Original Article

Polymeric organic coatings based on PANI-ES and PANI-ES/APP for fire protection

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ABSTRACT

Polyaniline (PANI) is an intrinsic semiconducting polymer with high potential for application in different areas, but its use in coatings for fire protection has been little explored so far. Therefore, the aim of this study was to investigate the use of this polymer in the preparation of organic coatings and their performance in fire protection. For this purpose, paints containing PANI-ES (emeraldine salt), PANI-ES/APP (ammonium polyphosphate) and APP in the formulation were formulated.

The synthesized polymers, PANI-ES and PANI-ES/APP, were evaluated by Fourier transform infrared spectroscopy (FTIR) analysis, electrical conductivity and thermogravimetric analysis (TGA).

The thermal protection of mild steel samples coated with organic coatings was evaluated after sample exposure to a Bunsen torch for 30 min. During the test, thermography images and temperature data for the steel surface were collected. The coatings were also evaluated by TGA. Due to the high corrosion protection potential offered by PANI, the corrosion behaviour of samples coated with organic coatings was also investigated through electrochemical impedance spectroscopy (EIS) measurements taken in a 3.5% NaCl solution.

It was found that the best fire protection was provided by the coating containing 10% PANI-ES and 10% APP, whose the steel substrate temperature after 30 min of assay did not exceed 330 °C. The coating containing 5% PANI-ES had the best anticorrosive performance. This behaviour can be attributed to the high porosity of the coatings.

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1. Introduction

The use of fire retardant coatings is an efficient way to protect materials from fire damage. The nature of these coatings can be organic and/or inorganic. Cementitious coatings, based on Portland cement and other minerals, have been already used to protect structural steel from fire. However, their weight and aesthetics limit their use in architectural applications [1]. Organic coatings are widely used as fire retardant coatings for many reasons, such as a lower weight when compared with the inorganic ones and ease of processing [2]. They can be applied for many materials, such steel [2-4], textiles [1] and wood [1,5].

It has been shown in many studies [4,6] that structural steel loses its mechanical properties at temperatures above 500 °C. Because of that, the construction industry desires more
effective alternatives to protect it [6]. Many studies [2,4,6-8] have analyzed the viability of intumescent coatings for fire protection of different substrates. These coatings are composed of three main components: an acid source, a carbon source and a blowing agent. When they are exposed to the heat source consecutive reactions occur, leading to the formation of the final carbonaceous layer [6,9]. Also, non-intumescent coatings are a less expensive alternative for fire protection. It has been showed by Green [10] that a material is more protected against fire even if it is painted with a conventional paint.

Popolyaniline (PANI) is an intrinsic semiconducting polymer that offers good anticorrosive properties for many metals such as steel, aluminium and their alloys [11–15]. The doped and conducting PANI offers anodic protection for the substrate due to formation of an oxide mixed layer [12,16]. Other applications for PANI-containing coatings have been studied recently. Baldissera et al. [17] studied the addition of PANI in the formulation of antifouling coatings. It was concluded by the authors that the addition of the conductive form of PANI in the paints containing Cu2O improved the efficiency of the antifouling systems. Stejskal et al. [18] studied the effect of the flame resistance of wood coated with a PANI-containing coating. For all the samples of wood containing PANI coatings, the mass loss during fire or high temperature exposure was lower than for the non-coated ones, showing that PANI coatings can improve the fire resistance of wood.

