

# Preliminary testing of corrosion characteristics of NiTi alloy coated with various polymers

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In this work are presented preliminary tests of corrosion characteristics of NiTi alloy coated with three different polymers coatings deposited by pulsed laser deposition. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) have been employed to study the corrosion performance of the NiTi coated samples in AFNOR artificial saliva. All the polymers coating showed a very corrosion resistance for a short-term immersion. The EIS results exhibited high impedance values (order of  $10^6 \Omega \text{ cm}^2$ ) obtained from medium to low frequencies which are indicative of the presence of a highly stable film on all coated NiTi alloys in the artificial saliva. The EIS spectra are fitted using an equivalent circuit. For NiTi coated samples maintained short time in artificial saliva, a two-layer model of an unsealed porous film is suitable.

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## 1. Introduction

Titanium and its alloys are one of the most widely studied and used metallic biomaterials [1-5]. Biomaterials consisting of NiTi [6] have found their place in orthopaedic surgery [7-11] cardiovascular surgery [12] and orthodontics [13]. Nitinol (NiTi) material with a composition of approximately 50 at.% Ni and can be described as a shape memory alloy [14, 15], superelastic and biocompatible material. Corrosion resistance of NiTi alloys is an important property for the long-term stability and biocompatibility of implants and medical devices. Some studies have shown that NiTi alloy exhibits excellent resistance against corrosion in physiological media, other has shown that it exhibits poor resistance [16-18]. It has been found that NiTi exhibits poor resistance to localized corrosion in chloride-containing environments, which arguably low pitting potential values. Surface modification used to improve the corrosion resistance of NiTi seems attractive. Coating of NiTi with TiN is known to improve corrosion behaviour of NiTi alloy [19].

The electrochemical tests (potentiodynamic polarization, EIS) are commonly used to study the in vitro corrosion of biomaterials [20].

In the present work the corrosion behaviour of Chitosan, Poly (methyl methacrylate) and Poly (L lactide) coated NiTi alloy, by pulsed laser deposition (PLD) process [21], in artificial saliva was studied. The

EIS test was used to detect the pores and pinholes in the polymers coated and assess their effect on the corrosion resistance behaviour over short immersion time.

## 2. Materials and methods

### 2.1. Materials

An equiatomic NiTi alloy (Nitinol) produced by the Saes Getters Group, USA was used in these tests as reference material [21].

The layers on NiTi alloy by PLD process were obtained from bulks samples of Chitosan, Poly (L lactide), “PLLA”, and Poly (methyl methacrylate), “PMMA” produced by Lactel Biodegradable Polymers, Birmingham U.S.A. The experimental set-up used to obtain thin layers of polymers by pulsed laser deposition process is described in [22].

In Figure 1 SEM micrography of a covered Nitinol wire with a thin layer of PMMA are presented. In Figure 1a) a general view of the obtained layer is represented at 200 $\mu\text{m}$  scale and in Figure 1b) a detail of polymer microstructure is evidenced at a 10000 times power amplification image. From images presented in Figure 1 can be observe some properties of polymer layer obtained by PLD method like smoothness, homogeneity and compacted aspect.

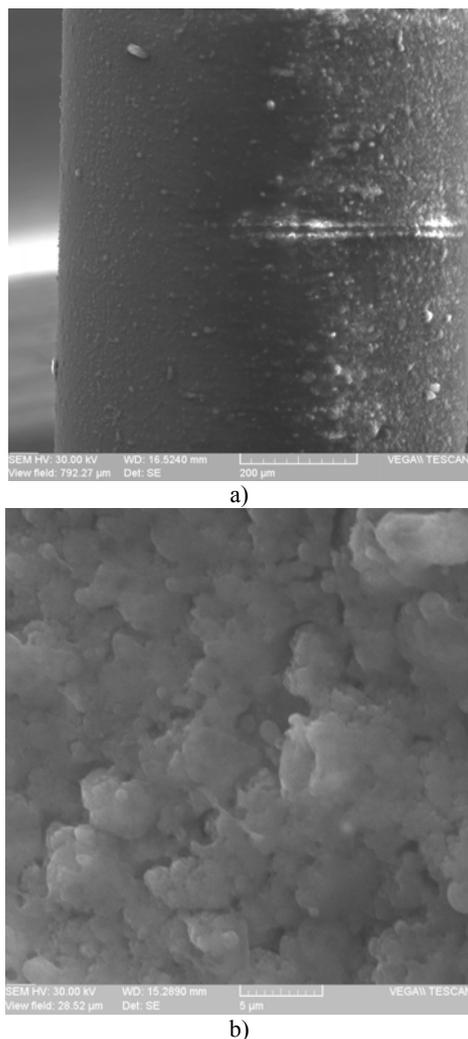


Fig. 1. SEM figures of a Nitinol wire covered with PMMA superficial layer a) 500 x and b) 10000 x power amplification.

