Synthesis and characterization of polypyrrole – TiO$_2$ coatings on AISI 304 stainless steel

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Abstract. The electrical properties of conducting polymers make them interesting materials to be used in a large number of technological applications. In recent years, an important effect on the anticorrosive properties of the conductive polymer was observed when inorganic particles such as nano-sized TiO$_2$ are incorporated in the conductive matrix. In the present study, polypyrrole films were synthesized in the presence of TiO$_2$ nanoparticles. A study of the electropolimerization conditions, thickness of the formed films and the effect of incorporation of TiO$_2$ nanoparticles on the structure of the polymer matrix by Raman spectroscopy was performed. These results show that it is possible to obtain the adherent coatings, with thicknesses between 3-4 µm. However, the presence of TiO$_2$ nanoparticles in the polymeric matrix influences the corrosion resistance of the polypyrrole coatings, destabilizing the natural passive capacity on the surface of AISI 304 stainless steel.

1. Introduction
Corrosion is an electrochemical process occurring between metal and a corrosive environment, which leads to structure degradation and therefore premature failure, as well as significant economics losses [1-2]. Among all metallic alloys, steel is still the most used material for industrial applications. For this reason, different strategies have been proposed to mitigate this phenomenon, such as the adequate selection of the material, followed by an effective design [3]. A particular example is stainless steels, which are iron alloys, with alloying elements such as chromium and nickel in various proportions. However, despite the corrosion resistance of stainless steel, in the presence of chlorides, these materials are susceptible to various types of localized corrosion, for this reason, it is important to consider other methods of protection against corrosion, such as the optimization of processes, the use of cathodic protection, corrosion inhibitors, or the application of coatings, both inorganic and organic; the latter method being the most effective route for the protection of metal surfaces [4].

Organic coatings exhibit good adhesion to the metal surface and controlled thicknesses, further their efficiency against corrosion can be busted by incorporation of inhibitory pigments [5]. In recent years, conductive polymers such as polyaniline (PANI), polythiophene (PT) and polypyrrole (PPy) have been widely studied as protective coatings, because they exhibit high conductivity, good environmental stability and extensive technological applications [6-7]. The PPy can be obtained by chemical and electrochemical polymerization. Electopolymerization is considered an effective
synthesis method that provides better control of the thickness and morphology of the films obtained and with good adhesion to the metallic substrate [8–12].

However, conductive polymers present some specific problems such as instability under exposure to oxygen and UV rays, poor mechanical properties, delamination, and porosity [13]. New strategies have been reported to improve their properties and extend their range of application, for example, through the chemical modification of the base monomer, the use of aqueous and non-aqueous solutions in the synthesis process, the incorporation of dopants, the synthesis of compounds and nanocomposites of conductive polymers with inorganic materials and their assembly in multilayers [14–15].

The incorporation of inorganic metal oxide particles such as MnO₂, V₂O₅, TiO₂, Fe₂O₃, Fe₃O₄ and WO₃ or metallic particles of Zn, Cu, Au, Pt is a promising method to improve mechanical strength, chemical resistance, thermal stability, and the homogeneity of the coating [2, 16]. It has been showed that the incorporation of nanoparticles of titanium dioxide (TiO₂), even at low concentrations (<10%wt.), provides better dispersion and greater anticorrosive protection in coatings, when they are in the presence of NaCl, due to its large surface area, low density and mechanical resistance [14, 17–18].

In the present work, polypyrrole (PPy) coating with additions of TiO₂ nanoparticles was electrodeposited onto AISI 304 stainless steel, studying the effect of nanoparticles concentration on the electrochemical behavior of the coating.

2. Experimental

2.1. Surface preparation of the substrate

AISI 304 stainless steel (SS) disks (18 wt.% Cr, 8.8 wt.% Ni, <2 wt.% Mn, <1 wt.% Si), of 19 mm in diameter were used as substrates. Samples were prepared by mechanical grinding to grade 600 with silicon carbide emery paper and degreased in an ultrasonic bath with ethanol for 10 min.