<table>
<thead>
<tr>
<th>Paint</th>
<th>Resin (%)</th>
<th>Pigment 1 Type</th>
<th>Pigment 2 APP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95</td>
<td>PANI-ES</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>PANI-ES</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>95</td>
<td>PANI-ES/APP</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>PANI-ES/APP</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>PANI-ES</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>85</td>
<td>PANI-ES/APP</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>PANI-ES</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>PANI-ES/APP</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Paint</th>
<th>Plate 1 (%)</th>
<th>Plate 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85.8 ± 4</td>
<td>748.0 ± 30</td>
</tr>
<tr>
<td>2</td>
<td>60.1 ± 7</td>
<td>829.3 ± 46</td>
</tr>
<tr>
<td>3</td>
<td>86.7 ± 3</td>
<td>632.5 ± 43</td>
</tr>
<tr>
<td>4</td>
<td>74.5 ± 7</td>
<td>600.4 ± 22</td>
</tr>
<tr>
<td>5</td>
<td>113.9 ± 16</td>
<td>613.4 ± 14</td>
</tr>
<tr>
<td>6</td>
<td>77.9 ± 9</td>
<td>706.4 ± 36</td>
</tr>
<tr>
<td>7</td>
<td>53.8 ± 4</td>
<td>917.3 ± 28</td>
</tr>
<tr>
<td>8</td>
<td>95.9 ± 10</td>
<td>450.9 ± 10</td>
</tr>
</tbody>
</table>

It has been verified that PANI is a multi-functional polymer that offers a large field of properties and studies. Due to its aromaticity and high amount of carbon atoms in its chemical structure, it is possible that PANI is an excellent carbon source in coatings for fire protection. Therefore, the aim of this work was to formulate and characterize coatings containing PANI in combination with a fire retardant (ammonium polyphosphate, APP). The corrosion protection of these coatings was also evaluated in order to determine a bi-functionality for these coatings on a steel substrate, namely their fire retardancy and anticorrosive properties.

![Fig. 1 – Fire resistance test (a) detail of the thermocouple and (b) thermography of the test.](image-url)
2. Experimental

2.1. Synthesis of PANI-ES and PANI-ES/APP

The PANI-ES was prepared by the polymerization reaction of aniline at temperatures between −4°C and 0°C for 6 h. A solution formed by an oxidizing agent [(NH₄)₂S₂O₈, PSA] in 1 M HCl was added slowly, under constant stirring, to a second 1 M HCl solution containing the monomer. The PANI-ES was filtered through porous glass funnel #G5, under low pressure to accelerate the process. The green powder was washed with distilled water and finally dried in an oven at 60°C for 24 h.

For the synthesis of PANI-ES/APP, APP was first solubilized in 1 M HCl at a concentration of 2.5% (w/v) under constant stirring and at 60°C. Thereafter, the aniline was added to this solution and cooled to approximately −4°C. The procedure was repeated for the synthesis of PANI-ES, i.e. the solution containing the oxidizing agent (PSA in 1 M HCl) was slowly added to the first solution under constant stirring. Finally, after 6 h of reaction, the solution was filtered and the green powder (PANI-ES/APP) was washed with distilled water and ethanol and oven dried at 60°C for 24 h.

2.2. Preparation of paints

The paints were prepared using suitable equipment for this purpose and the components were weighed according to the basic formulation described in Table 1.

<table>
<thead>
<tr>
<th>Paint</th>
<th>Thickness of coatings (μm)</th>
<th>Pull off resistance (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85.8 ± 4</td>
<td>1.30</td>
</tr>
<tr>
<td>2</td>
<td>60.1 ± 7</td>
<td>0.82</td>
</tr>
<tr>
<td>3</td>
<td>86.7 ± 3</td>
<td>1.68</td>
</tr>
<tr>
<td>4</td>
<td>74.5 ± 7</td>
<td>1.24</td>
</tr>
<tr>
<td>5</td>
<td>113.9 ± 16</td>
<td>0.93</td>
</tr>
<tr>
<td>6</td>
<td>77.9 ± 9</td>
<td>1.19</td>
</tr>
<tr>
<td>7</td>
<td>53.8 ± 4</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Fig. 3 – FTIR spectra of PANI-ES, APP and PANI-ES/APP.
It was not possible to evaluate Paint 6 with EIS because the extender removed all the paint from the metal surface, so the film did not form on the plate.

2.4. Fire resistance test

The fire resistance test was conducted for each coating in duplicate. The increase in temperature after application of the flame was measured on the backside of the metal substrate by a Thermomax thermocouple K-type, as shown in Fig. 1(a). A Fluke infrared thermography camera, model T4400, was also used to monitor the temperature profile of the sample. The thermography camera was used for the detection of the infrared spectral range, as shown in Fig. 1(b).

