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Enhancing the Stability of PPy Film on Ti by PEG Incorporation

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Composite films based on polypyrrole (PPy) and polyethylene glycol (PEG) were synthesized on titanium electrode, using various percentages of PEG, as the insulating material in order to enhance surface properties of the polymer composite films. The Fourier transform infrared spectroscopy (FT-IR) was performed to demonstrate the formation of a PPy-PEG composite film. The corrosion behaviour of coatings has been studied by Tafel tests and cyclic voltammetry. The PPy-PEG films/electrolyte interface was analyzed by electrochemical impedance spectroscopy (EIS) and the specific parameters of corresponding equivalent circuits were calculated. The polymeric layer morphology on titanium substrate has been evaluated using atomic force microscopy (AFM) and enhanced properties of the PPy-PEG films are discussed as the effect of PEG incorporation in the polypyrrole structure.

Keywords Electropolymerization; polyethylene glycol; polypyrrole; titanium

Introduction

Conducting polymers represent a novel class of materials that are intensively studied for their application in various domains: energy storage, electromagnetic screens, sensors, membranes, protective coatings [1]. In order to overcome the drawbacks relating to poor processability, to control and enhance the physical properties of a polymer, the most convenient tool in polymeric science, is the formation of a new composite material. The formation of a conducting polymer composites with new properties has been employed for the study of conducting polymer such as polypyrrole, polyaniline, polythiophene, etc., in combination with various polymers: poly(vinylalcohol) [2], poly(styrenesulphonate) [3], polycarbonate [4], poly(methyl methacrylate) [5], polyimide [6], polyethylene glycol [7]. Polypyrrole and its derivatives have attired the attention more than other conducting polymers due to their high electrical conductivity, stability in air, good redox reversibility and their easily synthesis both chemically and electrochemically [8,9]. Polypyrrole is important for its potential use in the next generation of modified electrodes, sensors, batteries, diodes,

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solar cells, tissue repair. Thus, applying its electrical and biological properties, polypyrrole can be used to create new bioengineering technologies [10,11]. However, the main problems with polypyrrole include its poor mechanical properties [12]. Several approaches have been considered to improve these drawbacks of conducting polymers [13–15]. An attractive route is to introduce an insulating polymer, due to the excellent processability, without losing its conductivity [16,17]. Polypyrrole is easily electrosynthesized on inert electrode such as gold, platinum [18,19] but is more difficult to generate PPy films with good adherence on other metals like Al or Ti and its alloys, that form a highly stable protective oxide layer that blocks electron transfer [20,21].

In order to change the structure, conductivity or chemical permeability of deposited films, a polypyrrole/polyethylene glycol composite coatings were proposed for platinum [8], and ITO surface [22,23].

In the present study, the polypyrrole-polyethylene glycol (PPy-PEG) composite films in which PEG was used as an insulting polymer were synthesized on titanium by electrochemical method. The aim of the paper was to study the effects of various concentration of PEG on electrodeposited composite film properties such as electrochemical behaviour, film stability, topography and wettability.

Experimental Part

Materials

The substrates were represented by commercially pure Ti discs of 1 mm thickness and 10 mm diameter (99.6% purity, Goodfellow Cambridge Ltd., UK). The surface of test specimens was polished with SiC paper to grade 4000. Before deposition, the discs were cleaned in acetone and rinsed well with distilled water.

The electrochemical deposition of polymeric and composite films was performed in aqueous solution of $0.2\,\text{mol}\cdot\text{L}^{-1}$ Py in $0.2\,\text{mol}\cdot\text{L}^{-1}$ oxalic acid. For composite PPy-PEG films electropolymerization of pyrrole was performed in the presence of PEG (400 molecular weight) with the following concentrations in the electrolyte solution: 0.5%, 1%, 2%, 3%, 4%, and 5%.

Pyrrole monomer was purchased from Merck, purity >98%, stored in the dark, at 0°C before use. All solutions were prepared using ultra pure deionised Milli-Q water. The composition of buffer solution used for electrochemical characterization was: NaCl 8.74 g/L; $NaHCO_3$ 0.35 g/L; $Na_2HPO_4\cdot 12H_2O$ 0.06 g/L; NaH_2PO_4 0.06 g/L.

