Recycled ABS Polymer Doped with Outdated Lansoprazole as a Corrosion Protection Composite Coating for Mild Steel in Chloride Solution

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Abstract—Acrylonitrile-butadiene-styrene (ABS) is a common waste polymer by-product from industry. Outdated medicines are usually discarded and could be a valuable asset for other applications such as metallic corrosion inhibition. The aims of the present work is to manufacture a recycled ABS polymer doped with outdated lansoprazole medicament as a corrosion protection composite coating. It was applied to mild steel and immersed in chloride solution, and evaluate its possible corrosion protection properties using different electrochemical techniques. The manufactured coating presents good corrosion protection properties showing an 80% efficiency as a function of time of immersion in the aggressive solution.

I. INTRODUCTION

In the industrial sector metallic corrosion has always been a great technical, economic and social problem. Through the years, the fight against corrosion by using chemical substances sometimes has been successful but as times passes by, often ended in toxic waste disposal harmful to the environment. Therefore, in the last few decades’ research has been looking into recycling and new natural organic substances and compounds to act for corrosion protection, friendlier to the environment.

It was found that some natural organic compounds are good corrosion inhibitors, as for example medicines when the active compound acts when is required [1]. Gastric secretion supresors (PPI: proton pump inhibitors) are among the most studied compounds, and within this group the derived family from triazoles are the main studied especially benzotriazole [2], fluconazole [3] and lansoprazole [4]. This is especially true in acid media and possibly in chloride containing neutral or near neutral solutions where localized attack may be present involving formation of hydrochloric acid within it [5].

As it was observed, organic inhibitors act over the metal surface influenced by it, the electrolyte and the inhibitor structure. In several studies, it is shown that the most efficient organic inhibitors contain nitrogen, sulphur or oxygen. Also, coatings have always been important for metallic corrosion protection due to its ease of application, good surface coverage and cost. This is so for recycled Acrylonitrile Butadiene styrene (ABS, C₈H₈·C₄H₆·C₃H₃N₃) [6] [7].

In recent times, interest for the preservation of the environment has grown, looking for manufacture of corrosion protection products and compounds more ecological, friendlier and less detrimental to the environment. This research evaluates the corrosion protection of an automobile industry waste polymer (ABS) as a coating doped with outdated discarded pharmaceutical lansoprazole, with possible recycling procedures [7]. This was done using electrochemical techniques.

II. EXPERIMENTAL PROCEDURE

A. Materials

Commercial 1018 steel (99.25% Fe, 0.18% C, 0.5% Mn, 0.03% P and 0.04% S by weight), coupons with an exposed area of 1.1cm² were embedded in epoxy resin. The coupons were polished with 600, empery paper to allow certain roughness on the metal surface to improve the coating adherence. Afterwards, the metal samples were cleaned with distilled water and then with acetone, to eliminate any residues present.

Outdated generic pharmaceutical drug capsules for gastritis treatment, 2·[(3-Methyl-4-(2,2,2-trifluoroethoxy)-2-pyridyl)-methylsulfinyl]benzimidazole] (lansoprazol) with a 15mg concentration, was dissolved in 20 ml N-N dimethyl-formamide (Sigma Aldrich 99.8%) at 1:1 ratio under agitation, for two hours. Electrochemical testing was performed for steel immersed in this solution at: 10, 25, 100 and 150ppm to determine the best corrosion inhibitor concentration.

Discarded ABS were cut in small pieces obtained as refuse from car industries, and dissolved in acetone (Sigma Aldrich 99.5%) at a 1:1 ratio. Afterwards it was characterized through FTIR spectrum using a Bruker spectrometer connected to a computer with a Opus 5.5 software. The ABS dissolved solution metal probes were dip coated after one-minute immersion retired for solvent evaporation and followed by a 15 second immersion to sealed remaining pores, obtaining a coating average thickness of 82 nm. These samples were kept in a desiccator ready for electrochemical measurements to evaluate coating corrosion protection.

After establishing the best inhibitor concentration, the two dissolving solutions were mixed. The dissolved 150ppm lansoprazole liquid solution was added to the one containing dissolved ABS, and left for 30 minutes under agitation to obtain a homogeneous mixture (Fig. 1). Resin embedded
steel probes were dip coated and left to dry at room temperature, as previously explained.