2.2. Electrodeposition of PPy and PPy-TiO₂ coatings

The coatings of PPy and PPy-TiO₂ were obtaining by different steps. The pyrrole monomer (Py) (reagent grade, Aldrich) was purged with nitrogen and stored below 0 °C. All other reagents such as oxalic acid, TiO₂ nanoparticles, were used as received. PPy and PPy-TiO₂ films were obtained by galvanostatic polarization applying a constant current density of 1.13 mA cm⁻². The electropolymerization was carried out at room temperature in a three electrode cell for 600 s. The pH of the solutions of PPy and PPy-TiO₂ in oxalic acid was 2.14. A platinum mesh was used as the counter electrode and an Ag/AgCl (3.0 mol L⁻¹ KCl) electrode as reference. A Gamry 750 potentiostat/galvanostat was used for the experiments. The electrolyte used in the synthesis of PPy and PPy-TiO₂ films was composed of 0.1 mol dm⁻³ pyrrole solution, 0.1 mol dm⁻³ oxalic acid solution and addition of nanoparticles. For the electropolymerization of PPy-TiO₂, nanoparticles were added by 1, 4 and 7% wt. they were dispersed in an oxalic acid solution before electrodeposition, using high intensity ultrasonic radiation for 2 h and subsequent mechanical agitation during the electropolymerization process.

2.3. Physicochemical characterization of PPy and PPy-TiO₂ coatings

The coatings were characterized by scanning electron microscopy (SEM) coupled with an energy-dispersive spectrometer (FEI Quanta 650 FEG) with a voltage of 10 kV. Raman Spectroscopy analysis of the effect of the TiO₂ nanoparticles on the structure of the polymer matrix was carried out in a HORIBA spectrometer system with 532 nm excitation and power of 50 mW. Thickness of the films were measured using an Eddy probe, Positector 6000.

2.4. Electrochemical characterization of PPy and PPy-TiO₂ coatings

The corrosion protection properties of the films were evaluated by electrochemical impedance spectroscopy (EIS) and linear potentiodynamic polarization. All measurements were performed in a solution of 3.5% wt NaCl at room temperature, using a three electrode cell, with an Ag/AgCl (3.0 mol
L\(^{-1}\) KCl) electrode as reference and a platinum wire as a counter electrode. EIS tests were carried out in a frequency range of 1 MHz to 3 mHz with a perturbation amplitude of 10 mV rms with an acquisition rate of 10 points per decade. The linear potentiodynamic polarization tests were carried out in a frequency range of -0.6 V to 1.6 V. All experiments were performed in a 100 mL cell at room temperature.

3. Results and discussion

3.1. Electrochemical polymerization of PPy and PPy-TiO\(_2\) coatings

The electropolymerization of PPy in oxalic acid was performed by galvanostatic polarization, applying a current density of 1.13 mA cm\(^{-2}\), for 600 s, evidencing the formation of a homogeneous polypyrrole film on the surface of the steel. During the formation of the film, the system reaches a constant potential of +0.6 to +0.8 V approximately, also reported in the literature. The oxidation of PPy on AISI 304 stainless steel occurs almost immediately the process initiates. Figure 1 shows the potentiometric curves for depositing polypyrrole with different concentrations of TiO\(_2\) nanoparticles onto the AISI 304 stainless steel. It can be observed that by increasing the concentration of nanoparticles in the polymer, the electropolymerization potential decreases, which suggests that less energy is required for the formation of the polymer [19].

![Figure 1. Potentiometric curve during the galvanostatic electrodeposition of PPy-TiO\(_2\) coatings onto AISI 304 stainless steel in 1 M oxalic acid solution for 600 s. a) PPy, b) 1% wt. TiO\(_2\)/PPy, c) 4% wt. TiO\(_2\)/PPy and d) 7% wt. TiO\(_2\)/PPy.](image)

3.2. Physicochemical characterization of PPy and PPy-TiO\(_2\) coatings

Figure 2 shows the scanning electron micrographs of polypyrrole coatings with 1, 4 and 7 % wt of TiO\(_2\) nanoparticles. The size of the nanoparticles is less than 100 nm. The polymer coating has a homogenous globular morphology, surrounded by deposits of TiO\(_2\) nanoparticles. Higher deposits are observed on the matrix as the concentration of nanoparticles in solution increases. It can be observed in all the micrographs that in the roughing lines, where roughness is generated, the atoms present electronic vacancies that are replaced by the atoms coming from the conducting polymer. Figure 2 (a'-c') shows the energy dispersive X-ray spectroscopy analysis. The presence of TiO\(_2\) nanoparticles on
the polymeric matrix is confirmed, as expected, the signal for Ti is more evident for the sample with higher concentration of TiO₂ nanoparticles.