The thermocouple K-type data collection was performed by a data logger module developed in the laboratory. The flame was applied for 30 min using an Orca Bunsen burner, model 770, with a methane flame. The methane torch reached the maximum temperature of 1300 °C.

2.5. EIS test

Electrochemical experiments were performed in a single compartment cell with three electrode configurations. The working electrode consisted of a steel plate coated with a dry film of the paint, with an exposed surface area of 0.785 cm² and the reference electrode was a saturated calomel

Fig. 4 – TG/DTG curves of PANI-ES, APP and PANI-ES/APP.

The resin and the additive were mixed for approximately 5 min using a DISPERMAT N1 disperser with a Cowles disc. Subsequently, pigment 1 was dispersed in the mixture at a speed of approximately 3000 rpm for an additional 1 h. The paints containing both pigments, 1 and 2, were dispersed for 2 h. The amount of solvent used in this process, only for viscosity adjustment of processing, was approximately 80.4 g for all formulations. The size of the dispersed paint particles was evaluated with a fineness of grind gage and was around 5 Hegman (40 μm).

2.3. Sample preparation

The specimens for the fire resistance test and corrosion protection test whit electrochemical impedance spectroscopy (EIS) were prepared following standard procedures. The paints were applied to steel plates, SAE 1010 with dimensions of 200 mm × 250 mm × 0.9 mm and 50 mm × 50 mm × 0.9 mm, that were previously degreased with xylene using an extender. Thereafter, the samples were stored in a dust-free environment until the complete drying. The film thickness was measured after evaporation of the solvent at room temperature using the diffuse current method in a Byko-7500 (BYK Gardner). The measurements were repeated eight times and the mean and standard deviation were calculated, as described in Table 2.

Fig. 5 – TG/DTG curves of paints and pure resin.
electrode (SCE). A platinum plate was used as the counter electrode.

The EIS measurements were performed with a potentiostat Metrohm Autolab, model PGSTAT 30, equipped with a frequency response analyser (FRA 2). The impedance data were measured periodically as the open circuit potential in 3.5% NaCl solution. A frequency range of $10^6$ to 0.1 Hz was used with the amplitude of the sinusoidal perturbation as 10 mV AC. A Faraday cage was used during the EIS experiments.

Simulations were performed using Nova 1.11 software. It was observed that the equivalent circuits to model the impedance data were the classic polymer organic coatings on metal substrates (Fig. 2). The coating resistances, $R_c$, were extracted directly from the Nyquist plots.

2.6. Characterization

Characterization of the polymers was carried out by Fourier transform infrared spectroscopy (FTIR) analysis (Perkin Elmer Spectrometer, model Spectrum 1000), electrical conductivity (Signatone model 5-301-6 associated with a source Keithley 6430, using the standard method of four points [19]) and thermogravimetric analysis (using a thermogravimetric analyser TA Instruments, model TGA Q50).

The TGA experiments were carried out in inert atmosphere ($N_2$) in the temperature range of 25 °C to 900 °C at a heating rate of 20 °C/min and used a sample mass of approximately 10 mg.

The coatings were evaluated for their adhesion to the metal substrate in accordance with ASTM D4541-17 [20] by optical microscopy (Zeiss Optical Microscope model Scope A1, with QImaging camera model Fast 1394), thermogravimetric analysis (TGA) and by SEM-EDS (scanning electron microscope Phenom World model Pro X – Phenom) with an acceleration voltage of 15 kV.

![Fig. 6 – Metal substrate temperature on the backside of samples (a) thermocouple and (b) thermographic camera.](image1)

![Fig. 7 – Coatings after the fire resistance test.](image2)
3. Results and discussion

3.1. Conducting polymers

3.1.1. Electrical conductivity
The conductivity of the PANI-ES was $5.4 \times 10^1 \, \text{S cm}^{-1}$. For the PANI synthesized in the presence of APP (PANI-ES/APP), the electrical conductivity was $7.5 \, \text{S cm}^{-1}$. Since APP is an insulating polymer, it was observed that the addition of it in the PANI synthesis process did indeed decrease the conductivity of the material.

