The Electrochemical Behaviour of NiTi Orthodontic Wires with Polytetrafluoroethylene Coating in Red Ruffled Pimiento Peppers Paste

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The corrosion behaviour of two NiTi orthodontic wires (uncoated and polytetrafluoroethylene-coated) in Red Ruffled Pimiento peppers paste was investigated using impedance and linear potentiodynamic techniques. Immersion tests were performed for 8 h. In addition, scanning electron microscopy (SEM) was employed to observe the surface morphology before and after polarization test in Red Ruffled Pimiento peppers paste. EIS studies showed high impedance values for both samples, increasing with exposure time. The polarization resistance (R_p) and the pseudo-capacitance (Q) were determined. Differences in the corrosion resistance of the uncoated orthodontic NiTi archwire as compared with polytetrafluoroethylene (PTFE)-coated orthodontic NiTi archwirwe were evaluated.

Keywords: Polytetrafluoroethylene Coating, NiTi Orthodontic Wires, Red Ruffled Pimiento Peppers Paste, Electrochemical Behaviour

Titanium (Ti) exhibits outstanding corrosion resistance in a wide variety of environments [1]. For this reason Ti is widely used as construction material in many fields of technology: surgery, aerospace, automotive, power generation, and oil and gas extraction. Corrosion resistance is an important property for biomaterials [1]. Many studies have been published recently on the corrosion of Ti and its alloys [2-6].

NiTi alloys have become important materials in biomedical applications as they possess properties, such as shape memory effect, superelasticity, and good biocompatibility [7-12]. Currently, NiTi alloys are used in orthopaedic, cardiovascular, urological surgery and orthodontics [13-16]. Actually, there are some controversy in relation with the reported resistance of NiTi, against corrosion, in physiological media, as some studies are reporting an excellent resistance, while others are claiming the opposite [17-19]. The low wear resistance of this material may cause some problems in the service condition. Nevertheless a major concern on dissolution properties on NiTi alloys still remains due to the high Ni content [20, 21]. Hence, it is necessary to enhance the surface properties of Ti material. Surface modification is a promising way to increase the surface hardness and wear resistance of titanium. This work presents the electrochemical study of uncoated NiTi alloy and PTFE-coated NiTi alloy in contact with *Red Ruffled Pimiento* peppers paste.

In order to obtain and characterizes the biocompatible coated polymer alloy, several on line (EIS- electrochemical impedance spectroscopy, and LPP-linear potentiodynamic polarization) and off line (SEM- scanning electrons microscopy) diagnosis tools have been used.

Experimental part

Materials and methods

Both uncoated and PTFE-coated equiatomic NiTi orthodontic wires were provided by Titanol® Cosmetic (Foresta*Dent*®, Germany).

Red Ruffled Pimiento peppers were harvested in the experimental greenhouses of Agronomical and Veterinary Medicine University from Iasi. An electric blender was used in order to obtain the peppers paste.

Electrochemical tests

Both uncoated and PTFE-coated NiTi orthodontic wires were placed in a glass corrosion flow cell kit (C145/170, Radiometer, France), which was filled with *Red Ruffled Pimiento* peppers paste (pH = 6.9 ± 0.1). A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum coil as the counter electrode. In this paper, the potentials are reported versus the SCE. The temperature of the electrochemical cell was maintained at 37 ± 1°C. Electrochemical measurements were performed using a potentiostat model PARSTAT 4000 (Princeton Applied Research, NJ, USA). The instrument was controlled via a personal computer and *VersaStudio*

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software. Electrochemical impedance spectra (EIS) were measured over a frequency range extending from 10^5 Hz to 10^{-2} Hz using a 10 mV amplitude AC voltage signal. The EIS tests were recorded at the open circuit potential developed by the samples after 1-h, and 8-h of immersion in test solution. Analysis of the spectra was performed in terms of equivalent circuit (EC) fitting using *ZSimpWin* version 3.22 software.

Linear potentiodynamic polarization (LPP) test were also carried out in *Red Ruffled Pimiento* peppers paste, after 8-himmersion time, at 37 ± 1°C. These measurements were conducted by stepping the potential using a scanning rate of 0.5 mV/s from - 0.6 V to + 1 V.

Surfaces SEM analysis

The surface morphology of both uncoated and PTFE-coated NiTi orthodontic wires before and after LPP test were assessed using scanning electron microscopy (Quanta 3D, FEI, Hillsboro, OR, USA).

Results and discussions

Electrochemical impedance spectroscopy (EIS) measurements offer useful information regarding the layer of both coated and uncoated NiTi samples (22-26). The Bode plot (magnitude and phase of impedance %Z% versus log of frequency) is usually used to represent the result. The EIS data of the uncoated and PTFE-coated NiTi orthodontic wires measured at two different immersion times in the *Red Ruffled Pimiento* peppers are presented in figures 1-2 in the form of Bode plots.

