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Corrosion Protection of Steel Panels by Commercial Primer Modified with Polyaniline and Cashew Nut Shell Liquid

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Abstract: The electrochemical behavior of primers modified with polyaniline (PANI) and Cashew Nut Shell Liquid (CNSL) was evaluated by using Tafel polarization curves and Electrochemical Impedance Spectroscopy (EIS) in 0.1 M HCl solution. The measurements carried out suggest that primer modified with combined PANI and CNSL mixture were a good corrosion inhibitor. The high concentrations (5%) in both modifier was capable corrosion inhibitor with highest inhibition efficiency, however, the mixture of these was more efficient. This results were reasonably agreement by measurements obtained with Tafel polarization curves and electrochemical impedance spectroscopy. The combination of PANI and CNSL inhibitors considerably improves the anticorrosive properties of commercial primers.

Key words: Corrosion, polyaniline, cashew nut shell liquid, steel, *Anacardium occidentale* L., considerably

INTRODUCTION

Corrosion is one of the processes of degradation more frequent in the metals and generates millions of dollars in economic losses (Li *et al*., 2007; Koch, 2017; Thompson *et al*., 2005). Corrosion can be controlled by different techniques or methods such as use of sacrificial anode, electrolytic coating with low corrosive metals (chrome plating, nickel plating), coating with films or anticorrosive paints, among others (Zhong and Clouser, 2014; Lozinguez *et al*., 2018; Li *et al*., 2007; Maab, 2011). The coating with organic substances is one of the most used methods for its easy application, low cost and effectiveness, since, it generates a barrier against moisture and contact with contaminants in the media to which the metal is exposed. These coatings can be a single or mixture substance which can eliminate or reduce corrosion (Maab, 2011; Nazeer and Madkour, 2018; Montemor, 2014).

The organic corrosion inhibiting substances are those that have a molecular structure with double bonds. In this sense, the Intrinsically Conducting Polymers (ICP) have been shown to be capable of inhibiting corrosion (Wuzei, 2017; Iqbal and Ahmad, 2017; Bai *et al*., 2015; Tavandashti *et al*., 2016; Raiz *et al*., 2014). In general terms, intrinsicallyconducting polymers are materials formed by long hydrocarbon chains with alternate single and double bonds (conjugated bonds); This architecture allows them to conduct the electric current when they have been doped by oxidation or reduction (Fujimoto *et al*., 2017; MacDiarmid, 2001). In this way these compounds combine in the same material, the properties of traditional polymers (lightness, processed at low temperature, absence of corrosion, etc.) and some of the properties of metals (electrical conductivity and electromagnetic properties).

The Polyaniline (PANI) is one of the most studied intrinsically conducting polymers and has been used to try to inhibit corrosion due to its excellent electrochemical properties, stability and easy synthesis and processability. Aniline is a substituted aromatic compound whose oxidation in an acidic medium produces its polymerization. The aniline polymer is therefore, a chain of phenylene rings joined together by an NH group which can be protonated and deprotonated through oxidation and reduction processes (MacDiarmid *et al*., 1987; Du *et al*., 1997).

The good stability and conductivity of polyaniline have made it a material with excellent technological expectations, giving rise to its use in multiple applications. Among them the most outstanding are: their use as electromagnetic protectors, smart windows, LEDs,

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biosensors, artificial muscles, anticorrosion coatings, etc., (Tanguy *et al*., 2017; Gautam *et al*., 2018; Beregoi *et al*., 2017; Langer *et al*., 2010).

Polyaniline has been used in anticorrosion treatments mainly as an electropolymerized polymer on stainless steel surfaces there are few investigations that report its incorporation in primers (Jafari *et al*., 2016; Mrad *et al*., 2017; Karpagam *et al*., 2008). Additionally, polyaniline have been combined with other substances to improve its anticorrosive properties. Polyaniline has been used in combination with graphene oxide, nickel oxide, montmorillonite, polyurethane, polyvinyl chloride, among others (Qiu *et al*., 2017; Bandeira *et al*., 2017; Haghdadeh *et al*., 2018; Zhang *et al*., 2013).