3.1.2. FTIR analysis
Fig. 3 shows the infrared spectra for PANI-ES, APP and PANI-ES/APP. The PANI-ES spectrum shows two strong absorption bands at 1554 and 1472 cm$^{-1}$ that were attributed to the C=C stretching of quinoid (Q) and benzenoid (B) aromatic ring groups, respectively. These values are similar to those previously reported in the literature [17,21]. The band at 1294 cm$^{-1}$ was assigned to vibrations of the C–N bonds, at 1241 cm$^{-1}$ was attributed to stretching of C–N–H bonds and at 1108 cm$^{-1}$ to the formation of polarons H$^+$N=Q=NH$^+$. The band around 793 cm$^{-1}$ is characteristic of a p-disubstituted benzene ring.

In the APP spectrum, the band at 1434 cm$^{-1}$ was attributed to the flexural vibrations of the N–H bonds. The bands at
1252 cm\(^{-1}\) and 1063 cm\(^{-1}\) were attributed to the symmetrical stretching of the P=O and P–O bonds, respectively. Finally, the bands at 881 cm\(^{-1}\) and 798 cm\(^{-1}\) were attributed to the vibrations of the PO\(_2\) and PO\(_3\) bonds, respectively [22].

As shown, the bands present in the spectrum of PANI-ES and APP are also present in the spectra for PANI-ES/APP, but with some displacements. This confirms the formation of the conducting polymer even with the addition of the APP. The bands at 1556 and 1470 cm\(^{-1}\) were attributed to the C=C stretching of aromatic ring groups Q and B. The band at 1294 cm\(^{-1}\) was assigned to the vibrations of the C–N bonds and the band at 1240 cm\(^{-1}\) was attributed to stretching of C–N–H bonds. The band at 1110 cm\(^{-1}\) was assigned to the formation of polarons H\(^+\)N=Q=NH\(^+\). The band around 794 cm\(^{-1}\) can be a bands overlapping of the P–O bond vibrations of APP and p-disubstituted benzene ring of PANI-ES.

3.1.3. Thermogravimetric analysis

This technique was used to obtain thermal behaviour of the polymers. Fig. 4 shows the TG/DTG curves for PANI-ES, APP and PANI-ES/APP.

The first thermal event in the TG/DTG curves for the PANI-ES, with a maximum degradation temperature around 75 °C, can be attributed to the moisture loss of the polymer. A second thermal event, with a maximum degradation temperature around 276 °C, is associated with the evolution of the dopant acid and degradation of oligomers. The third event in the TG curve for this polymer started at around 400 °C and is associated to a structural rearrangement where breakage at the ends of the chain may be occurring. The fourth thermal event, starting at approximately 500 °C, is associated with degradation of the polymer chain [23].

For the APP, the TG/DTG curves present a first thermal event associated with the elimination of NH\(_3\) and water, with a maximum degradation temperature around 350 °C. The second thermal event, with a maximum degradation temperature around 618 °C, is associated with the release of phosphoric, polyphosphoric and metaphosphoric acids in the degradation process of APP [24].

The PANI-ES/APP presents TG/DTG curves similar to pure PANI-ES and the same thermal events can be observed, however this polymer is thermally more stable. This fact may be associated with reactions that have occurred between the polymers during the synthesis, since the APP has a high number of functional groups. It can be noted that the residue content is higher in PANI-ES/APP (around 52%) while in PANI-ES it remained around 34%. This result also may evidence the presence of APP in the conducting polymer.

3.2. Organic coatings

3.2.1. Adhesion test

The adhesion test was done according to ASTM D4541-17 [20], which evaluates the pull off resistance (or adhesion) of a coating system on a metal substrate. Table 3 shows the thickness of coatings and pull off resistance values obtained in the
Fig. 11 – SEM/EDS micrograph of the charred surface of Paint 4.

