



# Article Synthesis and Characterization of Polyaniline-Based Polymer Nanocomposites as Anti-Corrosion Coatings

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**Abstract:** Polymer nanocomposites of polyaniline (PANI)-based metal oxides (SiO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub>A) were synthesized by in situ chemical oxidative polymerization by rapid mixing in a hydrochloric acid medium to evaluate and compare their performance as anti-corrosion coatings on commercial 1018 steel in a 3.5% NaCl medium. The anti-corrosion coatings were developed by dispersing synthesized nanocomposites on an alkydalic resin (AR) for their subsequent electrochemical characterization. X-ray diffraction (XRD) analyses show that PANI has a certain degree of crystallinity in its structure. The incorporation of metal oxide (MO) nanoparticles (NPs) into the polymer matrix was confirmed by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) analyses, while the interaction of nanoparticles with PANI was proven by Fourier transform infrared (FT-IR) and ultraviolet-visible (UV-vis). Thermogravimetric analysis (TGA) reveals that nanoparticles infer greater resistance to the thermal decomposition of PANI. Finally, the use of open circuit potential (OCP) study, Tafel curves, and electrochemical impedance spectroscopy (EIS) showed that coatings made with TiO<sub>2</sub>A NPs exhibit the best anti-corrosion properties as compared to those synthesized with SiO<sub>2</sub> and CeO<sub>2</sub> NPs.

Keywords: conducting polymer; nanocomposite; coating; anti-corrosion; EIS

#### 1. Introduction

Metals and alloys, like steel, are the primary support of the industrial infrastructure due to their mechanical properties, such as high hardness, toughness, and ductility. However, metals in adverse conditions like aggressive media are thermodynamically unstable and subject to corrosion. Economic losses from metal corrosion reach billions of dollars per year worldwide [1,2].

The corrosion process is inevitable; however, the useful life of materials can be extended using corrosion inhibitors, cathodic protection, anodic protection, or by the application of organic coatings. Protective coatings can be made of inert metals or polymers such as polyanilines, polyvinylamides, polycarboxylates, polysaccharides, and polysulfides, among others [3]. At present, conducting polymers (CPs) are arousing great interest regarding metal protection against corrosion since they are capable of passivating the metal substrate surface through protective oxide film formation. On the other hand, the use of organic composites as anti-corrosion coatings has also been suggested since the organic component, such as a polymer, provides a barrier effect, self-healing, and oxidation–reduction (redox) properties to the coating, while the protection against corrosion is afforded by inorganic pigments acting as inhibitors [4]. Thus, the development of polymer nanocomposites as anti-corrosion coatings, based on CPs and metal oxides, provides an improvement in the mechanical and physicochemical properties, such as barrier effect, adhesion, lower porosity, and hydrophobicity in some cases, because organic and



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). inorganic characteristics of the materials are more efficiently combined at the micrometer and nanometer scale [5].

The most extensively studied CPs are polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(ethylene dioxythiophene) (PEDOT), and their derivatives [6–8]. Besides, CPs have been evaluated as protective anti-corrosion coatings in mild steel [9–11], stainless steel [12–16], iron [17–20], copper [21], zinc [22,23], aluminum [24], and other metals [25], probably PANI and its derivatives being the most studied ones [26,27]. The use of dopants in the PANI has also been suggested to improve their conductivity and efficiency against corrosion. For example, Kalendova et al. [28] investigated anti-corrosion protection in different metals by adding inorganic pigments such as zinc, zinc phosphate, and calcium borate to PANI. They showed that the prepared composites achieved better efficiency in metal protection than the individually used materials due to a synergistic effect between the components.

On the other hand, Shi et al. [29] showed that  $SiO_2$  and  $TiO_2$  enhance organic coatings as anti-corrosion protection of mild steels. Caldas et al. [30] prepared PANI-SiO<sub>2</sub> hybrid materials by oxidative polymerization in situ, showing that they improve the anti-corrosion resistance of PANI as a coating deposited on carbon steel immersed in a 3.5% NaCl solution. Similarly, Radhakrishnan et al. [31] demonstrated that anti-corrosion coatings based on PANI and TiO<sub>2</sub> nanoparticles are more efficient in steel protection than PANI alone due to the increase in barrier properties and the interference in the charge transport between the substrate and the corrosive medium provided by NPs. The above findings are associated with the fact that  $SiO_2$  can improve the resistance to oxidation and acid corrosion of metals under different temperatures due to high resistance to heat and chemical resistance [32,33].  $TiO_2$ , in both anatase and rutile phases, is commonly used as an additive in paints since the nanoparticles of this metal oxide infer improvements in the coating's barrier properties. Nazeri et al. [34] prepared ceria and titania coatings deposited on 304 stainless steel and evaluated their performance as an inhibitor of pitting corrosion. Electrochemical measurements in NaCl and SEM and EDX analyses revealed that the composite is suitable for preventing cracking and increasing the resistance to pitting corrosion.

As was already mentioned, various methods of synthesis and oxide content have been used and dispersed in epoxy resin, so it is of interest to determine if these have a better effect on the anti-corrosive capacity of coatings. Therefore, in this study, we have synthesized anti-corrosion systems composed of PANI-based polymer nanocomposites by in situ chemical oxidative polymerization by rapid mixing, which is an effective synthesis method barely studied. Nanocomposites were prepared by mixing different NPs of MO (silica, ceria, and titania in anatase phase), each one separately, in a PANI matrix. So, three PANI-based nanocomposites (SiO<sub>2</sub>-PANI, CeO<sub>2</sub>-PANI, and TiO<sub>2</sub>A-PANI) were synthesized and characterized, together with PANI used alone, by techniques such as XRD, FTIR, UVvis, SEM-EDS, and TGA to learn about the aspects related to their structure, composition, and morphology. Afterward, these systems were evaluated and compared as coatings on 1018 carbon steel to establish that MO confer better anti-corrosion properties and performance a la PANI by electrochemical techniques, such as EIS and Tafel curves, and in this way, propose a new strategy in the development of anti-corrosion coatings based on MO-reinforced polymer nanocomposite. The anti-corrosion coatings were developed by dispersing nanocomposites synthesized in a commercial alkydalic resin (AR) and mechanically deposited onto the metal substrate using a commercial micrometer film applicator.

