Steel protection of two composite coatings: Polythiophene with ash or MCM-41 particles containing iron(III) nitrate as inhibitor in chloride media

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1. Introduction

While traditional coatings are designed to protect the metal substrates to which they are applied by providing a barrier between the surface and the environment, compelling innovations have been made with regard to “smart” coatings [1]. These novel coatings are far superior to the traditional ones in that they release corrosion inhibitors as required by the presence of damaged coating in corrosive environments. Recent work has focused on the self-contained corrosion control or “self-healing” potential of smart coatings [2,3], resulting in a new-generation of effective anti-corrosive systems. The new coatings possess nanocontainer functionality: an active passive matrix that responds to changes in the local environment. The main objective today is to employ nano-mesoporous structured materials dispersed in the polymer matrix of the coatings as corrosion inhibitor storage containers [1–3,21–25].

The study of the protection of metals and alloys from corrosion, using organic coatings, has been a research area of great interest leading to novel anti-corrosion paints and polymers [4–7]. Specifically, conducting polymers (CPs) are now starting to be used as organic coatings, where these form dense, adherent films with low porosity that restrict the entry of oxidizing agents and thus reduce metal corrosion [5,6]. These coatings provide corrosion resistance in saline and acid environments, with the added benefits of flexibility, insolubility and adhesion to the substrate [6,7]. Metals are severely damaged by localized corrosion in different environments, especially those containing chloride ions [8,9]. CPs form a passive film, a very thin metal oxide layer (iron oxide in the case of steel) which condenses on the metal surface, reducing naturally and to a great extent the corrosion rate of chloride ions. However, these films are not uniform, and the corrosion process of localized oxide breakdown persists through their fissures, resulting in a fast dissolution of metal [10,13]. The combined use of coatings and inhibitors dispersed in a polymer matrix has proved to be useful when deal-
ing with corrosion: the addition of nano- or mesoporous particles as inhibitor storage containers has resulted in smart, self-healing coating schemes which offer several advantages. Among them is the fact that used particles discarded as waste or byproduct materials can be recycled, thus contributing added value and benefiting the environment.

Recently, the application of electrochemical noise analysis (ENA) has been drawing considerable attention as a promising technique for analyzing and identifying corrosion intensity [11–20]. Electrochemical noise has been defined as stochastic fluctuations in the electrochemical potential of an electrode relative to a reference electrode. By contrast, electrochemical current noise has been defined as the stochastic oscillation of an electrochemical current between two nominally “identical” electrodes. Electrochemical noise measurements (ENM) are relatively simple; it is the retrieval of relevant information that often poses difficulties [15,16].

Electrochemical noise provides information about reaction kinetics, i.e., the rate of corrosion, and may assist in identifying types of corrosion as uniform, localized, or pitting [9]. It also yields information about reaction mechanisms [12,15,16–18]. Data on potential and current noise as a function of time (time series) can serve for statistical analysis purposes, specifically for calculating the standard deviation of data series. The Noise Resistance ($R_n$) can thus be obtained as a ratio of the potential standard deviation [$\sigma(V(t))$] over the current standard deviation [$\sigma(I(t))$]. These experimental data can be transformed from the time to the frequency domain by using the FFT to obtain the noise impedance [$Z_n$] [9,15,19,20].

Potential and current noise sampling are performed simultaneously, with the transformation of both divided directly to obtain the $R_n$ level as follows:

$$R_n = \frac{\sigma(V(t))}{\sigma(I(t))}$$

where $V(t)$ and $I(t)$ are the time series of potential and current fluctuations [12,15,19,20].

This analysis requires the signal to be stationary (that is, with the mean tending to zero), which is not always true in corrosion systems—especially at the beginning of exposure—thus posing difficulties in performing spectral estimations. A mathematical procedure is therefore used to remove the trend or shift the direct current (DC), usually by subtracting the data through linear regression.

