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Gravimetric and Electrochemical Investigation of the Anticorrosion Performance by Polystyrene Coating on E24 Carbon Steel in Acid Medium

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Abstract- Carbon steel is a well-known material and widely used in various industries. One of its major drawbacks is its corrosion in several middle and especially in acid solutions. In this work, we have studied the performance of polystyrene coating at different concentrations on E24 carbon steel against corrosion, in molar hydrochloric acid solution by gravimetric measurements, potentiodynamic polarization (PDP) and Electrochemical Impedance Spectroscopy (EIS) measurements. The effect of coating concentration, immersion time and temperature was examined. The viscosimetric molecular weight of polystyrene was investigated by measuring the intrinsic viscosity.The experimental results showed that the polystyrene coating acts as an effective anticorrosive coating of E24 carbon steel. The value of the protective efficiency reached 87,7% for 4.38 mmol/l of polystyrene coating with gravimetric tests. The stationary and the transient efficiencies reached 89.20% and 80.8% values respectively. The effect of temperature on the anticorrosion behavior of polystyrene film in the range 298-328 K, indicates that protective efficiency decreases with temperature.

Keywords- Corrosion, Carbon steel, Polystyrene coating, Gravimetric, Electrochemical, Hydrochloric Acid

1. INTRODUCTION

During the last years, many research on corrosion phenomenon find wide applications of nonmetallic and chemically stable materials, particular polymers as a corrosion inhibitor or protective film. Polymers in the form of structural material are used as protective coating to safeguard nonferrous metals and alloy steels used in various industries [1-3].

Polymeric coatings are used as a physical barrier against corrosive species (for example O_2 and H^+) on metal surfaces [4]. Polystyrene is low in oxygen, water vapor and low cost material [5].

Some researchers have successfully applied polystyrene as a protective coating against corrosion using different methods. Polystyrene layers applied by immersion on copper alloys (brass aluminum, copper-nickel 70/30) and 304 stainless steel, reacted as a barrier against corrosion [6]. Two-layer coatings, which contain polyaniline (PANI)/ polymethylmethacrylate (PMMA) and polystyrene as a topcoat on Q235 carbon steel, provide better anodic protection thanks to its special microstructure [7]. Other research has developed anticorrosive bio composites film such as montmorillonite added at different amount 1%, 3%, 5%, 10% and 20% to form protective polystyrene-montmorillonite film on Al 606 aluminum. Those coatings provide better protection against corrosion, even with high clay content [8]. New materials based on polystyrene and ecological clay are an effective way to prevent steel corrosion. Polystyrene-clay (3%) coating on carbon steel has the best anticorrosive properties with 99.94% of protective efficiency [9]. Furthermore, chemically modified polystyrene using succinic acid (SAH), phthalic anhydrides (PhAH) and a cationic catalyst BF_3-$O(C_2H_5)_2$ are used in way to upgrade its anticorrosive properties [7].

To obtain a uniform coating, several deposition techniques are used. A drop casting method has been adopted to apply a polystyrene coating on carbon steel [4] and on aluminum [8] by salvation. The sputtering technique was employed to deposit the polystyrene film on an aluminum substrate [10]. Then, we find the electrospinning technique followed by spin coating used to applicate the bilayer film on carbon steel Q235 [11].

In this study, the anticorrosive behavior of polystyrene coating deposed on E24 carbon steel in 1M hydrochloric solution was examined. In this regard, polystyrene films were prepared with various concentrations of polystyrene (2.19, 2.92, 3.65, 4.38 mmol/l). The protective efficiency was determined using gravimetric and electrochemical measurements in various conditions of immersion time (24, 72 and 120 h) and temperature (298, 308, 318, and 328 K). The viscosimetric molecular weight of polystyrene were carry out with measuring the intrinsic viscosity.

2. EXPERIMENTAL

2.1. Materials and reagents

The polystyrene coating was obtained by salvation of industrial polystyrene MC3500 from VALTRA in Toluene reagent (analytical grade). The polystyrene concentration range employed for was 2.19, 2.92, 3.65, 4.38 mmol/l. The solutions of Polystyrene was stirred for 1 h. Corrosive solution 1 M hydrochloric acid was prepared by dilution of an analytical grade of 37% hydrochloric acid with bi-distilled water.

2.2. Determination of the viscosimetric molecular weight of polystyrene

The intrinsic viscosity is commonly used in several polymer industries for estimation of the molecular weight MW of certain polymers. A viscosity profile of polystyrene coating solutions was measured at various concentrations 2.19, 2.92, 3.65, 4.38 mmol/l by using the Selecta STS 2011 Viscosimeter. The shear viscosities of the polystyrene coating solutions were measured at room temperature with a cylindrical spindle (L2) at viscometer speed of 200 rpm.