From the Bode plot, the phase angle is approximately zero at high frequency, indicating that the impedance is determined by solution resistance. The phase angle are between -70 to -80°. Therefore, slope between |Z| and log

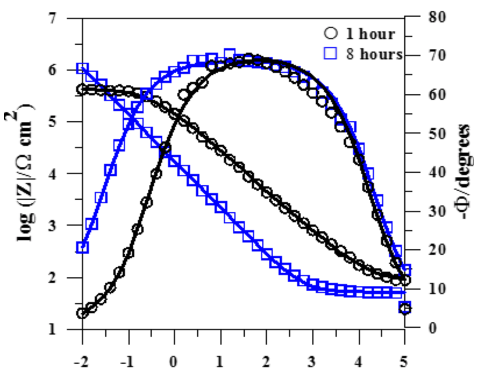

Fig. 1.Bode plots for EIS data of an: (A) uncoated NiTi orthodontic wires maintained different time periods in Red Ruffled Pimiento peppers paste at open circuit potential

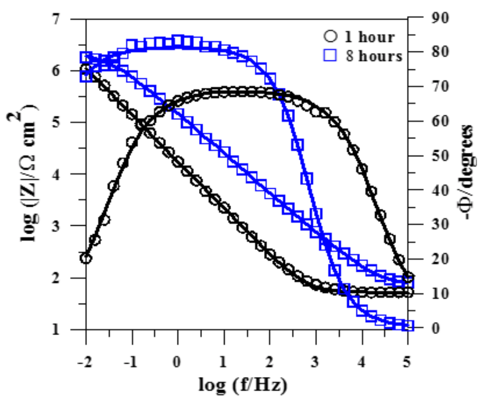

Fig. 2.Bode plots for EIS data of an: (A) PTFE-coated NiTi orthodontic wires maintained different time periods in Red Ruffled Pimiento peppers paste at open circuit potential

of frequency is less than -1 over a medium range of frequency, independent of time immersion, indicating that the passive film was not fully capacitive.

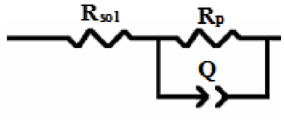

Fig. 3. Equivalent circuit (EC) used for fitting the measured impedance spectra

The electrochemical response of the uncoated sample was the best simulated by employing the equivalent circuit, $R_{sol}(R_pQ)$,with one time constant, as shown in figure 3.

The impedance spectra were fitted using the ZSimpWin software and the resultant EIS parameters are given in table 1.

In this EC, R_{sol} is the ohmic resistance of the electrolyte (around 5.7 ± 0.2 Ω cm²), R_p represents the polarization resistance and Q is the impedance related to a constant phase element (CPE). The constant phase element (CPE, Q) is introduced to replace the capacitor and to account for the less than ideal behaviour of the capacitance elements due to different physical phenomena. The (CPE, Q) is necessary due to the distribution of relaxation times resulting from heterogeneities at the electrode surface (e.g. distribution of the oxide layer thickness, distribution of the defects density in the oxide layer, surface roughness, impurities, dislocations and grain boundaries among others).

The more will increase the value of polarization resistance, the more the sample will resist corrosion.

Figure 4 and table 2 show the results of the electrochemical polarization measurements on untreated and PTFE-coated NiTi orthodontic wires in *Red Ruffled Pimiento* peppers paste at 37°C. The zero current potential (ZCP) and corrosion current density (j_{corr}) values were determined by Tafel analysis of both anodic and cathodic branches of the polarization plots. None of the materials exhibited a distinctive active–passive transition in the polarization curves following the Tafel region, but they entered directly into a stable passive regime. Probably, this fact indicates that uncoated and PTFE-coated NiTi archwire are passive from the beginning of the variation of potential in the positive direction. More negative values were determined for the ZCP with the untreated samples after 8 h immersion in *Red Ruffled Pimiento* peppers paste. A shift of ZCP to positive (noble) values was observed for coating sample. Although, more value of density corrosion currents were obtained for uncoated or coated samples in *Red Ruffled Pimiento* peppers paste. The polarization results were in agreement with EIS data.

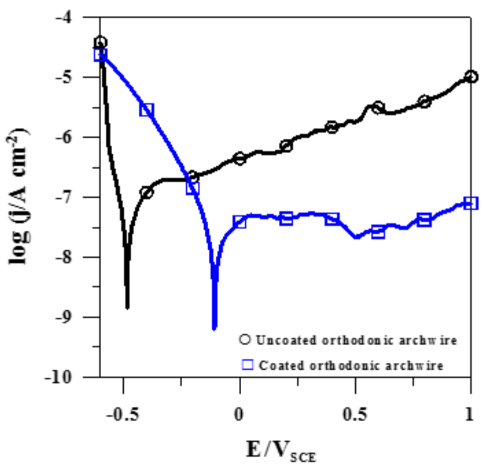

Fig. 4. Linear potentiodynamic polarization curves of the uncoated and coated orthodontic archwiere in aerated Red Ruffled Pimiento Peppers Paste at 37°C. Scan rate: v = 0.5 mV s^{-1}.

