Steel Corrosion Protection by Polymer Coatings.

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ABSTRACT   *The polyaniline, and ploy-N,N- dimethylaniline were chemically prepared in different solvents and deposited on a steel surface by cyclic voltammetric technique with different cycles. The tests for corrosion protection of the polymers coated and uncoated steel were investigated in 0.3 M NaCl solution by using Tafel polarization measurements. The experiments data showed, the studied polymers coating have ability to protect the steel against corrosion. Some factors, number of cycles of polymer preparation, solvent of polymer preparation, and the polymer type effect on the corrosion parameters, ícorr. (corrosion current), I.E.% (inhibition efficiency), and P (porosity) of the polymers coated steel in 0.3M NaCl solution. The all experiments were investigated at 30 0C.*

KEYWORDS : Corrosion protection; corr. resistant coatings; steel; electrodeposited film.

Introduction

Corrosion is a problem of great economic importance to industry. Corrosion protection is often afforded by isolating metals from the corrosive environment using polymer coatings. Practicals applications of conductive polymers have received considerable interest as corrosion protective coating on oxidizable metals in the most recent times [1-4]. This because these polymers are chemically stable, environmentally viable, and have good corrosion resistance [5]. Polyaniline is known as the most important inherently conducting polymer. Its excellent stability to air oxidation [6], controllable electrical conductivity [7], and simplicity of preparation from cheap materials make it superior to other conductivity polymers.

In our present work, we investigated the corrosion protection of polyaniline and ploy-N,N-dimethylaniline coatings steel in 0.3M NaCl aqueous solution. We studied also the effects of the polymers coating steel prepared under some conditions, such as the number of polymer film cycles formed by cyclic voltammetry, and different solvents of polymers preparation. This because these conditions exhibit influence on the properties of the coating polymer and, hence, effects on the steel corrosion protection.

Experimental
Material and Sample Preparation:

The steel working electrode is a disk with surface area 0.452 Cm^2. The steel (C; 0.06%, Si; 0.53%, Mn; 1.12%, S; 0.009%, Pb; 0.025%,Cu; 0.298%, Al; 0.026%, Ni; 7.78%, Cr; 18.09%, V; 0.095%, Mo; 0.137%) was cut as a cylindrical rode, and mounted into glass tube of appropriate diameter with epoxy resin. The disk surface was polished prior to any experiment with 600 grit SiC paper, rinsed with distilled water and polished with acetone- saturated paper towel to remove any grease and produce a relatively scratch free, smooth, shiny surface[8].

The Electrolyte Media:

All chemicals were of analytical grade. Bi-distilled water was used to prepare all solution, 0.1M aniline in 0.5M of HCl, HNO_3, and oxalic acids. We prepared also another solutions, 0.1M of N.N-dimethylaniline in the previous solvents of the same concentrations. The experiments were carried out at 30°C in all the tested electrolytes.

The Electrolytic Cell and Measured Potentials:

A conventional three- electrodes/ one- compartment glass cell consisting of a steel disk, a platinum wire, and Ag/AgCl electrode, were used as working, counter, and reference electrode respectively. The all potentials measured with respects to Ag/AgCl reference electrode.

Synthesis of Polymer Coating on Steel:

The polymers coatings were deposited on the steel by cyclic voltammetric technique, in solutions 0.1 M monomers in 0.5M of HCl, HNO_3, and oxalic acids using a potentiostat model PGZ100 from voltalab-Radiometer analytical with software Model Voltamaster 4 version (7.09). Some conditions affecting electrochemical polymerization such as number of cycles, electrolyte compositions, and monomer type were written in tables (1-8) to exhibit influence on the properties of the polymer coating.

Corrosion Experiments:

The potentiostatic polarization experiments (E-mV versus í-μA) were carried out for uncoated and polymer coated steel in aggressive medium of 0.3M NaCl aqueous solution.