Methods

The electrochemical data such as electrodeposition and electrochemical characterization were recorded at room temperature using a conventional three electrodes cell: a working electrode, a platinum counter-electrode and an Ag/AgCl, KCl reference electrode connected to Autolab PGSTAT 302 N potentiostat with general-purpose electrochemical system software. The following electrochemical parameters for the composite films were determined from Tafel plots: E_{cor} (corrosion potential), I_{cor} – corrosion current, R_p – polarisation resistance and v_{cor} – corrosion rate. The FT-IR spectroscopic analysis for the PPy-PEG composite films was done by a Perkin Elmer FTIR spectrophotometer (Spectrum 100 model) from 4000 to $600\,\text{cm}^{-1}$. The surface topography and roughness of polypyrrole films was studied with Atomic Force Microscope (AFM) from APE Research, Italy. The contact angle of a drop of water with the films surface was measured with a CAM 100 equipment.

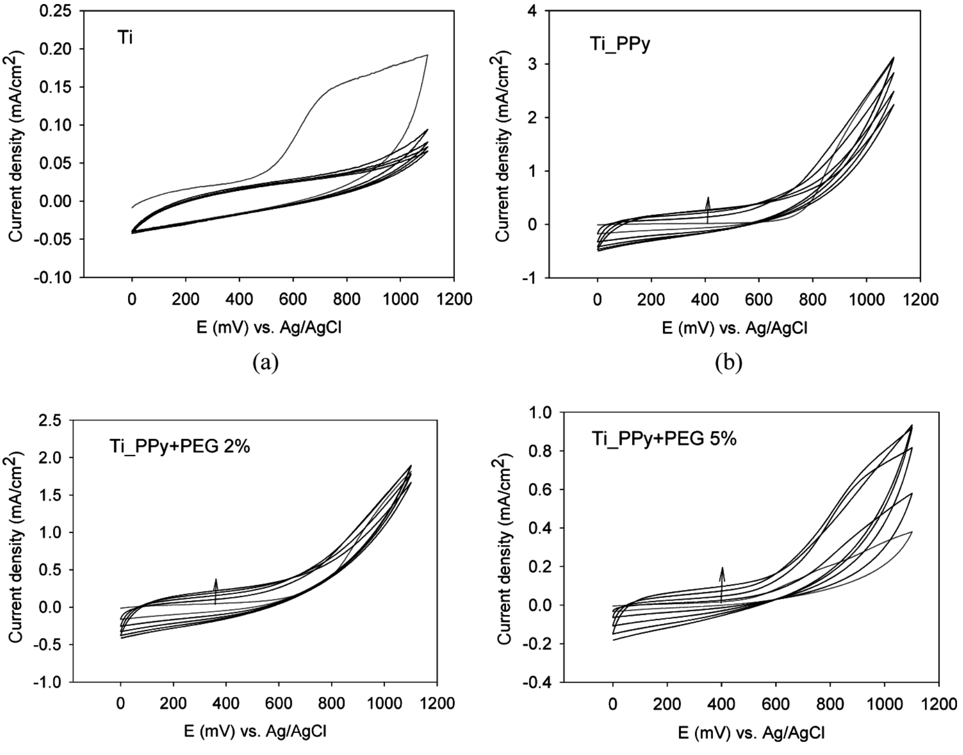
Results and Discussion

Electrochemical Deposition of Polypyrrole-Polyethylene Glycol Films on Ti Electrode

PPy and PPy-PEG films were deposited by potentiodynamic polymerization using as electrolyte solution oxalic acid aqueous solution in the presence of pyrrole, in which was added for composite films deposition, polyethylene glycol in different concentrations.

Figure 1a presents the electrochemical behavior of titanium electrode in oxalic acid aqueous solution without PPy. The first cyclic voltammogram is characterized by an sudden current increase around 0.6 V, on the anodic branch corresponding to the formation of a stable titanium oxide layer and then a passivation of the surface can be observed in the following 4 cycles.

The presence of pyrrole in the electrolyte solution changed the behaviour of the Ti electrode. The rapid increase of current starting with potentials of 0.7 V,



(a) (b)

(c) (d)

Figure 1. Cyclic voltammograms obtained on: (a) Ti in oxalic acid 0.2 M, (b) Ti in 0.2 M Pyrrole/0.2 M oxalic acid aqueous solution, (c–d) Ti in 0.2 M Pyrrole/0.2 M oxalic acid aqueous solution + different concentration of PEG. The first cycle is in a dashed line.

correspond to Py oxidation, Ti electrode surface being covered with a visible black films of polypyrrole during the 5 scans. In the presence of different concentration of polyethylene glycol, Figure 1(c–d) the current corresponding to electro-oxidation of pyrrole has almost four times decrease comparing to electro-oxidation in the absence of insulating PEG. Also, it was observed that the current density decrease proportionally with the increase in PEG concentration.

