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Influence of electropolymerization temperature on corrosion, morphological and electrical properties of PPy doped with salicylate on iron

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a b s t r a c t

In this work, the influence of the electropolymerization temperature on corrosion, morphological and electrical properties of polypyrrole (PPy) film is studied. Polypyrrole is electrochemically synthesized on iron in the pres-ence of sodium salicylate. The X-ray diffraction and scanning electron microscopy are performed in order to study the structure and morphology of electrodeposited PPy. The electroactive surface area, corrosion performance and resistance of the PPy film on iron are also investigated as a function of electropolymerization temperature. The results show that the synthesis temperature significantly affects the properties of the PPy film on iron. It is observed that at 25 °C amorphous PPy is formed, whereas lowering the temperature leads to the formation of a film containing crystallites of salicylic acid. The latter reveals lower corrosion protection and a much higher level of resistance compared to the amorphous one. These characteristics were associated with the presence of insulating salicylic acid crystals in the layer structure.

Keywords: Polypyrrole, Iron, Sodium salicylate, Electropolymerizatio, n Temperature, Resistance

1. Introduction

At present, the trend is to replace permanent, metallic, cardiovascular stents with their biodegradable forms [1–3]. The materials used for this purpose are active metals such as iron and its alloys [4,5], the subsequent biodegradation of the implant is based on the corrosion process [6,7]. However, the use of such materials in clinical applications requires the optimization of their degradation rate and biological performance [3,4].

Surface modification is one of the methods typically used to improve degradability or biocompatibility of biodegradable metal [3]. One promising solution is to coat the metal with conducting polymers [8–10].

The principal property of these polymers is their metallic-like conductivity due to the conjugated double bond in their backbone [11,12]. One especially promising example of a conducting polymer is polypyrrole (PPy). It exhibits high biocompatibility [13], excellent electrical, mechanical and thermal properties [14] and very good stability in different environments [8,15]. Because of its unique properties, PPy has been used in different applications including anti-corrosive coatings [16,17] and drug release systems [18].

The PPy film can be synthesized using chemical or electrochemical methods [19]. However, due to the simplicity of preparation and the possibility of controlling the properties of the film, the electrochemical technique is most frequently employed [20,21]. The synthesis method leads to the formation of a positively charged PPy backbone, and the polymer becomes oxidized. In order to achieve charge neutrality during this process, the incorporation of counter-anions into the polymer structure takes place [8]. Polypyrrole exhibits a redox switching ability between its reduced and oxidized states, and its behaviour depends significantly on its oxidation state [8,11]. The oxidation of the polymer backbone generates charge carriers, which confer electronic conductivity to the polymer. However, reduced PPy film behaves as an electronic insulator [8]. In order to change the properties of the polymer, it can be additionally re-oxidized (doped) or reduced (dedoped). These processes depend closely on the performance parameters and on the type of the electrolyte used [8,11].

It is well-known that many chemical and physical properties of electrodeposited polypyrrole can be varied to a significant extent by modifying the electropolymerization parameters including the solvent [21, 22], the supporting electrolyte [23], the electrodeposition potential/current density [24], and the monomer and electrolyte concentration [10]. One of these parameters is also the temperature. Its influence is very often neglected. However, the temperature has a very significant impact on the chemical and physical properties of electrodeposited conducting polymers. It also plays a very important role in the formation of nanostructures [25].

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According to the literature, there have been some attempts to study the influence of the electropolymerization temperature on different properties of conducting polymer films. For example, it was noted that changing the temperature influences the synthesis process [26,27], morphology [28,29] and electrical properties of the polymer film obtained [27,30]. Koinkar et al. [26] studied the influence of synthesis temperature on electrochemical polymerization of o-anisidine on low carbon steel from an aqueous solution of oxalic acid. The optical absorption spectroscopy reveals the formation of a mixed phase of emeraldine salt (ES) and pernigraniline base (PB) at 27 °C, whereas at lower temperatures the major portion of the coating constitutes the ES phase. Scanning electron microscopy images confirmed the changes in polymer morphology [26]. Kim et al. [32] observed that the level of molecular anisotropy may be enhanced through electropolymerization at reduced temperatures. Changes in structure and crystallinity were also observed in the case of PPy electropolymerized in propylene carbonate containing 0.1 M pyrrole and 0.5 M $LiClO_4$ on platinum or gold [32] and PPy synthesized in an aqueous solution of pyrrole and oxalic acid on stainless steel [33]. The results showed that the PPy film synthesized at low current density and at a reduced temperature showed a high degree of crystallinity [32,33]. This was not observed in the case of PPy prepared at room temperature. In this case, the PPy film exhibited an almost amorphous structure [32, 33]. This type of PPy structure produces better quality films with respect to adhesion, interconnected morphology, electrochemical activity and conductivity [31]. Some studies presented also reveal the influence of the electropolymerization temperature on the conductivity of conducting polymers. The polyaniline (PANI) synthesized in a non-aqueous solution of 1,2-dichloroethane (DCE) exhibited higher conductivity with decreasing electropolymerization temperature [27]. This was related to the smoother and denser structure of PANI film [27]. However, PPy synthesized inside the pores of track-etch membranes in an aqueous solution of 0.6 M pyrrole and 1.0 M ferric acid at 4 °C shows higher resistance (15 kΩ) compared to synthesis at 22 °C (~1 kΩ) [30]. This was associated with the fact that at lower reaction temperatures less polymer precipitates inside the pores, which leads to a higher initial resistance [30]. Another work observed that the polymerization rate and conductivity are significantly affected by the temperature of electropolymerization [25]. There were also some attempts to study the influence of temperature on the corrosion properties of PPy coated stainless steel [33]. The results showed that PPy film electropolymerized in an aqueous solution of pyrrole and oxalic acid at low current density and reduced temperature reveals lower corrosion current density, higher polarization resistance and pore resistance [33]. This was related to the high degree of crystallinity of the polymeric films obtained [33].