![Coating preparation](image)

**Fig. 1.** Coating preparation

### B. Electrochemical Measurements

All electrochemical tests were made in electrodes immersed in a 3% sodium chloride solution at room temperature. The free corrosion potential was registered during immersion in the electrolytic solution. Polarization resistance measurements were performed polarizing ±20 mV around the corrosion potential, at a scan rate of 1mV/s. Potentiodynamic polarization scans were performed with a scan rate of (1 mV/s), in the interval from -1000 mV up to +100 mV SCE. Impedance measurements (EIS) were performed using a 20mV amplitude sinusoidal signal and a frequency range 10000 to 0.01Hz. Complementary analysis was obtained using equivalent electric circuits. For all these measurements, a 3 electrode cell configuration with an auxiliary graphite and saturated calomel electrode (SCE) as reference electrodes, were used. For electrochemical noise (EN) a three `identical' electrode set-up was used with each EN time series comprising 1024 data points at a sampling rate of one sample/second. All measurements were performed using a Gill AC Electrochemical Instrument [8][9].

### C. Atomic Force Microscopy (AFM)

Coating surface topography was analysed using atomic force microscopy (AFM) WITec, Alpha300RA with 42 N/m constant force and a 330 kHz resonant frequency, and images were obtained at room temperature.

### D. Fourier Transform Infrared Spectroscopy (FTIR)

To identify and confirm the existence of lansoprazol functional groups the solution was analysed in the 400-4000 cm\(^{-1}\) frequency range in the transmittance mode using a Bruker spectroscope connected to a computer and using Opus 5.5 software [10].

### E. Scanner Electron Microscope (SEM)

The coated and metallic surfaces were analysed using a LEO1450VO scanner electron microscope (SEM) to observe coating degradation and metallic attack.

### F. Pull-off Tape Adhesion Test

The pull-off tape test gives information about metallic coating adequate adhesion to the substrate after the immersion period. The test was applied according to ASTM D3359 Standard [11], over a scratched ABS-150ppm lansoprazole coating surface over 1018 steel.

III. RESULTS

### A. Lansoprazole Characterization

Lansoprazole is a medicine belonging to a pharmaceutical group known as proton pump inhibitors (PPI), diminishing the stomach acid secretion, and used in the ulcer gastric and duodenal (peptic), Zollinger-Ellison syndrome treatment and other gastrointestinal ailments, where reduction in the gastric acid is advantageous [12]. Fig. 2 presents the lansoprazole chemical structure and FTIR spectrum used as inhibitor, where a wide band associated to vibrations from O-H couple stretching around 3400 cm\(^{-1}\), absorptions at 1449cm\(^{-1}\) corresponding to the triple coupling CΞN triazole rings, at 1230cm\(^{-1}\) the C-N couple stretching, and in 1000 cm\(^{-1}\) appeared the C-F couple stretching vibrations [3][10].

![Lansoprazole formula and FTIR spectrum](image)

**Fig. 2.** a) Lansoprazol formula; b) lansoprazole FTIR spectrum

To characterise lansoprazole as corrosion inhibitor, polarisation curves and EIS were performed in samples immersed in a 3% chloride solution at room temperature. Fig. 3 presents the polarisation curves for 1018 steel and different inhibitor concentration samples. Active potentials and slightly variable corrosion behaviour were observed without and with the presence of different lansoprazole concentrations. For the blank sample the anodic branch presents a polarising behaviour corresponding to the formation of corrosion products over the surface. With the presence of the inhibitor, the corrosion potential and the shape of the anodic branch remained similar, except for the 25ppm concentration where the corrosion potential becomes nobler and anodic depolarising condition was observed, but diminishing the active corrosion current density by almost one order of magnitude. For the other concentrations, the curves presented small changes in the anodic region and similar corrosion potentials though more cathodic with a 0.08 mA/cm\(^2\) corrosion current density [13]. Nevertheless the active region presenting the polarising conditions associated to the formation of corrosion products slightly changes, and the potential range increased up to the pitting potential [14][15].
EIS data analysis was done using equivalent electric circuits through the Zview software, to obtain the solution resistance (Rs), the inhibitor (Rinh) and charge transfer (Rct) resistance, as well as the inhibitor (Cinh) and double layer (Cdl) capacitance, respectively. The best adjustment was obtained for this well-known circuit (Fig. 5) under the experimental conditions [9][16][17]. These values were obtained from the circuit and presented in Table I.

With the values obtained the inhibitor efficiency was calculated according to equation:

\[
\%E = \left( \frac{|Z\text{inh}}{|Z\text{blank}|} \right) \times 100
\]

When two processes occur the Zinh is the total resistance (Rinh+Rct) with and without the inhibitor [18]. From Table I the parameters changes as a function of inhibitor concentration are clearly seen, where the greater charge transfer resistance (lower corrosion) obtained was for the 150ppm lansoprazole concentration with a 76% efficiency.