Results and Discussion:

Figure (1) displays the variation of applied potentials (E-mV) versus logarithm current (í-μA) of uncoated steel in aggressive medium of 0.3 M NaCl aqueous solution. Similar curves of figures (2-4) are obtained for coated steels by polyaniline film, formed by cyclic voltammetry of 10 cycles of 0.1 M aniline in 0.5M of different solvents, in aggressive medium of 0.3M NaCl solution. Others curves are obtained for coated steels by polyaniline films, formed by cyclic voltammetry of different cycles in 0.5M of oxalic and HNO_3 acids, in the same concentration of the aggressive medium (not shown). In like manner, similar curves are obtained for coated steel by poly-N,N-dimethylaniline films(not shown). The all curves related to the following Tafel equation (1),

$$\eta = a + b \log í \quad \text{.....................................(1)}$$

Where , η is the over-voltage; more positive and negative potentials with respect to the free corrosion potential (E_{corr}.), a is the intercept of Tafel line with the applied potential, b is the anodic and cathodic Tafel slope depends on the polarization values with respect to E_{corr}, Tafel constants (β_a, β_c). The anodic (β_a) and cathodic (β_c) Tafel slopes were calculated from the all figures. The values of E_{corr} and i_{corr} determined by the extrapolation of the linear portions of the anodic and cathodic Tafel curves of coated and uncoated steel. A polarization resistance (R_p) for the polymer coated steel could be estimated by the expression(2) [9],

$$R_p = \beta / í_{corr} \quad \text{.....................................(2)}$$

Where, $\beta = \beta_a \beta_c / 2.303 (\beta_a + \beta_c)$

The corrosion inhibition efficiency (I.E.%) was evaluated from the measured $í_{corr}$ values obtained from tafel polarization method using

the following relationship (3)[10],

$$I.E\% = \left(\frac{I_{corr} - I_{corr-}}{I_{corr}}\right) \times 100 \quad \dots\dots\dots(3)$$

Where icorr. and icorr-. are the corrosion current density without and with coated polymer. The porosity in the coating is very important parameter to determine whether a coating is suitable or not to protect the substrate against corrosion. In order to calculate the porosity of the polymer, we have used the following relationship (4) [11],

$$P = \frac{R_p \, (uncoated)}{R_p \, (coated)} \times 10^{\Delta E_{corr}/\beta_a} \quad \dots\dots\dots\dots(4)$$

Where P is the total porosity, (uncoated) and Rp (coated) denote the polarization resistance for uncoated and coated steel, respectively. Δ Ecorr. is the difference between corrosion potentials of coated and uncoated steel by volt and β_a is the anodic Tafel slope for uncoated steel substrate.

The all parameters of, Ecorr, icorr, β_a, β_c, β, R_p, I.E.% and P obtained from Tafel curves of the all figures were listed in tables (1-8).

Table (1, 2) display the effect of polyaniline coating thickness, formed by cyclic voltammetry of different cycles of 0.1M aniline in 0.5M of oxalic and HNO$_3$ acids, on steel corrosion resistance in 0.3M NaCl aqueous solution.

It is essential to note that the polyaniline coating thickness and the I.E.% of polyaniline increase with increasing the number of cycles of polyaniline preparation. There is a good correlation between porosity and thickness of the coating polymer, it shows that the porosity in the coating decreases with increasing in thickness of the polyaniline coating. The lower values of the porosity in polyaniline coatings permit an improvement of the I.E.% of polyaniline coating against steel corrosion by hindering the access of the corrosive chloride ions to the steel substrates[11]. It is essential to note that the corrosion current (values of coating steel were found to be lower than uncoated steel and also decrease with increasing the number of cycles of polyaniline preparation (enhancement of polyaniline thickness). This case was simply related to physical barrier behavior of polyaniline coating between the corrosive environment and underlying steel [12], and also due to improvement its inhibition properties against corrosion respectively. The results of tables (1, 2) clear that the polyaniline coating steel prepared in HNO$_3$ is more protective against corrosion in 0.3M NaCl solution than which prepared in oxalic acid at the all different cycles of preparation.

Tables (3,4) display P, I.E.%, and values of polyaniline and poly-N, N-dimethylaniline coating steel in 0.3M NaCl solution, the polymers coating prepared by cyclic voltammetry of 0.1M of aniline and N-N-dimethylaniline in 0.5M of different solvents, HCl, HNO$_3$, and oxalic acids. The porosity of polymers coating and the corrosion current values of polymers coating steel decrease due to the type of solvents of polymers preparation in the order of oxalic, HCl, and HNO$_3$ acids. On the other hand the inhibition efficiency values increase in the same order of solvents preparation. It is essential to note that porosity, inhibition efficiency, and the corrosion current of coating steel depend on the electrolyte type [13] of polymer preparation. This confirms to us that the type of solvent of polymer preparation is prerequisite to effect on the properties of the coating polymer. These results mean that the polyaniline and poly-N,N-dimethylaniline coating steel prepared by cyclic Voltammetric technique in HNO$_3$ is more protective barrier between steel and NaCl aggressive medium than which prepared in the other solvents. This may be to the packing efficiency of the polyaniline and the poly-N,N-dimethylaniline coating steel prepared in HNO$_3$ is the greatest than which prepared in the other solvents.

