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# Corrosion performance of chemically modified polymer coatings applied on mild steel

### **Punita Mourya**

Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad Dhanbad 826004, Jharkhand, India <u>mouryapunita025@gmail.com</u>, pmourya.rs.apc@itbhu.ac.in

Monika

Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi Varanasi 221005, Uttar Pradesh, India.

#### G. Udayabhanu

Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad B26004, Jharkhand, India.

### ABSTRACT

Corrosion resistant coatings are a promising solution to protect structural metals in severe corrosive environments. Modified polymer coatings made from PVC polymer are highly attractive due to the blood, cellular compatibility and the ability to work in various environments. This paper is focused on the use of modified PVC and PVC coatings for corrosion protection of mild steel (MS) in 0.5 M sulphuric acid. Their corrosion protection ability was examined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The results of these study clearly reveal that both act as protective coating on mild steel and reduces the corrosion current density effectively. These coatings on metal surface were characterised by Atomic force microscopy (AFM).

Keywords: EIS; AFM; Polymer

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#### INTRODUCTION

The corrosion of iron or mild steel in acidic media has been studied extensively, especially for its industrial relevance. Polymeric (or organic) coatings have been employed to protect metals against corrosion for a long time. The primary effect of a polymeric coating is to function as a physical barrier against aggressive species such as  $O_2$  and H<sup>+</sup>. However, all polymeric coatings are not permanently impenetrable, and once there are defects in the coatings, pathways will be formed for the corrosive species to attack the metallic substrate and localized corrosion will occur. Therefore, as a second line of defence for corrosion, various pigments with a lamellar or plate like shape such as micaceous iron oxide and aluminum flakes have been introduced into the polymeric coating to effectively increase the length of the diffusion pathways for oxygen and water as well as decrease the permeability of the coating [1].

A number of electrochemical measurements have been used as a tool to evaluate the anticorrosion performance of polymeric coatings including conjugated (e.g., polyaniline) or nonconjugated (e.g., polystyrene) polymers. For example, Wei et al. [2] demonstrated the anticorrosive performance of conjugated polyaniline and nonconjugated polystyrene by performing a series of electrochemical measurements of corrosion potential and corrosion current on the sample-coated cold-rolled steel (CRS) under various conditions. Lee and coworkers1 investigated the corrosion-resistance properties of polyaniline-coated mild steel in saline and acid by electrochemical impedance spectroscopy.

In previous work, we reported modification of Poly(vinyl chloride) (PVC) for alteration of its properties and developing its biocompatible forms such as PVC resin with thiosulphate, thiourea and sulphite [3]. The main principle behind the modification of PVC is a nucleophilic substitution reaction that provides an opportunity for the steady replacement of chlorine atoms through substitution with desired atoms or groups without any side reactions, resulting in modification of the surface charges that dominate at the interface between the biomaterial surface and biological environments. The newly synthesized polymer was characterized by examining the thermal stability, surface morphologies, hydrophilicity and antibacterial activity. These were found to be less stable thermally compared to the untreated polymer. The biocompatibility of the polymers was evaluated by assessing their wettability via contact angle measurements and by performing hemolysis and thrombogenicity assays.

In this paper, we present the first evaluation of the anticorrosive effect for PVC, PVC-TS (thiosulphate), PVC-TU (thiourea) and PVC-S (sodium sulphite) in form of coatings on mild steel in 0.5 M sulphuric acid medium by potentiodynamic polarization and electrochemical impedance spectroscopy measurement. Further, the surface morphology of spin coated polymers films were examined by atomic force microscopy (AFM).

#### EXPERIMENTAL

#### Materials and Sample preparation

The used MS samples for all the experiments had 0.253% C, 0.12% Si, 0.013% P, 0.024% S, 0.012% Cr, 0.03% Mn and balance Fe; all by weight. For electrochemical measurements MS substrate were cut into 3 cm × 1 cm × 0.1 cm dimensions, respectively. Exposed surface area of 1 cm<sup>2</sup> was used as working electrode for electrochemical measurements. These substrates were abraded with emery papers ranging from grade size 320 to 2000 and then degreased with acetone, washed with double distilled water and dried in air before immersing in the electrolyte. The corrosive solution, 0.5 M H<sub>2</sub>SO<sub>4</sub> was prepared by dilution of analytical grade H<sub>2</sub>SO<sub>4</sub> of predetermined normality with triple distilled water. The volume of electrolyte used in each experiment was 150 ml.

#### **Preparation of Coatings and Electrochemical Measurements**

PVC and modified PVC polymer were dissolved in THF to give typically 1 wt % solutions for improving the film formation. Coating solutions were applied on the surface with Apex Spin NXG-P1 spin coater with 1500rpm for 2 min to obtain smooth and uniform film. The coated samples were cured at room temperature for twelve hours and heated in a hot air oven at a temperature of 100 °C for 5 min to ensure complete curing [4].