On the other hand, the ability of the Cashew Nut Shell Liquid (CNSL) to inhibit corrosion has been few studied (Balgude *et al*., 2014; Philip *et al*., 2001). CNSL is a vegetable oil, economic, non-toxic and not dangerous extracted from the plant of Marañonor cashew (*Anacardium occidentale* L.), its main components are cardanol, cardol and anacardic acid, these are phenolic derivatives with hydrocarbon Chain (C15) polyunsaturated substituents. The aim of this research was to evaluate the capacity of polyaniline combined with the cashew nut shell liquid in a primer to inhibit corrosion in stainless steel panels.

MATERIALS AND METHODS

The nuts were collected and proceeded to open them to have only the shell. The shells were milled until an average size of 5 mm was obtained.The raw cashew nut shells was loaded into a hydraulic press and a high was applied pressure to release CNSL from shells.

Polyaniline was synthesized chemically by oxidation of aniline with Ammonium Persulfate (APS). For this, 0.1 mol of aniline and 0.1 mol of oleic acid were added in 250 mL of ultrapure water, this mixture was maintained with constant agitation for 2 h. Then 50 mL of aqueous solution containing 0.1 mol of APS was added dropwise and stirred for 4 h. The product obtained was filtered and washed with water and ethanol (1:1) repeatedly. The obtained polyaniline was dried at 40°C for 24 h under vacuum. The 5 g of polyaniline were taken and dissolved in 100 mL of thinner, stirring them by ultrasound in a time of 15 min.

In this study different proportions of polyaniline and CNSL were tested. For it were used proportions of 3% and 5% of each modifier (PANI and CNSL). Eighteen testwere carried out; Six treatments with three replicates each (Table 1).

Table 1: Proportions of mixtures used in the corrosion assays

	Proportions (%)		
Assay codes	PANI	CNSL	Primer
A1	5.0	0.0	95.0
A2	5.0	3.0	92.0
A3	5.0	5.0	90.0
A4	3.0	5.0	92.0
A5	0.0	5.0	95.0
A6	0.0	0.0	100.0

*Each test was done in triplicate

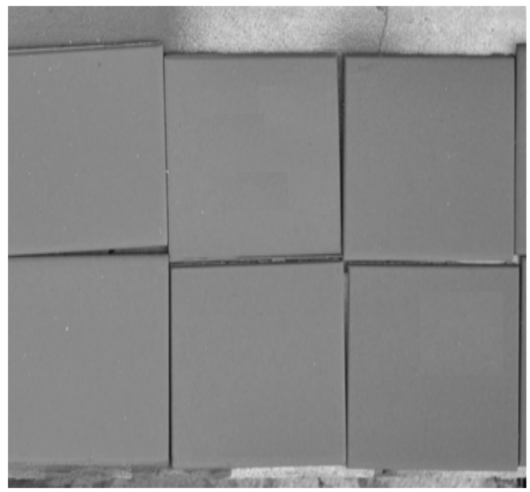

Fig. 1: Images of steel panels painted with PANI and CNSL treatments

The coatings with modified primer were applied onto steel panels with ASTM specification (7.6×9.5×0.15 cm). Each panel was cut with polishing discs. To prepare the surface, the SSPC-SP1 method was first applied in which with a polishing disc oils, grease or other chemicals present in said surface were removed and solvent was used to remove soluble contaminants. Subsequently, the SSPS-SP2 method was applied, passing abrasive paper over the surface to remove all loose mill scale, rust, paint and other contaminants.

The anticorrosive primer in the different tests was applied by spraying with an airbrush on both sides of the panels. Figure 1 shows a series of painted panels.

In order to evaluate the corrosion process was carried out by an accelerated corrosion test. The painted steel panels were submerged in a 0.1 M HCl solution by 10 days, to simulate a strongly corrosive environment and accelerate the corrosion process. In the determination of the corrosion inhibition efficiency, the electrochemical tests impedance spectroscopy and Tafel polarization were used.