All changes and relationships between the electropolymerization temperature and conducting polymer properties are significantly affected by the synthesis conditions. However, there are still a lack of literature reports which study the influence of temperature on the properties of polypyrrole film synthesized on an iron substrate in the presence of an aqueous solution of sodium salicylate. In our previous work, the PPy film was electrosynthesized under different conditions on the surface of biodegradable iron (PPy/Fe) [10]. The corrosion properties of the PPy film were optimized for the purpose of producing a biodegradable metallic stent [10]. The influence of various synthesis parameters, excluding temperature, on corrosion, electrical [10] and redox [8,11] properties has been investigated. However, to obtain fully optimized PPy/Fe material with the parameters and properties needed for a specific application, all electropolymerization conditions should be studied.

In this work, the influence of the electropolymerization temperature on morphological, corrosion and electrical properties of polypyrrole doped with salicylate on iron is investigated for the first time. Polypyrrole is electrochemically synthesized on iron in the presence of sodium salicylate, which is incorporated into the coating. The corrosion performance was studied at 37 °C in phosphate buffer saline solution (pH 7.4), which simulated body fluid conditions. The relationship between the morphological, corrosion and electrical properties is discussed. This information is key for the synthesis of a polymeric film on an iron substrate with certain desirable properties for several possible applications.

2. Experimental

The following chemicals were used: pyrrole monomer (≥99%, Acros Organics), sodium salicylate (≥99.5%, EMSURE), phosphate buffer saline pH 7.4 (PBS, Sigma Aldrich) with 2.7 mM KCl, 137 mM NaCl and 10 mM phosphate buffer. All solutions are made with Milli-Q water.

The substrate is a pure iron plate (≥99.8%, Chempur Feinchemikalien und Forschungsbedarf GmbH).

The iron plate was embedded in an epoxy resin. The iron electrode was mechanically polished with abrasive papers 220, 500 and 1200 SiC grade (Struers), rinsed with ethanol and dried. After the polymerization experiments, the sample was rinsed with Milli-Q water and dried in an N_2 stream.

The electrochemical polymerization, cyclic voltammetry and potentiodynamic polarization measurements were performed in a one-compartment water-jacketed cell with three electrode system controlled by a VersaSTAT4 potentiostat. The working electrode for these measurements was the iron with an exposed area of 38 mm^2. A $Ag/AgCl_{sat}$ in 3 M KCl solution was used as a reference electrode and a platinum sheet (10 mm × 10 mm), as a counter electrode.

The polymer films were electrochemically synthesized on iron in a one-step process at 1.2 V vs. $Ag/AgCl_{sat}$ from aqueous solution of 0.1 M pyrrole and 0.1 M sodium salicylate (pH 7) ($Q = 6.37C \cdot cm^{-2}$) at 5, 10, 15, 20 and 25 °C. The choice of the monomer and electrolyte concentration, deposition charge and potential were chosen based on our previous study [34]. The temperature during the electropolymerization and measurements was controlled by a JULABO F12 thermostat.

The characterization of corrosion protection of the polymeric film was carried out by potentiodynamic polarization at potentials from −300 mV to 1 V (vs. OCP) with a 3 $mV \cdot s^{-1}$ scan rate under conditions of simulated tissue environment: phosphate buffer saline (PBS) aqueous solution (pH 7.4) at 37 °C.

The electroactive surface area (ESA) of PPy/Fe was determined by performing the cyclic voltammetry of this electrode in 5 mM $K_3Fe(CN)_6$/0.1 M KCl solution with a potential range from −1.2 V to 1.2 V rel. OCP and a scan rate of 50 $mV \cdot s^{-1}$ at 23 °C [35,36] [Supplementary material].

The re-oxidation and reduction of the PPy were performed at +0.8 and −0.8 V in a monomer-free aqueous solution of 0.1 M sodium salicylate at room temperature for 1, 2 and 3 min, respectively. The potentials were chosen based on the cyclic voltammograms obtained in the aqueous solution of 0.1 M sodium salicylate presented in previous work [8].

The determination of polymer resistance was based on electrochemical impedance spectroscopy (EIS) measurements, which were carried out in a 2-electrode system controlled by Gamry Instrument - Interface 1000. The working electrode for this measurement was an iron double-band and was prepared based on the description provided by Kankare and Kupila [37]. The electrode consists of two separated iron plates (each with a dimension of 18 mm × 1.5 mm) with a gap between the sheets of 80 μm. All surrounded by epoxy resin with leads attached to each sheet. The construction of a double-band electrode allows for resistance measurements of a polymer film deposited between the iron plates. EIS measurements were performed in the frequency range of 10 kHz–0.01 Hz. The perturbation signal applied was a 3 mV RMS variation around the open circuit potential. Because the resistance measured in situ is a combination of the polymer resistance, the supporting electrolyte and the double layer capacitance [38,39], the impedance measurements were conducted in the air. Determination of the polymer resistance from the impedance spectra was performed at the frequency of 10 Hz. It is the impedance value for which the phase angle is 0°, and therefore, the modulus of impedance was assumed to be the resistance

of the polymer film [8,39]. Because the resistance of the conducting polymer film is dependent on its dry state [39], each sample was measured at the same condition: after the polymer deposition, each sample was immediately removed from the solution, dried in a warm air stream for approximately one minute and then the impedance was measured. More details about the method of polypyrrole resistance determination can be found in Supplementary material and in previous work [39].

Scanning electron microscope FEI QUANTA FEG 250 was used to examine the morphology of the deposits. The film thickness is measured from cross-sectional scanning electron microscope (SEM) images, using JEOL JSM-IT300LV with a tungsten filament source.