Once the intrinsic viscosity is known, the viscosimetric molecular weight MW of the polymer can be obtained using the Mark-Houwink-Sakurada equation (1).

$$[\eta] = K\, M_w^{\alpha} \quad (1)$$

where K and α are two parameters that depend on the solvent, polymer, and temperature reported in the literature [12].

The intrinsic viscosity [η] can be obtained using the Kraemer–Huggins plot by computing the relative viscosity ηr and the specific viscosity ηs from the viscosity measured for different polystyrene concentrations solutions, using the following equations (2-3) [12].

$$\eta_r = \frac{\eta}{\eta_{sol}} \quad (2)$$

$$\eta_{sp} = \eta_r - 1 \quad (3)$$

η_{sol} is the solvent viscosity.

2.3. Substrate Preparation

E24 carbon steel used had the chemical composition of 0.17% C, 1.4% Mn, 0.045% P, 0.045% S, 0.009% N and the remainder ion Fe. The E24 Steel specimens (20 mm×20 mm×2 mm) were used for gravimetric measurements. Before each experiment samples were ground with emery papers (400, 600 and 1200) gradually, ultrasonically cleaned in acetone, ethanol and bi-distilled water for 10 min, respectively.

2.4. Corrosion weight loss tests

The initial weight of each specimen was noted before immersion using an analytical balance (precision±0.1 mg), then the specimens were immersed in 1 M hydrochloric acid solution without and with different concentration of polystyrene coating. After 24 h, 72h and 120 h of immersion at room temperature and after 2 h of immersion at 298 K, 308 K, 318 K and 328 K, the specimens were washed, dried and reweighed. In order to get good reproducibility, experiments were carried out in triplicate. The influence of coating concentration, temperature and immersion time were valued by various parameters [13].

The corrosion rate W_{corr} (mg/cm2 h), the protective efficiency %E and the recovery rate θ were calculated using Eq (4), (5) and (6) respectively.

$$W_{corr} = \frac{m_b - m_a}{S \times t} \quad (4)$$

$$\%E = \left(1 - \frac{W_{corr}}{W^0_{corr}}\right) \times 100 \quad (5)$$

$$\theta = \frac{E}{100} \quad (6)$$

where mb, ma S, t, W_{corr} and W^0_{corr} are mass of the specimens before immersion and mass of the specimens after immersion, exposed surface area of E24 steel specimens, immersion time, corrosion rate of uncoated E24 steel and corrosion rate of coated of E24 steel, respectively.

2.5. Electrochemical measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with: E24 steel specimens as the working electrode with an exposed area of 2 cm^2, a platinum auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The corrosive medium was 1 M HCl and the temperature was maintained at 298 K using a water bath. The scanning speed was 1 mV/s. The determination of the electrochemical parameters (i_{corr}, E_{corr}, βc and βa) from the polarization curves is done using a nonlinear regression. The protective efficiency EI% was evaluated from the measured i_{corr} values using the relationship (7) [14].

$$EI\% = \frac{i^0_{corr} - i^i_{corr}}{i^0_{corr}} \times 100 \quad (7)$$

where, i°_{corr} and i^i_{corr} are the corrosion current density in absence and presence of polystyrene coating, respectively.

The electrochemical impedance spectroscopy were made in Nyquist mode with a signal amplitude (10 mV). The explored frequency range varied from 100 kHz to 10 mHz. Protective efficiency η was calculated using equation (8).

$$\eta = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \quad (8)$$

R°_{ct} and R_{ct} are the transfer charge resistances in the absence and in the presence of different polystyrene coating concentration, respectively.

3. RESULTS AND DISCUSSION

3.1. Intrinsic molecular weight determination of PS

Many measurements have been made for the viscosity of different concentrations of polystyrene in toluene solutions. Using Eq (1) and taking (α=0.72 and k=2.27×10^4) [15]. The intrinsic molecular weight for polystyrene was found in the average of 41 073 g/mol.

3.2. Weight loss measurements

3.2.1. Effect of concentration

The effect of polystyrene concentration on the protective efficiency of polystyrene coating was studied for E24 carbon steel without and with coating by gravimetric measurements, at different concentrations after 24 h of immersion and at room temperature. The corrosion parameters including W_{corr}, %E and θ are presented in

Table **1**. It is clear from the results that the application of the polystyrene coating causes a decrease of the corrosion rate. The increase in polystyrene concentration is accompanied by a decrease in corrosion rate, this decrease is important even at low coating concentration (2.19 mmol/l). The polystyrene coating was able to reduce the corrosion rate to almost four times its initial value.