Electrochemical measurements of corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy on sample-coated MS coupons were performed on a Electrochemical Analyser CHI604C model in a three necked corrosion cell equipped with platinum wire as counter electrodes and a silver-silver chloride electrode (3 M KCI) as the reference electrode as well as the working electrode.

The working electrode was vertically immersed in the test solution and open circuit potential (OCP) was evaluated from potential-time curve when potential became virtually constant with respect to time. After this, Tafel plots were obtained by scanning the electrode potential from -250 to +250 mV versus OCP at the rate of 0.5 mV s<sup>-1</sup>. The linear Tafel segments of anodic and cathodic curves were extrapolated till the point of intersection to obtain corrosion potential (*E*<sub>corr</sub>) and corrosion current density (*i*<sub>corr</sub>). The values of  $\eta$  were calculated by using corrosion current densities *i*<sub>corr</sub> and *i*<sup>0</sup><sub>corr</sub> values using in following equation.

$$\eta^{0} = \frac{i_{corr}^{o} - i_{corr}}{i_{corr}^{o}} \times 100 \tag{1}$$

where,  $i_{corr}^{o}$  and  $i_{corr}$  are the corrosion current densities values of uninhibited and inhibited solutions.

EIS measurements were conducted under potentiostatic conditions in the frequency range from 100 kHz to 100 mHz, with an amplitude of 10 mV, using an alternating-current signal at OCP. Zsimpwin software was used to analyze the impedance data. The impedance measurements were started after keeping the electrode dipped in the electrolyte for sufficient time till OCP was attained. The diameter of the semicircle of the Nyquist plot corresponds to the charge transfer resistance ( $R_{ct}$ ).

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$$\eta\% = \frac{R_{ct} - R_{ct}}{R_{ct}} \times 100$$
(2)

where,  $R_{ct}^{\circ}$  and  $R_{ct}$  are the charge transfer resistance values of uninhibited and inhibited solutions.

#### Surface Characterization

A contact mode atomic force microscope (model no. BT 02218, Nanosurf Easyscan 2 Basic AFM, Switzerland) with a Si<sub>3</sub>N<sub>4</sub> cantilever (Nanosensor, CONTR type) having a spring constant of ~ 0.1 Nm<sup>-1</sup> and tip radius more than 10 nm was used to investigate roughness of blank and coated MS surfaces.

#### **RESULTS AND DISCUSSION**

#### Potentiodynamic polarization measurement



# Figure 1. Potentiodynamic polarization curves of bare MS surface, MS surface coated with PVC and modified PVC in 0.5 M $H_2SO_4$ solution.

Figure 1 represents potentiodynamic polarization curve of the bare MS surface, PVC, PVC-TS, PVC-S and PVC-TU coated in 0.5 M sulphuric acid solution. The coating properties such as corrosion potential ( $E_{corr}$ ) and corrosion current densities ( $i_{corr}$ ) were calculated by Tafel extrapolation method and data listed in Table 1. The corrosion current density and corrosion potential of the bare surface was found to be 2397µAcm<sup>-2</sup> and -456mV. Whereas, corrosion current density values of

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coated mild steel sample with PVC, PVC-TS, PVC-S and PVC-TU are 238, 163, 139 and 80 µAcm<sup>-2</sup>, respectively; and corrosion potential are 488, 562, 570 and 586mV, respectively. It is evident from the numerical values of potentiodymanic parameters, that the extent of corrosion process was suppressed largely due to application of coating. From the obtained values it can be understood that among the four coating systems PVC-TU showed the best performance due to the presence of hydrophobic thiol group [5].

Table 1.	Potentiodynamic	polarization	parameters	of	bare	MS	and	polymer	coated	MS
surface and protection efficiency values in 0.5 M H <sub>2</sub> SO <sub>4</sub> solution.										

	Potentiodynamic polarization						
	-E <sub>corr</sub>	İ <sub>corr</sub>	βa	-β <sub>c</sub>	η		
	mV vs. Ag/AgCl	µA cm <sup>-2</sup>	mV dec <sup>-1</sup>	mV dec <sup>-1</sup>	%		
Blank	456	2397	109	150			
PVC	488	238	121	154	90.0		
PVC-TS	562	163	173	188	93.2		
PVC-S	570	139	167	261	94.2		
PVC-TU	586	80	180	157	96.6		

#### Electrochemical Impedance Spectroscopy measurement

Electrochemical impedance spectroscopy is used to investigate the electrochemical interactions at the coating metal interface at a preset potential, usually the open circuit potential. The corrosion behavior of coated and non-coated substrates was studied by electrochemical impedance spectroscopy in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The impedance spectra consist of large capacitive loop at high frequencies followed by a small inductive loop at low frequencies. The high frequency impedance spectra correspond to the protective properties of the polymer coating layer but low frequency range impedance spectra explore the property of the interface layer. On the other hand, the low frequency inductive loop is attributed to the relaxation process caused by adsorption of species like FeSO<sub>4</sub> or inhibitor species on the electrode surface [6]. The charge-transfer resistance ( $R_{ct}$ ) values are listed in Table 2 were calculated from Nyquist plots by taking the difference in impedance at the lower and higher frequencies.