In order to study the phase composition of crystalline phases present in the samples, X-ray diffraction method (XRD) using the Phillips X'Pert Pro MPD with CuKα1 and CuKα2 radiations was used. For this examination, the PPy films electropolymerized at 5, 15, and 25 °C were mechanically removed from the iron support.

3. Results and discussion

3.1. Morphological properties of PPy/Fe synthesized at different temperatures

3.1.1. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of the samples synthesized at 5, 15 and 25 °C are presented in Fig. 1.

It may be observed that the higher the electropolymerization temperature, the lower the crystallinity of the materials. In the case of PPy synthesized at 25 °C, a broad hump of a low intensity is present at about 2θ = 25° (Fig. 1a). It is typical of amorphous polypyrrole [40–42]. This hump is not seen in the diffractograms of the samples obtained at electropolymerization temperatures of 5 and 15 °C. This indicates that the amount of amorphous polypyrrole in the studied samples increases with the increase in electropolymerization temperature.

The XRD pattern of the sample obtained at 25 °C (Fig. 1a) also shows a few very weak reflections. The 2θ reflections at about 35 and 41° could be caused by the presence of iron oxide [43,44], whereas the 2θ reflections at 45 °C may be related to the presence of iron [ICDD File Card No. 01-071-3763]. The former might be formed on the surface of iron prior to PPy deposition [10], whereas the latter originates from the residuals of iron support. The passivation layer inhibits the dissolution of the iron substrate and allows for a stable PPy deposition [10,16,34].

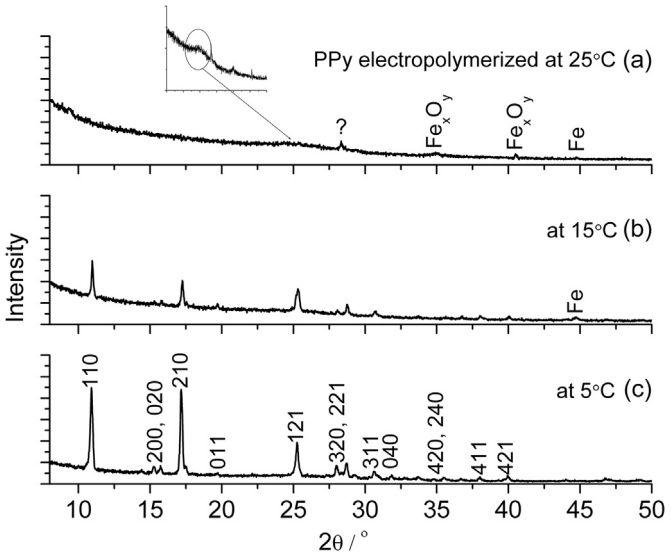

Fig. 1. The results of XRD analysis of the samples synthesized at a temperature of 25 (a), 15 (b) and 5 °C (c). Miller indices shown in (c) mark the XRD reflections characteristic of salicylic acid.

The origin of the reflection at 2θ = 28.4° is probably a reflex from the silicon holder [ICDD File Card No. 00-005-0565].

In the case of polymeric films prepared at 5 and 15 °C reflections characteristic of salicylic acid can be seen (Fig. 1b and c). The intensity of the salicylic reflections increases with decreasing temperature. This indicates that lowering the electropolymerization temperature results in an increase in the number of salicylic acid crystals in the polymer structure. Therefore, electropolymerization of pyrrole on iron at lower temperatures probably includes both monomer oxidation and the formation of salicylic acid. The formation of salicylic acid crystals were also observed in the case of PPy synthesized on stainless steel at 0.8 V in the presence of 0.25 M Py and 0.5 M sodium salicylate (pH 7) at 25 °C [45]. One of the reasons for the electrocrystallization of salicylic acid may be its lower solubility at a reduced temperature. It is known that the solubility of salicylic acid decreases from about 2 g/l to 1 g/l between 25 and 5 °C [46]. On the other hand, it was also noticed that no salicylic acid crystals were formed during the polarization of bare iron in monomer free solution of 0.1 M sodium salicylate at a reduced temperature. This indicates that salicylic crystals can only be formed in the presence of sodium salicylate and pyrrole during the electropolymerization process.

The electrocrystallization of dopant during the conducting polymer electrosynthesis was also observed in the case of a poly(3,4-ethylenedioxytiophene) (PEDOT) film in the presence of 2,2′-azino-bis-3-ethylbenzothiaxoline-6-sulfonic acid (ABTS) [31]. In this case, the electrodeposition of crystals was dependent on the deposition potential. The increase in the concentration of crystalline ABTS in the polymeric film resulted in the poor adhesion, disconnected morphology, low electroactivity and conductivity of the deposited PEDOT film [31].

3.1.2. Scanning electron microscopy analysis

The morphology of the polypyrrole electrochemically synthesized in the presence of sodium salicylate at temperatures of 5, 10, 15, 20 and 25 °C was analysed by scanning electron microscopy (SEM). In all cases, the average thickness of the synthesized PPy-salicylate film was determined to be ~20 μm. The PPy film could not be electrodeposited on iron at a temperature higher than 25 °C (data not shown). It was noted that the higher temperatures did not allow for the deposition of a good quality PPy coating, despite the use of the same electropolymerization charge as for lower temperatures. There is a high degree of probability that the higher temperatures inhibit the oxidation of the monomer, and therefore the formation of PPy on iron in an aqueous solution of pyrrole and sodium salicylate. As a result, PPy films with much lower thicknesses were obtained, this made it impossible to compare them with the PPy film synthesized under alternative conditions.

