Development of Highly Hydrophobic and Anticorrosive Conducting Polymer Composite Coating for Corrosion Protection in Marine Environment

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Abstract　Present work is directed towards the synthesis of hydrophobic polyaniline-SiO$_2$ composites (HPSC) by chemical oxidation polymerization. HPSC coating were evaluated for protection of mild steel from corrosion in 3.5 % NaCl aqueous solution. Suitable coating with HPSC was formed on mild steel using epoxy resin by powder coating technique. Hydrophobic properties of HPSC were investigated by contact angle measurement. Corrosion protection efficiency of mild steel coated HPSC in 3.5 % NaCl aqueous solution has been evaluated using Tafel Extrapolation method, salt spray test and weight loss methods. The results reveal that the HPSC coating showed the significant reduction in the corrosion current density reflects the better protection of mild steel in marine environment. Protection efficiency of the coating containing HPSC was 93.3 % in 3.5 % NaCl solution after 60 days of immersion and 85 % in the salt spray test of 35 days. The high performance of HPSC containing coating is attributed to the passivation of steel by polyaniline. Higher protection efficiency up to 96 % has been achieved by using HPSC coated mild steel at 6.0 wt. % loading of HPSC in epoxy. Coating performance and corrosion rate of mild steel has been investigated by using immersion and salt spray test indicating that HPSC coated mild steel revealed better performance from corrosion.

Keywords　Conducting polymer, Composites, Corrosion inhibitor, Tafel Extrapolation method

1. Introduction

Conducting polymers, such as polypyrrole, polythiophene, polyaniline, have been studied in great details for past two decades for variety of applications. Coatings on the surface of metals by polymeric materials have been widely used in industries for the protection of these materials against corrosion [1-2]. Some specific conducting polymers, e.g. polyaniline and its derivatives, have been found to display interesting corrosion protection properties. In the past decade, the use of polyaniline as anticorrosion coatings had been explored as the potential candidates to replace the chromium-containing materials, which have adverse health and environmental concerns [3-6]. Fabrication of hydrophobic polyaniline film has attracted considerable attention as surface wettability is one of the determinative factor for different application. For over a decade hydrophobic surfaces have been extensively studied in the

prospect of applications such as self-cleaning and anticorrosion [7, 8]. Number of method have been reported to fabricate hydrophobic surface including solvent casting of polymers, electrodeposition [9], layer-by-layer deposition and colloidal assemblies [10], sol-gel process [11], phase separation[12], chemical etching and chemical grafting[13]. Most of those methods cannot be easily developed and they need very strict conditions of preparation, and low adhesion coatings are often obtained.

Corrosion protection using conductive polymers was first suggested by MacDiarmid [14], Wei et al. [15] demonstrated the corrosion protection effect of polyaniline through a series of electrochemical measurements on the doped or undoped polyaniline-coated cold rolled steel (CRS) under various conditions. Wessling [16] demonstrated full mechanism of the corrosion protection of polyaniline on steel which is attributed to an increase in the corrosion potential and to the redox catalytic property of polyaniline in the formation of passive layer of metal oxide.

A polymer acts as a barrier when it exists in the electronically and ionically insulating state. An important feature of the polymer coating in its conductive state is the ability to store large quantity of charge at the interface

formed with a passive layer on a metal. This charge can be effectively used to oxidize base metal to form a passive layer. Thus, the conducting polymer film was also capable of maintaining a stationary potential of the protected metal in the passive range [17]. Recently; many researchers improved anticorrosion properties of PANI through composites of PANI with other active pigments such as glass flake, which is used with epoxy coatings in the marine atmosphere [18] Polyaniline-Fe_2O_3 composite is reported to offer excellent corrosion protection [19]. Shi et al. [20] have investigated that TiO_2 and SiO_2 have been used for reinforced organic coating (epoxy) to protect mild steel from corrosion.

Application of conducting polymers like polyaniline to corrosion protection of metals is, however, subject to some limitations. First, charge stored in the polymer layer (used to oxidize base metal and to produce passive layer) can be irreversibly consumed during the system's redox reactions. Consequently, protective properties of the polymer coating may be lost with time. Also, porosity and anion exchange properties of conducting polymers could be disadvantageous, particularly when it comes to pitting corrosion caused by small aggressive anions (*e.g.*, chlorides). An interesting alternative is to consider conducting polymer based composite systems. Composite materials play an important role due to their light weight and improved corrosion resistance. These materials usually comprise of a polymer matrix in which fibres and/or small filler particles are thoroughly dispersed. Silicon dioxide particles, for example, comprise one of the common fillers in composite materials such as plastics and films. Conducting Polyaniline/inorganic composites have also attracted more and more attention. A number of different metals and metal oxide particles have so far been encapsulated into the shell of conducting PANI to produce a host of composites materials. These composite materials have shown better mechanical, physical and chemical properties, due to combining the qualities of conducting PANI and inorganic particles [21-23].

Among various inorganic particles, SiO_2 particles have attractive attention due to their excellent reinforcing properties for polymer materials [24]. However, SiO_2 is an insulator and a lot of work has been done to expand the applications of insulator SiO_2 as fillers and improve the processability of polyaniline [25-29]. Corrosion protective coatings on the mild steel surface by electrochemical deposition of conducting polymers have been extensively studied [30-34]. These types of coatings lack long lasting ability of metals in a corrosive medium. In order to improve the adherence ability and efficiency of conducting polymer coating on the metal surface, the use of liquids paints have also been performed by many researchers[35-38].

Present work is based on the preparation of hydrophobic polymer nanocomposite coating onto the mild steel surface by using powder coating techniques. Powder coatings are often used as an alternation to liquids paints finishing or traditional liquid finishing. The key benefits of powder coating techniques are cost effective, environmentally friendly, excellence of finish and performance. This shows

single coat finishes with no primer or any other solvent required and high film thickness can be achieved with single coat. Preparation of PANI/SiO_2 nanocomposite (HPSC) was carried out by in situ polymerization using fluorinating dopant i.e. PFOA to introduce the water repellent property in polymer composite. Corrosion protection performance of these nanocomposite were compared with that of the polyaniline by performing Tafel extrapolation method, weight loss method, salt spray test and surface morphology studies in 3.5-5.0 % aqueous NaCl solution. The HPSC materials were characterized by cyclic voltammetry, FTIR spectroscopy (FTIR), Scanning electron microscopy (SEM), TEM and contact angle measurements. Coating performance of powder coated polymers was investigated by immersion and salt spray test for 60 days and 35 days respectively.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS) (Merck, India), Ethanol (Merck, India), aqueous ammonia (Merck, India), Aniline (Loba Chemie, India) was freshly distilled before use. Perfluoro-octanoic acid (PFOA, Merck, India), Ammonium persulfate (APS, Merck, India). Aqueous solutions were prepared from the double distilled water having specific resistivity of 1MΩ-cm.

