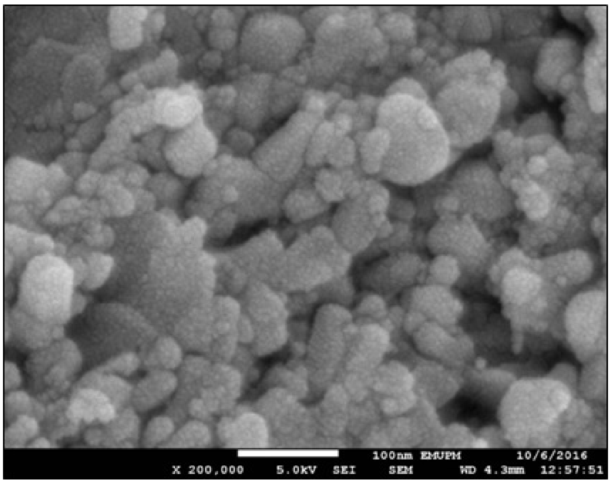

Figure 4. FESEM image of hybrid nanocomposite at x200k magnification

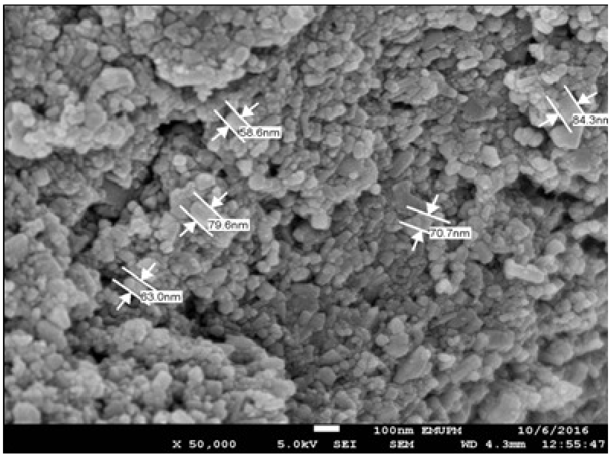

Figure 5. FESEM image of hybrid nanocomposite at x50k magnification

ement comes from both ZnO and PEDOT structure. High percentage of zinc element was detected due to agglomeration of ZnO structure in nanocomposite. The sulphur element detection is consistent from three spectrums indicates ZnO is uniformly coated with PEDOT. This shows ZnO was successfully loaded with PEDOT and in agreement with the FESEM and TEM analysis.

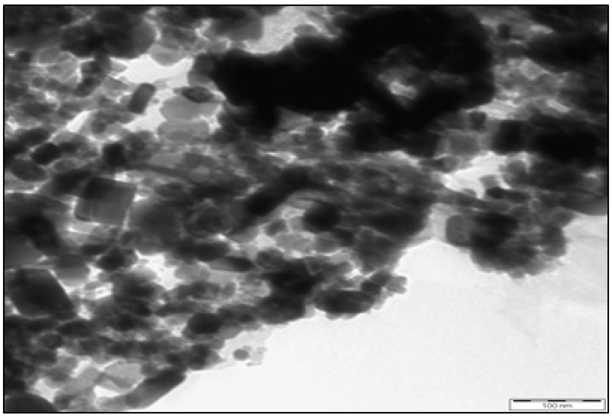

Figure 6. TEM image of hybrid nanocomposite at x63k magnification

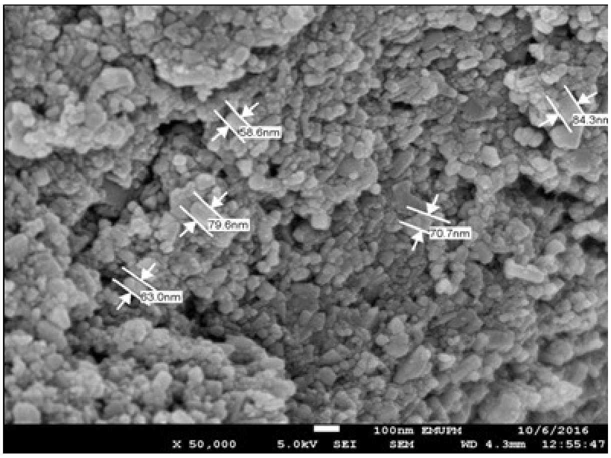

Figure 7. TEM image of hybrid nanocomposite at x200k magnification

B. Corrosion Protection Performance of ZnO-PEDOT:PSS Hybrid Nanocomposite

Potentiodynamic Polarization

Potentiodynamic polarization analysis was done to observe the basic rule of metal corrosion. By using DC polarization technique, generated Tafel curves able to provide a good comparison of coating protection properties using varies wt.% hybrid nanocomposite in epoxy matrix. In