Fig. 12 – SEM/EDS micrograph of the charred surface of Paint 7.
adhesion test for the coatings. The test was carried out for the samples that were used for the EIS analysis, but in a region where the coating had no contact with the saline solution.

In the Paints 2, 5 and 8, corrosion products were observed on the metal substrate where the coating was removed. This fact may have contributed to the lower adhesion of the coating, such that less force was required to pull the film off of the substrate. The pull off resistance for the coatings was 0.82 MPa, 0.93 MPa and 0.62 MPa, respectively.

3.2.2. Thermogravimetric analysis

Fig. 5 shows the TG/DTG thermograms of Paints 1, 3, 5 and 6 that contained 5% of conducting polymer (PANI-ES and PANI-ES/APP) in the formulation and pure resin.

In the TG/DTG curve for the epoxy resin, a first mass loss was observed with a maximum degradation temperature around 97 °C and attributed to the loss of moisture and evaporation of the solvent present in the sample. The second thermal event, with a maximum degradation temperature around 443 °C, was associated with degradation of the polymer chain [17,25].

The paints exhibited behaviour similar to the pure resin because the degradation events of the PANI used as a pigment were in the same temperature range of the resin, as seen previously. However, the paints containing APP in the formulation (Paint 3, 5 and 6) had their maximum degradation temperatures displaced to lower values due to the degradation of APP components (NH₃, phosphoric acid, polyphosphoric acid and metaphosphoric acid).

3.2.3. Fire resistance test

The assay was performed as previously described and the temperature profiles obtained by thermocouple (a) and thermographic camera (b) as a function of time throughout the test are shown in Fig. 6. As can be seen, there is a difference of approximately 100 °C between the methods, but the behaviour was similar in both. This difference can be attributed to the fact that the thermocouple has a small physical contact with the metallic substrate, while the thermographic camera captures a larger area of the surface.

Uncoated steel, after 3 min of flame exposure, had a temperature above 400 °C, which stabilized at approximately 460 °C after 10 min of the test (Fig. 6(a)). In this temperature range, the structural properties of the steel would be compromised [26,27]. Similar temperatures for the uncoated substrate were also found by Ullah et al. [28]. The plates coated with Paints 1, 2 and 3 exhibited similar behaviour to uncoated steel, but the temperature took around 5 min to reach 400 °C and stabilized at approximately 380 °C. The plate coated with Paint 4 showed the worst performance and reached 400 °C with only 1 min of assay. Although the addition of APP in the PANI-ES synthesis improved the thermal stability of the polymer (PANI-ES/APP), as observed in the TGA of Fig. 4, in the fire resistance test the performance of the coatings with this polymer was not higher than that of PANI-ES.

However, the Paints 5, 6, 7 and 8 showed superior performance among the evaluated coatings. All these paints were prepared with 10% APP in the formulation, which is the organophosphorus agent that acts as the flame-retardant compound [22,29]. It was observed that the performance of this compound was an effective fire retardant initially because
the temperature increase was slower than for the other formulations. This action of the flame retardant can be explained by the fact that during its decomposition there is the release of PO\(^*\) radicals, which react with the oxidants and reduce the exothermicity. This reduces the decomposition of the coating, as discussed by Schartel [30].

The best performance in the fire resistance test was presented by steel plate coated with Paint 7, whose temperature after 30 min of assay did not exceed 330 °C. This paint was formulated with 10% PANI-ES and 10% APP. The temperature of the steel plate coated with Paint 5, similar to Paint 7 but containing 5% less of PANI-ES in the formulation, remained at about 380 °C at the end of the assay. Therefore, it is possible to affirm that a greater amount of PANI-ES in the paint improves the fire protection of the coating, which can be attributed to the greater carbon source provided by the polymer in the paint. In addition, PANI doped with HCl may be acting as an acid source in the formulation, which also favours the fire protection of the coating.

In Figs. 7 and 8, it is possible to observe the appearance of the coatings as well as the backside of the steel plates after the fire resistance test.