2.2. Synthesis of the SiO_2 Nanoparticles

The synthesis of monodiperse uniform- sized SiO_2 particles was carried out in the presence of ammonia as catalyst and ethanol as solvent using hydrolysis method of tetra-ethylorthosilicates (TEOS) [39]. Aqueous ammonia (0.1M) was added to a solution containing ethanol (1.0 M) and 20 ml of deionized water which was stirred for 1 hour then 0.05M TEOS was added and again stirred for 1 hour at room temperature. Appearance of white turbid suspension indicating the formation of silicon dioxide, this suspension was retrieved by centrifugation and further calcination at 823 K for 6 hours. The formation of SiO_2 nanoparticles was confirmed by FTIR spectroscopy and SEM analysis.

2.3. Preparation of PANI-SiO_2 Composites

The doped PANI-SiO_2 composites have been prepared by chemical oxidative polymerization using PFOA as a surfactant dopant. For preparation of PANI-SiO_2 composite, the weight ratio of aniline and SiO_2 was taken as 1:1 in the presence of 0.2 M PFOA in distilled water. The mixture has been homogenized using high speed blender rotating at 10,800 rpm for 30 min to form an emulsion. The emulsion solution has been transferred to double walled glass reactor under constant stirring. The polymerization has been initiated by the drop wise addition of ammonium peroxydisulfate (APS) (0.1 mol), $(NH4)_2S_2O_8$) in 100 mL distilled water. The polymerization was carried out at a temperature of 0-3 °C for a period of 4-6 h. The synthesized polymer composite was isolated from reaction mixture by

filtration and washed with distilled water to remove oxidant and oligomers and followed by drying in the vacuum oven at 60 °C.

2.4. Preparation of PANI/SiO₂ Composites (HPSC) Coated Mild Steel

Mild steel coated with HPSC electrode of dimension 1 cm x 1 cm were employed to carry out the corrosion studies. Surface treatments were applied on the samples including the cleaning of the electrode was carried out by 1/0, 2/0, 3/0 and 4/0 grade emery papers. The electrodes were then thoroughly cleaned with acetone and trichloroethylene to remove any impurities on the surface. The powder polymer was mixed with epoxy formulation in various proportions ranging from 1.0 % to 6.0 wt. %. The polymer-epoxy powder coating was applied to a thickness of 45 ± 3 m using an electrostatic spray gun. After obtaining uniform coverage of the powder the powder-coated panels were placed in air drying oven for curing at 140 °C for 20 min. The adhesion of the coating was tested by tape test as per ASTM D3359-02 and found to pass the test.

2.5. Electrochemical Polymerization

The electrochemical polymerization of 0.1 M aniline and aniline in the presence of SiO₂ in 0.2 M PFOA was carried out at 0.9 V on platinum electrode vs. Ag/AgCl reference electrode. The polymer film growth was studied by sweeping the potential between −0.20 and 0.9 V on Pt electrode at a scan rate of 20 mV/s. Prior to polymerization, the solution was deoxygenated by passing argon gas through the reaction solution for 30 min. Peak potential values of the corresponding polymer and HPSC were recorded in PFOA medium.

2.6. Characterization

The electrochemical behavior of PANI/SiO₂ composites were investigated by cyclic voltametry using Autolab 100, Potentiostat/Galvanostat. NICOLET 5700 FTIR spectrophotometer was used for the structural characterization of polymers. Contact angle measurements was used to check the hydrophobic nature of the nanocomposite coated mild steel by the Sessile drop method [38] and [39] using a drop shape analyzer (DSA 100, DSA/V 1.9). Electrochemical polymerization and electrochemical characterizations were carried out using (Autolab 100, Potentiostat/Galvanostat, Netherlands). All measurements were carried out at room temperature. The surface morphology of the polymers coated mild steel samples was observed using SEM (Leo).

3. Corrosion Study

The corrosion protection performance of HPSC and PANI coated mild steel samples was carried out at room temperature in aqueous solution of 3.5 % NaCl solution using Tafel extrapolation, salt spray taest and weight loss methods. Experiments were carried in a conventional three electrode cell assembly using Autolab Potentiostat/ Galvanostat, PGSTAT100 (Nova Software) with pure mild steel of dimension 1 cm x 1 cm as working electrode coated with conducting polymers (HPSC/PANI formulated with epoxy resins) by powder coating method, Pt as counter electrode and saturated calomel electrode (SCE) as reference electrode. The linear Tafel segments to the anodic and cathodic curves (-0.2 to + 0.2 V versus corrosion potential) were extrapolated to corrosion potential to obtain the corrosion current densities. The corrosion current density [i_{corr} (A/cm²)] was calculated with the Stern-Geary equation [40]. The corrosion protection efficiency (% P.E.) was determined from the measured i_{corr} (corrosion current densities with blank mild steel electrode (i^0_{corr}) without coatings and corrosion current densities with a mild steel electrode coated with polymer coated (i^c_{corr}) values by using the following relationship;

$$P.E.(\%) = \frac{i^0_{corr} - i^c_{corr}}{i^0_{corr}} \times 100 \qquad (1)$$

3.1. Weight Loss Method

The weight loss methods have also been performed for corrosion study. Polymer coated mild steel specimens of dimension 4 x 3.5 cm² have been tested for same span of time by immersing the samples in aqueous 3.5 % NaCl solution for 60 days. The uncoated and polymers coated mild steel specimens were weighed in an electronic balance with an accuracy of 0.1 mg. before immersion in saline medium. After the 60 days of immersion the mild steel specimens were withdrawn from the tested solution, washed thoroughly with distilled water followed by acetone and dried with air, then weighed again. The performance of the coating was examined visually and through calculation of the weight loss. Weight loss (W.L) is expressed as the loss in the weight per unit area or per unit area per unit time (g cm⁻² h⁻¹) as follows:

$$W.L = \frac{w_0 - w_1}{a.t} \qquad (2)$$

Where, w_0 = initial weight of the sample before immersion (g); w_1 = weight of the sample after immersion (mg); a= surface area (cm²) of specimen; t = end time (h) of each experiment.

If we introduce the density of metal; d (g/cm³), the loss in the thickness of metal per unit time can be calculated. Corrosion rate (C.R) in mm/year can also be calculated by weight loss method as follows:

$$C.R(mm/year) = \frac{(w_0 - w_1) \times 87.6}{a.t.d} \qquad (3)$$

3.2. Salt Spray Tests

Coated mild steel panels were prepared by coating on fully finished mild steel specimen dimension 15.0 cm×10.0 cm×0.12 cm. The coated panels were exposed to salt spray of 5.0 % NaCl solution as per ASTM B117 method.