This work presents the results of an electrochemical noise evaluation of two composites formed by polythiophene (P1 polymer derived of 3-hexylthiophene and (S)-(−)-1-(4-nitrophenyl) pyrrolidin-2-yl)methyl-2-(thiophen-3-yl) acetate, in an 89/11 monomer ratio. Iron(III) nitrate was used as a corrosion inhibitor in both cases: one included cigarette ashes and the other, MCM-41 mesoporous particles as inhibitor containers.

2. Experimental approach

Compounds purchased from Sigma-Aldrich and Ferment were used without further purification. Polymer synthesis was performed in an atmosphere of dry nitrogen, using conventional Schlenk techniques. Chloroform and nitromethane solvents were dried by distillation from anhydrous CaCl$_2$ or MgSO$_4$. NMR studies were carried out with Varian Inova 200 MHz and Mercury 400 MHz multinuclear instruments. The P1 polymer was dissolved in CDCl$_3$ (ca. 5–10 mg of polymer in 0.5 mL) in 5 mm (o.d.) tubes and measured at 25 °C with TMS as the internal standard. Chemical shifts were stated in parts per million. IR spectra (4000–400 cm$^{-1}$) were recorded on a Perkin Elmer Spectrum 400 spectrophotometer (ATR reflectance mode) and a Bruker Vector 22 FT spectrophotometer with OPUS 5.5 software. The molecular weight of P1 polymer was measured by means of gel permeation chromatography (GPC, Alliance 2695; eluent, THF; temperature, 30 °C; injection volume, 25 μL; 2 linear PL gel columns; UV detector) calibrated with 580–3,250,000 monodispers polystyrene standards. UV–vis spectrum was measured with a Thermo Electron Corporation GENESYS 10 UVS scanning apparatus with Vision lite software. Thermal stability measurements were carried out on a SDT Q600 V8.2 Build 100 thermo-gravimetric analyzer under a nitrogen flow (50 mL/min); mode: DSC-TGA Standard, with sapphire as calibration material and an alumina crucible. The Universal V4.2E program was used. To determine the working inhibitor concentration, two polarization curve tests were performed on an ACM GiliAC instrument controlled by GiliAC software.

2.1. Synthesis of polythiophene derivative

**Synthesis of polymer (P1) derived from 3-hexylthiophene and (S)-(−)-1-(4-nitrophenyl) pyrrolidin-2-yl)methyl-2-(thiophen-3-yl) acetate**

A solution of 6.65 g (39.8 mmol) of iron (III) chloride was cooled at 10 °C in a three-neck flask under a constant flow of dry nitrogen gas in 90 mL of chloroform and 20 mL of nitromethane, with an added solution of 0.87 g (2.51 mmol) of monomer (S)-(−)-1-(4-nitrophenyl) pyrrolidin-2-yl)methyl-2-(thiophen-3-yl) acetate in 22 mL of chloroform. Then, a solution of 1.21 g (7.12 mmol) of 3-hexylthiophene in 40 mL chloroform was added dropwise. Polymerization was carried out for 24 h, under constant stirring, at a temperature ranging from 10 °C to 25 °C. The reaction was finalized by adding methanol (1 L). Consequent to precipitation, the polymeric product was separated by filtration and washed with methanol.

To eliminate the ferric salt, the P1 polymer was treated with 100 mL of a NH$_3$ (aq)/MeOH mixture for 1 h. It was then filtered and washed again with methanol. The soluble part of the neutral polymer was extracted with a chloroform solvent in a soxhlet apparatus, and the solvent was evaporated. The product was obtained in the form of a colored plastic solid. It was finally dried to achieve a constant mass providing 0.69 g (38%) of pure P1 polymer.

Fig. 1 presents the chemical structure of the P1 polymer derived from 3-hexylthiophene and (S)-(−)-1-(4-nitrophenyl) pyrrolidin-2-yl)methyl-2-(thiophen-3-yl) acetate. P1 polymer was used in

![Fig. 1. P1 polymer structure.](image-url)
smart coatings to study its corrosion protection behavior on 1018 carbon steel in a 3 wt% sodium chloride solution.