None of the formulations tested showed an intumescent behaviour because the carbonaceous layer did not expand due to the decomposition of the carbon source (resin and PANI) during exposure to the flame. This fact can be attributed to the absence of an expanding agent in the formulation of the paints and to the low generation of expansion gases during the decomposition of the coating [31].

Table 4 shows the diameter of the thermally affected zone measured on the backside of steel plates (Fig. 8) after the assay.

It was observed that the growth of the thermally affected zone was smaller for Paints 5, 6 and 7, indicating the thermal protection of these coatings. In comparison with the uncoated plate (Fig. 9), that had a diameter of 102 mm, only the plates coated with Paints 3 and 4 had higher diameters of 143 and 112 mm respectively. The low efficiency of these coatings in the fire resistance test can be attributed to the fact that the coatings were not completely cured at the time of testing. Solvent was still present along the thickness of the coating, propitiating the burning of the entire coating, as can be seen in Fig. 7.

3.2.4. SEM-EDS

This technique was used to evaluate the products formed after the combustion of the coatings in the fire resistance test. The area evaluated was the central ring formed by the direct incidence of the flame in the coating, which can be visualized in Fig. 7. Figs. 10–13 show SEM/EDS micrographs of the charred surface of some coatings.

Paint 2 in Fig. 10 shows a surface coated by oxides. Due to the thermal oxidation, it is possible to associate the oxide formation with the high temperature reached on the surface of the substrate. Meanwhile, a different structure was observed in Paint 4 (Fig. 11) with PANI and APP, where there are areas with exposed steel and some fractures on the substrate surface. However, oxide formation on the substrate is also observed.

The presence of phosphorus on the surface of Paint 7 indicates a solid phase action of APP during the decomposition, as seen in Fig. 12. This behaviour helped to slightly reduce the substrate temperature and protect the surface from the flame. The formation of pores was not observed but due to the insufficient intumescence of the coating, the thermal oxidation of the steel could not be avoided.

Paint 8 demonstrated a similar behaviour as the other samples (Fig. 13). The SEM images indicate that the PANI and APP were not able to protect the substrate from the fire damage. Although the presence of PANI increased the residue formation per the TGA results, it is clear that an expansion is necessary to promote a protective layer.

3.2.5. EIS analysis

This technique evaluates the corrosion stability of the coatings when in contact with an electrolyte, which in this case was a 3.5% NaCl solution. Figs. 14 and 15 presents the Nyquist diagrams for the coatings after different times of exposure to the solution. The values of the resistance of the coatings were

Fig. 14 – Nyquist plots recorded for paints after 24 h and 48 h of exposure to 3.5% NaCl.
extracted directly from the Nyquist diagrams by the method of extrapolation of the capacitive arc from the relationship:

$$R_c = Z_{r,w \to 0} - Z_{r,w \to \infty}$$  \hspace{1cm} (1)

where $R_c$ is the coating resistance, $Z_{r,w \to 0}$ and $Z_{r,w \to \infty}$ is the impedance when the frequency tends to zero and to infinity, respectively.

The Nyquist diagrams and the resistance values of the coatings obtained after the formation of the capacitive arc show that after electrolyte penetration into the film, all samples displayed minimal polarization resistance after 24 h of exposure of the coatings to 3.5% NaCl solution, except Paint 1 (Fig. 14). The resistance of the coatings remained around $1.2 \times 10^4 \, \Omega$, $6.5 \times 10^5 \, \Omega$, $1.4 \times 10^6 \, \Omega$, $2.1 \times 10^6 \, \Omega$ and $1.0 \times 10^4 \, \Omega$ for the coatings formed from Paints 2, 3, 4, 5 and 7, respectively. The coating formed from Paint 8 was extremely inefficient, with a resistance below 300 $\Omega$.

![Fig. 15 – Nyquist plots recorded for paints after 96 h and 168 h of exposure to 3.5% NaCl.](image)

After 48 h of exposure of the coatings to 3.5% NaCl solution, a decrease in the coating resistance for the samples and a tendency to form a capacitive arc for Paint 1 were noted.