The current density increased with cycle's number, as a proof of polymeric and composite film growth on titanium surface.

Structure of PPy-PEG Composite Films

The infrared spectra of the samples were recorded in the wavenumber range from 4000 to 400 cm^{-1}. The FT-IR spectra of PEG, PPy and PPy-PEG films are presented in Figure 2. In the IR spectrum of PEG (Fig. 2a) are evidenced: the absorption bands at 3384 cm^{-1} corresponding to stretching vibration of OH group, the band at 2864 cm^{-1} corresponding to stretching vibration of CH_2 and the absorption band at 1107 cm^{-1} corresponding to stretching vibration of C–O bond. In the case of PPy spectrum (Fig. 2b), it was observed the NH stretching band of pyrrole ring at 3425 cm^{-1}. The bands between 1000–1600 cm^{-1} show the characteristic polypyrrole absorption. The band at 1626 cm^{-1} is assigned to C=C ring of pyrrole. Figure 1c shows the FT-IR absorption spectrum of PPy-PEG film. This presents peaks that are characteristic both to PPy (3425 cm^{-1}, 1626 cm^{-1}) and to PEG (2864 cm^{-1}, 1107 cm^{-1}), indicating that PEG was incorporated into the PPy film, forming a PPy-PEG composite film.

Electrochemical Characterization

Cyclic Voltammetry. The stability of the electrodeposited polymeric films was checked in buffer solution with a pH of 6.5. The cyclic voltammograms were

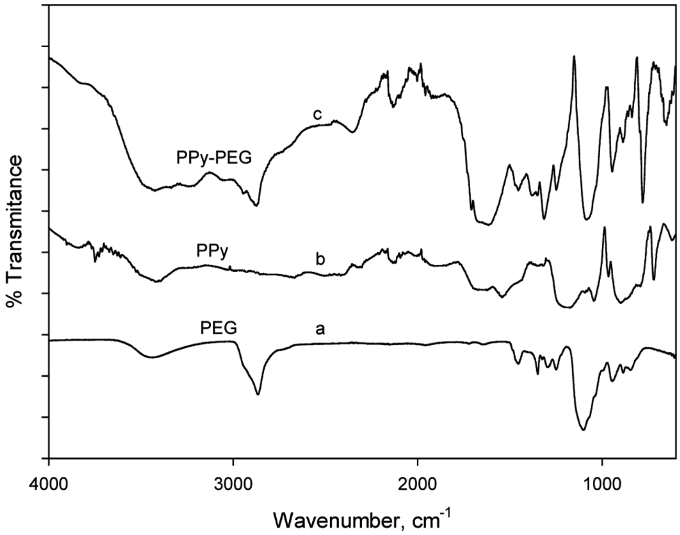


Figure 2. FT-IR spectra of PEG (a), PPy (b) and PPy-PEG films (c).