4. Result and Discussion

The PANI-SiO$_2$ composites have been prepared by in situ polymerization in the presence of fluorinating agent i.e. PFOA which act as surfactant as well as dopant. Therefore, interaction of PFOA with SiO$_2$ particles leads to formation micelles which act as a soft template with formation of emulsion. The addition of water soluble oxidant, i.e., APS initiates the polymerization reaction, which starts from the surface of the micelles and then propagates inside the bulk of the aniline dissolved in the micellar phase. The oxidation of monomer aniline leads to formation of anilinium radical cations which on combination with another unit form neutral dimer molecule. Further oxidation of this dimer and subsequent addition of monomer unit leads to the formation of a trimer, tetramer, and finally the conducting polymer composite, i.e., HPSC. The schematic representation of formation of HPSC coating onto electrode surface is shown in Scheme 1.
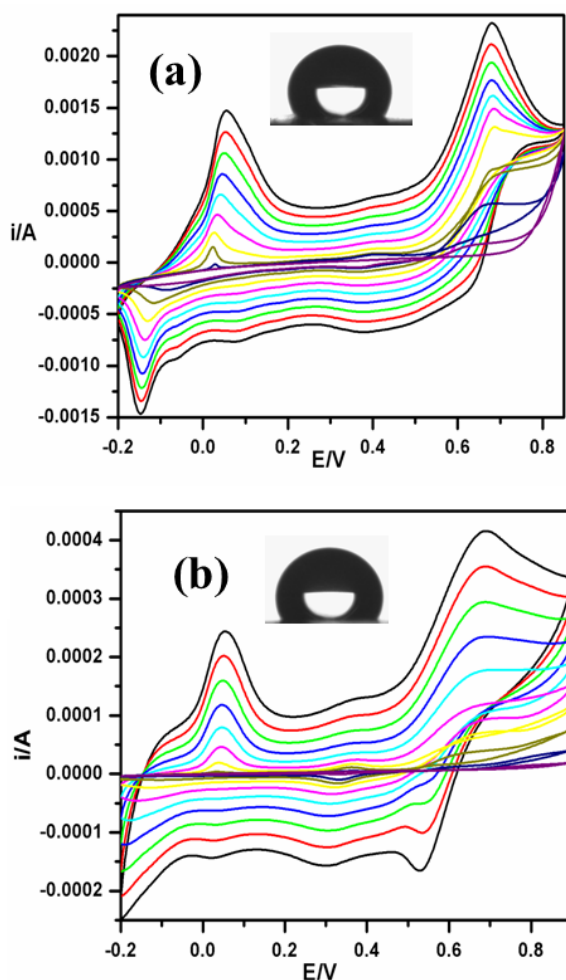
4.1. Electrochemical Behaviour

Figure 1 shows the electrochemical growth behavior of aniline and aniline-SiO$_2$ in 0.2 M PFOA solution. Electrochemical polymeriztion was carried out at 0.9 V on platinum electrode vs Ag/AgCl reference electrode. The polymer film growth was studied by sweeping the potential between -0.20 and 0.9 V on Pt electrode at a scan rate of 20 mV/s. Peak potential values of the corresponding PANI and HPSC were recorded in PFOA medium. First anodic peak (oxidation peak) corresponds to the oxidation of monomer. The intensity of this peak gradually decreases with subsequent scans. During the first reverse sweep, a reduction peak appears which shows that the formation of oligomers and polymer on electrode surface as shown in Figure.1. After the first scan, well defined oxidation and reduction peaks of polymers between 0.2 and 0.6 V vs. Ag/AgCl appeared. The current values of each oxidation and reduction peaks are greater than that of a previous cycle which indicate the built up of an electroactive polymeric material on the electrode surface. Moreover, it was observed that current value of PANI film (Figure 1a) was found to be higher than that of HPSC film (Figure 1b) which revealed higher conductivity of PANI as compare to HPSC coating on electrode surface.
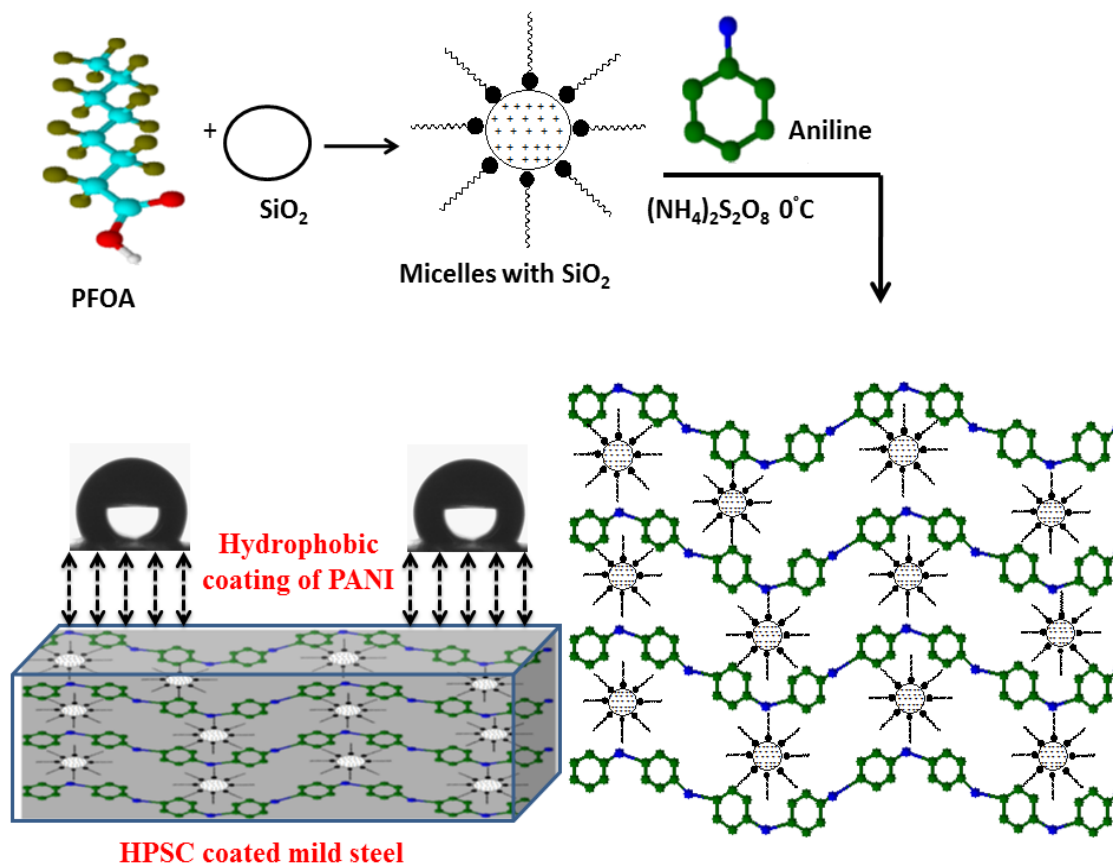
Scheme 1. Pictorial representation for the development of Hydrophobic Polyaniline-SiO$_2$ composite