2.2. Preparation of inhibitor solutions

To select the working inhibitor concentration, the electrochemical technique of polarization curves was applied in a 3% sodium chloride solution, adding 0, 5, 10, 20, 50 and 100 ppm of iron(III) nitrate.

2.3. Cigarette ashes and MCM-41 particles loaded with inhibitor: their preparation for smart coatings

To load containers with the inhibitor for the purpose of studying the ashes and MCM-41 particles [26–32] as inhibitor containers, the following sequence was followed: 20 mg and 60 mg of particles were used in two acetone solutions: one with ashes, the other with MCM-41 particles. The solutions were complemented with 10 mL of iron(III) nitrate (5 ppm). They were filtered, evaporated and dried at 100 °C for one hour, and then taken to SEM to characterize the particles. Elemental mapping and a scan line were carried out on each. To avoid agglomeration, sodium dodecyl sulfate (SDS, C_{12}H_{25}NaO_{4}S) was used as a dispersant agent or surfactant. Each inhibitor container with P1 polymer (50 mg) diluted in 1 mL of toluene was mixed during 24 h at room temperature, with a rotation frequency of 300 rpm.

2.4. Electrode preparation

To obtain an electrochemical response, 1018 carbon steel working electrodes in the form of circular probes were cut and abraded until forming 600-grade-silicon-carbide (SiC) emery paper. They were then encapsulated in a commercial MC-40 resin with a 1 cm² area exposed to the 3% chloride solution. The P1 polymer matrix or
**Fig. 4.** EDX-SEM mapping: (a) ash particles and (b) MCM-41 particles, showing the presence and distribution of the inhibitor elements: Fe, N and O.

**Fig. 5.** FT-IR spectra for (a) ash with inhibitor, (b) P1<sub>ash</sub>, (c) MCM-41 with inhibitor, and (d) P1<sub>MCM-41</sub>.

**Table 1**

<table>
<thead>
<tr>
<th>Monomer ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Molecular weight</th>
<th>Thermal stability</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Mw</td>
<td>PDI</td>
</tr>
<tr>
<td>89%:11%</td>
<td>1600</td>
<td>91000</td>
<td>5.8</td>
</tr>
</tbody>
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<sup>a</sup> Obtained by 1H NMR; the relation between monomers was incorporated into the polymer; 3-HT: functionalized thiophene.
protective coating (50 mg dissolved in 1 mL of toluene), mixed with each of the two composites—one containing ash particles (P1_MCM-41) or the other MCM-41 particles (P1) with an inhibitor (iron(III) nitrate) — was prepared and applied to a steel metal surface using a small brush. After the first application, the electrode was left to dry, and a second coating was applied with a total average thickness of 12 microns. Other metal samples were coated with the P1 polymer in absence of inhibitor containers and, finally, a layer of acrylic spray enamel was applied to all the probes. For comparison purposes, a blank metal surface was also observed. Before immersion, in order to evaluate the performance of the smart inhibitor coating system, a duplicate of each probe was prepared scratching the coating surface with a cutter to simulate in-service coating damage and trigger corrosion conditions. This is a common procedure for evaluating anti-corrosion passive films and coatings [33].

2.5 Electrochemical measurements

The electrochemical measurement was conducted in an electrochemical cell arrangement containing a mild steel probe with an exposed area of 1 cm² as the working electrode. A graphite bar was used as counter electrode, and an Ag/AgCl as reference electrode. The tip of a platinum electrode was used as a second electrode for current noise measurement.