Table I: EIS parameters obtained from the electric equivalent circuit adjusted for different lansoprazole inhibitor concentrations

<table>
<thead>
<tr>
<th>Sample conc.</th>
<th>Rs (Ω cm²)</th>
<th>Cinh (F/cm²)</th>
<th>Rinh (Ω cm²)</th>
<th>Cdl (F/cm²)</th>
<th>Rct (Ω cm²)</th>
<th>% E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>12</td>
<td>---</td>
<td>---</td>
<td>0.00054759</td>
<td>171</td>
<td>-</td>
</tr>
<tr>
<td>10 ppm</td>
<td>48</td>
<td>0.000033029</td>
<td>32</td>
<td>0.00057409</td>
<td>422</td>
<td>59</td>
</tr>
<tr>
<td>25 ppm</td>
<td>14</td>
<td>0.000036934</td>
<td>16</td>
<td>0.00040718</td>
<td>555</td>
<td>69</td>
</tr>
<tr>
<td>100 ppm</td>
<td>14</td>
<td>0.00032765</td>
<td>11</td>
<td>0.0044132</td>
<td>105</td>
<td>76</td>
</tr>
<tr>
<td>150 ppm</td>
<td>16</td>
<td>0.00017791</td>
<td>15</td>
<td>0.0065337</td>
<td>714</td>
<td>76</td>
</tr>
</tbody>
</table>

To describe the inhibitor interaction with the metal surface, adsorption isotherms namely: Langmuir, Temkin, Frumkin and Freundlich are used for corrosion inhibitor protection [19]. These adsorption isotherms were tried with the experimental data, the inhibitor efficiency representing the degree of surface coverage (\(\chi\)) for different inhibitor concentrations such as:

\[
\chi = \frac{\text{Rct (inh)} - \text{Rct (blank)}}{\text{Rct (inh)}}
\]

The best adsorption isotherm model obtained (Fig. 6) with the experimental data, was the Frumkin adsorption isotherm model:

\[
K_{ad} C = (1 - \chi) e^{\chi f}
\]

where \(K_{ad}\) is the adsorption equilibrium constant, \(C\) the inhibitor constant, \(f\) the molecular interaction constant and \(\chi\) surface coverage. A linear regression analysis was performed (Fig. 6) with a correlation factor \(R^2 = 0.95\), obtaining the \(K_{ad}\). This is substituted in the following equation to obtain the free energy of adsorption \(\Delta G_{ads}\):

\[
\Delta G_{ads} = -RT \ln K_{ad}
\]
where $\Delta G_{ads}$ is the Gibbs free energy, $R$ and $T$ are the universal constant for gases and temperature, respectively; characterising the interaction between the inhibitor molecules and the metal surface. Values equal or more positive than -20 kJ/mol are related to physisorption and equal or more negative than -40 kJ/mol to a chemisorption process [3][19]. In this case, $\Delta G_{ads} = -5.05$ kJ/mol was obtained, meaning a physisorption process of the inhibitor is taking place over the metal surface, common in organic inhibitors [20][21]. Therefore, a physical barrier is formed, changing the percent coverage of the metal surface, and consequently the double layer capacitance changes. From the Frumkin isotherm model, this change is generated when the water molecules present in the metal surface were displaced and replaced by the inhibitor organic molecules thus protecting the metal surface [19][21].

B. ABS Coating Characterisation

In Fig. 7 the ABS compound IR spectrum is presented where the characteristic peaks are observed: acrylonitrile at 2237 cm$^{-1}$, styrene at 1602, 1497, 761 y 699 cm$^{-1}$ and butadiene at 967 cm$^{-1}$[22].

![Fig. 7. a) ABS chemical formulation and b) ABS FTIR spectrum](image)

Fig. 8 presents the polarisation curves for steel 1018 without and with ABS coating in 3% NaCl solution. It is clearly seen the effect of the ABS coating over the metal surface, diminishing the overall corrosion current density more than two orders of magnitude. The corrosion potential became more anodic from -700 up to -10 mV, and less likely to a corrosion process as compared to the bare metal surface.

![Fig. 8. Polarisation curves for steel 1018 without and with ABS coating in 3% NaCl solution](image)

Fig. 9 presents the EIS measurements obtained for 1018 steel without and with ABS coating in a 3% NaCl solution. Two depressed semicircles were obtained for both samples, shown in the Nyquist plots, confirmed by the associated phase angles presented in Fig. 9b. The Bode plots present the total impedance value where a difference of two orders of magnitude can be observed confirming the results obtained from the polarisation curves. The ABS coating sample presents a highly resistive behaviour (30 kohm*cm$^2$) along the frequency range considered, as compared to the blank total impedance (250 ohms*cm$^2$) [4].