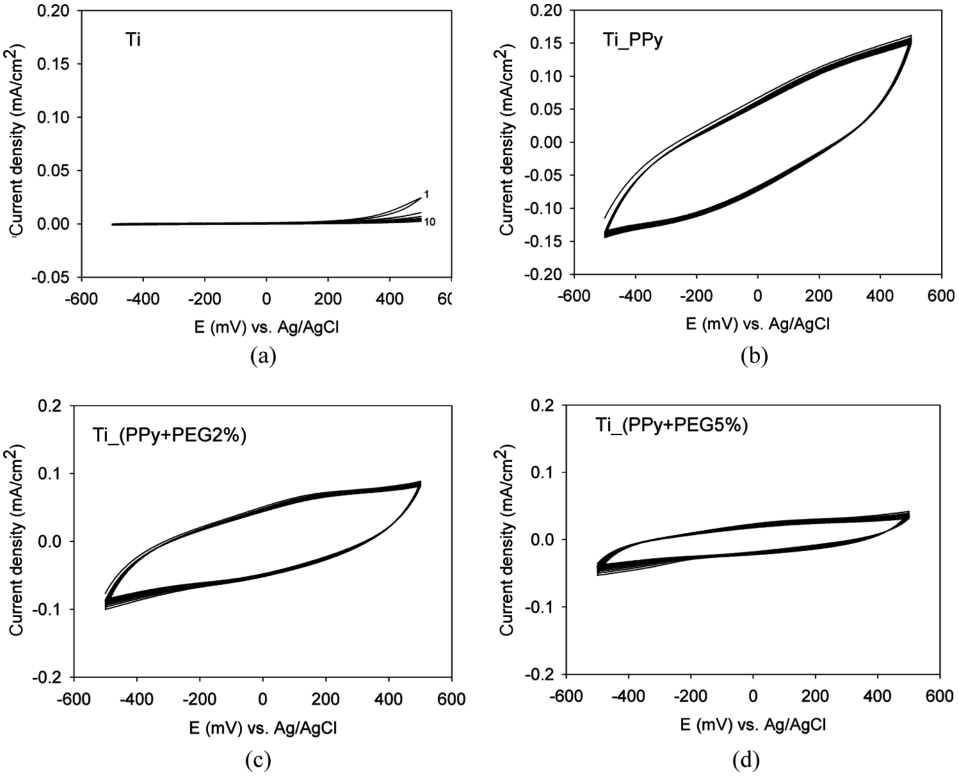


Figure 3. Cyclic voltammetric curves (10 scans) on: (a) untreated Ti, (b) Ti-PPy film and (c–d) Ti_PPy films with PEG added in different concentrations. Potential scan rate: $0.05\,Vs^{-1}$.

repeated ten times. From the Figure 3a it was observed that uncoated Ti is rapidly passivated by the formation in the aqueous solution of TiO_2 passive film, beginning with 0.3 V that increases the stability of the Ti substrate.

The PPy and PPy/PEG films present a good electrochemical behaviour on – 0.5–0.5 V domain, all films remaining stable during the 10 CV scans as shown in Figure 3. The PPy films present a better capacitive character comparing with PPy/PEG composite films. The increase in polyethylene glycol concentration results in a reduction of capacitive character of the composite films while the stability of the film remains unchanged. Modification of titanium surface from a TiO_2 poor conductive coating to a conducting composite surface and the electrochemical stability on this potential range create premises of using this electrode in sensor applications.

Tafel Plots. In order to evaluate if the modifications of titanium electrode does changed corrosion stability, Tafel plots were recorded in buffer solution both for uncoated and coated titanium electrodes, as shown in Figure 4. The untreated Ti sample presents the specific behaviour of a valve metal, having the highest values for the polarization resistance, due to TiO_2 passive oxide film which act as a barrier inhibiting the redox process [9].

From the Tafel plots an increase of the corrosion potential in anodic direction with about 200 mV for Ti/PPy surface. This potential shift is associated with an increase of corrosion current increase with approximately two orders of magnitude

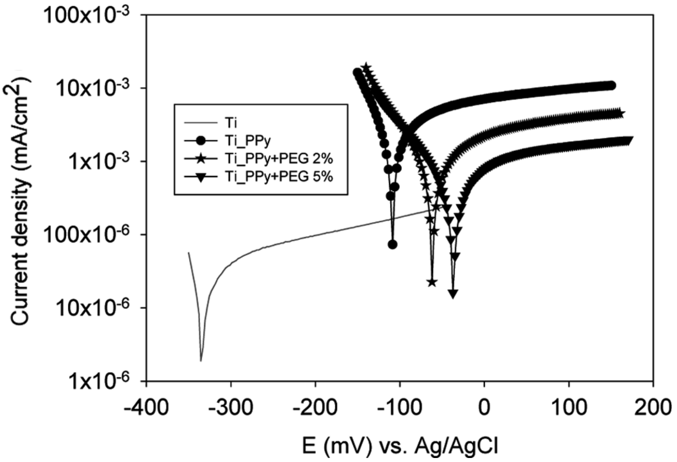


Figure 4. Tafel plots for uncoated titanium, Ti covered with PPy film and PPy + PEG films.

for Ti/PPy surface comparing with titanium natural passivated surface due to replacing of low conducting TiO_2 layer with PPy conducting polymer. The corrosion rate is also increasing as can be seen in Table 1, but the polymer film also contributes to the exchange current density and thus this means only an apparent contribution to the corrosion rate, and not a real reduction of stability. Such trend and shift in current densities and corrosion rate are in perfect concordance with literature data [24] which explain such exchange current for the complex process due to several electroactive species and surfaces with structural and morphological exchanges.