The electrolytic medium was prepared with 3% by weight of sodium chloride in distilled water the resulting pH of this solution was 7. Measurements were taken at room temperature by immersing the three electrodes in the electrolyte solution in the absence and presence of different concentrations of iron(III) nitrate (0, 5, 10, 20, 50 and 100 ppm). Polarization resistance curves were obtained by applying a potential sweep from −900 mV to 200 mV of 1018 mild steel, with a sweep rate of 0.5 mV s⁻¹. The corrosion potential (Ecorr) was calculated for the different systems being studied, and the Tafel slopes in the anodic curves were extrapolated down to the corrosion potential to obtain the corrosion current density (icorr). A Gill ACM Instruments AC-Sequencer software and potentiostat, galvanostat and zero resistance ammeter was used.

Electrochemical Noise Measurements (ENMs) as a function of time of immersion in a 3% sodium chloride solution were recorded using a coated working electrode, a platinum electrode as second working electrode and a copper-copper sulfate reference electrode for the different immersion periods. Electrochemical Noise Measurements were simultaneously performed at a sampling rate of one point per second for a period of 1024 seconds. An Automated Zero Resistance Ammeter (ZRA) and ACM instruments were used. Rn, inversely proportional to the corrosion rate, was calculated as the ratio of the standard deviation of the potential over the standard deviation of the current (Rn = σv/σi).

3. Results and discussion

3.1. P1 polymer analysis

The spectroscopic NMR results showed that the P1 polymer has 89% of 3-hexylthiophene and 11% of functionalized thiophene, (S)-(–)-(1-(4-nitrophenyl) pyrrolidin-2-yl)methyl–2-(thiophen–3-yl) acetate. This is a favorable result considering the molar feed ratio used in the polymer synthesis: 2.8 (7.12 mmol): 1 (2.51 mmol) of (3-hexylthiophene: functionalized thiophene). Both monomer signals are illustrated in Fig. 2. A similar polymer was synthesized in our research group, but with a ratio of 74% of 3-hexylthiophene and 26% of functionalized thiophene, lower regioregularity, and a dyads configuration of 64% [35].

1H NMR (200 MHz, CDCl3), 3-TH: δ = 6.98, 7.00, 7.03, 7.05 (H4-4), 2.56, 2.80 (Hc), 0.91, 1.35, 1.43, 1.58, 1.70 (H4-1). Functionalized thiophene: δ = 8.00 (H17, H19), 6.57 (H16, H20), 3.23, 3.44, 3.72, 3.81, 4.11, 4.32 (H12, 12.5, 10.5): UV-vis: λmax = 418 nm, 589,500 cm⁻¹ M⁻¹ (chloroform solution); FT-IR (cm⁻¹): 3056 (−C-H st), 2922, 2853 (C-H st), 1738 (C=O st), 1653, 1598 (C=C st), 1510 (NO2 st as), 1456 (CH3 δas, CH2 δ), 1377 (CH2 δsym), 1311 (NO2 st sym), 1112 (C-O st), 824 (ar CH δoop), 753, 724 (CH2 γ).

The regioregularity, meaning the monomer units arrangement (percentage of H-T dyads and HT-HT triads), molecular weight distribution (Mn and Mw) and thermal properties (Tg and Td) in this study were similar to those normally found in PTs synthesized under the same regio-selective method; that is, through oxidative polymerization with FeCl3 [36–39]. Table 1 summarizes the physicochemical properties observed.

3.2. Analysis of the inhibitor containers

3.2.1. SEM Characterization: mapping of inhibitor containers

Fig. 3 shows the distribution of the inhibitor container particles in an amorphous form. The containers were also analyzed through EDX mapping (Fig. 4) to locate the inhibitor components in the container matrix.

Firstly, as can be noted, the scattering of the ashes and MCM particles improved with the use of a surfactant agent (SDS, sodium dodecyl sulfate). Iron(III) nitrate inhibitor components and dispersion can be observed in Fig. 4. These results clearly demonstrate that ashes and MCM-41 particles can function as inhibitor containers and, when treated appropriately, can also form composites that serve for smart coatings.