#### 2. Experimental Procedure

#### 2.1. Reagents and Materials

Analytical grade (ACS) or high purity reagents were purchased from Sigma Aldrich (St. Louis, MO, USA). Aniline (ACS  $\geq$  99.5%, CASRN: 62-53-3). Amorphous silica (SiO<sub>2</sub>, CASRN: 7631-86-9) with an average nanoparticle size of 7.42 nm, titania anatase phase (TiO<sub>2</sub>A, CASRN: 1317—70-0) with an average nanoparticle size of 12.97 nm, and cerium

oxide (CeO<sub>2</sub>, CASRN: 1306-38-3) with an average nanoparticle size of 22.23 nm. Ammonium persulfate (APS, CASRN: 7727-54-0) and solvents were purchased from FER-MONT\_MÉXICO (Monterrey, NL, México).

#### 2.2. Synthesis of PANI and Polymer Nanocomposites

PANI can be synthesized by chemical or electrochemical polymerization reactions [35]. Depending on the degree of oxidation or protonation, PANI exhibits different forms subject to other redox states, which regulate its various properties. The most important form is the protonated emeraldine (ES) and its corresponding non-protonated base (LB), which is electronically conductive, and this feature is responsible for the active control of corrosion in metal substrates [36,37].

## 2.2.1. PANI Synthesis by Rapid Mixing Oxidative Polymerization of Aniline

Aniline was polymerized using HCl as a catalyst and ammonium persulfate (APS) as an oxidizing agent. Two equimolar solutions of aniline (4.56 mL) and APS (11.409 g) were prepared in 50 mL HCl 1M under magnetic stirring for several minutes. Then, the APS solution was suddenly added to the aniline solution at low temperature ( $\approx 0$  °C), under constant stirring (for approximately 4 to 6 h, see Figure 1). Finally, a green precipitate was obtained, filtered through a Buchner funnel (Sigma Aldrich, St. Louis, MO, USA) connected to the vacuum source, and washed several times with deionized water and HCl 1M until the filtrate was almost colorless. Subsequently, the product was dried in an oven for 12 h at an approximate temperature of 60 °C [38].



Figure 1. Schematic representation of PANI synthesis by rapid mixing oxidative polymerization of aniline.

2.2.2.  $SiO_2$ ,  $TiO_2$ , and  $CeO_2$ /PANI Nanocomposites Synthesis by In Situ Chemical Oxidative Polymerization by Rapid Mixing

An equimolar solution of aniline with HCl 1M was prepared under magnetic stirring. Before the in situ polymerizations of aniline, quantities of metal oxides to be used (SiO<sub>2</sub>, CeO<sub>2</sub>, or TiO<sub>2</sub>A) were added in a ratio of 0.25% in volume. Then, the solutions were sonicated by ultrasound for 45 min to prevent the agglomeration of nanoparticles and allow the HCl-doped aniline to deposit on the surface of NPs via electrostatic interactions. Finally, the in situ polymerization was carried out by sudden addition of the APS solution to HCl 1M and further continuing the procedure through stirring (Figure 2), filtering, washing, and drying described in the PANI synthesis by rapid mixing [38,39].



**Figure 2.** Schematic representation of SiO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub>-PANI nanocomposites synthesis by in situ chemical oxidative polymerization by rapid mixing.

### 2.2.3. Coating Development

The metal substrate was 1018 low carbon steel with the following chemical composition in weight percent: C = 0.18%, Mn = 0.6-0.9%, P = 0.04%, S = 0.05%, and Fe = balance. Metal samples of  $2 \times 2 \text{ cm}^2$  and 1/8'' thickness were cut. The samples' surface was mechanically polished using silicon carbide paper with different grits (320, 400, and 600) until obtaining a homogeneous surface. Afterward, the samples were degreased with isopropanol and left to dry for 24 h at room temperature. The anti-corrosion systems (Figure 3) were developed by mixing PANI and the formulated nanocomposites in an alkydalic resin (AR), using magnetic stirring until a homogeneous mixture was obtained. All the formulated coatings were made with the nanocomposite ratio of 0.5 wt.% concerning to the resin employed. The coatings were deposited on metal samples using a commercial Elcometer 3570/1 micrometer film applicator, allowing depositing coatings in a uniform and reproducible manner and fixing the thickness of the wet film at 3 µm.



**Figure 3.** Photography of (**a**) bare metal and anti-corrosion systems of: (**b**) PANI/AR, (**c**) SiO<sub>2</sub>-PANI/AR, (**d**) CeO<sub>2</sub>-PANI/AR, and (**e**) TiO<sub>2</sub>A-PANI/AR.

#### 2.3. Characterization of PANI and Polymer Nanocomposites

The diffraction patterns (XRD) of different materials were measured in a range of  $2\theta = 20^{\circ}$  to  $100^{\circ}$  with  $0.02^{\circ}$  increments, using a Bruker D8 Focus X-ray diffractometer with Cu*K* $\alpha$  radiation. Infrared spectra were run in a spectral range of 4000–600 cm<sup>-1</sup>, in a PERKIN ELMER FTIR 2000 Spectrometer (Waltham, MA, USA), from powder samples to determine the chemical structure of synthesized materials. The UV-vis spectra were recorded in a PERKIN-ELMER Lambda-35 Spectrophotometer (Waltham, MA, USA), dispersing 0.001 g of sample in deionized water (10 mL) by sonication. Thermogravimetric analyses were performed in a METTLER TOLEDO Thermobalance (Columbus, OH, USA) with the temperature ramp 25–900 °C, at a heating rate of 10 °C min<sup>-1</sup> under air atmosphere (75 mL min<sup>-1</sup>). The morphology and elementary analysis of coatings were characterized by a JEOL JSM 7800F Ultrahigh Resolution Scanning Electron Microscope (*Akishima*, TYO, Japan), equipped with an EDAX EDS detector.

#### 2.4. Electrochemical Characterization

A three-electrode cell made of acrylic was used for the characterization of materials. The steel samples coated with PANI, nanocomposites, and the bare steel samples were used as working electrodes ( $3.142 \text{ cm}^2$ ); a graphite rod was employed as a counter-electrode, and a saturated calomel electrode (SCE, Hg/Hg<sub>2</sub>Cl<sub>2</sub>) was the reference electrode. The corrosive medium was a brine composed of 3.5% NaCl solution, and before the electrochemical evaluation, open circuit potentials (OCP) were measured. Electrochemical tests were performed using an Autolab/PGSTAT302N potentiostat/galvanostat (Herisau, AR, Swiss) coupled to a PC with NOVA 2.0. software.