Figure 1. Electrochemical growth behaviour of (a) 0.1M aniline in 0.2M PFOA medium and (b) aniline- SiO$_2$ in 0.2M PFOA medium in potential range between -0.2 V to 0.9 V vs. Ag/AgCl at scan rate of 20 mV/s and inset shows contact angle of polymer
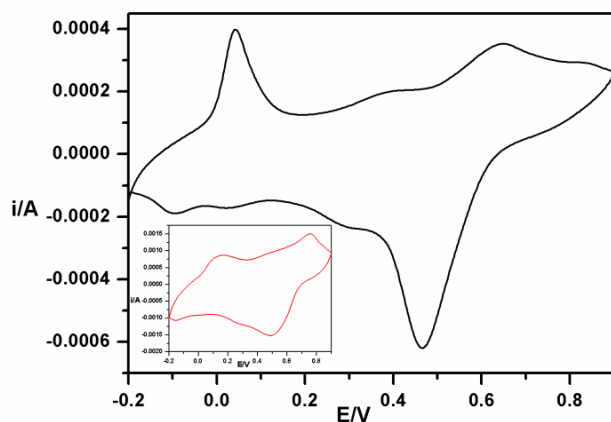
Figure 2. Cyclic voltammogram of HPSC and inset shows the cyclic voltammogram of PANI in PFOA medium at a scan rate of 20 mV/s

Figure 2 shows the cyclic voltammogram of PANI-SiO$_2$ composite and the inset in Figure 2 gives the cyclic voltammogram of PANI in PFOA medium. The comparison of peak potential data of PANI and HPSC in PFOA medium,

indicates that the first peak potential value of PANI in PFOA medium lies at 0.15 V. Incorporation of SiO$_2$ particle in PANI, the first peak potential value shifted from 0.15 V to 0.041 V vs Ag/AgCl, This implies that the polymerization of aniline leads to larger peak potential shift as compared to the aniline in presence of SiO$_2$ which indicates the presence of SiO$_2$ particles in the polymer chain induce some change in configurations along the polymer backbone which is responsible for the negative shift in the oxidation potential.

4.2. Contact Angle Studies

The contact angle measurements were carried out using Sessile drop method. The change in the value of the contact angle reveals the hydrophobic/hydrophilic character of the surface, which in turn can be related to corrosion inhibition of polymer composite. The inset image of Figure 1 indicates the contact angle of 2 µl water droplet on the corresponding surface. Contact angle values of PFOA doped PANI and PANI-SiO$_2$ film on the electrod surface was found to be in range of 126° and 115° respectively.

4.3. FTIR Spectra

Figure 3 shows the FTIR spectra of SiO$_2$, PANI and PANI-SiO$_2$. PANI showed the main characteristics bands at 1554 and 1438 -1440 cm^{-1} attributed to the stretching mode of C=N and C=C, the bands at 1250 cm^{-1} indicating the C–N stretching mode of benzenoid ring. The FTIR spectra of SiO$_2$ indicated that the characteristic peak at 1081 cm^{-1} and 807 cm^{-1} are assigned to the stretching and bending vibration of Si–O–Si respectively. These peaks were also observed in HPSC indicating the interaction of SiO$_2$ particles in polyaniline chain.
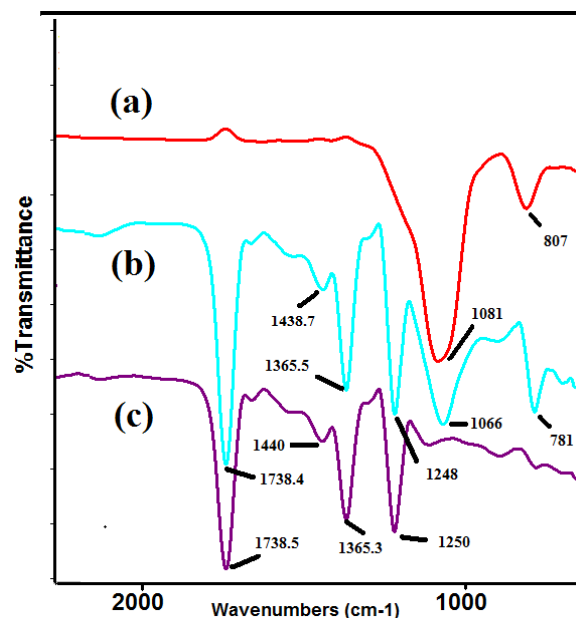
Figure 3. FTIR spectra of (a) SiO2 (b) HPSC and (c) PANI

HPSC and PANI showed a characteristic strong peak at 1738 cm^{-1} due to C=O stretching mode and peak at 1365 cm^{-1}due to C-F starching mode , which indicates the
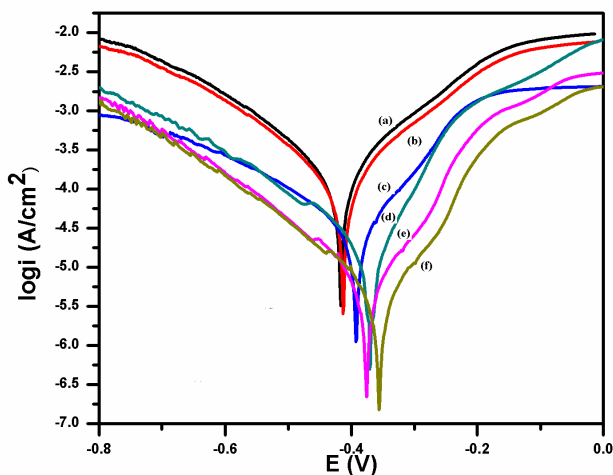
interaction of PFOA dopant in the polymer chain.

4.4. Anticorrosive Properties of HPSC Coated Mild Steel

4.4.1. Tafel Extrapolation Method

Tafel polarization behaviour of mild steel in 3.5 % NaCl solution with uncoated, epoxy coated, PANI and HPSC coated mild steel are shown in the Figure 4 & Figure 5.
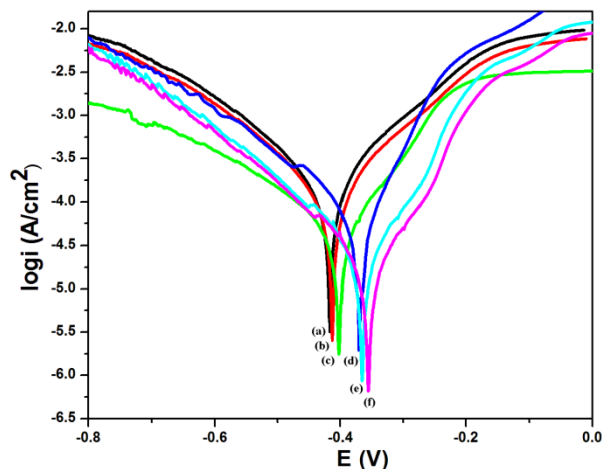
Figure 4. Tafel curves of PANI coated mild steel electrode with different loading level of PANI in epoxy resin (a) blank mild steel (b) epoxy coated mild steel (c) 1.5% (d) 3.0% (e) 4.5% (f) 6.0% in 3.5% NaCl solution

sample to 98 μA/cm^2 for epoxy coated mild steel sample to 4.36 μA /cm^2 for HPSC coated mild steel samples.