Tables (5,6) reveal the effect of poly-N,N-dimethylaniline coating thickness, formed by cyclic voltammetry of different cycles of 0.1M N,N-dimethylaniline in 0.5M of oxalic and HNO$_3$ acids respectively, on the values of corrosion parameters of the tested steel in 0.3M NaCl aqueous solution.

The results clear that the corrosion parameters, P , I.E.% and icorr. of poly-N,N-dimethylanline behave the same trend of the corrosion parameters of polyaniline coating steel with respect to the number of cycles of polymer preparation. The corrosion parameters in tables (5,6) clear also that the poly-N,N-dimethylaniline coating steel prepared in HNO$_3$ is more corrosion protection than which prepared in oxalic acid at the all different cycles of preparation.

Tables (7,8) display the corrosion parameters, P, I.E.% and icorr. of coated steel by difference polymers (polyaniline and poly-N,N-dimethylaniline) prepared by cyclic voltammetry of 10 cycles of 0.1M of corresponding monomer in 0.5M oxalic and nitric acid, in 0.3M NaCl solution.

The data show that the corrosion parameters of polymers coating depend on the polymer category and the solvent of polymer preparation under the same condition of electropolymerization. This may be to the adhesion differences of polymers to steel surface. The porosity values of polymers coating steel decrease in the order polyaniline and poly-N,N-dimethylaniline which prepared in the same solvent. It is essential to note that the porosity values of prepared polymers, depend also on the type of solvent of polymer preparation; decrease in the order oxalic and nitric acid. This case was simply related to the packing efficiency of each polymer, which depends on the size of monomer unit in polymer chain and on the physical properties of the polymer preparation.

It is essential also to note that the I.E.% and icorr. values of polymer coating steel increase and decrease, in the order of polyaniline and poly-N,N-dimethylaniline due to the type of solvent of polymer preparation in the order of oxalic and nitric acid. This is due to the difference of the porosity values of polymer coating steel, which associated with the polymer type and the solvent of polymer preparation. The lower values of porosity of polymer coating steel increase the inhibition efficiency and, hence, decrease the corrosion current by hindering the access of the chloride ions to attack the steel surface [11].

Conclusions:
The following conclusions can be drawn from this work:
1- The corrosion resistance of polymer coatings steel was higher than of uncoating steel.
2- There is a good correlation between the porosity (p) values of polymer coatings steel and the degree of corrosivities. High porosity show high corrosion current, however low porosity tend to retard corrosive action of chloride ions.
3- The corrosion parameters, i_{o}, I.E.%, and P of polymers coating steel in 0.3M NaCl solution depend on, number of cycles of polymer preparation, solvent of polymer preparation, and polymer type.
4- Our observed experimental results reveal the inhibition efficiency of the poly-N,N-dimethylaniline coating steel of different solvent preparation is more corrosion protective than the polyaniline coating steel at the same conditions.
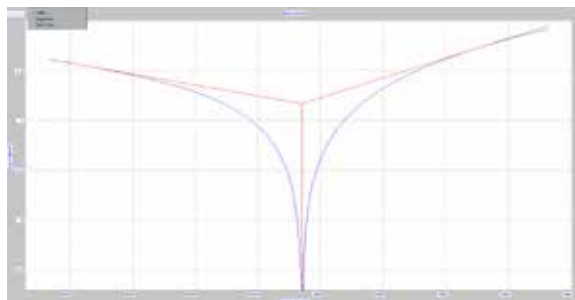

Fig (1): Tafel plot of potential (E - mV) versus log current (í - μA) of uncoated steel in aggressive medium of 0.3M NaCl aqueous solution.

Fig (2):Tafel plot of potential (E - mV) versus log current (i - μA) of coated steel by polyaniline film, formed by cyclic voltammetry of 10 cycles of 0.1M aniline in 0.5M oxalic acid, in aggressive medium of 0.3M NaCl aqueous solution.