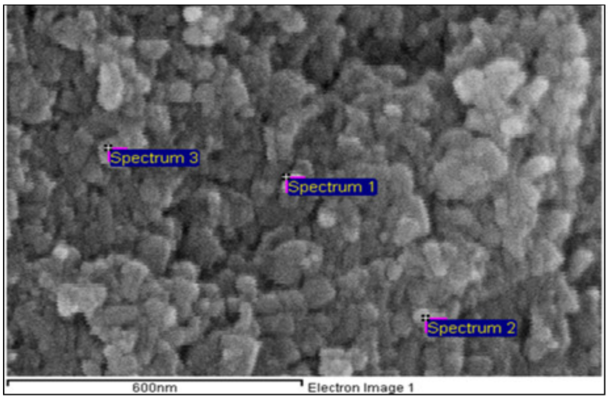

Figure 8. Elementary analysis of hybrid nanocomposite

Table 1. Elementary analysis of hybrid nanocomposite.

Spectrum	C	O	S	Zn	Total
1	18.18	26.02	0.71	55.09	100.00
2	17.41	25.36	0.80	56.43	100.00
3	18.16	24.70	0.85	56.29	100.00

this study, basic corrosion behaviour of 316L and protection ability of hybrid nanocomposite incorporation can be explained from Tafel curve. Basically, Tafel curve explained the anodic and cathodic process within the system either from corrosion of the stainless steel or/and the applied coating. Extrapolation of Tafel curve provides the i_{corr}, E_{corr} and corrosion rate (CR) values. The corresponding parameters from this analysis are as tabulated in Table 2. From Table 2, E_{corr} value of polished uncoated substrate was -0.3450 V which is in the active site of stainless steel 316L. Active state of substrate has high sensitivity towards corrosion rate so it is ideal to highlight the properties of the coating to protect against corrosion. The i_{corr} value of uncoated substrate is $2.77x10 - 5Acm^{-2}$ and the CR is 0.3221 mm/yr

From Figure 9, application of physical barrier coating enhanced the corrosion protection significantly. The presence of barrier coating reduces the i_{corr} value of coated substrates compared to uncoated substrate. The decrease in i_{corr} value is due to decrease of an active area of substrate covered by the coating thus inhibit both cathodic and anodic reaction [22]-[23]. Protective coating also protects substrate from direct exposure of chloride ion, Cl^{-} presence in seawater. Addition of 1 wt.% reduce i_{corr} value and shifts E_{corr} to more positive value showing improve corrosion protection provided by the coating. As the wt.% of nanocomposite increases, i_{corr} value continue to drop to the lowest value given i_{corr}, E_{corr} and CR values is 2.07 x 10^{-7} Acm^{-1} -0.2646 V and 0.0022 mm/yr; respectively. The presence of PEDOT:PSS with strong oxidative properties act as oxidant accepts electron release from anodic site then further oxidize the substrate creates a protective passive oxide layer at the interface of the metal/polymer hence provide anodic protection to substrate [24]-[25]. PEDOT:PSS helps to poise the substrate in the passive range in the absence of any redox reaction. Corrosion initiation will occur when PEDOT:PSS discharge resulting negative shifting value of corrosion potential. Furthermore, the dispersion of the hybrid nanocomposite throughout epoxy coating increased the tortuosity of corrosive elements to

Table 2. Parameters value from Tafel plot.

Days of immersion	Loading of hybrid nanocomposite wt (%)	Corrosion Potential E_{corr}(V)	Corrosion current density,i_{corr} (Acm^{-2})	Corrosion rate, *CR (mm/yr)*
-	Bare SS	-0.3450	2.77 E-5	0.3221
0 days (optimization)	1	-0.3340	9.10 E-6	0.0966
	2	-0.2646	2.07 E-7	0.0022
	3	-0.2754	3.29 E-7	0.0035
	4	-0.3084	5.16 E-7	0.0055
	5	-0.3379	2.97 E-6	0.0315
15 days	1	-0.1877	1.60 E-7	0.0017
	2	-0.1492	4.05 E-8	0.0004
	3	-0.2362	3.80 E-5	0.4038
	4	-0.3661	2.93 E-6	0.0312
	5	-0.2848	2.50 E-5	0.2655
30 days	1	-0.3385	9.75 E-6	0.1035
	2	0.0259	1.38 E-7	0.0015
	3	-0.1076	3.10 E-7	0.0033
	4	-0.2432	5.39 E-6	0.0070
	5	-0.2975	5.81 E-5	0.6170

penetrate the coating. The tortuous path increase reaction time for corrosive elements to reach anodic site of the substrate [26].