#### 2.4.1. Tafel Polarization Curves

The polarization curves were recorded in a potential range of  $\pm 250$  mV with respect to OCP at a scan rate of 0.00166 V s<sup>-1</sup>. Subsequently, electrochemical parameters like corrosion current (*i*<sub>corr</sub>) and potential (*E*<sub>corr</sub>), anodic slope ( $\beta_A$ ), and cathodic slope ( $\beta_C$ ) were obtained by the Tafel extrapolation method to calculate the corrosion rate (*CR*) and protection efficiency,  $\eta_{PROT}$ (%), as shown in Equations (1) and (2).

$$CR = \frac{i_{corr} \cdot K \cdot EW}{\rho} \tag{1}$$

where  $i_{corr}$  represents the corrosion current of the evaluated sample, *K* is a constant that defines the corrosion rate units, 0.1288 mils  $\mu A^{-1} \text{ cm}^{-1} \text{ year}^{-1}$  (=) *mpy*, *EW* is the average steel equivalent weight, 27.92 g eq<sup>-1</sup>, and  $\rho$  represents its density, 7.86 g cm<sup>-3</sup>.

$$\eta_{PROT}(\%) = \frac{i_{corr}^0 - i_{corr}^{coat}}{i_{corr}^0} \times 100$$
<sup>(2)</sup>

where  $i_{corr}^0$  represents the corrosion current of uncoated steel sample, and  $i_{corr}^{coat}$  represents the corrosion current of coated steel sample.

#### 2.4.2. Electrochemical Impedance Spectroscopy (EIS)

Impedance measurements were carried out with an amplitude perturbation of  $\pm 10$  mV, a frequency range from 100 kHz to 10 mHz, and 10 points per decade. The FRA (Frequency Response Analyzer System)-NOVA 2.0 software was used for the analysis of the results. The simulation of impedance diagrams was performed using equivalent circuits and the ZSimpWin 3.22 software.

The protection efficiency,  $\eta_{PROT}(\%)$  was calculated as shown in Equation (3), using the  $R_{ct}$  values obtained from the fitting process.

$$\eta_{PROT}(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$
(3)

where  $R_{ct}$  and  $R_{ct}^0$  represent the charge transfer resistance of the coated and uncoated samples, respectively.

# 3. Results and Discussion

#### 3.1. X-ray Diffraction (XRD) Study

Figure 4a shows the typical XRD pattern of PANI. This pattern exhibits two visible peaks at  $2\theta = 20^{\circ}$  and  $25^{\circ}$ , which belong to the planes (100) and (110), respectively [40,41]. These peaks can be attributed to the parallel and perpendicular periodicity of the polymer chain and are characteristic of the protonated form of PANI [42–44]. PANI is highly rigid due to its linear structure and not very flexible chains, which induces its crystallinity. The percentage of PANI crystallinity was determined (33.27%) from the diffraction pattern in Figure 4a, which support that PANI is in its protonated form, consistent with the peaks at low angle values  $2\theta$  [44].



**Figure 4.** XRD patterns of (**a**) PANI, (**b**) SiO<sub>2</sub>, SiO<sub>2</sub>-PANI, (**c**) CeO<sub>2</sub>, CeO<sub>2</sub>-PANI, and (**d**) TiO<sub>2</sub> A, TiO<sub>2</sub>A-PANI; nanoparticles (black) and nanocomposites (red).

Figure 4b shows the diffraction patterns of the  $SiO_2/PANI$  nanocomposite and amorphous silica NPs. The comparison of the patterns indicates that the incorporation of silica NPs induces no new order into the polymer due to their low concentration.

Figure 4c exhibits a comparison of XRD patterns of the  $CeO_2/PANI$  nanocomposite and  $CeO_2$  NPs. The nanocomposite patterns show a preferential orientation in the planes corresponding to  $CeO_2$  (111, 200, 220, 311, 222, etc.). However, an increase in the intensity of oxide diffraction peaks is related to the deposit of PANI on the surface of  $CeO_2$  NPs, which does not influence in their crystalline behavior [45]. Nevertheless, there are two small, almost imperceptible bands in an angular position between 20° and 25°, attributed to the typical PANI diffraction pattern mentioned before, thus confirming the polymer interaction with cerium NPs.

XRD patterns of titania anatase phase (TiO<sub>2</sub>A) NPs and the TiO<sub>2</sub>A/PANI nanocomposite are shown in Figure 4d. Similarly, those of CeO<sub>2</sub> nanocomposite and the TiO<sub>2</sub>A patterns are not significantly influenced by the presence of PANI since the crystallinity of this compound is dominated by the original pattern of titanium oxide, planes (101), (004), (112), (105), (211), (204), (116), etc., which is corroborated by the absence of the polymer's characteristic peaks located at  $2\theta = 20^{\circ}$  and  $25^{\circ}$  [46].

#### 3.2. FTIR Spectroscopic Study

Figure 5 shows FTIR spectra for PANI and formulated nanocomposites. The modes of vibrational bands are explained as follows: the bands characteristic of PANI (Figure 5a) appear at 3310–3265 cm<sup>-1</sup>, corresponding to the stretching of N–H aromatic amines in the benzenoid ring [41,47,48]; those at 2153 and 2016–1973 cm<sup>-1</sup> are due to the stretching of C=N and C=C bonds in quinoid and benzenoid rings [41,47,48], respectively. The bands at 2550–2420 cm<sup>-1</sup> belong to symmetric stretching of C–H bonds of the aromatic group [41,47]. The band at 1629 cm<sup>-1</sup> represents specifically the stretching of C=N bonds in the quinoid ring. The bands related to the stretching of C–N bonds in the benzenoid ring appear between 1300 and 1200 cm<sup>-1</sup>. In this region, a band characteristic of the conducting protonated PANI (1240) appears as well [41,47,48], whereas between 860–830 cm<sup>-1</sup>, bands correspond to vibrational flexions out of the plane of C–H bonds [41]. Finally, vibrations of C–C and C–H bonds in the aromatic ring are found in the region of 750–650 cm<sup>-1</sup> [47].

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The FTIR spectrum of SiO<sub>2</sub>/PANI nanocomposite is shown in Figure 5b. In addition to the vibrational bands described in Figure 5a, the band characteristic of silica is observed at the wavenumber of 988 cm<sup>-1</sup>, attributed to the anti-symmetric stretching of Si–O–Si bonds [48]. On the other hand, some bands of the nanocomposite spectrum (Figure 5b) present slight displacements compared to those of PANI (Figure 5a), attributed to the interaction existing between the SiO<sub>2</sub> nanoparticles and the polymer, which is likely to occur due to N–H bonds of PANI and O–Si on the electronegative surface of SiO<sub>2</sub> nanoparticles [49].