Table 2. Impedance parameters and protection efficiency values of bare MS and polymer coated MS surface in  $0.5 \text{ M H}_2SO_4$  solution.

				EIS				
	$R_{ m s}$ $\Omega~ m cm^2$	$R_{ m ct}$ $\Omega~ m cm^2$	L H cm <sup>2</sup>	$\frac{CPE}{Y_0}$ $\mu \ \Omega \ s^n \ cm^{-2}$	n	Chi square	η %	
Bare MS	2.43	6.02	222	280.0	0.900	0.0192		
PVC	2.42	52.5	151	160.6	0.823	0.0178	88.5	
PVC-TS	12.79	70.0	178	155.0	0.726	0.1009	91.4	
PVC-S	9.48	114.0	153	114.0	0.767	0.0569	94.7	
PVC-TU	19.52	175.4	518	35.0	0.773	0.0988	96.5	



Figure 2. Nyquist plots of bare MS surface, MS surface coated with PVC and modified PVC in  $0.5 \text{ M H}_2\text{SO}_4$  solution.

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where,  $R1 = R_s = Solution Resistance$   $R2 = R_{ct} = Charge Transfer Resistance$   $R3 = R_L = Layer Resistance$  L1 = InductanceQPE1 = CPE = Constant Phase Element

# Figure 3. Equivalent circuit used to fit the EIS data for bare MS surface, MS surface coated with PVC and modified PVC in 0.5 M $H_2SO_4$ solution.

The impedance data obtained above were analyzed using an electrochemical equivalent circuit shown in Figure 3 where,  $R_s$ ,  $R_{ct}$ ,  $R_L$ , *L* and *CPE* stand for solution resistance, charge transfer resistance, layer resistance, inductance and constant phase element, respectively. The term *CPE* has been introduced to replace a double layer capacitance ( $C_{dl}$ ) for more accurate fit [7]. The impedance of the *CPE* is defined as follows:

$$Z_{CPE} = Y_0^{-1} (i\omega)^{-n}$$
(3)

where,  $Y_0$  is a proportionality factor and 'n' has the meaning of phase shift. The value of 'n' represents the deviation from the ideal behavior and it lies between 0 and 1 [8, 9]. The values of R<sub>ct</sub> obtained for coated MS samples are 52.5, 70.0, 114.0 and 175.4  $\Omega$  cm<sup>2</sup> for PVC, PVC-TS, PVC-S and PVC-TU, respectively, which was too high than bare MS 6.0  $\Omega$  cm<sup>2</sup>. From Table 2, it is observed that the CPE values was found to be correspondingly lesser for coated MS than bare MS sample. Whereas, for coated samples, one well defined time constant was observed which can be assigned to the capacitance of polymer coating layer. The impedance results are in good conformation with potentiodynamic polarization results.

#### **Surface Characterization**

Three dimensional morphology and roughness of the PVC and modified PVC coatings on MS surface was assessed by Atomic Force Microscopy (AFM). Roughness of the coatings was determined to analyse the smoothness of surface, which revealed that all coating surfaces were very smooth. Due to the exclusion of three-dimensional clusters or nano sized islands, a decrease in the roughness of bare MS (514.5 nm) surface after coating of polymer on MS surface was measured. The measured roughness values of coatings shown in Figure 4 are 104.2 nm, 67.5 nm, 56.5 nm, and 41.6 nm for PVC, PVC-TS, PVC-S and PVC-TU, respectively. It was inferred from roughness analysis that polymer coated surfaces were comparatively much smoother than uncoated mild steel surface.

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Figure 4. AFM images of bare MS surface, MS surface coated with PVC and modified PVC in 0.5 M  $H_2SO_4$  solution.

#### CONCLUSIONS

The present investigation led to the following conclusions. A simple room temperature process involving the spin coating of polymeric solutions comprising PVC and modified PVC on mild steel resulted an adherable thin protective coating. The surface morphological analysis was indicating the fact that a smooth and crack free surface of the polymer film on mild steel could be achieved by adapting a simple coating methodology. Measured roughness value indicates that the coating surfaces are very smooth. PVC-TU coatings on mild steel were found to be superior in anticorrosion over those of PVC, PVC-TS, PVC-S on the basis of potentiodynamic polarization and electrochemical impedance spectroscopy measurements of corrosion current and impedance parameters in 0.5 M sulphuric acid solution.

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