Table 1. Tafel parameters for corrosion of mild steel in 1.0 M HCl with different loading level of PANI & HPSC in epoxy resin

Sample name	Loading level of polymer (%)	I_{corr} (μA/cm^2)	Corrosion rate (mm/ year)	Protection efficiency (%)
Blank mild steel	-	106.5	1.51	0
Epoxy coated mild steel	0	98.0	1.39	7.9
PANI	1.5	64.5	0.91	39.43
	3.0	61.6	0.87	42.16
	4.5	30.2	0.42	71.6
	6	20.4	0.28	80.84
PANI-SiO$_2$ Composite	1.5	32.6	0.45	69.39
	3.0	12.8	0.17	87.98
	4.5	6.16	0.08	94.21
	6	4.36	0.06	96.0

The corrosion current values (i$_{corr}$) decreased with increasing the concentration of HPSC in epoxy resin. i$_{corr}$ value decreased from 32.6 μA/cm^2 at 1.5 wt. % to 4.36 μA/cm^2 at 6.0 wt. % loading of conducting material in epoxy resin.

Figure 5. Tafel curves of HPSC coated mild steel electrode with different loading level of HPSC in epoxy resin (a) blank mild steel (b) epoxy coated mild steel (c) 1.5% (d) 3.0% (e) 4.5% (f) 6.0% in 3.5% NaCl solution

Figure 6. Tafel curves of (a) blank mild steel (b) epoxy coated mild steel (c) & (d) are PANI and HPSC coated mild steel electrode with 6.0 % loading level in epoxy resin in 3.5% NaCl solution
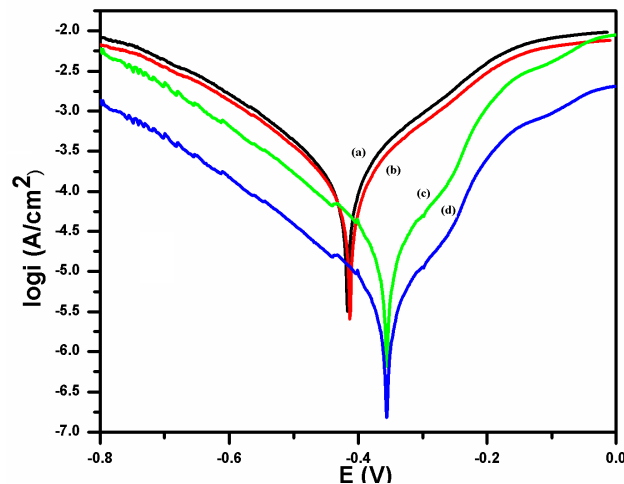
The corrosion kinetic parameters derived from these curves are given in the Table 1. As shown in Table 1 the HPSC coated mild steel sample showed a remarkable current density shift from 106.5 μA/cm^2 to 4.36 μA /cm^2 versus Ag/AgCl in the corrosion current (I$_{corr}$), relative to the value of the uncoated mild steel. The significant reduction in the corrosion current density (i$_{corr}$) in polymer coated mild steel indicated the effective corrosion protection performance of these polymers. The corrosion current values (i$_{corr}$) found to be decreased from 106.5 μA/cm^2 for uncoated mild steel

While PANI coated mild steel showed the i$_{corr}$ in the range of 20.4 μA/cm^2 at 6.0 wt. % loading. The corrosion protection efficiency calculated from Tafel parameter revealed that PANI coated mild steel showed the protection efficiency 39.4 % at 1.5 wt.% loading while HPSC coated mild steel showed 69.4 % P.E at

the same loading level. Up to 96 % protection efficiency have been achieved by using 6.0 wt. % HPSC in epoxy resin. While in case of PANI, only 80.84% protection has been achieved at 6.0 wt.% loading as shown in Figure 6.

4.4.2. Weight Loss Method

SEM images of uncoated, epoxy coated and polymer coated samples before and after the immersion test of 60 days have been shown in Figure 7 & Figure 8. These images clearly show the formation of large pits on the surface of mild steel after immersion. These pits and cracks were developed during the corrosion of mild steel in saline medium. When epoxy coated mild steel sample was immersed in the saline medium for 60 days, detachment of coating from mild steel substrate have been observed. The

pits were also appeared on the metal surface as shown in Figure 8.

In case PANI coated sample, few pits still appeared on mild steel surface. While, HPSC coated mild steel samples did not show any cracks and pits on the metal surface. No detachment of coating from mild steel substrate was also observed after the immersion of these samples in 3.5 % NaCl medium for 60 days of immersion indicating strong adherence of HPSC composite to the mild steel substrate and it is resistant to corrosion in aqueous 3.5 % NaCl.
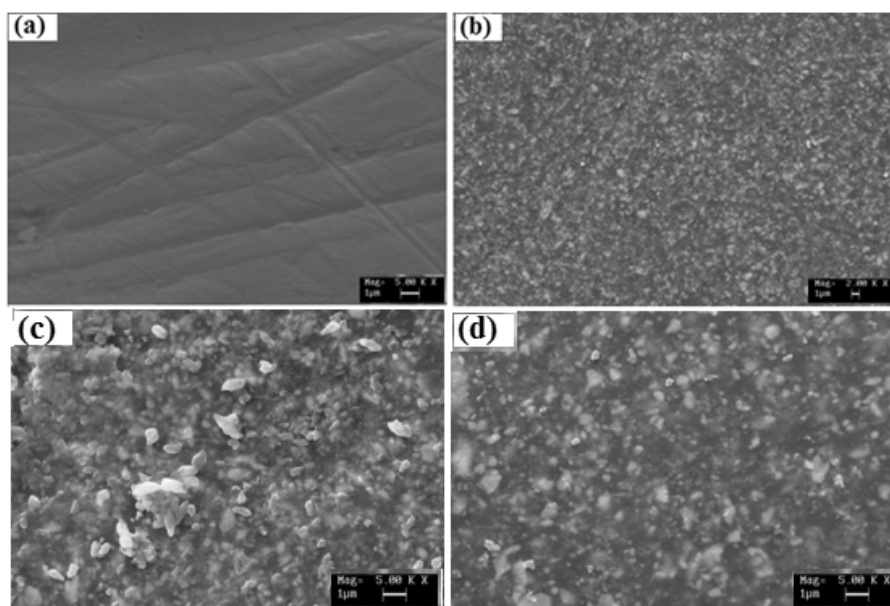
Figure 7. SEM micrographs of (a) blank mild steel electrode (b) blank epoxy resin coated electrode (c) PANI coated (d) HPSC coated electrode before immersion in 3.5% NaCl solution
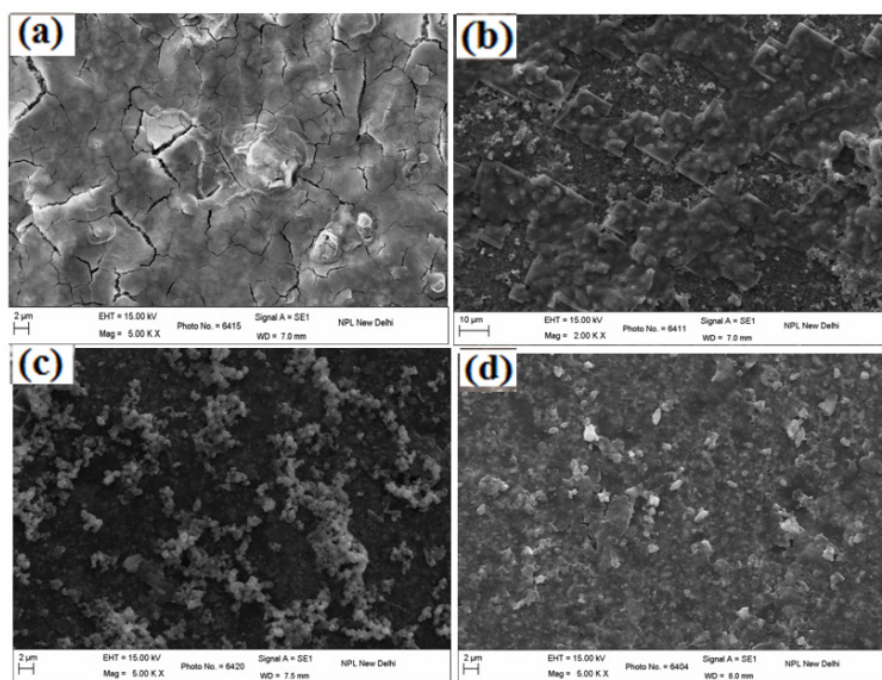
Figure 8. SEM micrographs of (a) blank mild steel electrode (b) blank epoxy resin coated electrode (c) PANI coated (d) HPSC coated electrode after immersion in 3.5% NaCl solution for 60 days