Figure 5c,d exhibit the FTIR spectra for CeO<sub>2</sub>/PANI and TiO<sub>2</sub>A/PANI nanocomposites, respectively. As in Figure 5b, the spectra are dominated by the presence of bands characteristic of PANI. However, in the case of the CeO<sub>2</sub> nanocomposite (Figure 5c), the typical bands of Ce–O vibrational stretching at 848 and 521 cm<sup>-1</sup> are seen [50], thus confirming the incorporation of CeO<sub>2</sub> into the PANI matrix. Likewise, for the TiO<sub>2</sub>A/PANI nanocomposite (Figure 5d), vibrational bands characteristic of anti-symmetric stretching for Ti–O–Ti bonds appear at 740 cm<sup>-1</sup> [40].



**Figure 5.** FTIR spectra for (**a**) PANI and nanocomposites of (**b**) SiO<sub>2</sub>-PANI, (**c**) CeO<sub>2</sub>-PANI, and (**d**) TiO<sub>2</sub> A-PANI.

#### 3.3. UV-vis Study

Figure 6 shows UV-vis spectra for PANI and synthesized nanocomposites. In the case of PANI (Figure 6a), the absorption spectrum displays the three bands characteristic of the polymer, observed at the wavelengths of 364, 457, and about 900 nm [40,47,50]. The first band (364 nm) corresponds to  $\pi$ - $\pi$ \* electron transition within the segments of benzenoid rings; the second (457 nm) is due to polaron- $\pi$ \* transition, probably attributed to the protonation of PANI chains, whereas the third (900 nm) is associated with a  $\pi$ -polaron transition, attributed to the polymer doping process [40,47]. Figure 6b exhibits the UV-vis spectrum for the SiO<sub>2</sub>/PANI nanocomposite, displaying the bands characteristic of PANI

(Figure 6a). A slight displacement is observed in bands, wavelengths, and intensity due to  $SiO_2$  NPs incorporated into the polymer mesh, which induce an effect on doping of the conducting PANI.



**Figure 6.** UV-vis spectra for (**a**) PANI and nanocomposites of (**b**) SiO<sub>2</sub>-PANI, (**c**) CeO<sub>2</sub>-PANI, and (**d**) TiO<sub>2</sub> A-PANI.

For the CeO<sub>2</sub>/PANI nanocomposite spectrum (Figure 6c), similarly to that in Figure 6b, the displacement in bands characteristic of PANI results from polaron-based electronic transitions induced by CeO<sub>2</sub> NPs. They produce an effect of electron distribution in segments of benzenoid rings, creating a large conjugated system due to the incorporation of the nanoparticles into the polymer [51]. Likewise, in the above UV-vis spectra, the use of TiO<sub>2</sub>A (Figure 6d) as a doping agent in the polymer matrix generates displacements in the bands of PANI spectra due to the interaction of NPs with polyaniline. They diminish the degree of orbital overlapping of  $\pi$  electrons and phenyl rings with a single nitrogen atom and generate a reduction in the extended conjugated system of PANI. It confirms that the presence of NPs influences the level of PANI doping independently of the crystalline structure they exhibit [48].

#### 3.4. Morphological Study of PANI and Nanocomposites by SEM

The morphology of PANI and nanocomposites was studied by analyzing the samples by SEM. Figure 7a,b show PANI micrographs obtained at 20,000 and 30,000 magnifications, respectively. As can be observed, the products obtained exhibit a compact structure with different types of morphology, mostly nanofibers and irregularly shaped nanoparticles, as well as agglomerated nanofibrous structures. It is consistent with the findings described in the literature [42] for products obtained via rapid mixing synthesis.



Figure 7. SEM micrographs of PANI: (a) 20,000 and (b) 30,000 magnification.

Figure 8 shows micrographs of nanocomposites studied at 20,000 magnification and EDS analyses globally performed for each sample.



**Figure 8.** EDS spectra and micrographs obtained at 20,000 magnification of nanocomposites: (a) SiO<sub>2</sub>/PANI, (b) CeO<sub>2</sub>/PANI, and (c) TiO<sub>2</sub>A/PANI.

Based on the micrographs in Figure 8a–c, a substantial modification of the original structure of PANI can be seen because the polymeric mesh induces a particular ordering of nanoparticles (SiO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub>A) incorporated in its microstructure due to electrostatic interactions existing between both substances. The presence of NPs in the polymer can be distinguished because of the contrast of tones in the image, where brighter areas represent metal oxides. In general, it can be corroborated by EDS spectra obtained for each case (see Figure 8a–c), which evidence the presence of each element in the analyzed

samples. The NPs of SiO<sub>2</sub> and TiO<sub>2</sub>A exhibit sizes below 20 nm, whereas those of CeO<sub>2</sub> can reach 50 nm.

#### 3.5. Thermogravimetric Analysis of Nanocomposites

Figure 9 shows thermogravimetric curves of PANI and nanocomposites of SiO<sub>2</sub>-PANI, CeO<sub>2</sub>-PANI, and TiO<sub>2</sub>A-PANI.



**Figure 9.** TGA curves of (**a**) PANI (olive green) and nanocomposites of (**b**) SiO<sub>2</sub>-PANI (blue), (**c**) CeO<sub>2</sub>-PANI (yellow), and (**d**) TiO<sub>2</sub>A-PANI (burgundy).

The nanocomposites show three stages of weight loss in the studied temperature range by TGA. According to the thermograms, in the first stage of approximately 25 to 100 °C, there is a 10% weight loss of PANI and 6–13% of nanocomposites, attributed to the ejection of water molecules from the structure of the materials. In the second stage, weight losses of 12% for PANI and 9–12% for nanocomposites can be observed, occurring up to 280 °C and related to the loss of dopant (HCl), and low molecular weight remnants. In the third stage, taking place from 280 to 700 °C, the thermal stability is different, the weight loss varies from 14 and 28% for nanocomposites, whereas for PANI, it is 41%.

These results indicate that the nanocomposites of CeO<sub>2</sub>-PANI and TiO<sub>2</sub>A-PANI exhibit higher resistance to thermal degradation because they exhibit a total mass loss of 31 and 41%, respectively, at 700 °C. On the contrary, the SiO<sub>2</sub>-PANI nanocomposite shows a greater mass loss (53%) at the same temperature, just below PANI's, which exhibits the greatest value (63%) of all studied samples. The improvement in nanocomposites' thermal stability can be attributed to the strong interaction between the nanoparticles and free chains of PANI. It has been demonstrated that nanoparticles of SiO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub> exhibit strong thermal stability in the range of studied temperatures [52–54].