In order to carry out the electrochemical characterization the steelpanels specimens were used as working electrodes, a Saturated Calomel Electrode (SCE) and a platinum electrode were used as reference and counter electrode, respectively. All potentials were given on the SCE scale. The electrochemical studies were carried out with a potentiostat/galvanostat EG&G PARSTAT 273A. The Tafel polarization (potentiodynamic polarization) and electrochemical impedance spectroscopy were carried out used a 0.1 M HCl solution. The potentiostate/galvanostate was controlled with PowerSuite Software and the electrochemical data were analyzed with ZSimpWin.

RESULTS AND DISCUSSION

The electrochemistry impedance spectroscopy measurements of steel panels subjected to the effects of primer in the absence and presence of various concentrations of PANI and CNSL were made after 10 days of immersion in 0.1 M HCl at 25°C. The Nyquist plots are shown in Fig. 2a-f where it canbe observed that the EIS spectra have some similarity, shows an incomplete or not perfect semi circle at high frequency. It is clearly observed that the diameter of the semi circle increases with the addition of modifier being higher when primers modified with CNSL.

The semi circles have a center under the real axis when the semi circle is projected completely which corresponds to a capacitive phenomenon. This phenomena correspond to surface heterogeneity due a surface roughness, dislocations, distribution of the active sites or adsorption of inhibitors. In order to analyze the EIS response an equivalent circuit was selected. The equivalent circuit models corresponding to this impedanciometric process is shown in the Fig. 3. This circuit is generally used to describe the steel corrosion interface model with a parallel combination of double-layer capacitance C1 and R2 polarization resistance (charge transfer resistance) in series with the solution Resistance (R1). It can be seen that the polarization Resistance, R2 increases when the modifier were present in the primer, its values were higher when CNSL was present.

Table 2 show electrochemical impedance parameters R2 and C1 of the complex plane plots of the test carried out in the steel panels.

The inhibition efficiency (%IEimp) in different test were calculated from the charge transfer resistance according to equation:

$$\%IE_{imp} = \frac{R2-R2^0}{R2} \times 100$$

where, R2 and $R2^0$ represent the charge transfer resistance in the presence and absence inhibitor, respectively. The values of R2 increase with increasing of CNSL and PANI concentrations and the results indicate that charge transfer process mainly controls the corrosion process. Efficiency of inhibition ($\%IE_{imp}$) is observed from Table 1, this value increase when modifier concentration highest.

The polarization behavior of steel panels with and without adition of inhibitors is show in the Fig. 4. It is possible observe that Ecorr varies between -0.41 and -0.63 V, the most positive value being the one corresponding to the modification of the primer with the mixture of 5% CNSL and 5% polyaniline and the most negative value corresponding to the unmodified primer.

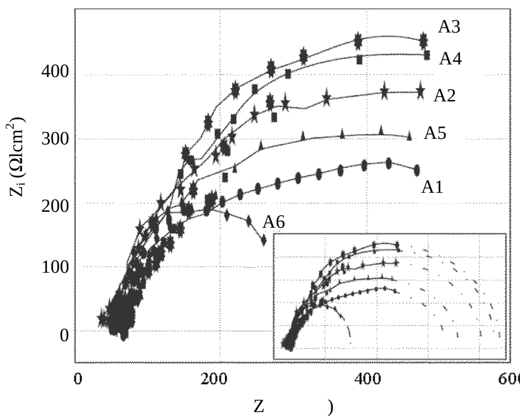

Fig. 2: Electrochemical impedance spectra of steel panels in 0.1 M HCl solution: a) Assay 1; b) Assay 2; c) Assay 3; d) Assay 4; e) Assay 5 and f) Assay 6