SEM images of PPy films synthesized in the temperature range 5–25 °C are presented in Fig. 2. It may be observed that the polymeric structures obtained differ, depending on the applied temperature. The film deposited at 5 °C reveals a very rough surface which consists of a significant number of randomly located crystals, which are salicylic acid crystals (Fig. 2a and b). Based on observations from SEM analysis, it may be observed that increasing the deposition temperature results in a decrease in the number of crystals in PPy structures. On the other hand, the inhibition of the crystallization process results in the formation of a more homogenous PPy structure. A polymer synthesized at 15 °C exhibits a much lower number of crystals in its structure (Fig. 2d, e, f) compared to those obtained at lower temperatures, whereas no crystals at all are observed in the case of PPy synthesized at 25 °C (Fig. 2g, h, i). PPy coatings prepared under the latter conditions are the most homogenous and their surfaces are characterized by a typical cauliflower-like structure constituted by spherical grains with a magnitude of a few micrometers (R_a = 130 nm, R_q = 165 nm) [AFM images, Supplementary material, Fig. C].

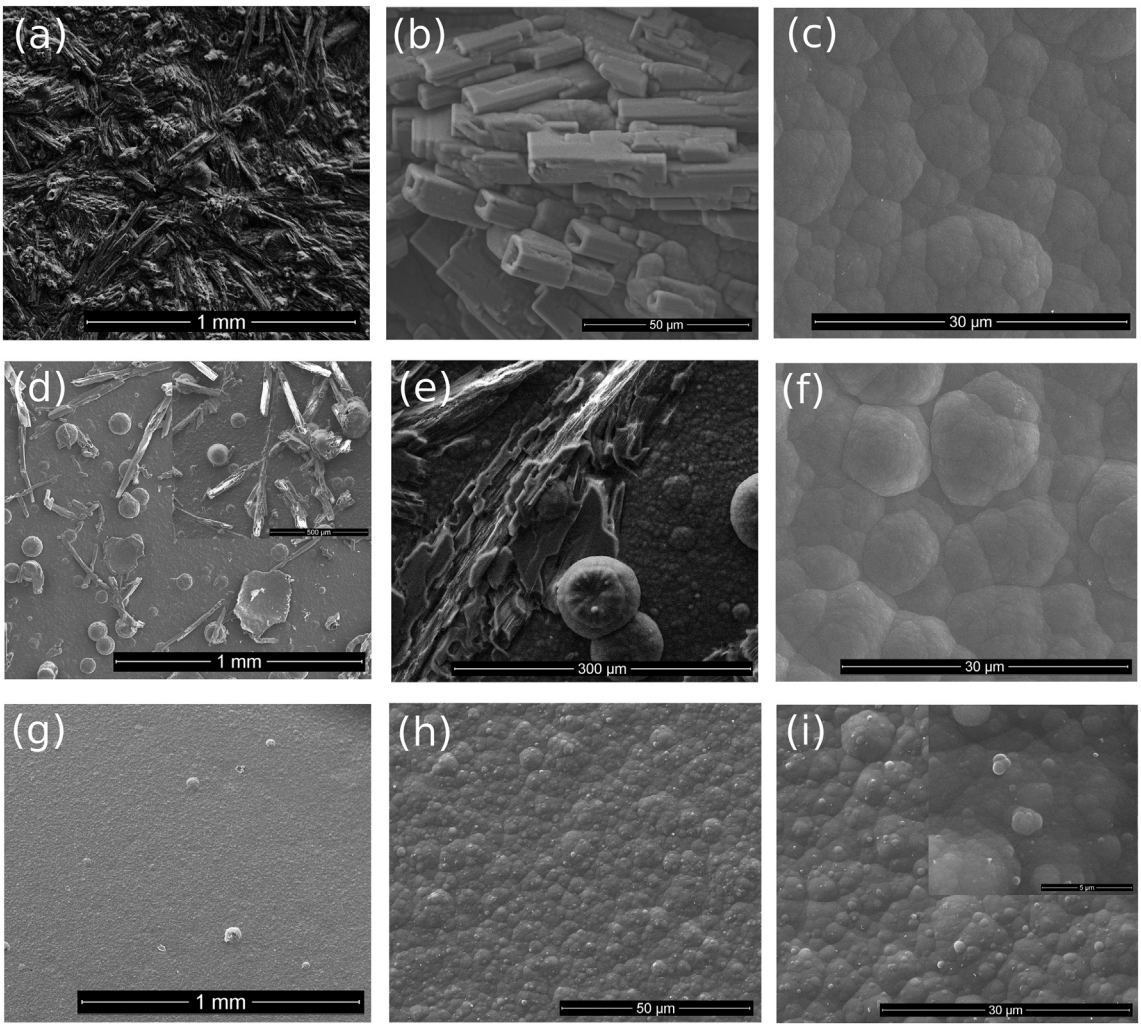

Fig. 2. SEM images of PPy films synthesized potentiostatically at 1.2 V in aqueous solution of 0.1 M pyrrole and 0.1 M sodium salicylate at the temperature of 5 °C (a, b, c), 15 °C (d, e, f) and 25 °C (g, h, i).

The SEM results are in agreement with the previously presented XRD analysis. The results indicate that the obtained PPy-salicylate structure is strongly influenced by the temperature applied during the electropolymerization process.