![Figure 2](image_url)

**Figure 2.** SEM images and the corresponding EDS analysis of PPy/TiO₂ coatings electrodeposited onto AISI 304 stainless steel in 1 M oxalic acid solution. (a), (a’) 1% wt. TiO₂, (b), (b’) 4% wt. TiO₂ and (c), (c’) 7% wt. TiO₂.

The PPy/TiO₂ coatings are homogeneous and adherent to the stainless steel surface. The thickness of the coatings are about 3-4 μm.

Raman results for TiO₂/PPy coatings electrodeposited onto AISI 304 stainless steel, with concentrations of 1, 4 and 7 wt% of TiO₂ nanoparticles are presented in Figure 3. The spectra show characteristic bands for the PPy in vibration modes, located at 931, 982, 1047, 1252, 1318, 1381 and 1591 cm⁻¹. The structural behavior of the chains of PPy in oxidized state and the presence of polaron and bipolaron states are associated with the intermediate energy levels that arise within the electronic band gap of the polymer due to oxidation [20]. There are also bands at 1318, 1252 and 1047 cm⁻¹ with a mixed vibration of C=C and inter-ring C-C. The band at 931 cm⁻¹ is characteristic of the oxidized state of the polymer (quinoid form) and assigned to out of plane C-H. The bands at 982 and 1047 cm⁻¹ are characteristic of the reduced state of the polymer (benzoid form), assigned to ring deformation mode C-H in plane deformation. As the concentration of nanoparticles increases, these bands increase in intensity [21]. The bands at 441 and 623 cm⁻¹ are possibly attributed to the addition of TiO₂ nanoparticles, rutile phase [22].

3.3. Evaluation of the corrosion resistance of PPy and PPy-TiO₂ coatings

Figure 4 shows the Nyquist diagrams of PPy coatings with addition of 1, 4 and 7% wt. of TiO₂ nanoparticles. The impedance diagrams of the bare stainless steel exhibit higher capacitance, which is attributed to good corrosion resistance of the stainless steel due to the presence of chromium oxide on its surface. On the other hand, when the stainless steels substrate was covered with the coatings showed lower resistance to load transfer. The coated samples have low impedance values, indicating that the passive layer naturally formed on the surface of the steel is destabilized [7]. This effect is more evident as the amount of TiO₂ nanoparticles in the PPy coatings increases. Diffusion processes occur for the PPy coatings with 1 and 4% wt. TiO₂ nanoparticles, associated to the transport of loads.
through the coatings and a possible detachment of the coating. Further work is necessary to clarify the role of TiO$_2$ nanoparticles on the corrosion protection of PPy coatings for AISI 304 stainless steel.

![Figure 3. Raman spectra of the PPy/TiO$_2$ coatings electrodeposited onto AISI 304 stainless steel in 1 M oxalic acid solution. a) 1% wt. TiO$_2$, b) 4% wt. TiO$_2$ and c) 7% wt. TiO$_2$.](image)

![Figure 4. Impedance diagrams for AISI 304 stainless steel with and without PPy/TiO$_2$ coatings in 3.5% wt NaCl solution. (a) Bare, (b) PPy, (c) 1% wt. TiO$_2$/PPy, (d) 4% wt. TiO$_2$/PPy and (e) 7% wt. TiO$_2$/PPy.](image)

4. Conclusions

By means of the electrochemical synthesis of PPy/TiO$_2$, it was possible to obtain homogeneous and adherent coatings with thicknesses ranging between 3-4 μm onto AISI 304 stainless steel. A large number of TiO$_2$ nanoparticles anchored to the surface of the polymer and encapsulated within the polymer matrix are observed. Using the Raman spectrum, it was possible to identify the characteristic bands attributed to PPy in the presence of TiO$_2$ nanoparticles and it was observed that the polymer is in the oxidized state and has aromatic and quinoid structures as reported by the literature. The presence of TiO$_2$ nanoparticles in the polymer matrix influences its corrosion resistance. The PPy/TiO$_2$
coating affects the stability of the naturally formed oxide of stainless steel making it more susceptible to corrosion. Further work it necessary to clarify the role of the TiO$_2$ nanoparticles.

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