The same behaviour was observed after 96 h of exposure of the films to the solution (Fig. 15), where the resistance of the coatings decreased to approximately $8.0 \times 10^3 \, \Omega$, $5.9 \times 10^5 \, \Omega$, $9.0 \times 10^4 \, \Omega$ and $5.0 \times 10^2 \, \Omega$ for the coatings formed from Paints 2, 3, 5 and 7, respectively. This trend was a consequence of the progressive degradation of the coating by diffusion of the electrolyte through the pores of the films. After the corrosive attack, the coating resistance for Paint 4 increased to $2.4 \times 10^5 \, \Omega$, probably due to the formation of corrosion products that block the pores and make ion transport more difficult, which was observed in previous studies [32,33].

After 168 h of exposure of the coatings to 3.5% NaCl solution, it was observed that Paint 1 tends to form the capacitive arc and that the resistance of the film, extrapolating the capacitive arc, is around $1.3 \times 10^6 \, \Omega$. For the other samples, a decrease in the coating resistance was noted.

From these results, it was observed that the coating obtained from Paint 1 (containing 5% PANI-ES in the formulation) had the best anticorrosive performance, i.e. the barrier effect of the coating to the passage of the electrolyte was more efficient compared to the other paints evaluated in the 168 h test range.

3.2.6. Film morphology

Figs. 16 and 17 show the morphology of the paint films obtained by optical microscopy before and after being
submitted to the immersion experiments. As all paints displayed approximately the same fineness, their morphology was similar before they were exposed to the corrosive solution.

The micrographs indicate a high number of pores on the surface of the films before exposure to the saline solution, regardless of the type of polymer used in the paint formulation, which compromises the efficiency of the coatings. The pores accelerate the formation of diffusion paths and facilitate the passage of the electrolyte through the coating that attacks the metal surface. These results corroborate the low resistance of the films evaluated by the electrochemical impedance test.

Larger pores were observed in all coatings after the samples were exposed to 3.5% NaCl solution for 168 h, indicating degradation of the coatings. It is also possible to observe pores where the total degradation of the coatings occurred for the Paints 4 and 8 (Figs. 16 and 17 respectively), exposing the metallic substrate (indicated by yellow circles in the figures).

The paints with the highest amount of PANI in the formulation (Paints 2, 4, 7 and 8) presented films with larger pores after 168 h in contact with 3.5% NaCl solution. A greater amount of pigment in the coating increased its permeability and facilitated the corrosion process of the material to be protected. The Paint 1 presented the smallest pores in relation to the other samples, which corroborates the better efficiency in the electrochemical impedance test.

4. Conclusion

The aim of this study was to mix electronic conductive polymers, in this case PANI-ES, with a classic polymer used to produce paints and subsequently form a protective coating. The mixture should take advantage of the electrochemical and electrical properties of the polymeric material to protect surfaces exposed to aggressive environments.

In this study, it was demonstrated that PANI-ES could improve the fire protection of the coatings, which can be attributed to the greater carbon source provided by the polymer in the paint. In addition, PANI doped with HCl may be acting as an acid source in the formulation, which also favours the fire protection of the coating. The best performance was presented by the coating whose paint was formulated with 10% PANI-ES and 10% APP, where the temperature after 30 min
of assay did not exceed 330 °C. It was observed that none of the formulations tested showed an intumescent behaviour, as the carbonaceous layer did not expand due to the decomposition of the carbon source (resin and PANI) during exposure to the flame. However, the results obtained so far are very promising.

Regarding EIS results, it was observed that the coating containing 5% PANI-ES had the best anticorrosive performance, i.e. the barrier effect of the coating on the passage of the electrolyte was more efficient, compared to the other evaluated paints.

In this study, the paint that provided the best fire protection was not the one that presented better corrosion protection; this could be attributed to the greater amount of pigment in the coating, increased its permeability and facilitated the corrosion process of the material to be protected.

**Conflicts of interest**

The authors declare no conflicts of interest.

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