Fig (3):Tafel plot of potential (E - mV) versus log current (i - μA) of coated steel by polyaniline film, formed by cyclic voltammetry of 10 cycles of 0.1M aniline in 0.5M HCl acid, in aggressive medium of 0.3M NaCl aqueous solution.
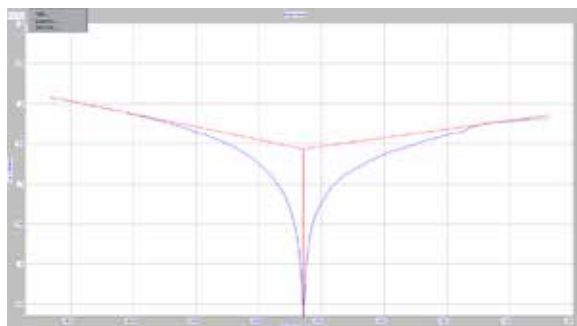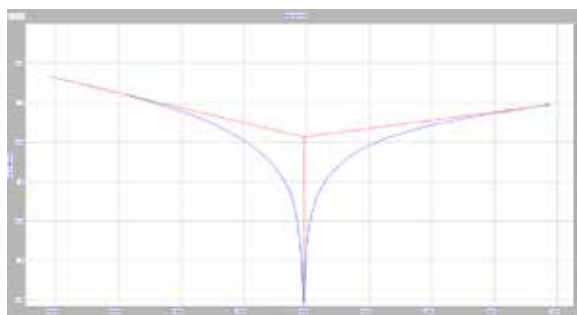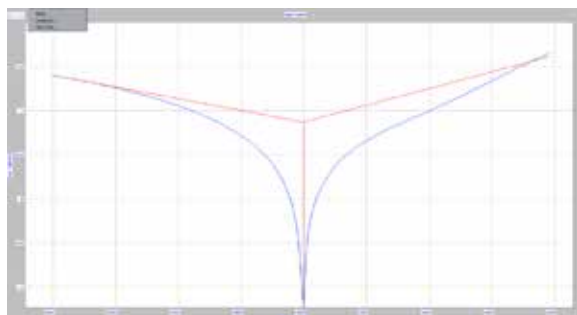

Fig (4):Tafel plot of potential (E - mV) versus log current (i - μA) of coated steel by polyaniline film, formed by cyclic voltammetry of 10 cycles of 0.1M aniline in 0.5M HNO$_3$ acid, in aggressive medium of 0.3M NaCl aqueous solution.

Number of cycles of polyaniline Preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.45555	0.07051993	14.7869	4.77	-0.465	---	---
5 cycles	0.2299	-0.3993	0.063051314	13.1402	4.82	-0.235	11.1%	8.06%
10 cycles	0.5875	-0.3734	0.099131129	10.3946	9.54	-0.279	29.7%	2.96%
15 cycles	0.2883	-0.2508	0.058238328	8.3124	7.01	-0.320	43.8%	2.55%
20 cycles	0.3811	-0.3086	0.074042437	7.4734	10.32	-0.370	81.5%	1.73%

Table (1): Corrosion parameters of uncoated and coated steel by polyaniline film, formed by cyclic voltammetry of different cycles of 0.1M aniline in 0.5M oxalic acid, in aggressive medium of 0.3M NaCl aqueous solution

Number of cycles of polyaniline Preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.45555	0.07051993	14.7869	4.77	-0.465	---	---
5 cycles	0.8736	-0.2811	0.09234436	10.0047	9.23	-0.278	32.34%	2.6%
10 cycles	0.2597	-0.3759	0.066669088	7.4829	8.91	-0.355	49.4%	1.46%
15 cycles	0.2303	-0.3514	0.86040915	3.7484	16.12	-0.399	74.65%	0.54%
20 cycles	0.3242	-0.2015	0.05395804	2.9863	18.07	-0.426	79.8%	0.38%

Table (2): Corrosion parameters of uncoated and coated steel by polyaniline film, formed by cyclic voltammetry of different cycles of 0.1M aniline in 0.5M nitric acid, in aggressive medium of 0.3M NaCl aqueous solution.

Solvent of polyaniline preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.4555	0.070519934	14.7869	4.77	-0.465	---	---
0.5M HCl	0.1833	-0.2979	0.04927349	8.2261	5.99	-0.370	44.4%	1.89%
0.5M HNO₃	0.2897	-0.3759	0.066669088	7.4829	8.91	-0.401	49.4%	0.96%
0.5M oxalic acid	0.5875	-0.3734	0.099131129	10.3946	9.54	-0.270	29.7%	2.96%

Table (3): Corrosion parameters of uncoated and coated steel by polyaniline film, formed by cyclic voltammetry of 10 cycles of 0.1M aniline in 0.5M of different solvents, in aggressive medium of 0.3M NaCl aqueous solution.