Table 2. The weight loss parameter of coated mild steel samples with different loading level of PANI & HPSC in epoxy resin during the immersion test in 3.5% NaCl for 60 days

Sample Name	Loading Level of polymers	Initial Weight	Weight after Immersion in NaCl for 60 days	Weight Loss (mg)	Weight Loss (%)	C.R (mm/year)	Protection efficiency (%)
Blank mild steel	-	32632.1	21478.45	11153.7	34.18	4.18	0
Blank epoxy	0	30918.7	21918.27	9000.4	29.11	3.56	14.83
PANI	1.5	32798.2	24913.5	7884.7	24.04	2.94	29.67
	3.0	30416.2	23502.6	6913.6	22.73	2.78	33.49
	4.5	32678.1	26642.5	6035.6	18.47	2.26	45.93
	6	31567.2	28369.4	3197.8	10.13	1.24	70.33
PANI-SiO$_2$ Composite	1.5	31494.2	25541.8	5952.4	18.9	2.32	44.50
	3.0	30566.5	25935.7	4630.8	15.15	1.86	55.50
	4.5	32929.7	29926.5	3003.2	9.12	1.12	73.20
	6	30804.7	30102.4	702.3	2.28	0.28	93.30

Table 2 shows the values of the weight loss from mild steel samples during the immersion test for 60 days in 3.5 % NaCl. The results revealed that HPSC coated samples were more protectable to mild steel than that of only PANI coated samples in same immersion time. It was found that the HPSC content has a great influence on the anticorrosive performance of the coating. The corrosion protection effect of HPSC coated mild steel sample improved slowly when HPSC content in epoxy formulation increases from 1.5 to 3.0 wt. % Afterward, an excellent corrosion protection effect appears at 6.0 wt. % loading of HPSC content in epoxy resin After the immersion of coated and uncoated samples in 3.5 % NaCl solution for 60 days, it was observed that uncoated and epoxy coated samples showed the maximum weight loss of 34.18 % and 29.11 % respectively. PANI coated mild steel showed the weight loss up to 10.13 % at 6.0 wt. % loading while HPSC coated samples at the same loading level showed negligible weight loss (i.e < 3 %) after 60 days of immersion in 3.5 % NaCl medium. Corrosion rate (C.R) in mm/year have also been calculated by weight loss method. It was observed that the corrosion rate was highest for uncoated mild steel in 3.5 wt. % NaCl medium. After 60 days of immersion, the C.R value of uncoated mild steel was found to 4.18 mm/year. Epoxy and PANI coated samples showed C.R. value of 3.56 mm/year and 1.24 mm/year respectively. While in the case of HPSC coated sample in 6.0 wt. % loading, C.R. value reduced to 0.28 mm/year.

4.4.3. Salt Spray Test

The appearance of the uncoated and HPSC coated mild steel samples after exposure to salt spray fog for 35 days is shown in Figure 9. It was observed that epoxy coated and PANI coated (at 6.0 wt. % loading) mild steel have more corrosion extended area from the scribes as shown in Figure 9 (a) and 9 (b) while HPSC coated mid steel (at 1.0 wt. % loading) showed less corrosion extended area as compared to

epoxy and PANI coated coated mid steel as shown in Figure 9(c).
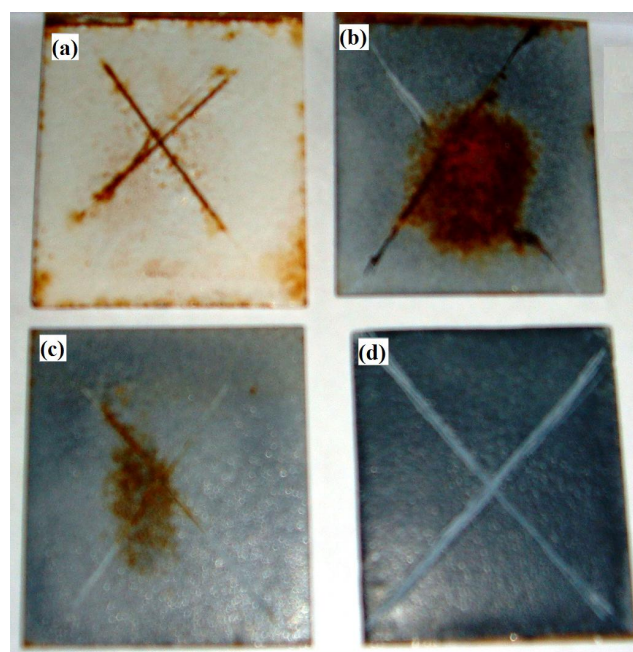
Figure 9. Salt spray images of powder coated sample of (a) Epoxy coated (b) PANI coated at 6% loading, (c) & (d) HPSC coated at 1.5 and 6% loading level

However, HPSC containing coating sample (at 6.0 wt.% loading) were found to be free from rust and blister as shown in Figure 9 (d). Moreover, there was no spreading of rust along the scribed area.