Table 1. Effect of polystyrene concentration on the corrosion parameters of E24 carbon steel in 1 M HCl solution

Coating polymer	concentration (mmol/l)	W_{corr} (mg/cm^{2}h)	E%	θ
Polystyrene	**Blank**	0.69		
	2.19	0.31	54.5	0.545
	2.92	0.29	57.5	0.575
	3.65	0.19	72.8	0.728
	4.38	0.08	87.7	0.877

An increase of the protective efficiency and the recovery rate is observed with the increase in the concentration of polystyrene. The protective efficiency reaches his maximum value of 87.7% for a concentration of 4.38 mmol/l of polystyrene according to Fig. 1. The 4.38 mmol/l polystyrene coating was chosen as an optimal concentration based on their protective efficiency.

Generally, steel corrosion is defined by two processes, the dissolution of the metal and the formation of iron oxides as indicated in equations (9-11).

$$Fe \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (9)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (10)$$

$$2Fe + O_2 + 2H_2O \rightarrow 2FeO_2H + 2H^+_{(aq)} \quad (11)$$

These reactions are initiated by the increase in the rate of H_2O and O_2 molecules in the environment that diffuse onto the surface of the coating. In the presence of Cl^- ions, the substitution of water molecules on the surface of the carbon steel by Cl^- ions lead to the probability of rapid rusting of the surface of the carbon steel. If one of these processes is prevented, corrosion is inhibited and the coating becomes effective for corrosion prevention [14,15].

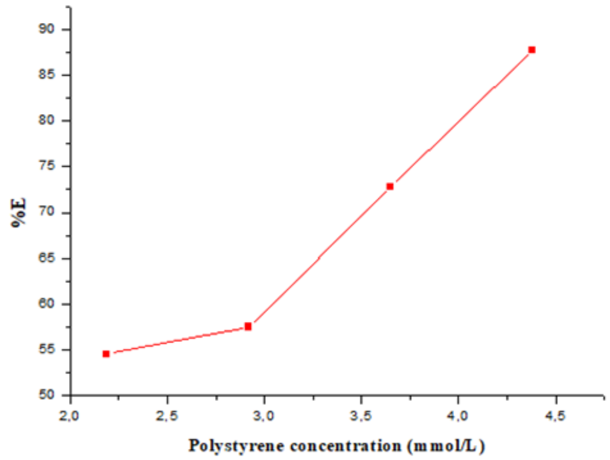

Fig. 1. Variation of protective efficiency with polystyrene concentration for 24 h

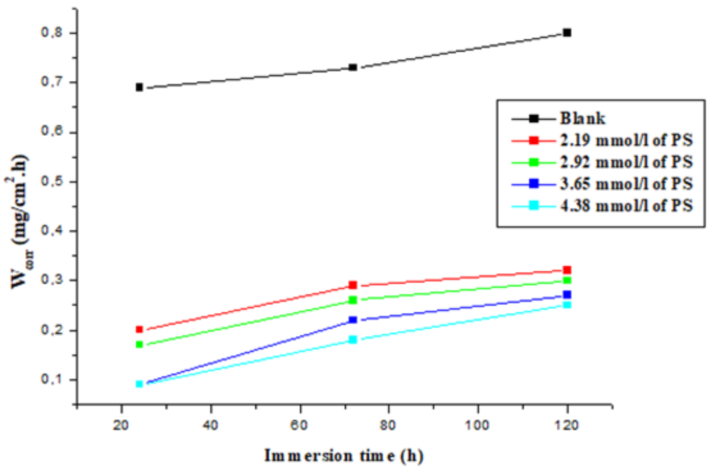

Fig. 2. Variation of corrosion rate with immersion time for different polystyrene concentration

3.2.2. Effect of immersion time

The variation of corrosion rate with immersion time 24, 72 and 120 h at room temperature in 1 M hydrochloric acid solution is shown in Fig. 2.

The study of those curves shows that the corrosion rate increases slightly with the increasing of the immersion time for different polystyrene concentration, which implied a decrease of the protective efficiency of polystyrene coating. It can be seen that for the 4.38 mmol/l of polystyrene coating, the average corrosion rate during various immersion times decreased by 31% compared to uncoated steel. This is caused by the continuous dissolution of the metal in the corrosive environment.

3.2.3. Effect of temperature

To evaluate the effect of temperature on the corrosion behavior of E24 carbon steel without and with polystyrene coating in 1 M hydrochloric acid, the gravimetric measurements were carried out in the temperature range of 298 K-328 K.