The corrosion medium was an aerated artificial saliva AFNOR/NF (French Association of Normalization) having the composition: NaCl – 0.7 g/L, KCl – 1.2 g/L, Na<sub>2</sub>HPO<sub>4</sub>H<sub>2</sub>O – 0.26 g/L, NaHCO<sub>3</sub> – 1.5 g/L, KSCN – 0.33 g/L, urea – 1.35 g/L.

The pH was measured with a multiparameters analyzer CONSORT 831C. The pH of this saliva was 8.2.

## 2.2. Electrochemical measurements

The investigation of the corrosion characteristics of the polymers - coatings deposited on NiTi substrates was studied by electrochemical impedance spectroscopy (EIS). Electrochemical measurements were carried out in aerated artificial saliva at 25°C using a Princeton Applied Research potentiostat (Model 263 A) connected with a Princeton Applied Research 5210 lock-in amplifier controlled by a personal computer and a specific software package called Electrochemistry Power Suite (Princeton Applied Research). A glass corrosion cell kit with a platinum counter-electrode and a saturated calomel

reference electrode (SCE) were used to perform the electrochemical measurements. The specimen area exposed to electrolyte solution was 0.307 cm<sup>2</sup> of the Chithosan covered sample, 0.329 cm<sup>2</sup> for PLLA covered sample and 0.329 cm<sup>2</sup> for PMMA covered sample. The EIS measurement was performed at the open circuit potential after one hour immersion in the electrolyte solution. All potentials referred to in this article are with respect to SCE. The EIS spectra were recorded in the 10<sup>-2</sup> Hz to 10<sup>4</sup> Hz frequency range. The applied alternating potential signal had amplitude of 10 mV.

In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used. The quality of fitting to the EC was judged first by the  $\chi^2$  value that was  $< 5 \times 10^{-4}$ , and second by the error distribution versus frequency comparing experimental with simulated data.

## 3. Results and discussion

The oral environment is conducive to the formation of corrosion products. The human artificial saliva can vary to a considerable degree and is dependent on the age and sex of the patient, the time of day, eating habits, medication and oral hygiene [23]. Artificial saliva (AFNOR) was selected for this study.

EIS measurements offer useful information regarding the superficial layer of the coated sample. EIS measurements were performed at the open circuit potential in artificial saliva. Typical impedance spectra obtained of the various coated layer are shown in Figure 2. They are presented as Bode plots of the logarithm of impedance magnitude (Log Zmod) and of the phase angle as a function of the frequency's logarithm. The advantage of the Bode plot is that the data for all measured frequencies are shown and that a wide range of impedance values can be displayed.

Generally, three frequency regions referring to the high, medium and low frequency values are distinguished from impedance spectra. The high frequency plateau of the impedance values at frequency higher than 10<sup>3</sup> Hz, yields the value of the solution resistance ( $R_{sol}$ ). In the Bode plot, impedance at medium frequency represents the response of the coating, while at the low frequency limit; the information about process is related to the reaction on the substrate/electrolyte interface [24].

The high impedance values (10<sup>6</sup>  $\Omega$  cm<sup>2</sup> orders) obtained from medium to low frequencies for all the coated samples suggest a high corrosion resistance in AFNOR artificial saliva. The phase angle maximum observed for all NiTi coated samples was found to lie in the range of approximately  $-75^\circ$  to  $-85^\circ$ . The values of the phase angle maximum span three frequency decades (0.1-100 Hz), indicating a capacitive response for all the samples and suggests the presence of a coating layer on the surface acting as a barrier. The low-frequency domain evidences the processes taking place at the substrate/electrolyte interface. Such behaviour is typical

for a metallic material covered with a porous film, which is exposed to an electrolytic environment.

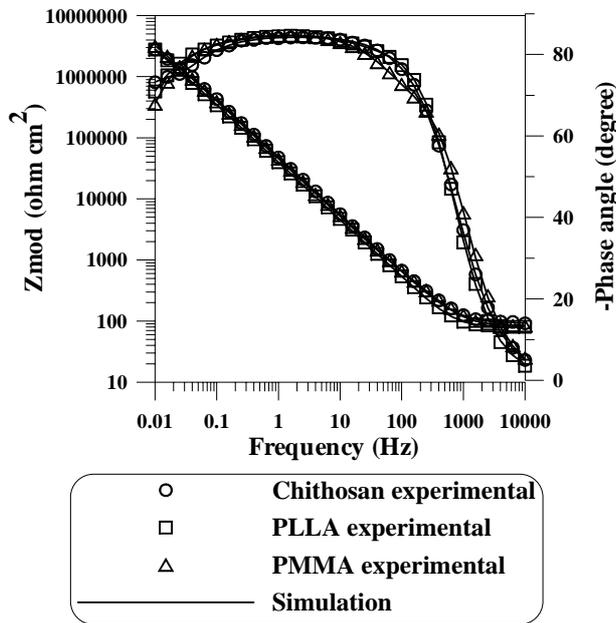


Fig. 2. Bode plot of the coated/NiTi samples in artificial saliva measured at open circuit potential.