3.1.3. Determination of electroactive surface area

The electroactive surface area (ESA) of the PPy film synthesized at different electropolymerization temperatures (5, 10, 15, 20, 25 °C) was determined based on the Randles-Sevcik equation. This is a

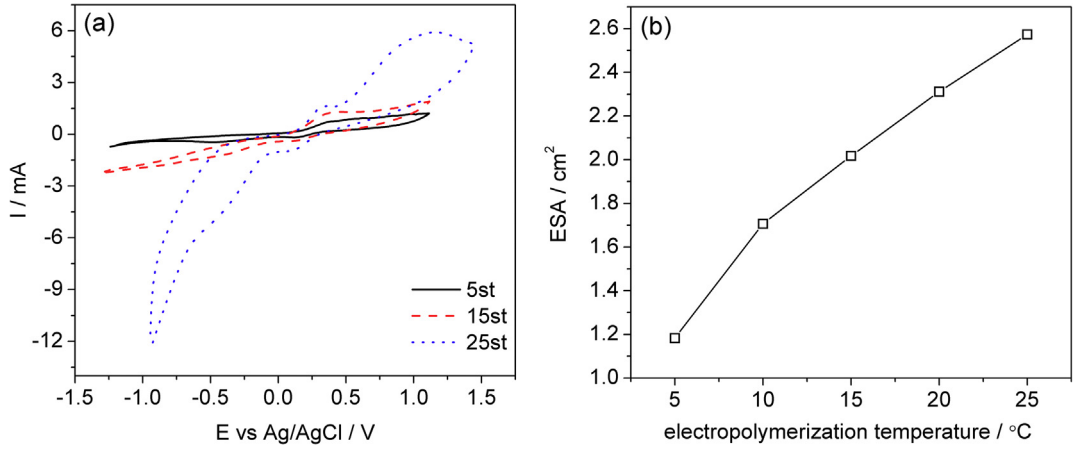

Fig. 3. Examples of cyclic voltammograms of PPy/Fe synthesized at a temperature of 5, 15 and 25 °C in 5 mM $K_3Fe(CN)_6$/0.1 M KCl solution (a), electroactive surface area (ESA) of PPy/Fe synthesized at different electropolymerization temperature (b). Measurements were performed at 23 °C.

common electrochemical method for estimating the electroactive surface area of different electrode materials [20,35]. For this purpose, cyclic voltammetry of the PPy/Fe electrode in 5 mM $K_3Fe(CN)_6$/0.1 M KCl solution was performed.

An example of the cyclic voltammograms obtained for the film synthesized at a temperature of 5, 15 and 25 °C are presented in Fig. 3a. The redox peaks related to the oxidation/reduction of the ferrocyanide ions occur in a potential range between the −0.2 and +0.5 V vs. Ag/AgCl [36]. The remaining peaks are related to redox reactions of the polymer, which is a typical behaviour in the case of conducting polymer materials [8].

Based on the graphs in Fig. 3a it may be observed that increasing the electropolymerization temperature results in a higher intensity of oxidation/reduction peaks of both ferrocyanide ions and polymer. This may be associated with the fact that a higher temperature produces a higher surface area and a more electrochemically active polypyrrole coating.

Fig. 3b presents the change in ESA for PPy films obtained at 5, 10, 15, 20 and 25 °C. It may be observed that with increasing electropolymerization temperature, the ESA of the film increases. The highest ESA value is obtained in the case of 25 °C (~2.6 cm^2). It means that the polymeric film obtained at higher temperatures has a higher electrochemical activity. This may be associated with changes in surface area of the material and with the number of salicylic acid crystals in the PPy structures. For lower electropolymerization temperatures, when the PPy film consists of a significant number of crystals, the electroactive surface area is lower either due to the insulating area introduced by the salicylic crystals or the lower surface area of PPy.

3.2. Corrosion and electrical properties of PPy/Fe synthesized at different temperatures

The corrosion performance of bare iron and polypyrrole coated iron (PPy/Fe) synthesized at different electropolymerization temperatures was assessed by potentiodynamic polarization in an aqueous solution of phosphate buffer saline (PBS, pH 7.4) at 37 °C (Fig. 4). The corrosion performance of the PPy/Fe material differs depending on the electropolymerization temperature applied during synthesis. The oxidation and reduction branches of the polarization curve are well defined, although the specific redox reactions involved are uncertain at this time. Redox processes may involve oxidation of the metal and/or polymer (anodic branch) and reduction of oxygen and/or polymer (cathodic branch) [48]. The corrosion potential E_{corr} and corrosion current density i_{corr} were calculated based on the Tafel plots from Fig. 4 in order to assess the initial corrosion performance of the polymer/iron system. The redox processes of the polymer were not taken into account. The

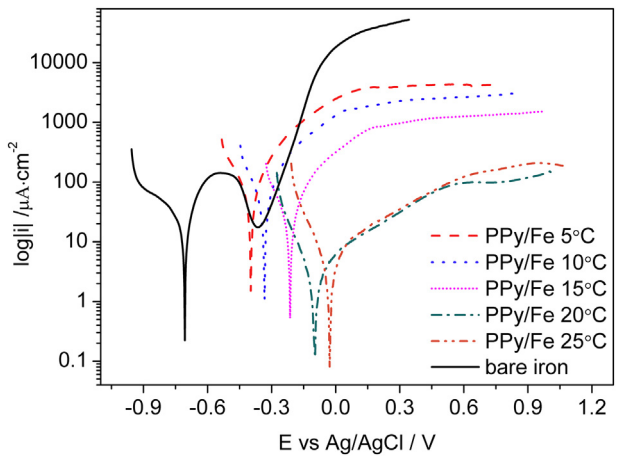

Fig. 4. Tafel plots of PPy/Fe synthesized at a temperature of 5, 10, 15, 20, 25 °C and bare iron measured in PBS solution (pH 7.4) at 37 °C.

E_{corr} and i_{corr} for bare iron were determined to be −0.71 V and 14.41 $\mu A \cdot cm^{-2}$, respectively.