#### 3.6. Open Circuit Potential (OCP) Study

Figure 10A shows the OCP variation of the studied samples (uncoated 1018 steel and coatings of PANI/AR, SiO<sub>2</sub>-PANI/AR, CeO<sub>2</sub>-PANI/AR, and TiO<sub>2</sub>A-PANI/AR) at different times of immersion in 3.5% NaCl. The bare steel displays a gradual change in the potential toward more negative values, reaching -0.74 V vs. SCE at the end of immersion (72 h). This change of OCP could be due to the oxidation of the metal directly exposed to NaCl solution. On the other hand, the OCP values of all coated samples exhibit more noble potentials than the bare steel, indicating the presence of a barrier (coating) acting as a water-resistant barrier between the metal surface and the electrolyte. The coatings of CeO<sub>2</sub>-PANI/AR and SiO<sub>2</sub>-PANI/AR show decay of OCP in the first hours of immersion (8 h), recording -0.651 and -0.65 V, respectively; after that time, the OCP values reach a

steady-state (-0.658 and -0.647 V vs. SCE) at the end of the test. Likewise, the coatings of PANI/AR and TiO<sub>2</sub>A-PANI/AR exhibit negative displacements of OCP in the first 24 h but later shift toward more positive values, reaching -0.571 V and -0.412 V, respectively; this latter one is exhibiting the most positive potential. The OCP variation toward more positive potentials is attributed to the metal surface protection and anti-corrosion properties of the coatings [55].

#### 3.7. Tafel Curves

The potentiodynamic polarization (Tafel) curves for the uncoated 1018 steel sample and PANI/AR, SiO<sub>2</sub>-PANI/AR, CeO<sub>2</sub>-PANI/AR, and TiO<sub>2</sub>A-PANI/AR coatings are given in Figure 10B. The electrochemical parameters, such as  $i_{corr}$ ,  $E_{corr}$ ,  $\beta_A$ , and  $\beta_C$ , were obtained by the Tafel extrapolation method and shown in in Table 1, including the parameters of *CR* and  $\eta_{PROT}$ (%), according to Equations (1) and (2).



**Figure 10.** (**A**) OCP variation and (**B**) Tafel curves of: (**a**) uncoated 1018 steel (red), coatings of (**b**) PANI/AR (olive green), (**c**) SiO<sub>2</sub>-PANI/AR (blue), (**d**) CeO<sub>2</sub>-PANI/AR (yellow), and (**e**) TiO<sub>2</sub>A-PANI/AR (burgundy).

From these, it can be seen that the value of  $i_{corr}$  for the PANI/AR coating (0.079  $\mu$ A cm<sup>-2</sup>) is much lower compared to that of uncoated steel (2.418  $\mu$ A cm<sup>-2</sup>), which proves that this coating has good properties as a barrier for ion diffusion [56]. The coatings made of SiO<sub>2</sub> and TiO<sub>2</sub>A nanoparticles show a decrease of  $i_{corr}$  values compared to the PANI/AR coating, which is indicative of a better anti-corrosion protection provided by these nanocomposites, unlike the CeO<sub>2</sub>-PANI/AR coating that exhibits the highest  $i_{corr}$  value (0.147  $\mu$ A cm<sup>-2</sup>). These results show that the TiO<sub>2</sub>A-PANI coating has the best anti-corrosion properties with  $i_{corr}$  of 0.018  $\mu$ A cm<sup>-2</sup>, followed by SiO<sub>2</sub>-PANI/AR with the value of 0.073  $\mu$ A/cm<sup>2</sup>.

**Table 1.** Tafel parameters obtained for uncoated steel and PANI-base coatings immersed in 3.5%

 NaCl solution.

			Tafel Param	eters		
Samples	E <sub>corr</sub> (V)	i <sub>corr</sub> (μA cm <sup>-2</sup> )	$egin{array}{c} eta_A \ (\mathrm{V~dec^{-1}}) \end{array}$	$egin{array}{c} eta_C \ (V \ dec^{-1}) \end{array}$	CR (mpy)	<i>¶р</i> гот (%)
1018 STEEL	-0.698	2.418	0.515	0.060	1.106	-
PANI/RA	-0.522	0.079	0.225	0.188	0.036	97.10
SiO <sub>2</sub> -PANI/RA	-0.479	0.073	0.385	0.124	0.033	97.35
CeO2-PANI/RA TiO2A-PANI/RA	$-0.637 \\ -0.362$	$0.147 \\ 0.018$	0.194 0.195	0.119 0.192	0.067 0.008	94.28 98.63

As was mentioned above,  $E_{corr}$  of the formulated coatings shift toward more positive values with respect to the bare sample, which can be interpreted as better control of the

anodic and cathodic reactions in the corrosion process due to the barrier properties of the coatings [57]. This can be confirmed by the values of anodic slopes  $\beta_A$ , and to a smaller extent, those of cathodic slopes  $\beta_C$ , which decrease: that is, the anti-corrosion systems studied exhibit a mixed control in the obtained Tafel curves. On other hand, it can be observed that the system with the highest corrosion rate is due to bare steel (1.106 mpy) exposed to the corrosive medium, where the probable formation of different iron compounds (i.e., oxides) would be expected. On the contrary, the corrosion rate decreases by up to two or three orders of magnitude in the presence of the different nanocomposites.

Finally, the calculations of anti-corrosion protection efficiency  $\eta_{PROT}(\%)$  shown in Table 1 demonstrate that the TiO<sub>2</sub>A-PANI/AR system has the best corrosion resistance properties (98.63%), followed by the SiO<sub>2</sub>-PANI/AR (97.35%) and PANI/AR systems (97.10%), with CeO<sub>2</sub>-PANI/AR being the least efficient (94.28%), which is consistent with the values of *CR* described previously.

#### 3.8. Electrochemical Impedance Spectroscopy

Figure 11 shows Nyquist and Bode diagrams (phase angle vs. frequency) for the uncoated 1018 steel sample and the PANI/AR, SiO<sub>2</sub>-PANI/AR, CeO<sub>2</sub>-PANI/AR, and TiO<sub>2</sub>A-PANI/AR coatings.