Solvent of poly-N,N-dimethylaniline preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.4555	0.070519934	14.7869	4.77	-0.465	---	---
0.5M HCl	0.3477	-0.2708	0.066102777	6.9203	9.55	-0.345	53.2%	1.49%
0.5M HNO₃	0.5872	-0.2848	0.083275189	2.9766	27.98	-0.427	79.9%	0.24%
0.5M oxalic acid	0.3719	-0.2616	0.066684263	7.8048	8.54	-0.522	47.2%	2.06%

Table (4): Corrosion parameters of uncoated and coated steel by poly-N,N-dimethylaniline film, formed by cyclic voltammetry of 10 cycles of 0.1M N,N- dimethylaniline in 0.5M of different solvents, in aggressive medium of 0.3M NaCl aqueous solution.

Number of cycles of poly-N,N-dimethylaniline Preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% Of polymer coating	P Of polymer coating
Uncoated steel	0.2524	-0.4555	0.070519934	14.7869	4.77	-0.465	---	---
5 cycles	0.5546	-0.3541	0.093840718	9.2462	10.15	-0.241	37.5%	3.62%
10 cycles	0.3719	-0.2616	0.066684263	7.8048	8.54	-0.322	47.2%	2.06%
15 cycles	0.5161	-0.2488	0.060451817	5.7443	10.52	-0.395	61.2%	1.29%
20 cycles	0.22318	-0.2680	0.103894095	4.7147	11.2	-0.446	68.1%	0.55%

Table (5): Corrosion parameters of uncoated and coated steel by poly-N,N-dimethylaniline film, formed by cyclic voltammetry of different cycles of 0.1M N,N- dimethylaniline in 0.5M oxalic acid, in aggressive medium of 0.3M NaCl aqueous solution.

Number of cycles of poly-N,N-dimethylaniline Preparation	β_a V/decade	β_c V/decade	β Volt	i_{corr} µA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.45555	0.07051993	14.7869	4.77	-0.465	---	---
5 cycles	11.8277	-0.2514	0.106889995	5.9878	17.85	-0.380	59.51%	0.58%
10 cycles	0.5872	-0.2848	0.08327519	2.9766	27.98	-0.427	79.87%	0.24%
15 cycles	0.6405	-0.2663	0.08167419	2.5684	31.80	-0.439	82.63%	0.19%
20 cycles	0.4867	-0.233	0.068418228	1.2320	55.53	-0.453	91.67%	0.10%

Table (6): Corrosion parameters of uncoated and coated steel by poly-N,N-dimethylaniline film, formed by cyclic voltammetry of different cycles of 0.1M N,N- dimethylaniline in 0.5M nitric acid, in aggressive medium of 0.3M NaCl aqueous solution.

Type of coating polymer	β_a V/decade	β_c V/decade	β Volt	I_{corr} μA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.4555	0.070519934	14.7869	4.77	-0.465	---	---
Poly aniline coated steel	0.5875	-0.3734	0.099131129	10.3946	9.54	-0.279	29.7%	2.96%
poly-N,N-dimethylaniline coated steel	0.3719	-0.2616	0.066684263	7.8048	8.54	-0.322	47.2%	2.06%

Table (7): Corrosion parameters of uncoated and coated steel by difference type of polymer film, formed by cyclic voltammetry of 10 cycles of 0.1M corresponding monomer in 0.5M oxalic acid, in aggressive medium of 0.3M NaCl aqueous solution.

Type of coating polymer	β_a V/decade	β_c V/decade	β Volt	I_{corr} μA/cm²	R_p KΩ/cm²	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated steel	0.2524	-0.4555	0.070519934	14.7869	4.77	-0.465	---	---
Poly aniline coated steel	0.2597	-0.3759	0.0666/9008	7.4829	8.51	-0.481	49.4%	0.96%
poly-N,N-dimethylaniline coated steel	0.5872	-0.2848	0.08327589	2.9766	27.98	-0.427	79.9%	0.24%

Table (8): Corrosion parameters of uncoated and coated steel by difference type of polymer film, formed by cyclic voltammetry of 10 cycles of 0.1M corresponding monomer in 0.5M nitric acid, in aggressive medium of 0.3M NaCl aqueous solution.

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