3.2.2. FT-IR analysis of inhibitor containers

According to the FT-IR analysis performed on each composite constituted by containers (whether ash or MCM-41), iron(III) nitrate inhibitor and P1 polymer (Fig. 5), the FT-IR spectra of iron oxides were well established. It has been observed that absorption bands attain a high wavenumber region as a result of OH stretching and a low wavenumber region as a result of Fe-O lattice vibration. In our study, the FT-IR spectrum of magnetite exhibited two strong infrared absorption bands. According to Ishii et al., this behavior can be attributed to the Fe–O stretching mode of the tetrahedral and octahedral sites for the band at 570 cm⁻¹ and the Fe–O stretching mode of the octahedral site for the band at 390 cm⁻¹, provided that Fe³⁺ ion displacements at tetrahedral sites are negligible [34,42]. Table 2 summarizes possible FT-IR peaks for different iron oxides.

Considering the above, it was possible to assign the corresponding signals to the ash container with iron(III) nitrate inhibitor: 3225 (O–H st), 1796 (OC=O st), 1407 (O–H δ), 1036 (C=OH st), 873 (N=O st) and 602, 570, 446 (magnetite Fe–O). The ash container with
inhibitor and P1 polymer presented the following bands: 3263 (O–H st), 2954, 2923, 2853 (C–H st), 2795 (O=C=O st), 1736 (C=O st), 1598 (C=C st), 1416 (O–H δ, CH₂ δas, CH₂ δ), 1312 (NO₂ st sym), 1111 (C=O st), 873 (ar C=N st), 823 (ar CH δoop) and 603, 570, 444 (magnetite Fe–O). The MCM-41 container with iron(III) nitrate inhibitor gave rise to the following bands: 3388 (SiO–H st), 1635 (OH bending), 1055 (C–O st), 962 (Si–O st), 797 (Si-N st) and 558, 444 (Fe–O).

Finally, the MCM-41 container with inhibitor and P1 polymer presented the following bands: 3385 (SiO–H st), 3059 (=C–H st), 2954, 2923, 2854 (C–H st), 1727 (C=O st), 1599 (C=C st), 1510 (NO₂ st as), 1455 (CH₂ δas, CH₂ δ), 1377 (CH₂ δsym), 1311 (NO₂ st sym), 1261, 1072 (ar C–H st), 963 (Si–O st), 822 (ar CH δoop) and 615, 570, 464 (Fe–O).

**Fig. 7.** Noise resistance ($R_n$) as a function of time (0–72 h) for mild steel coated with (a) P1_ash and (b) P1_MCM-41.

**Fig. 8.** Smart coating in chloride solution: corrosion potential as a function of time for (a) P1_ash samples and (b) P1_MCM-41 samples.

**Fig. 9.** Noise resistance ($R_n$) as a function of time (0–400 h) for mild steel composite coatings and as a function of time of immersion in chloride solution for (a) P1_ash and (b) P1_MCM-41.
The inhibitor performance at several concentrations [5–100 ppm] was evaluated by polarization curves. Triplicate curves were obtained and an average curve is presented (1.5% deviation). As can be observed in Fig. 6, in the case of 5 ppm, there is an active corrosion potential around −780 mV; after that, the potential increases forming a passivation zone until −400 mV; for that reason we selected this inhibitor concentration. The current limit in the cathodic region was associated to the effect of oxide diffusion. By contrast, the anodic region in the presence of inhibitor showed pseudo-passivation due to the possible formation of corrosion products associated to the different inhibitor concentrations. Consistent with the literature, this study found that the inhibitor promoted a protective oxide film formation against corrosion on the surface of the metal [40,41].

The \( I_{corr} \) was calculated using the well-known slopes method in the active Tafel region reached 1.480 mA/cm\(^2\) [43], in the case of solutions without inhibitor, but dropped to 0.105 mA/cm\(^2\), 0.350 mA/cm\(^2\), 0.225 mA/cm\(^2\), 0.185 mA/cm\(^2\) and 0.207 mA/cm\(^2\), respectively, for the solutions with the different inhibitor concentrations specified above.