4.4.4. Surface Morphology of HPSC and HPSC Coated Samples

The scanning electron micrographs of SiO$_2$ particles, PANI and HPSC are shown in Figure 10. SiO$_2$ particles showed spherical shaped morphology and PANI showed uniform net like morphology. Morphology of PANI was

entirely different with incorporation of SiO$_2$ particles in PANI matrix as shown Figure 10c & 10d. SEM image of HPSC revealed that the entrapment of SiO$_2$ particles in the globular space of PANI matrix during insitu polymerisation of polyaniline.

SEM images of uncoated, epoxy coated and polymer coated samples before and after the immersion test of 60 days have been shown in Figure 7 and 8 respectively. These images clearly show the formation of large pits on the surface of mild steel after immersion. These pits and cracks were developed during the corrosion of mild steel in NaCl medium. When epoxy coated mild steel sample was immersed in the saline medium for 60 days, detachment of coating from mild steel substrate have been observed. The pits were also appeared on the metal surface as shown in Figure 8 (a). In the case PANI coated sample, few pits still appeared on mild steel surface. While, HPSC coated mild steel samples did not show any cracks and pits on the metal surface. No detachment of coating from mild steel substrate

was also observed after the immersion of these samples in 3.5 % NaCl medium for 60 days of immersion indicating strong adherence of HPSC composite to the mild steel substrate and it is resistant to corrosion in aqueous 3.5 % NaCl medium. It was found that the HPSC content has a great influence on the anticorrosive performance of the coating. The corrosion protection effect of HPSC coated mild steel sample improved slowly when HPSC content in epoxy formulation increases from 1.5 to 3.0 wt. % Afterward, an excellent corrosion protection effect appears at 6.0 wt. % loading of HPSC content in epoxy resin.

Corrosion protection property of these coating may be attributed to the HPSC content in epoxy resin. HPSC can react with epoxy to form highly adherent, dense and non porous polymer film on the mild steel surface. In the other hand, presence of SiO$_2$ particles entrapped in PANI chain provide the reinforcement to PANI chain which reduce the degradation of polymer chain in saline condition.
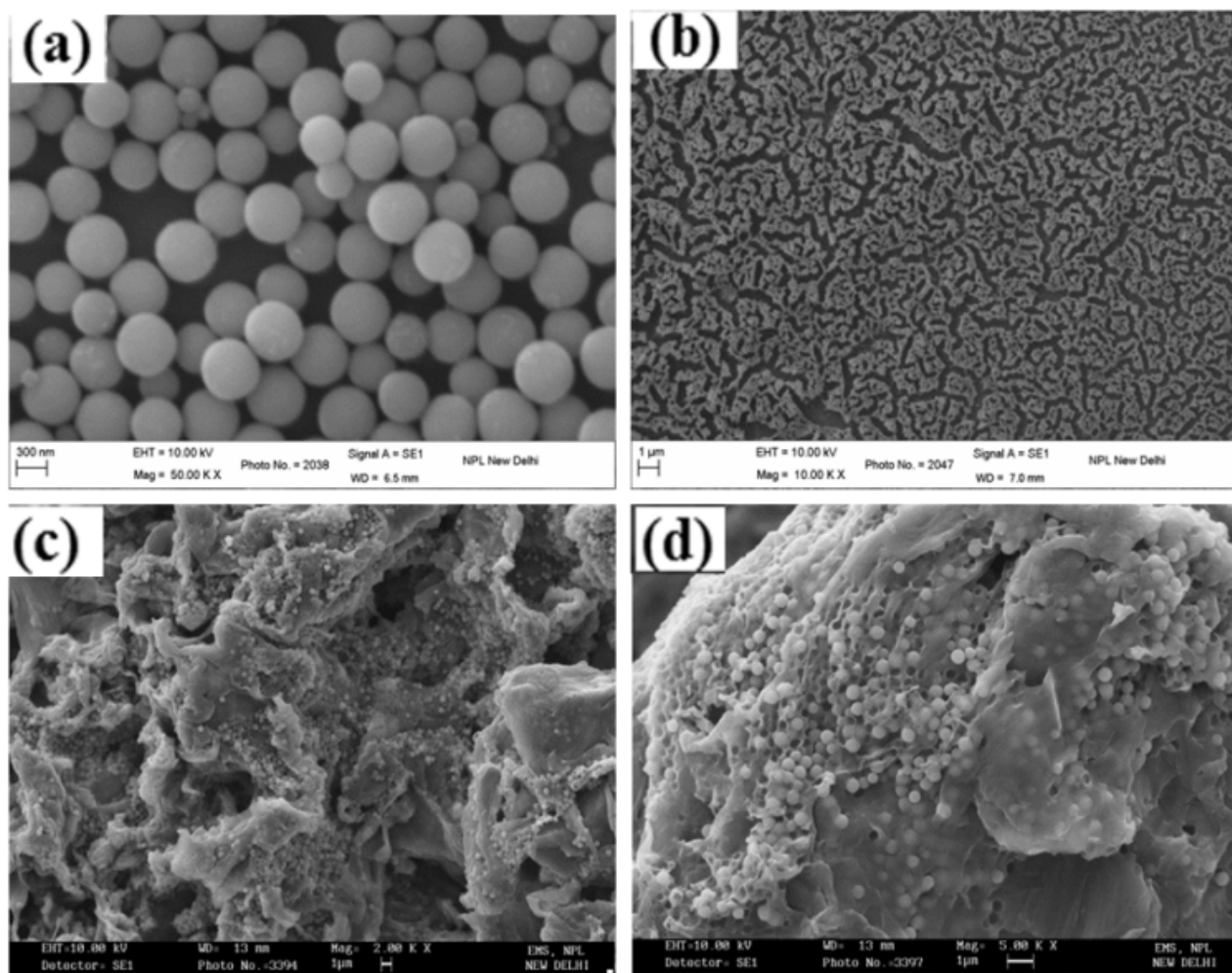
Figure 10. SEM micrographs powder sample of (a) SiO$_2$, (b) PANI, (c) & (d) HPSC

The corrosion studies show that the HPSC containing coating showed better corrosion protection as compared to PANI coating which may be due to the redox property and uniform distribution of PANI in the coating containing HPSC. Earlier studies [41-43] have shown that the redox property of PANI coating onto metal surface plays an important role to protect the metal by passivating the pin holes. Corrosion protection of metals occurs via reduction of PANI–Emeraldine salt (PANI–ES) to PANI–Leucosalt (PANI–LS). PANI–LS is assumed to undergo a subsequent re-oxidation by dissolved oxygen to PANI–ES. Due to this cyclic reaction, the coating containing PANI is able to offer higher corrosion protection. But in the case of HPSC containing coating, these composites have a dual protection mechanism; forming a passive layer and simultaneously acting as a physical barrier. HPSC containing coating onto metal surface act as a barrier between metal surface and corrosive environment. Water repellant property of HPSC coating inhibit the entrance of water and corrosive ions on the metal surface. Due to uniform distribution of PANI, the possibility of forming uniform passive layer on the mild steel surface is more since PANI has been shown to protect the mild steel surface by passive film formation. Furthermore, Powder coating technique also plays an important role for achieving high quality, durable and good anticorrosive coatings.