In the case of PEG incorporation the increase of corrosion potential in anodic direction is about 300 mV, and the Ti/PPy + PEG composite presents better stability with the increase of PEG concentration. For 2% PEG the corrosion rate decrease is not a significant one, but increasing PEG concentration from 2% to 5%, induces a two times decrease of corrosion rate from 46 µm/year to 24.7 µm/year as can be seen in Table 1.

Electrochemical Impedance Spectroscopy. The EIS measurements were made at free potential in buffer solution, the frequency domain being 0.01 Hz–100 kHz and the amplitude ±10 mV. EIS analysis was discussed in term of Nyquist representations and parameters resulted after the fitting of EIS spectra. Nyquist spectra for Ti electrode covered with pyrrole film and those covered with composite films are presented in the Figure 5.

Table 1. Electrochemical parameters for the composite films from Tafel plots

Sample	E_{cor}, V	I_{cor}, A	R_p, Ω	v_{cor}, mm/year
Ti	−0.335	$4.08 \cdot 10^{-8}$	$4.94 \cdot 10^{5}$	$1.18 \cdot 10^{-3}$
Ti_PPy	−0.130	$1.71 \cdot 10^{-6}$	$6.12 \cdot 10^{3}$	$4.95 \cdot 10^{-2}$
Ti_PPy + PEG 2%	−0.062	$1.58 \cdot 10^{-6}$	$7.43 \cdot 10^{3}$	$4.6 \cdot 10^{-2}$
Ti_PPy + PEG 3%	−0.065	$1.28 \cdot 10^{-6}$	$7.19 \cdot 10^{3}$	$3.72 \cdot 10^{-2}$
Ti_PPy + PEG 4%	0.032	$8.76 \cdot 10^{-7}$	$1.55 \cdot 10^{4}$	$2.54 \cdot 10^{-2}$
Ti_PPy + PEG 5%	−0.037	$8.51 \cdot 10^{-7}$	$3.59 \cdot 10^{4}$	$2.47 \cdot 10^{-2}$

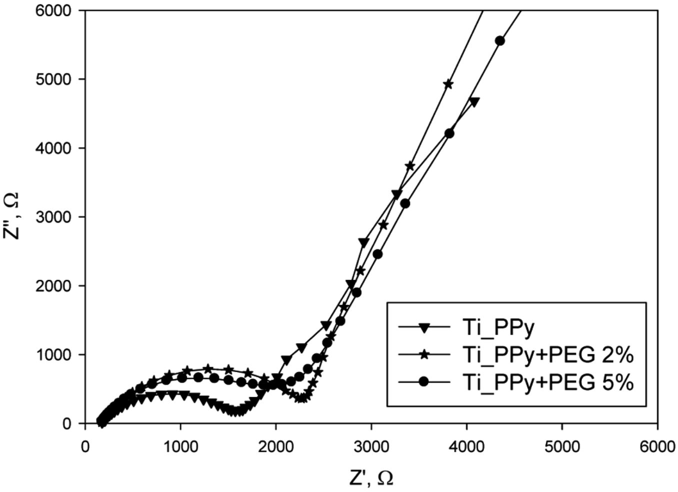


Figure 5. Nyquist plots of the PPy and PPy + PEG films.

For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (CPE) was used.

Electrical parameters of equivalent circuits obtained by fitting the experimental results of EIS test are presented in the Table 2.

From the recorded EIS data for polymeric and composite films, it was proposed the corresponding equivalent electric circuits as shown in Figure 6.

In the case of uncoated Ti, the circuit contains only the buffer solution resistance (R_1), a charge transfer resistance (R_2) in parallel bonded with a double layer CPE (Q_1). In case PPy film and PPy-PEG films, the equivalent electric circuit contains a supplementary constant phase element (Q_2) corresponding to the composite coating, indicating the capacitive behaviour of this film.

The charge transfer resistance values from EIS data are in concordance with polarization resistance values obtained from Tafel plots. The value of this parameter is influenced by the presence of PEG in different concentrations.

However, changes in charge transfer resistance were observed for Ti/PPy comparing with Ti/PPy + PEG coating for higher difference of PEG concentrations.

Surface Analysis – Atomic Force Microscopy

The polymeric and composite films were investigated with the contact mode AFM that provided interesting information about the PPy-PEG films topography.