**Figure 11.** Nyquist and Bode diagrams of: (**a**) uncoated 1018 steel (gray) and coatings of (**b**) PANI/AR (olive green), (**c**) SiO<sub>2</sub>-PANI/AR (blue), (**d**) CeO<sub>2</sub>-PANI/AR (yellow), and (**e**) TiO<sub>2</sub>A-PANI/AR (burgundy). The continuous line represents the fit of experimental diagrams.

Nyquist plots (Figure 11) exhibit significant variations in impedance diagrams of different coatings containing PANI mainly. In the case of uncoated steel, the apparent formation of a semicircle is evident across the entire frequency range with lower impedance values (Figure 11a), which indicates an active behavior in the oxidation of steel. On the contrary, the samples coated with PANI and nanoparticles of metal oxides display higher impedance values, where different semicircles are formed across the entire frequency range. The capacitive behavior at high frequencies is related to the anti-corrosion properties of each material, while in the region of low frequencies, this contribution could be due to a diffusion process at the metal/coating interface [58], mainly diffusion of oxygen and/or corrosive (i.e., chloride) ions. In both cases, the larger the impedance magnitudes, the greater the steel protection. Taking into consideration that the TiO<sub>2</sub>A-PANI/AR system exhibits the highest impedance values, this coating might be deemed to offer the highest protection of steel immersed in 3.5% NaCl solution.

Bode diagrams obtained for steel, PANI/AR, SiO<sub>2</sub>-PANI/AR, CeO<sub>2</sub>-PANI/AR, and TiO<sub>2</sub>A-PANI/AR are showed in Figure 11. In these plots, at least two angle maximums

are detected in the entire range of frequencies. Additionally, in the presence of different coatings, an increase in angle values is seen from the beginning of the scan (high frequencies), related to the semiconducting properties of the coating, that is, the higher the angle value, the greater is its contribution and/or the lower the electron conductivity. Moreover, other maximums appear due to phenomena occurring through the metal/coating/solution interface, as will be discussed further below.

To analyze impedance diagrams, equivalent circuits shown in Figure 12 were used, where  $R_s$  is the solution resistance,  $Q_{coat}$  and  $R_{pore}$  represent the capacitance and resistance of coating pore, except for steel, in where the likely formation of iron oxides can be considered. The  $Q_{dl}$  element is the double-layer capacitance of the metal surface, and  $R_{ct}$  is the metal charge transfer resistance. Figure 12b also exhibits a third arrangement of the constant phase element  $Q_{dif}$  and a resistance  $R_{dif}$ , associated with the diffusion process through the metal/coating interface.



**Figure 12.** Equivalent circuits for the systems of (**a**) uncoated 1018 steel; coatings of (**b**) PANI/AR, SiO<sub>2</sub>-PANI/AR, CeO<sub>2</sub>-PANI/AR, and TiO<sub>2</sub>A-PANI/AR.

The constant phase element (*CPE*) is generally used to describe a phase change independent of the frequency between an applied potential and its response in the current, which can be represented as a function of impedance:

$$Z(CPE) = Y_0^{-1} (j\omega)^{-n} \tag{4}$$

where  $Y_0$  is a constant value of *CPE*,  $\omega$  is the angular frequency (in rad s<sup>-1</sup>), *j* is the imaginary number  $j^2 = -1$ , and *n* is the *CPE* exponent. According to the *n* values, *CPE* can represent resistance (*Z*(*CPE*) = *R*, *n* = 0), capacitance (*Z*(*CPE*) = *R*, *n* = 1), inductance (*Z*(*CPE*) = *R*, *n* = -1), or Warburg impedance for *n* = 0.5 [59].

The  $Y_0$  value can be related to the coating capacitance  $C_{coat}$  through the Equation:

$$C_c = Y_0 (\omega^n \cdot m)^{n-1} \tag{5}$$

where  $\omega^n \cdot m$  is the angular frequency at which the maximum imaginary impedance Z'' occurs.

The fittings performed to Nyquist and Bode plots for bare steel, and PANI-based anti-corrosion systems, are represented by a continuous line in Figure 11, showing a good fit for all experimental impedance diagrams. The parameters obtained from the simulation are given in Table 2.

From the values shown in Table 2, it is worth mentioning that the measurement of  $R_{pore}$  and  $Q_{coat}$  parameters are of utmost importance for each system since both are related to the semiconducting properties of the coatings. As can be seen, the resistive parameter  $R_{pore}$  increases for PANI-based coatings in relation to the uncoated steel because the coatings applied on metal samples act as a barrier that prevents free substrate corrosion. In this case, the TiO<sub>2</sub>A-PANI/AR coating is the one exhibiting the highest pore resistance (6140  $\Omega$  cm<sup>2</sup>), followed by SiO<sub>2</sub>-PANI/AR (5028  $\Omega$  cm<sup>2</sup>) and CeO<sub>2</sub>-PANI/AR

(3700 $\Omega$ cm <sup>2</sup> ), whereas the PANI/AR system shows the lowest $R_{pore}$ of all evaluated coat-
ings (3400 $\Omega$ cm <sup>2</sup> ). However, the bare steel exhibits far lower resistance than the others
$(70.54 \ \Omega \ cm^2)$ due to the formation of iron compounds on the steel surface because of the
lack of any barrier between its surface and the corrosive medium.

Table 2. EIS parameters obtained for uncoated steel and PANI-based coatings immersed in 3.5% NaCl solution.

Samples	EIS Parameters										
	$R_s$ ( $\Omega \ \mathrm{cm}^2$ )	$Q_{coat}$ (F cm <sup>-2</sup> )	n	$R_{pore}$ ( $\Omega \ \mathrm{cm}^2$ )	$Q_{dl}$ (F cm <sup>-2</sup> )	n	$R_{ct}$ ( $\Omega \ \mathrm{cm}^2$ )	$Q_{dif}$ (F cm <sup>-2</sup> )	n <sub>dif</sub>	$R_{dif}$ ( $\Omega \ \mathrm{cm}^2$ )	<sup>¶</sup> PROT (%)
1018 STEEL	49.5	$1.34  imes 10^{-3}$	0.80	70.54	$1.72 \times 10^{-3}$	0.81	1143	-		-	-
PANI/RA	157	$6.71  imes 10^{-9}$	0.79	3400	$6.63 imes10^{-6}$	0.80	$1.78  imes 10^4$	$4.74 imes10^{-6}$	0.60	$1.54 \times 10^5$	93.58
SiO <sub>2</sub> -PANI/RA	203	$9.67 imes10^{-7}$	0.44	5028	$2.36 imes10^{-7}$	0.85	$4.556  imes 10^4$	$4.56 imes10^{-5}$	0.40	$1.11  imes 10^5$	97.49
CeO2-PANI/RA	194	$4.75  imes 10^{-7}$	0.71	3700	$6.40 imes10^{-7}$	0.67	$3.804  imes 10^4$	$2.11  imes 10^{-6}$	0.78	$5.68  imes 10^4$	96.99
TiO <sub>2</sub> A- PANI/RA	168	$1.06  imes 10^{-8}$	0.77	6140	$6.40  imes 10^{-7}$	0.44	$6.882  imes 10^4$	$8.83  imes 10^{-6}$	0.48	$3.84  imes 10^5$	98.34