Table **2** shows the effect of temperature on the corrosion parameters of specimens with and without 4.38 mmol/l of polystyrene coating after 2 h of immersion.

Table 2. Parameters corrosion of E24 carbon steel with 4.38 mmol/l of PS coating in different temperature

T(K)	**W_{corr} (mg/cm^2 h)**	**E%**	**θ**
298	0.35	77.6	0.776
308	0.48	73.1	0.731
318	1.12	64.6	0.646
328	2.35	59.5	0.595

As detected from Table 2, the protective efficiency decreases with increasing of the temperature in 1 M hydrochloric acid. This behavior suggests that the polystyrene coating was desorbed at a higher temperature, which allows us to conclude that the temperature factor disadvantage the protection of corrosion.

3.3. Polarization behavior

Fig. 3 shows the potentiodynamic polarization curves that represent the protective effect of E24 carbon steel in 1 M HCl environment by different concentration of PS coating.

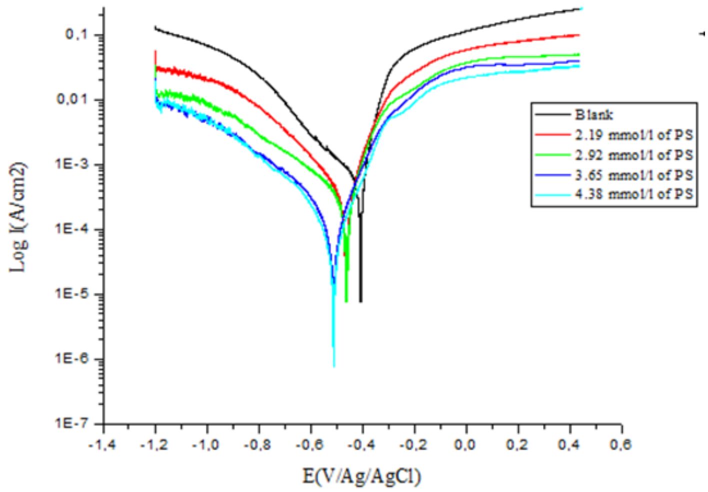

Fig. 2. Polarization curves of carbon steel in 1 M HCl in the absence and the presence of different concentrations of PS coating at 298 K

From Table 3, the stationary polarization curves showed that the application of the polystyrene coating causes a displacement of the potential to higher negative values and a significant decrease in current density in the cathodic and anodic domains, this allowed us to conclude that the polystyrene coating acts as a mixed protective coating [18].

Table 3. Electrochemical parameters obtained from the polarization curves

Coating polymer	**concentration (mmol/l)**	**-E_{corr} (mV/Ag/AgCl)**	**i_{corr} ($\mu A/cm^2$)**	**β_a (mV/dec)**	**β_c (mV/dec)**	**EI%**
Polystyrene	Blank	405.5	2298	62.0	279.0	
	2.19	461.3	1444.8	100.7	237.2	37.1
	2.92	459.5	855.1	82.2	277.1	62.8
	3.65	510.5	361.2	110.3	174.0	84.3
	4.38	510.7	248.1	115.4	154.4	89.2

The protective mechanism of carbon steel corrosion by the polystyrene coating can be explained by the diffusion of corrosive species (OH^- and Cl^-) through the protective film. In the case of the 9% polystyrene film, it is found that the corrosion of carbon steel is primary in view of i_{corr}=1444.8 $\mu A/cm^2$ and EI%=37.1%, the diffusion of corrosion species is slowed down by the increase in the concentration of PS and the protective efficiency has reached 89.2% with the 4.38 mmol/l polystyrene coating [19,20]. Additionally, the decrease of corrosion current density implies the increase of protective efficiency.

3.4. Electrochemical impedance spectroscopy (EIS)

The electrochemical characterization of the protective organic coating is usually performed by Electrochemical Impedance Spectroscopy (EIS). Fig. 4 present the Nyquist plots for E24 steel specimens coated with different concentration of polystyrene. The curves reveals clearly one capacitive loop at hight to low frequencies for all polystyrene concentration coating, all the samples exhibited the same behavior, which could be attributed to a single charge transfer [21]. The diameters of the semicircles for the coated E24 specimens increases with increasing of polystyrene concentration, this behavior indicates that the charge transfer phenomenon reported or slow down due to the adsorption of polystyrene film at the interface of metal-electrolyte which results in an increase in corrosion resistance [22], The depression in the semicircles indicated a frequency depression that have been attributed to roughness and in himogeneities of solid surface [23]. A simplified Randles equivalent circuit in Fig. 4 consists of a parallel combination of a charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}), both in series with solution resistance (R_s) was used for fitting Nyquiest plots [24]. Excellent fit are obtained for all the samples, as an example, the Nyquist plot for the 2.92 mmol/l of polystyrene coating are presented in Fig. 4. The parameter values obtained for all protective coating are summarized in Table 4.