In this case, the electrochemical interface can be subdivided into sub-interfaces: electrolyte/coated layer and electrolyte/substrate. This type of EIS spectra is best modelled by an equivalent circuit (EC) proposed by Liu et al [25] for the two sub-electrochemical interfaces, as shown in Figure 3.

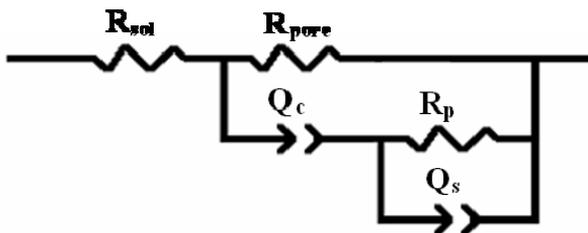


Fig. 3. Equivalent circuit for two-layer model: a compact inner layer and a porous outer layer, with unsealed pores

The impedance spectra were fitted using the ZSimpWin software. The results of the analysis are shown in Table 1. The fitting quality of EIS data was estimated by both the chi-square ( $\chi^2$ ) test (between  $10^{-4}$  and  $10^{-5}$ ) values and the comparison between error distribution versus frequency values ( $\pm 2\%$  for the whole frequency range) corresponding to experimental and simulated data. The  $R_{pore}$  and  $Q_c$  ( $c$  means coating) parameters describe the processes occurring at electrolyte/coating layer. The parameter  $R_p$  coupled with  $Q_s$  ( $s$  means substrate) describes the processes at the substrate layer at the

electrolyte/substrate layer interface.  $R_{pore}$  is the charge transfer resistance associated with the penetration of the electrolyte through the pores or pinholes existing in the coating, and  $R_p$  is the polarization resistance at the electrolyte/substrate interface in the pores or pinholes.  $Q_c$  corresponds to capacitance of the coating layer and  $Q_s$  to the capacitance at the electrolyte/substrate layer interface, which seems to be associated to the double layer formation.  $R_{sol}$  is the ohmic resistance of the electrolyte. The same  $R_{sol}$  value, that is  $81 \pm 3 \Omega$ , was noticed in all the cases.

Table 1. Electrochemical parameters obtained from EIS spectra using the selected EC for the coated/NiTi samples in artificial saliva at open circuit potential

Polymers	Chithosan	PLLA	PMMA
$R_{pore}$ ( $\Omega \text{ cm}^2$ )	$6.1 \times 10^3$	$3.5 \times 10^3$	$2.5 \times 10^3$
$Q_c$ ( $\text{F s}^{n-1} \text{ cm}^2$ )	$3.6 \times 10^{-5}$	$3.8 \times 10^{-5}$	$3.9 \times 10^{-5}$
$n_c$	0.94	0.96	0.97
$R_p$ ( $\Omega \text{ cm}^2$ )	$2.9 \times 10^6$	$2.7 \times 10^6$	$3.2 \times 10^6$
$Q_s$ ( $\text{F s}^{n-1} \text{ cm}^2$ )	$6.8 \times 10^{-6}$	$6.9 \times 10^{-6}$	$6.5 \times 10^{-6}$
$n_s$	0.89	0.86	0.89

The symbol  $Q$  signifies the possibility of a non-ideal capacitance (CPE, constant phase element). The CPE relies on the fact that, experimentally, the protective film never exhibits the theoretically expected phase shift of  $-90^\circ$  and a slope of  $-1$  for an ideal dielectric. The following equation [26] calculates the CPE impedance:

$$Q = Z_{CPE} = \frac{1}{C(j\omega)^n} \quad (1)$$

where, when  $n = 1$ , the  $Q$  element reduces to a capacitor with a capacitance  $C$ , and when  $n = 0$  it is reduced to a simple resistor. This  $n$  is related to a slope of the  $\log(Z_{mod})$  versus  $\log(\text{Frequency})$  Bode-plots,  $\omega$  is the angular frequency and  $j$  is an imaginary number ( $j^2 = -1$ ).

Future experiments will be made concerning the electrochemical behavior of the polymers coating for NiTi alloy of long-term immersion in Ringer solution.

#### 4. Conclusions

The electrochemical process of the polymers coatings for NiTi alloy in artificial saliva has been investigated. Over the frequency range applied the equivalent circuit employed for the description of the coated samples provides the best fitting of the experimental data. Two-layer models satisfactorily describe the electrochemical behaviour of the systems by considering a porous on the metallic NiTi substrate. The coating offered high corrosion

protection ( $R_p$  are more than  $10^6 \Omega \text{ cm}^2$ ) for a short-term immersion.

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