In another instance, the values of  $Q_{coat}$  reflect that the uncoated material shows the greatest tendency toward electrolyte absorption ( $1.34 \times 10^{-3}$  F cm<sup>-2</sup>) compared to the anti-corrosion systems, which diminish several orders of magnitude, the PANI/AR system having the lowest capacitance value ( $6.71 \times 10^{-9}$  F cm<sup>-2</sup>). However, the systems based on nanoparticles and PANI (TiO<sub>2</sub>A-PANI, SiO<sub>2</sub>-PANI/AR, and CeO<sub>2</sub>-PANI/AR) also exhibit low capacitance values ( $1.061 \times 10^{-8}$ ,  $9.67 \times 10^{-7}$ , and  $4.75 \times 10^{-7}$  F cm<sup>-2</sup>), indicating that these materials have low electrolyte absorption tendency.

The charge transfer resistance ( $R_{ct}$ ) is associated with the kinetics of electrochemical reactions at metal-coating-electrolyte interfaces. According to the results shown in Table 2, all anti-corrosion systems increase by several orders their values of  $R_{ct}$  compared to the bare steel (1143  $\Omega$  cm<sup>2</sup>), which reflects the protective properties of the coatings. Thus, the TiO<sub>2</sub>A-PANI/AR system exhibits the highest charge transfer resistance ( $6.88 \times 10^4 \Omega$  cm<sup>2</sup>), followed by the SiO<sub>2</sub>-PANI/AR ( $4.56 \times 10^4 \Omega$  cm<sup>2</sup>), CeO<sub>2</sub>-PANI/AR ( $3.80 \times 10^4 \Omega$  cm<sup>2</sup>), and PANI/AR ( $1.78 \times 10^4 \Omega$  cm<sup>2</sup>) systems. This is supported by the low double-layer capacitance values ( $Q_{dl}$ ) for all the anti-corrosion systems, suggesting a low transfer of species at the interface.

On the other hand, the diffusion parameter  $R_{dif}$  is related to the capacity of a coating to prevent the free diffusion of ions between the metal surface and the electrolyte; this means that greater protection of the coating is related to lower mobility of ions through it, which, like other resistances ( $R_{pore}$  and  $R_{ct}$ ), is related to the barrier properties of the material. Thus, the TiO<sub>2</sub>A-PANI/AR system is the one exhibiting the highest diffusion resistance ( $3.84 \times 10^5 \Omega \text{ cm}^2$ ), followed by PANI/AR ( $1.54 \times 10^5 \Omega \text{ cm}^2$ ), SiO<sub>2</sub>-PANI/AR ( $1.11 \times 10^5 \Omega \text{ cm}^2$ ), and CeO<sub>2</sub>-PANI/AR ( $5.68 \times 10^4 \Omega \text{ cm}^2$ ). According to these values, the diffusion process through the coating is lower for the TiO<sub>2</sub>A-PANI/AR system, offering greater protection of the steel compared to other nanocomposites.

Additionally, the coatings protection efficiency  $\eta_{PROT}$  (%) was determined using Equation (3). The higher efficiencies are determined for the coatings based on nanoparticles and PANI (TiO<sub>2</sub>A-PANI/AR, SiO<sub>2</sub>-PANI/AR, and CeO<sub>2</sub>A-PANI/AR), reaching values of (98.34, 97.49, and 96.99%, respectively); whereas the lowest efficiency (93.58%) is obtained for PANI/AR coating, which is consistent with impedance parameters reported previously.

#### Anti-Corrosion Mechanism of Coatings

The barrier properties of anti-corrosion systems studied are due to the synergistic effect existing between their components (PANI/AR and NPs/PANI/AR). The formation of a uniform barrier film of the alkydalic resin strongly bound to the steel surface and PANI is expected, thus enhancing a uniform protective film [60]. On the other hand, there is a sense that the incorporation of metal oxide nanoparticles into the polymer matrix inhibits the electrolyte permeation through the metal-coating interface, improving not only the

efficiency of corrosion protection of the material but also its adhesion to the substrate. The use of additives at the nanometer scale is known to improve the barrier properties of polymers by diminishing their porosity [61].

#### 3.9. Immersion Tests

In addition, Table 3 shows the variation of Tafel parameters obtained at different immersion times (3, 8, 24, and 72 h) of the anti-corrosion systems studied.

**Table 3.** Tafel parameters obtained for PANI-based coatings immersed in 3.5% NaCl solution for 3, 8, 24, and 72 h.

Samples	Tafel Parameters	Immersion Time (h)			
		3	8	24	72
	$i_{corr}$ (µA cm <sup>-2</sup> )	0.079	0.112	0.070	0.075
	$E_{corr}$ (V)	-0.522	-0.596	-0.679	-0.680
PANI/RA	$\beta_A$ (V dec <sup>-1</sup> )	0.225	0.174	0.108	0.081
	$\beta_C$ (V dec <sup>-1</sup> )	0.188	0.197	0.205	0.149
	$\eta_{PROT}$ (%)	97.10	95.73	97.48	97.27
	$i_{corr}$ (µA cm <sup>-2</sup> )	0.073	0.123	0.096	0.069
SiO <sub>2</sub> - PANI/RA	$E_{corr}$ (V)	-0.479	-0.650	-0.726	-0.699
	$\beta_A$ (V dec <sup>-1</sup> )	0.385	0.172	0.117	0.096
	$\beta_C$ (V dec <sup>-1</sup> )	0.124	0.189	0.224	0.170
	$\eta_{PROT}$ (%)	97.35	95.28	96.40	97.52
6-0	$i_{corr}$ (µA cm <sup>-2</sup> )	0.147	0.163	0.135	0.227
	$E_{corrr}$ (V)	-0.637	-0.683	-0.737	-0.750
$CeO_2$ -	$\beta_A$ (V dec <sup>-1</sup> )	0.194	0.162	0.110	0.071
I AINI/ KA	$(V dec^{-1})$	0.119	0.122	0.167	0.162
	η <sub>PROT</sub> (%)	94.28	93.62	94.78	90.96
TiO2A- PANI/RA	$i_{corr}$ ( $\mu$ A cm <sup>-2</sup> )	0.018	0.139	0.074	0.059
	$E_{corr}$ (V)	-0.362	-0.498	-0.616	-0.662
	$\beta_A$ (V dec <sup>-1</sup> )	0.195	0.264	0.149	0.119
	$\beta_C$ (V dec <sup>-1</sup> )	0.192	0.192	0.232	0.221
	$\eta_{PROT}$ (%)	99.63	94.61	97.31	97.93