The coating systems were subjected to different periods of short-term immersion in the solution to obtain the electrochemical resistance noise level as a function of time (Fig. 7). For the P1ash coating system (see Fig. 7(a)), \( R_n \) decreased after 24 h of immersion for each sample, suggesting a bond disbondment of the coatings from the metal surface. The best performance of \( R_n \) was 10\(^7\) ohm-cm\(^2\) for the P1 polymer and P1ash (60 mg) coating systems, with up to 24 h of immersion. During the first hours of immersion the polymer coating presents barrier effect, the inhibitor will act only when the coating has been damaged and the corrosion has started due to longer immersion periods. The worst performance was 10\(^4\) ohm-cm\(^2\) for the P1ash (20 mg) system, with 48 h to 72 h of immersion, which presented a similar behavior to that of the blank sample. Similarly, in the case of the P1MCM-41 coating system (Fig. 7(b), the best behavior was registered in the P1 polymer coating without particles, which maintained an \( R_n \) value between 10\(^7\) to 10\(^6\) ohm-cm\(^2\) throughout the 72 h of immersion in the solution. For the P1MCM-41 systems, \( R_n \) values were between 10\(^5\) to 10\(^6\) until 24 h of immersion. Subsequently, \( R_n \) declined to values around 10\(^4\) ohm-cm\(^2\) with 48 h to 72 h of immersion. These results suggest that the coating begins to degrade or disband after 24 h of immersion, and corrosion protection diminishes shortly after immersion. Hence, it can be concluded that the coatings containing 60 mg particles offer a favorable condition, while the P1 polymer coating without particles offers a comparatively superior overall performance.

Fig. 8 presents the corrosion potential as a function of time for the mild steel samples without coating (blank), P1 polymer and with smart coating: P1ash and P1MCM-41, both containing iron(III) nitrate. All samples were covered with acrylic enamel as well. The

### Table 2

<table>
<thead>
<tr>
<th>Iron oxide/hydroxide</th>
<th>Band wavenumbers (cm(^{-1}))</th>
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<tbody>
<tr>
<td>Magnetite (Fe(_2)O(_4))</td>
<td>Broad bands at 570 and 400 cm(^{-1})</td>
</tr>
<tr>
<td>Maghemite ((\gamma)-Fe(_2)O(_3))</td>
<td>700, 630–660 range (Fe-O range)</td>
</tr>
<tr>
<td>Hematite ((\alpha)-Fe(_2)O(_3))</td>
<td>540, 470 and 352 cm(^{-1})</td>
</tr>
<tr>
<td>Goethite ((\alpha)-FeOOH)</td>
<td>1124, 890 and 810 cm(^{-1}) for OH stretch</td>
</tr>
<tr>
<td>Lepidocrocite ((\gamma)-FeOOH)</td>
<td>1018 cm(^{-1}) (in-plane vibration) and 750 cm(^{-1}) (out-of-plane vibration)</td>
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</table>

**Fig. 10.** Corrosion products FT-IR spectra for a) P1ash and, b) P1MCM-41.
corrosion product, promoted by inhibitor liberation from the container particles. The best experimental conditions were composite coatings with 60 mg inhibitor loaded particles. The electrochemical tests as a function of immersion time, showed good performance of the coating systems presenting noise resistance values around 10 o/m-cm². The particles acting as containers, releasing the inhibitor and retarding the corrosion process of the metal during short immersion periods (72 h with acrylic enamel).

Acknowledgments

The authors would like to thank Ciq-Uaem for the spectroscopic analysis and René Guardian Tapia for SEM micrographs. They also gratefully acknowledge PROMEMP/1035.0/07/2674 and CONACYT (Grant No. CB2007-81383-Q) for funding the project. In particular, J.L. Gutiérrez-Díaz is indebted to CONACYT for its support through a scholarship.

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