5. Conclusions

PANI/SiO$_2$ composites were prepared by chemical oxidation polymerization of aniline and SiO$_2$ by using ammonium persulfate (APS) as an oxidant in the presence of PFOA medium. FTIR, cyclic voltammetry and SEM techniques confirmed the interaction of PANI with SiO$_2$ particles. The excellent corrosion protection performance by HPSC coated mild steel could be due to the strong adherence of polymer film which uniformly covers the entire electrode surface as evident by the surface morphology. The corrosion current densities were lowered several orders of magnitude with these coatings. The coating had good protective efficiency which increased with increasing the loading of HPSC to the maximum of 96 % at 6.0 wt.% loading and reduced to about 93.3 % after 60 days of immersion in highly corrosive environment confirming the improved coating performance. Weight loss method also revealed that HPSC coated samples showed very low weight loss as well as negligible corrosion rate as compared to PANI coated samples at same immersion time, which indicates the better protection and adhesion of HPSC onto the mild steel surface as compared to PANI.

Presences of SiO$_2$ particles entrapped in polymer matrix provide the reinforcement to PANI chain which reduce the degradation of polymer in corrosive medium. Hydrophobic HPSC coating protect metal by dual mechanism by forming passivating layer as well as act as a physical barrier which inhibits the entrance of water onto metal surface.

Furthermore, Powder coating technique also plays an important role for achieving high quality, durable and good anticorrosive coatings. These studies clearly reveal that the polymer has excellent corrosion protection properties and it can be considered as a potential material for corrosion protection of mild steel in corrosive medium like.3.5 % NaCl solution.

REFERENCES

[1] Jones DA, Principles and Prevention of Corrosion, Macmillan Publishing, Chap. 1, New York (1992).

[2] Lacroix JC, Camalet JL, Aeiyach S, Chane-Ching KI, Petitjean J, Chauveau E, Lacaze PC. J. Electroanal. Chem 2000; 481:76.

[3] Deberry DW. J. Electrochem. Soc 1985; 132:1027.

[4] Wessling B. Synth. Met 1991; 41:907.

[5] Elsenbaumer RL, Lu WK, Wessling B, Int. Conf. Synth.Met., Seoul, Korea, Abstract No. APL (POL) 1-2, (1994).

[6] Wrobleski, DA, Benicewicz BC, Thompson KG, Byran C. J. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1994; 35:265.

[7] Fan H, Zhao N, Wang H, Li X, Xu J. Materials Letters 2012;78: 42.

[8] Schmit, D. L.; Coburn, C. E.; Benjamin, M. D. Nature 1994; 39:368.

[9] Zhu Y, Li J, Wan M, Jiang L. Polymer 2008; 49:3419.

[10] F. Shi, Y.Y. Song, J. Niu, X.H. Xia, Z.Q. Wang, X. Zhang. Chem. Mater. 2006; 18 1365.

[11] L.B. Zhang, H. Chen, J.Q. Sun, J.C. Shen. Chem. Mater. 2007; 19: 948.

[12] S.X. Lu, Y.L. Chen, W.G. Xu, W. Liu. Appl. Surf. Sci. 2010; 256: 6072.

[13] Z.J. Wei, W.L. Liu, D. Tian, C.L. Xiao, X.Q. Wang. Appl. Surf. Sci. 2010; 256: 3972.

[14] Q. Wang, B.W. Zhang, M.N. Qu, J.Y. Zhang, D.Y. He. Appl. Surf. Sci. 2008; 254: 2009.

[15] MacDiarmid AG, 1985. Suny, New Platz, NY.

[16] Wei Y, Wang J, Jia X, Yeh J-M, Spellane P. Polymer 1995; 36:4535.

[17] Wessling B. Adv. Mater 1994; 6:226.

[18] Spinks GM, Dominis AJ, Wallace GG, Tallman DE. J. Solid

State Electrochem 2002; 6:85.

[19] Sathiyanarayanan, S, Syed Azim S, Venkatachari G. Electrochimica Acta 2007; 53:2087.

[20] Sathiyanarayanan S, Syed Azim S, Venkatachari G. Synth. Met 2007;157: 751.

[21] Shi, H, Liu F, Yang L, Han E. Progress in Organic Coatings 2008; 62:359.

[22] Majumdar, G, Goswami M, Sarma TK, Paul A, Chattopadhyay A. Langmuir 2005; 21: 1663.

[23] Chowdhury D, Paul A, Chattopadhyay A. Langmuir 2005; 21:4123.

[24] Feng XM, Yang G, Xu Q, Hou WH, Zhu JJ. Macromol Rapid Commun 2006; 27:31.

[25] Hasan M, Zhou Y, Mahfuz S, Jeelani S. Materials Science and Engineering: A 2006; 429:181.

[26] Li X, Dai N, Wang G, Song X. Journal of Applied Polymer Science 2008; 107:403.

[27] Xia HS, Wang Q. J Appl Polym Sci 2003; 87:1811.

[28] Zengina H, Erkan B. Polym. Adv. Technol 2010; 21:216.

[29] Stejskal J, Kratochvı'l P, Armes SP, Lascelles SF, Riede A, Helmstedt M, Prokes J, Krˇivka I. Macromolecules 1996; 29:6814.

[30] Al-Dulaimi AA, Hashim S, Khan MI. Sains Malaysiana 2011; 40:757.

[31] Beck F, Michaelis R, Scholoten F, Zinger B. Electrochimica Acta 1994; 39:229.

[32] Camalet JL, Lacroix J.C, Aeiyach S, Chane-Ching K, Lacaze PC. Synth. Met., 1998; 93:133.

[33] Kilmartin PA, Trier L, Wright GA. Synthetic Metals 2002; 131: 99.

[34] A. Meneguzzi A, C.A.Ferreira, M.C.Pham, M. Delamar, P.C. Lacaze. Electrochim. Acta 1999; 44:2149.

[35] Bhandari H, Choudhary V, Dhawan SK. Thin Solid Film, 2010; 519:1031.

[36] Kinlen PJ, Menon V, Ding Y. J. Electrochem. Soc., 1999; 146:3690.

[37] Talo A, Passiniemi P, Forse´n O, Yla¨saari S. Synth. Met., 1997; 85:1333.

[38] Wessling B, Posdorfer J. Electrochim. Acta, 1999; 44:2139.

[39] Rao KS, El-Hami K, Kodaki T, Matsushige K, Makino K, Journal of Colloid and Interface Science, 2005; 289 :125.

[40] Stern M, Geary A, Electrochemical polarization, J. Electrochem Soc. 1957; 104:56.

[41] Wessling B, Posdorfer J, Electrochim. Acta 1999; 44:2139.

[42] D. Huerta-Vilca, S.R. Moraes, A.J. Motheo, J. Braz. Chem. Soc. 2003; 14: 52.

[43] T.P. McAndrew, S.A. Miller, A.G. Gilleinski, L.M. Robeson, Polym. Mater. Sci. Eng. 1996; 74: 204.