Table 2. Experimental results from EIS analyse

Sample	R_1, Ω	Q_1, F/cm^2	N_1	R_2, Ω	Q_2, F/cm^2	N_2
Ti	141.9	$1.5 \cdot 10^{-5}$	0.70	$1.3 \cdot 10^{6}$	–	–
Ti_PPy	167	$2.5 \cdot 10^{-5}$	0.65	1510	0.17	0.73
Ti_PPy + PEG 1%	160.5	$1.8 \cdot 10^{-5}$	0.67	1192	$1.08 \cdot 10^{-3}$	0.77
Ti_PPy + PEG 2%	173.2	$1.2 \cdot 10^{-5}$	0.75	2169	$8.65 \cdot 10^{-4}$	0.83
Ti_PPy + PEG 5%	172.4	$1.1 \cdot 10^{-5}$	0.74	1892	$3.01 \cdot 10^{-4}$	0.76

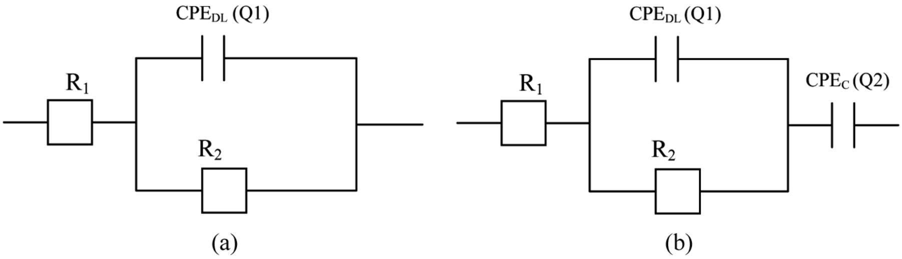


Figure 6. Proposed equivalent circuit for (a) uncoated titanium; (b) Ti covered with PPy film and PPy + PEG films.

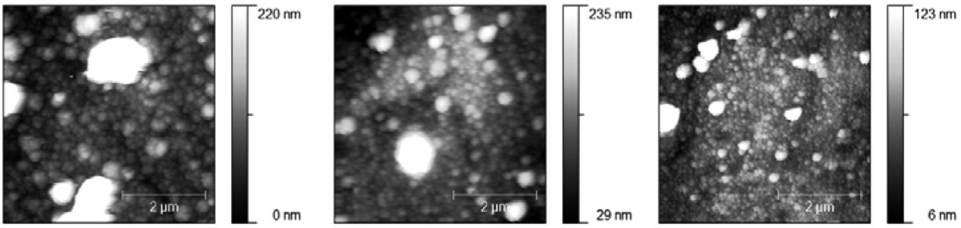
Figure 7 shows two-dimensional images for polypyrrole and polypyrrole/polyethylene glycol composite films deposited on titanium surface. Figure 7a correspond to a polypyrrole film without PEG which shows that the film surface has a granular structure. When the PPy film is produced in presence of PEG, the dimension of grains is reduced, resulting in a denser composite layer.

In the case of the film with higher concentration of PEG (5%), an agglomeration of the grains and a formation of big clusters it were observed (Fig. 7). Probably, this is the reason for which a non adherent composite film was obtained for higher concentration of PEG than 5%. In the Figure 8 is presented a three-dimensional AFM image of $5 \times 5\,\mu m^2$ scans for PPy + 6% PEG films showing an agglomeration of PEG macromolecules which entail a non adherent composite coating.

In the Table 3 the roughness as root mean square parameter R_q, and the roughness average (R_a) are presented as function of PEG concentration. A reduction of average roughness from 57 nm to 16 nm can be observed on 0–4% PEG concentration range and then an increase of roughness appear for higher concentration of PEG. Taking into account that roughness value from Table 3 associated with Table 2 data we can propose as a stable coating without agglomeration, the PPy films + PEG 4%, this one having a more electropositive corrosion potential as well. In such way surface analysis sustained electrochemical stability data.

Contact Angle Measurement

The wettablility of the composite films was appreciated by measuring the contact angle of a drop of water deposited on the film surface. The values of contact angle



(a) 0 % PEG (b) 1 % PEG (c) 4 % PEG

Figure 7. Two-dimensional AFM images (contact mode) of $5 \times 5\,\mu m^2$ scans for PPy films in the presence of different concentration of PEG: (a) without PEG (only PPy films); (b) 1% PEG; (c) 4% PEG.