Incorporating of more than 2 wt.% ZnO-PEDOT:PSS shows an increment in i_{corr} value, shifting of E_{corr} value towards negative side and also increase *CR*. This can be related due to formation of perlocation network. A slight increase of conductive particle increases the pathway in the conducting network. However, further increase of conductive particles cause the conducting domain to increase without any significant increase in the pathway for electrons leading to monotomic increase in conductivity [27]. Excessive additive in this system leads to enhance corrosion process due to increase in conductivity. Hence, 2 wt.% loading of ZnO-PEDOT:PSS give optimum corrosion protection to 316L. By using the same range of nanocomposite additives, the samples were tested in real environment and

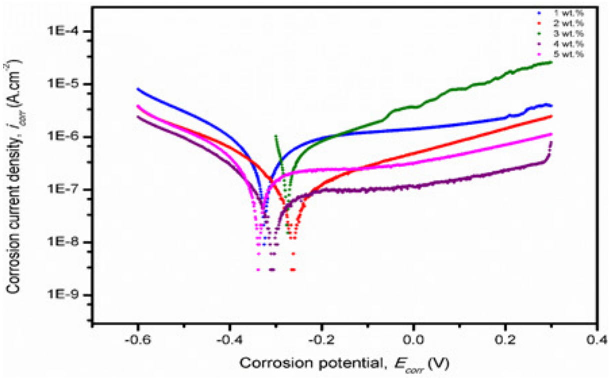

Figure 9. Tafel curves of different wt.% loading of hybrid nanocomposite

were evaluated for every 15 days. Based on Figure 10 and Figure 11 30 days of immersion duration, it can be deduced that coating behaviour with different wt.% hybrid nanocomposite is almost the same as in optimization part. The presence of 2 wt.% of nanocomposite in epoxy based coating provide the best corrosion protection performance with lowest i_{corr} value compared to other wt.% in both 15 and 30 days immersion duration. However, as immersion duration increased, the CR value increases. Increase in immersion duration leads to loses in coating integrity due to water uptake resulting corrosion.

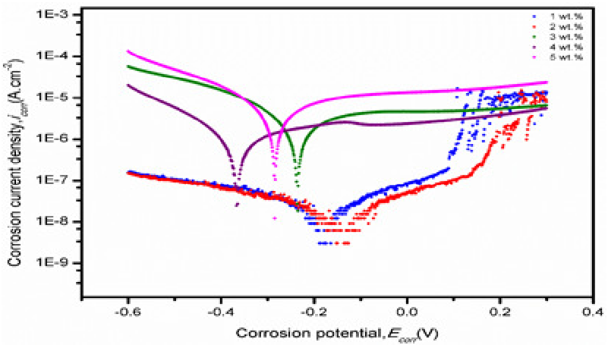

Figure 10. Tafel curves at 15 days immersion duration

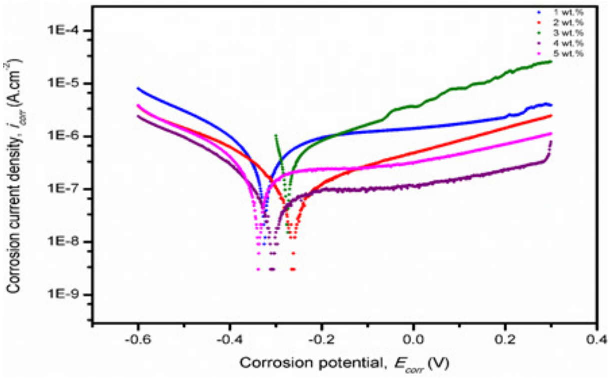

Figure 11. Tafel curves at 30 days immersion duration

IV. SUMMARY

Conducting polymer, PEDOT:PSS and ZnO is successfully formed as hybrid nanocomposite. Addition small amount of ZnO has no effect on coating amorphousness thus ensure the effectiveness of physical barrier protection. Formation of core-shell structure contributed to p-n junction formation which retarded the corrosion process. Addition of 2 wt.% ZnO-PEDOT: PSS provide optimum corrosion protection to stainless steel 316L. This amount of wt.% also provided best corrosion protection with 15 and 30 days immersion duration in real environment. Hence, application of epoxy/ZnO-PEDOT:PSS coating was able to protect stainless steel against corrosion especially when exposed to chloride environment.

V. ACKNOWLEDGEMENT

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