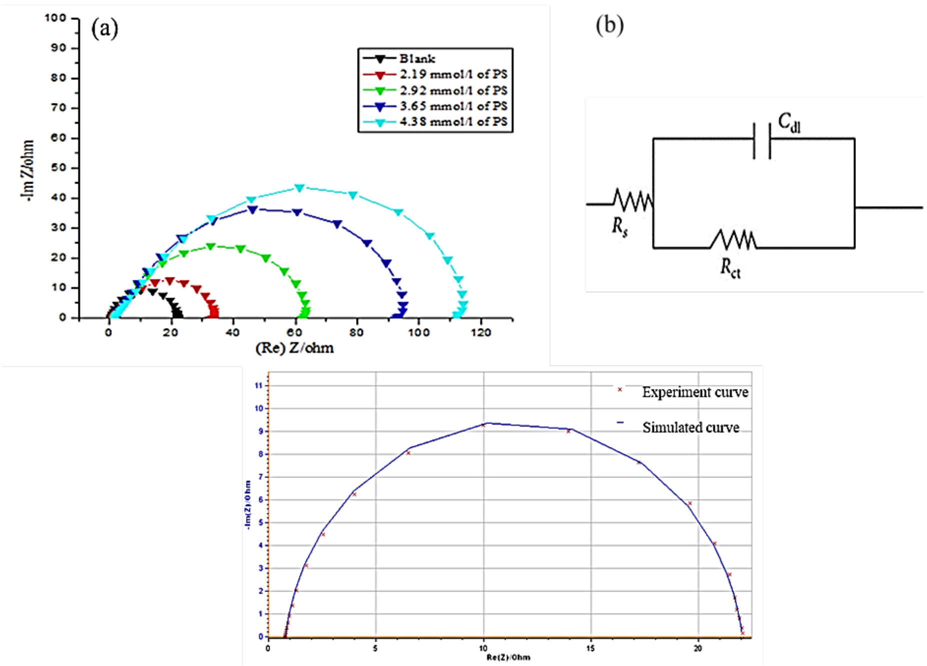

Fig. 4. (a) Nyquist plots of E24 steel in 1 M HCl with different concentrations of PS coating; (b) Electrical circuit equivalent to the metal/PS/HCl interface and (c) Nyquiest plot fitted using the electrical circuit

Table 4. Electrochemical impedance parameters for E24 steel in 1 M HCl solution with various concentrations of PS coating at 298 K

Coating polymer	concentration (mmol/l)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	a	C_{dl} (μF cm^{-2})	η
Polystyrene	Blank	0.79	21.28	0.92	771	
	2.19	1.39	31.1	0.76	751	**31.57**
	2.92	2.03	63.36	0.75	485	**66.41**
	3.65	2.29	93.61	0.79	272	**77.26**
	4.38	3.13	111.6	0.81	179	**80.93**

We observe from Table 4, that the charge transfer resistance values of samples increases when the concentration of the polystyrene coating increases, this indicated that the increase in polystyrene film charge transfer resistances. charge transfer resistance leads to the best protection of the metal [16]. The protective efficiency reaches a value of 80.8% with 4.38 mmol/l of polystyrene coating. This behaviour is due to a limited barrier effect due to the presence of micropores and deformations in the coating, and/or poor adhesion between the coating and the metal substrate which can lead to delaminating areas in the coating, particularly at the frontier. The resultant low adherence generates a slight increase in the resistance values to charge transfer. This behavior confirms the results obtained by the potentiodynamic polarization curves. The polystyrene film provides a high protective efficiency by increasing concentration [25].

4. CONCLUSION

Polystyrene coating acts as an effective protective film for corrosion of E24 carbon steel in 1 M of hydrochloric acid solution. From the experimental results, it can be concluded that the increase of polystyrene concentration is accompanied by an increase of the protective resistance. The increase in temperature and immersion time results with a low increase in the corrosion rate. The protective efficiency trend of polystyrene coating obtained from gravimetric, electrochemical studies are in good agreement. The maximum protective efficiency was given by 4.38 mmol/l of polystyrene concentration coating. These results, combined with the availability and low cost, show that polystyrene convenient protective coating against corrosion.

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