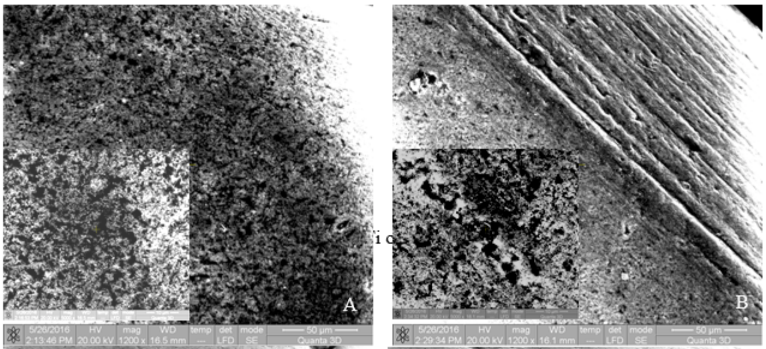

Fig. 5. SEM micrographs of PTFE-coated NiTi orthodontic wires: (A) before LPP tests, and (B) after LPP tests

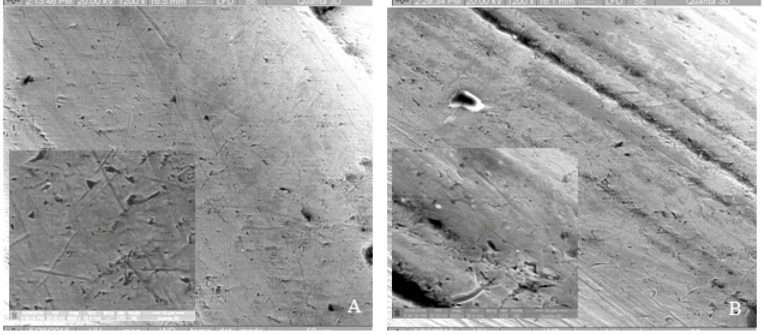

Fig. - 6. SEM micrographs of uncoated NiTi orthodontic wires: (A) before LPP tests, and (B) after LPP tests

Table 1

ELECTROCHEMICAL PARAMETERS OBTAINED FROM EIS SPECTRA USING THE SELECTED EC FOR THE PTFE COATED AND UNCOATED NiTi ORTHODONTIC WIRES AFTER DIFFERENT IMMERSION TIME IN RED RUFFLED PIMIENTO PEPPERS PASTE AT OPEN CIRCUIT POTENTIAL (37 °C)

Samples	Immersion time	$10^5 Q$ (S cm^{-2} s^n)	n	$10^{-6} R_p$ (Ω cm^2)
Uncoated NiTi orthodontic wires	1-hour	1.1	0.82	0.5
	8-hours	0.94	0.84	1.2
PTFE coated NiTi orthodontic wires	1-hour	0.93	0.84	1.4
	8-hours	0.89	0.85	2.2

Table 2

THE MEAN VALUES OF PARAMETERS MEASURED AND CALCULATED FOR THE PTFE COATED AND UNCOATED NiTi ORTHODONTIC WIRES IN RED RUFFLED PIMIENTO PEPPERS PASTE (37 °C)

Sample	ZCP (V)	$10^7 j_{corr}$ (A/cm^2)
Uncoated NiTi orthodontic wires	-0.49	1.2
PTFE coated NiTi orthodontic wires	-0.11	0.4

Representative SEM micrographs of uncoated and PTFE-coated NiTi orthodontic wires before and after polarization in *Red Ruffled Pimiento* peppers paste determinated at +1 V are shown in figure 5-6(A-B).

No deterioration of both samples was observed for positive polarization up to 1V in *Red Ruffled Pimiento* peppers paste at 37°C. This indicates that the anodic polarization tests had no major effect on the characteristics of the layer of the uncoated and PTFE coated NiTi orthodontic wires.

Conclusions

The electrochemical behavior of uncoated and PTFE coated NiTi orthodontic wires immersed in Red *Ruffled Pimiento* peppers paste at 37 °C has been investigated.

The linear potentiodynamic polarization curves demonstrated an improvement in corrosion resistance of PTFE coated NiTi alloy. Electrochemical impedance spectroscopy is a useful technique for studying the corrosion behavior on biomaterials, even they are coated with a polymeric material. The coating offered good protection for NiTi substrate at the immersion (8-hours) in *Red Ruffled Pimiento* peppers paste.

The zero corrosion potential (ZCP) of an PTFE coated NiTi orthodontic wires is nobler than of NiTi orthodontic wires one, and the corrosion current density (j_{corr}) of uncoated sample is more than three times larger than that of coated one.

The results of EIS showed that the resistance of PTFE coated NiTi orthodontic wires increases slowly then the uncoated NiTi orthodontic wires, after 8 h immersion in *Red Ruffled Pimiento* peppers paste, fact highlighting that PTFE coating provide a more effective barrier against metallic substrate dissolution.

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