![Fig. 9. EIS measurements for 1018 steel without and with ABS coating in 3% NaCl solution](image)
C. ABS +150ppm Lansoprazole Characterisation

Fig. 10 presents the FTIR spectrum for ABS/150ppm lansoprazole where characteristic ABS peaks were observed, but at lower intensities: acrylonitrile at 2237 cm\(^{-1}\), styrene at 1602, 1497, 761 and 699 cm\(^{-1}\) and butadiene at 967 cm\(^{-1}\). At 3040 cm\(^{-1}\), C-H stretching aromatic rings are visible, absorption at 1449 cm\(^{-1}\) corresponding to C=N triazole rings double coupling. Also observed, carbonile compound stretching vibrations at 1710 cm\(^{-1}\), as well as small aliphatic signals with carbonile torsion and C-F bonds [4].

Electrochemical measurements namely: open circuit corrosion potential, polarisation resistance, EIS and electrochemical noise (ENM) as a function of time for 2000 hours, were applied to 1018 steel bare metal and ABS+150 ppm lansoprazole coated samples. In Fig. 11a the OCP for bare steel presented a common active potential throughout the time of immersion, around -600mV. More anodic potentials were obtained for the coated sample around -500 mV as expected, oscillating from time to time. These in turn, is reflected in the polarisation resistance measurements (corrosion rate), where stable values near 1000 ohms*cm\(^{2}\) were obtained for the blank sample. Higher variable values (lower corrosion rate) were observed for the coated sample, around an average 1kohm*cm\(^{2}\) with extreme values from 300 to 3 kohms*cm\(^{2}\), maintaining its range along the time of immersion, as seen in Fig. 11b. These variations observed are probably due to pores or defects of the film coating [23].

To complement the previous measurements, EIS and ENM were also performed, and total impedance as well as noise resistance were plotted as a function of time of immersion (Fig. 12 a and b) [8][9]. The total impedance for bare steel sample (blank) remained fairly stable along the test, from 1000 ohm*cm\(^{2}\) decreasing slowly to 400 ohm*cm\(^{2}\) after 2000 hours of immersion. Noise resistance obtained in the bare steel sample lies between 2 to 10 kohms*cm\(^{2}\), showing a slight trend to decrease as a function of time of immersion. For the coated sample data oscillate from 10 up to 500 kohms*cm\(^{2}\) with an average value of approximately 90 kohms*cm\(^{2}\). These variability is associated to localised breakdown events from pores, defects or local corrosion attack and film growth taking place over the coated film. ENM is especially susceptible to register these events compared to other electrochemical techniques. Values observed in the noise resistance obtained are in general one order of magnitude higher compared to EIS total impedance data obtained, commonly encountered and reported [6][7].

EIS electric equivalent circuit (Fig. 13) fitting and analysis was also performed and presented, where the first RC loop corresponds to the coating in series with a second RC loop associated to the metal surface corrosion process [9][24][25]. Table II presents the values obtained where it can be seen a decrease in the coating and charge transfer resistance values and consequently in the coating and double layer capacitance, for the different times of immersion. Nevertheless, the coating efficiency remained high above
84% throughout the test, confirmed from the overall electrochemical measurements data obtained and presented.

![Graph](image1.png)

Fig. 12. Steel sample without and with ABS+150ppm Lansoprazole coating, a) EIS total impedance and b) ENM noise resistance

![Graph](image2.png)

The ABS+150ppm Lansoprazole coating topography was obtained through AFM after the end of the immersion period. Fig. 14a present the surface coating analysis revealing a homogeneous and well bonded to the metal surface, with just a few pores all along. This is also seen and confirmed in the SEM micrograph obtained (Fig. 14b) [26].

![Image](image3.png)

Fig. 14. ABS Lansoprazole 150ppm coating a) AFM topography and b) SEM micrograph

![Image](image4.png)

Fig. 15 presents the coated steel surface after the experimental immersion where a few corroded areas are clearly visible (Figure 15a), and the good adhesion obtained after the scratched surface pull-off tape procedure where only two spots disbonded were visible from local coating failure (Fig. 15b) [11].

![Image](image5.png)

**Fig. 15.** ABS +150ppm Lansoprazole coated steel a) coated surface after immersion and b) scratched surface pull off tape adhesion test
IV. CONCLUSIONS

Discarded pharmaceutical Lansoprazole provides adequate protection as corrosion inhibitor forming a stable film through a physisorption process. Recycled ABS as a thin film corrosion coating is highly efficient to protect 1018 steel against corrosion. The combination of ABS and Lansoprazole as a composite corrosion coating performs well as corrosion protection system after 2000 hours of immersion in the chloride solution, maintaining high efficiency and good adherence throughout the experimental conditions.

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REFERENCES