The corrosion parameters for PPy coated iron obtained at different temperatures are presented in Fig. 5. The increase in the corrosion potential in the direction of a more noble potential and the decrease of the corrosion current density indicate a higher corrosion resistance of the material. From Fig. 5 it may be observed that increasing the temperature results in an increase in the E_{corr} from approximately −0.4 V for 5 °C to −0.03 V for 25 °C and a decrease in the i_{corr} from approximately 40 $\mu A \cdot cm^{-2}$ for 5 °C to 2.5 $\mu A \cdot cm^{-2}$ for 25 °C. This indicates that lowering the electropolymerization temperature results in a decreased corrosion resistance of the coating. The highest level of corrosion resistance is obtained in the case of PPy coatings synthesized at 25 °C. It is has been established that by changing the synthesis conditions such as electrolyte and monomer concentration or deposition potential and current density results in different corrosion properties of polypyrrole doped with salicylate on iron [10]. In this particular case, it is observed that the corrosion parameters of PPy coated iron may also be tailored by changing the electropolymerization temperature during polymer synthesis.

The resistance evolution of PPy films synthesized on iron at different temperatures has also been investigated. Fig. 6 presents the changes in the PPy resistance depending on the electropolymerization temperature. The electrical properties of PPy also depend closely on the temperature. With increasing polymerization temperature, the resistance of PPy decreases from approximately 40 kΩ for 5 °C to approximately 840 Ω for 25 °C. Therefore, the most conductive polymeric film is obtained in the case of 25 °C. At this temperature, corrosion protection also reached its highest level.

An increase in PPy conductivity with an increasing tendency of the material to corrode is not a very typical behaviour in materials engineering. H. Nguyen Thi Le et al. [16] relates high levels of corrosion protection with the insulating properties of the material because of its poor ionic and electronic conductivity. However, the mechanism of corrosion protection of iron or steel by a conducting polymer depends on the polymer/metal electrochemical system [34]. In the case of a PPy-salicylate coating deposited on oxidizable iron, the corrosion protection of this material is obtained as a result of galvanic coupling-between the coating and the metal [34]. The reactions between the polymer and metal lead to the formation of corrosion products on the base of the polymer pores, which isolate the substrate from the corrosive medium and in this way the corrosion process of iron is inhibited [34]. The detailed explanation of the corrosion protection mechanism and the degradation of PPy on iron can be found in previous work [34]. Such a mechanism was also reported in the case of PPy-oxalates on iron [47] or polyaniline deposited on steel [48].

Besides, as in any polymer system, the properties of the resultant films are also inextricably linked to the nature of the molecular organization [49]. The latter is highly dependent on dopant anions and deposition conditions [50]. For example, in the work of A. Ashrafi et al. [33], high crystalline PPy doped with oxalate ions deposited on stainless steel shows higher levels of corrosion protection and resistance compared to the amorphous one. Therefore, all changes in the corrosion and electrical properties of the salicylate doped PPy/iron system studied here are influenced by the type of dopant, synthesis conditions and are also closely dependent on its resultant morphology, obtained at different electropolymerization temperatures.

The electrical properties of the PPy-salicylate/Fe system established here may be explained based on the general properties of conducting polymers. It is well known that the overall conductivity of conducting polymers includes the mobility and number of both the electronic and ionic charge carriers. Because the resistance measurements of PPy in this work were performed in air, it is assumed that the conductivity in the system is determined by the predominant electronic charge carriers.

It is generally accepted, that conductivity in these systems involves charge transport along the chains, as well as the hopping of carriers

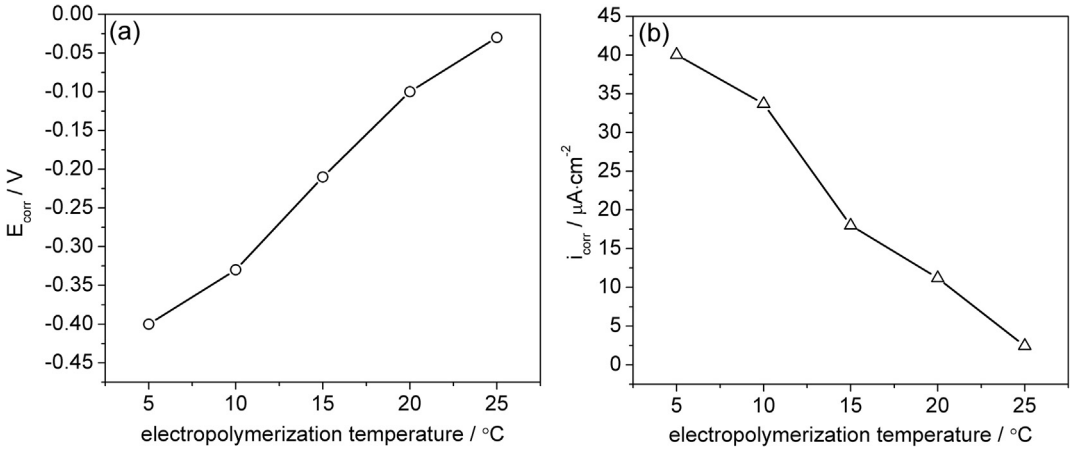

Fig. 5. Evolution of the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for PPy/Fe synthesized at different electropolymerization temperature.

(holes, polarons, bipolarons etc.) from one polymer chain to another. These indicate that polymer morphology and chain arrangements play a significant role in determining the electrical properties of the material [50].

In this case, the PPy film may be described as a composite material containing two different phases, highly conductive polymeric islands, which are separated by insulating regions in the form of salicylic acid crystals. The lower resistance found in the PPy synthesized at higher temperatures is due to the larger conducting regions and thus lower insulating barriers. The opposite phenomena may be observed for PPy prepared at a reduced temperature, in which a large number of salicylic acid crystals is present.

3.3. Corrosion and electrical properties of re-oxidized or reduced PPy/Fe synthesized at different temperatures

The corrosion and electrical properties of PPy synthesized in the presence of sodium salicylate at different temperatures have also been studied after its additional reduction and re-oxidation processes. Fig. 7 presents the changes in the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for re-oxidized (Fig. 7a, b) or reduced (Fig. 7c, d) PPy/Fe synthesized at a temperature of 5, 15 and 25 °C. The corrosion parameters have been determined based on the Tafel plots recorded in PBS (pH 7.4) at 37 °C [Supplementary material, Fig. D].

