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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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ABSTRACT

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 presence 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.

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) ($Q = 6.37 C \cdot cm^{-2}$) 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