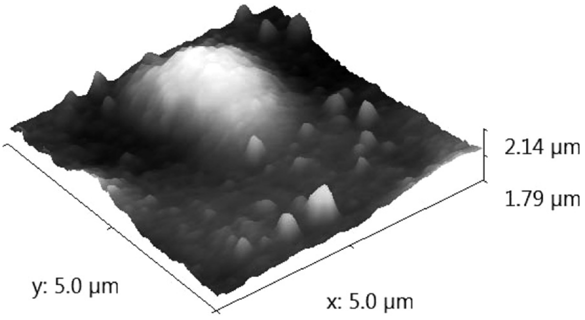


Figure 8. Three-dimensional AFM image (contact mode) of $5 \times 5\,\mu m^2$ scans for PPy + 6% PEG films.

Table 3. Statistical parameters from AFM images

		PPy films + PEG					
Roughness	Ti_PPy	0.5%	1%	2%	3%	4%	5%
Ra, (nm)	57.8	38.5	31.4	30.8	29.2	16.3	49.5
Rq, (nm)	94.4	54.8	43.3	41.6	39.7	26.6	67.0

decreased from 61 degree in the case of the surface of uncoated Ti, to 32 degree for film deposited on Ti that contain only polypyrrole and continued to decrease with the increase in PEG concentration, to a quasi total spreading of the drop of water in the last case, with 5% PEG (Fig. 9). This behaviour suggests that PEG concentration plays an important role in determining the surface energy.

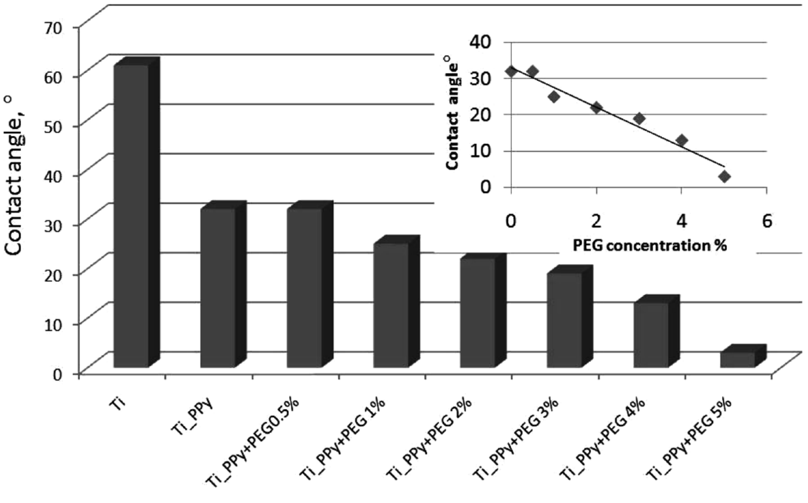


Figure 9. Contact angle measurement for uncoated titanium, titanium with PPy films and PPy and different concentration of PEG added. Inset – linear evolution of contact angle with PEG concentration on the range 0–5%.

A quasi linear decreasing of contact angle with concentration in following equation:

$$y = 5.46x + 32.95, \quad R = 0.9589 \ (y - \text{contact angle; } x - \text{PEG concentration})$$

was observed when the PEG concentration increase on the range 0–5%.

This fact is a very interesting aspect for the biocompatibility applications, taking into account that wettability is an important contribution on surface biocompatibility.

Conclusions

1. The present paper shows that polypyrrole-polyethylene glycol conducting polymer composite films with good electrical conductivity can be synthesized from an aqueous pyrrole solution containing polyethylene glycol on titanium electrode.
2. The PPy-PEG film presents peaks that are characteristic both to PPy and to PEG, indicating that PEG was successfully incorporated into the PPy film, forming a PPy-PEG composite film.
3. The presence of polyethylene glycol in the polymerization solution acts both in reduction of polypyrrole grains and roughness of the surface on the concentration range 0–4% PEG.
4. For a 4% PEG incorporation was obtained the best stability of film PPy-PEG. Surface analysis sustained electrochemical data from Tafel plots and EIS technique.
5. The wettability of the composite films PPy-PEG is drastically changed while increasing of the amount of PEG added. This parameter is in direct connection with surfaces roughness and especially with surface chemistry. A quasi linear decreasing of contact angle with concentration was observed.
6. The switching between different wettability characters is a premise for PPy-PEG films application in tissue engineering.
7. Modification of titanium surface from a TiO_2 poor conductive coating to a conducting composite surface and the electrochemical stability on this potential range create premises of using this electrode in sensor applications.

Acknowledgments

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