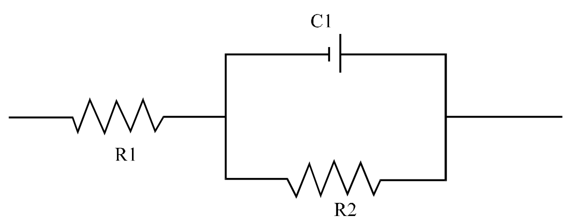

Fig. 3: Equivalent circuit model of steel panels in 0.1M HCl solution

Table 2: Electrochemical impedance parameters of corrosion steel in HCl 0.1 M solution

	Impedance parameters			
Assay	R1 (Ω cm²)	R2 (Ω cm²)	C1 (μF cm²)	IE_{imp} (%)
A1	2.2	825	453	67.5
A2	2.4	1109	305	75.8
A3	2.9	1550	105	82.7
A4	3.0	1398	203	80.8
A5	2.1	997	247	73.1
A6	2.3	268	521	-

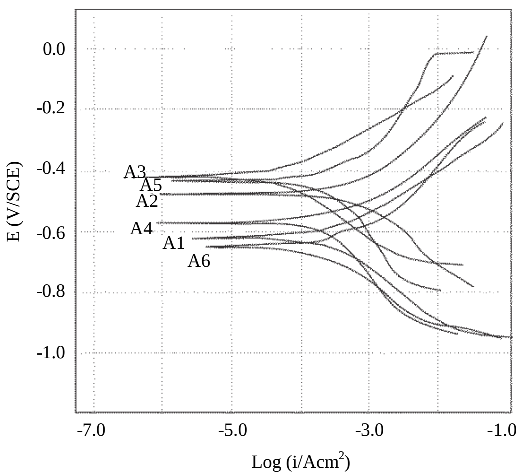

Fig. 4: Tafel polarization curves of steel panels in HCl 0.1 M solution: a) Assay 1; b) Assay 2; c) Assay 3; d) Assay 4; e) Assay 5 and f) Assay 6

Table 3: Tafel polarization values for corrosion steel panels in 0.1 M HCl solution

	Polarization parameters		
Assay	E_{cor}	I_{corr}	IE_{Taf} (%)
A1	-0.62	221	68.6
A2	-0.48	169	76.0
A3	-0.41	114	83.8
A4	-0.58	151	78.6
A5	-0.43	194	72.4
A6	-0.64	705	-

Values of associated electrochemical parameters such as corrosion density (J_{corr}) and corrosion potential (E_{corr}) obtained by extrapolation of the Tafel lines and the calculated inhibition efficiency (%IE_{Taf}) are presented in Table 3. The inhibition efficiency were calculated according to equation:

$$\%IE_{Tap} = \frac{J^0_{corr} - J_{corr}}{J^0_{corr}} \times 100$$

where, J_{corr} represent the corrosion current density in the presence of inhibitor and J^0corr is corrosion current density without the presence of inhibitor, estimated by Tafel extrapolation. Efficiency of inhibition (%IE_{taf}) is observed from Table 3 to increase with modifier concentrationin accordance with the obtained with the impedance spectroscopy.

These data show corrosion current density (J_{corr}) of panel steel decreased with increasing the concentration of the modifier CNSL and PANI and there was not a specific relation between E_{corr} and inhibitors concentration. It can observed that both, CNSL and PANI are good inhibitor for steel in HCl 0.1 M and the mixture of them have a better performances, the inhibition efficience reaches its highest value at a concentration of 5% of both modifier.

CONCLUSION

The electrochemical measurements of electrochemical impedance spectroscopy and Tafel polarization supplied consistent results about the inhibition capacity of PANI and CNSL mixture. The measurements showed that the modifiers have excellent inhibition properties about corrosion process of steel in HCl 0.1 M solution. The inhibition become or make greater when inhibitor concentration increases (5%).

Electrochemical impedance measurements suggest a better inhibition action when PANI and CNSL are combined in the primer mixture. The anticorrosive protection provided by CNSL was higher that PANI effect. Tafel polarization measurement showed that the CNSL and Pani act as corrosion inhibitor agent and its mixture increases the anticorrosive effect.

Finally, the inhibiting efficiencies (%IE) determined by Tafel polarization and electrochemical impedance are reasonably good agreement.

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