According to the parameters, the  $i_{corr}$  values for all cases exhibit a slight decrease in their magnitudes, and the TiO<sub>2</sub>A-PANI/AR system still has the best anti-corrosion properties, given the lowest value of  $i_{corr}$  (0.059 µA cm<sup>-2</sup>). The displacement of  $E_{corr}$ toward more negative values as well as the decrease in anodic slopes  $\beta_A$  and increase in the cathodic ones  $\beta_C$  suggest a mixed control of anodic and cathodic reactions of the system due to the dense thin film formed by the coating, adhered to the metal surface. Furthermore, a slight decrease in the protection efficiency ( $\eta_{PROT}$ ) through the immersion time is observed. Thus, the TiO<sub>2</sub>A-PANI/AR system exhibits the highest efficiency (97.93%) and the CeO<sub>2</sub>-PANI/AR, the lowest (90.96%), at the end of immersion (72 h). Despite these results, it can be interpreted that all the systems have good anti-corrosion properties due to the barrier effect they provide and the tendency to passivate the metal surface [62,63].

According to the diffusion process through the coatings is lower for the TiO<sub>2</sub>A-PANI/AR system, offering greater protection of the steel compared to other nanocomposites. Based on the Tafel parameters, the coatings made with NPs of TiO<sub>2</sub>A and SiO<sub>2</sub> present the highest protection efficiencies, even for the initial and final immersion times (98.63 and 97.93% for TiO<sub>2</sub>A/AR and 97.35 and 97.52% for SiO<sub>2</sub>/AR), followed PANI/AR (97.10 and 97.27%), showing variations of less than 1% in their efficiencies. It is also important to note that these efficiencies are obtained using only a percentage of 0.5 wt.% of MO NPs compared to the works mentioned above. The lowest efficiencies are those exhibited by CeO<sub>2</sub>-PANI/AR (94.28 and 90.96%) with a variation of no more than 5%, but they are higher than the corresponding referenced above.

Similarly, the results obtained by EIS reflect admissible protective properties of the studied systems, despite the smaller magnitudes of the  $R_{ct}$  values shown in Table 2 compared to those cited in the literature, since, as mentioned in the work of Sasikumar et al. [64], the  $R_{ct}$  values increase as the concentration of nanocomposite or NPs in the coating increases, and it should be remembered that in this study, low concentrations were used (0.5% in wt), trying not to significantly influence the anti-corrosion contribution of the studied materials. This is confirmed by the high protection efficiency ( $\eta_{PROT}$ ) shown for all the systems evaluated.

To sum up, the  $TiO_2A$ -PANI/AR coating has the best anti-corrosion properties of all the systems studied since it exhibits a constant behavior in different electrochemical evaluations and the most efficient results for all corrosion tests. The anti-corrosion properties exhibited by the coatings made in this work are attributed to the composition and the synthesis method used.

#### 4. Conclusions

Nanocomposites of PANI-based MO (SiO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub>A) were synthesized by in situ chemical oxidative polymerization by rapid mixing. The XRD, FTIR, and UV-vis analyses show that the protonated form of PANI (ES) was obtained. They also confirm the incorporation of MO in the polymeric mesh due to the observed displacements of peaks and bands of the spectra involved, resulting from the interaction of NPs with polymer macromolecules. The micrographs obtained by SEM and EDS results corroborate the incorporation of NPs into PANI. The electrochemical evaluation by Tafel curves and EIS demonstrated that all the coatings studied exhibit good anti-corrosion properties, having those produced with NPs (SiO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub>A) the highest protection efficiencies. However, according to the results of immersion tests, the TiO<sub>2</sub>A-PANI/AR coating proved to have the best anti-corrosion properties of all the systems studied. Based on the results obtained with the synthesized anti-corrosion coatings, we propose as a strategy to evaluate other formulations using alkyd resins as dispersing medium and as an alternative synthesis route, and in situ chemical oxidative polymerization by rapid mixing for preparation of PANI and MO-based polymeric nanocomposites, in order to obtain successful syntheses in less time and also evaluate their performance at longer immersion times.

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# Nomenclature

ACS	Analytical grade
APS	Ammonium persulfate
AR	Alkydalic resin
CPE	Constant phase element
CPs	Conducting polymers
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ES	Protonated emeraldine
FRA	Frequency Response Analyzer System
FT-IR	Fourier transform infrared
LB	Non-protonated base
МО	Metal oxide
NP	Nanoparticle
NPs	Nanoparticles
OCP	Open circuit potential
PA	Polyacetylene
PANI	Polyaniline
PEDOT	Poly(ethylene dioxythiophene)
PPv	Polypyrrole
PTh	Polythiophene
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV-vis	Illtraviolet-visible
XRD	X-ray diffraction
Symbols	in the second se
Cast	Coating capacitance
CR	Corrosion rate
E.	Corrosion potential
FW	Average steel equivalent weight
<i>i</i>	Corrosion current
i0	Corrosion current of uncoated steel sample
icoat	Corrosion current of coated steel sample
<sup>c</sup> orr K	Constant that defines the corresion rate units
i i	Imaginary number
) 11	CPF exponent
	Capacitance of coating pore
Qcoat	Double-layer canacitance of the metal surface
Qal	Diffusional capacitance
Qaif R	Charge transfer resistance of a coated sample
$R_{ct}^0$	Charge transfer resistance of an uncoated sample
R <sub>ct</sub>	Diffusional resistance
R <sub>dif</sub>	Paristance of coating pore
K <sub>pore</sub> V-	Constant value of CPE
10 7/	Pool impodence
L 7//	
L' Creal: Symbols	inaginary inpedance
	Anadiaslana
PA R -	Cathadia alana
PC	Protection officionay
//PROT( <sup>7</sup> 0)	Front density
ρ	Sieer density
ω	Angular frequency

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