Both the re-oxidation and reduction processes of the polymer have an influence on the corrosion properties of the PPy coated iron material.

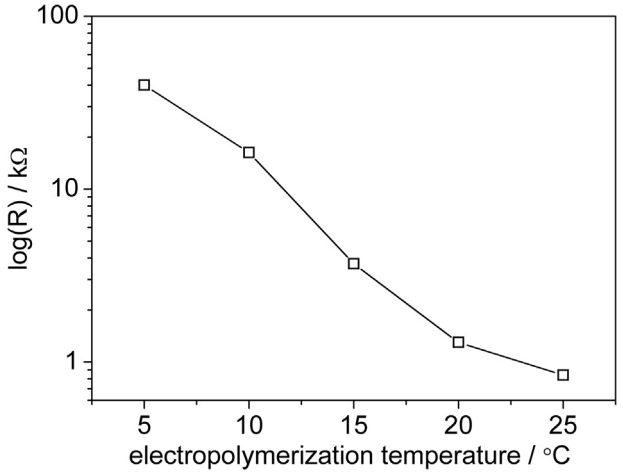

Fig. 6. Evolution of the PPy resistance synthesized at different electropolymerization temperature.

It may be observed that the re-oxidation of the PPy leads to a decrease in the corrosion potential and an increase in the current density for each electropolymerization temperature (Fig. 7a, b). This means that the re-oxidation process leads to a decrease in the corrosion protection of iron coated with PPy. After 1 min of re-oxidation, the E_{corr} decreases for all of the temperatures and with longer re-oxidation times it remains constant. The i_{corr} in these cases increases after 1 min of re-oxidation and then remains virtually constant.

The changes in corrosion parameters following PPy reduction may be seen in Fig. 7 c, d. In this case, the behaviour of E_{corr} and i_{corr} is very similar for each electropolymerization temperature. The reduction of the polymeric film leads to a decrease in the corrosion potential and an increase in the corrosion current density. The rate of these changes differs depending on the deposition temperature. The resistance of differently re-oxidized and reduced PPy films has also been studied (Fig. 8). The reduction of the polymeric film leads to an increase in its resistance, which may be observed for each electropolymerization temperature. This is a typical behaviour in the case of conducting polymers [11].

Re-oxidation of the PPy for one minute leads to an increase in its resistance, which later becomes constant. This may be observed at temperatures of 15 and 25 °C. The results are in agreement with the changes in the corrosion parameters of PPy prepared under these conditions. It is well known that oxidation of the conducting polymer backbone generates charge carriers, which confer electronic conductivity to the polymer [8]. However, re-oxidation of already oxidized PPy can lead to its irreversible anodic degradation (overoxidation) [8]. Overoxidized PPy loses its unique properties which makes changing its properties impossible [8,11,51]. That is the reason why both the corrosion parameters and resistance of the PPy do not change after one minute of re-oxidation. Another behaviour of re-oxidation may be observed in the case of PPy synthesized at 5 °C. In this case, the resistance of the polymeric material decreases significantly after one minute of re-oxidation and then it increases slightly.

Generally, the re-oxidation and reduction of PPy synthesized at 15 and 25 °C leads to both a decrease in the corrosion protection properties of the PPy film and an increase in the resistance of PPy. The re-oxidation behaviour is mainly due to the irreversible overoxidation process of the polymeric film. During polymer reduction, the release of the salicylate anions takes place [11]. Therefore, such a PPy can also act as an anti-inflammatory drug in possible medical applications [8,10,11]. The greater the reduction time, the higher the resistance and the lower the corrosion protection of PPy obtained. Reduction of the PPy film, for a longer time, causes its instability due to the large amount of anions released. This gradually leads to the weaker adhesion of the polymeric material to the iron substrate, which results in a lower corrosion resistance of the metallic material [8]. The corrosion and electrical behaviour of reduced PPy are similar for all temperature cases.

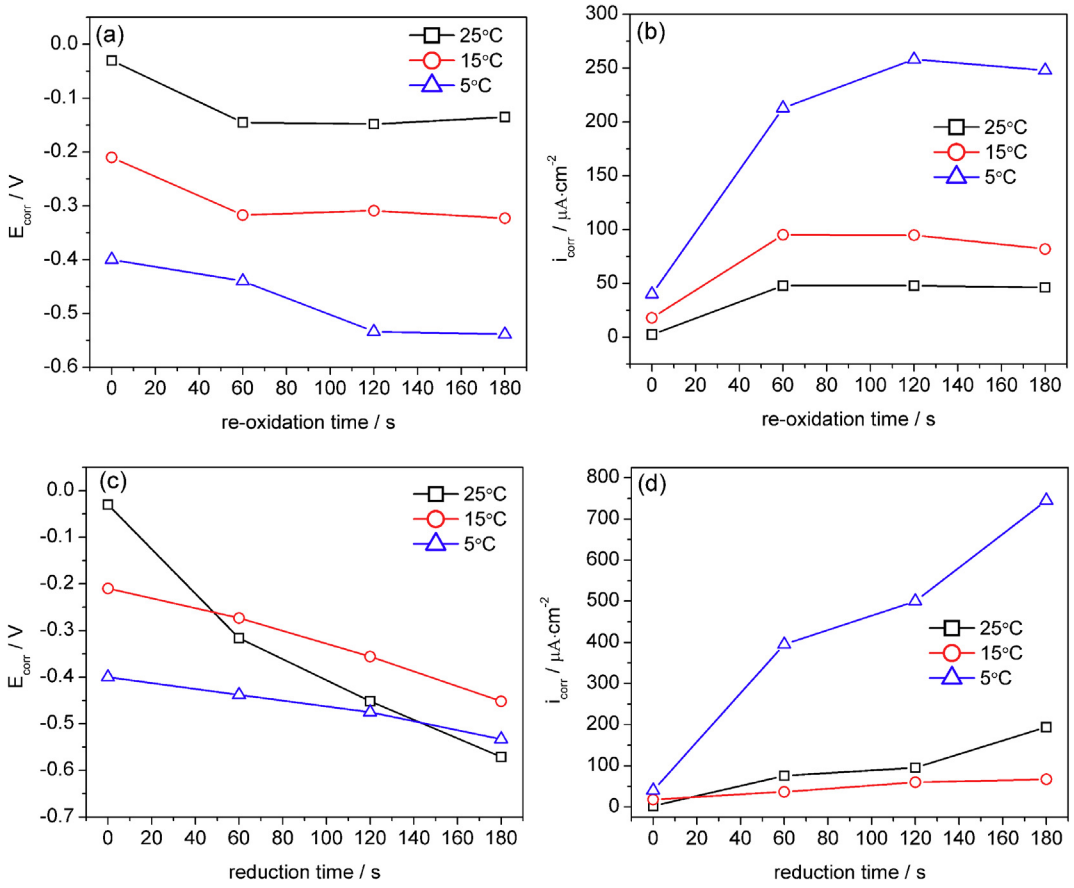

Fig. 7. Evolution of the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for re-oxidized (a, b) or reduced (c, d) PPy/Fe synthesized at a temperature of 5, 15 and 25 °C.

Another behaviour is observed in the case of re-oxidized PPy film, which was synthesized at 5 °C. In this case, the evolution of the E_{corr} and i_{corr} is slightly different. The resistance changes differ significantly compared to those measured at other temperatures. The resistance of the polymeric material decreases significantly after one minute from re-oxidation and then it increases slightly, which was not observed at 15 and 25 °C. Such behaviour is probably associated with the large number of insulating salicylic acid crystals in the polymeric structure which significantly prevented and hindered the initial oxidation process of the PPy film compared to the oxidation process of salicylate. Re-oxidation of this PPy film allows the polymeric material to be fully oxidized which results in a significant decrease in its resistance. A further increase in resistance is related to the overoxidation process, which, at this temperature, is much more gradual than at 15 and 25 °C. Because of this, PPy is gradually and partially degraded. This is another proof that the oxidation state of the PPy is different depending on the temperature applied during its synthesis.

4. Conclusions

In the present work, the polypyrrole film on iron has been successfully electrosynthesized in aqueous sodium salicylate solution at different temperatures. The XRD and SEM experiments showed that different compositions and structures of PPy may be obtained depending on the

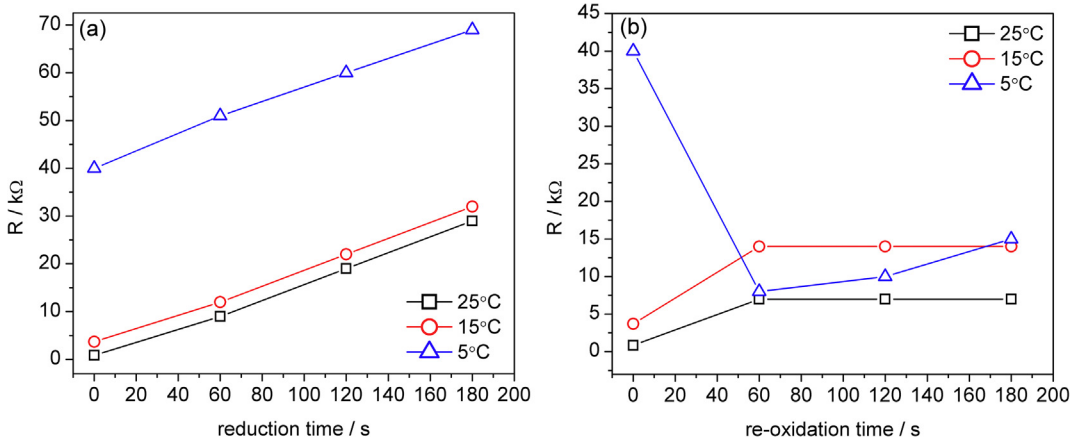

Fig. 8. Evolution of the resistance of reduced (a) or re-oxidized (b) PPy/Fe synthesized at a temperature of 5, 15 and 25 °C.

applied electropolymerization temperature. The film synthesized at a reduced temperature reveals a rougher morphology and a higher degree of crystallinity, compared to the PPy prepared at higher temperatures due to the presence of salicylic acid crystals in its structure. It has been noted that increasing the deposition temperature results in a decreased number of crystals in the PPy structures. The inhibition of the crystallization process at higher temperatures resulted in the formation of an amorphous, more homogenous and highly electroactive PPy film on iron. No salicylic acid crystals were observed in the case of PPy synthesized at 25 °C. PPy coatings prepared under the latter conditions were the most homogenous and their surfaces were characterized by a typical cauliflower-like structure.

It was also noted that PPy with incorporated crystals shows lower corrosion protection and much higher resistance compared to the amorphous one. This was associated with the presence of insulating salicylic acid crystals incorporated into the polymer structure. The film studied here might be described as a composite material containing two different phases, highly conductive polymeric islands, which are separated by insulating regions in the form of salicylic acid crystals.

The outcome of the present study shows that the morphological, corrosion and electrical properties of PPy doped with salicylates on iron may be significantly affected by the electropolymerization temperature. It means that the properties of this material may be additionally tuned by changing the electropolymerization temperature, for possible medical applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.surfcoat.2017.08.055.

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