Degradation Characteristics of Poly-tetrafluoroethylene Coatings on Stainless Steel Orthodontic Wires Immersed in Tuna Fish Derived Products

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This paper objective was to evaluate the degradation characteristics of polytetrafluoroethylene (PTFE) coatings on stainless steel orthodontic wires with memory shape while immersed in tuna fish derived products. EIS was the major investigative technique, since it has the potential to discover new information on the processes occurring, while not interfering significantly with the mechanism operating. The spectra of uncoated and coated orthodontics stainless steel wires were recorded, and the data were analyzed in order to evaluate the equivalent circuit (EC) parameters and subsequently the degradation characteristics of each material. The corresponding corrosion morphologies after polarization test was also observed using scanning electron microscopy (SEM). Comparison of the electrochemical behaviour, in the condition of exposure to aggressive media, for stainless steel orthodontic wires with memory shape, coated with a PTE porous layer versus the uncoated alloy sample was done. The coatings stainless steel orthodontic wires samples exhibited more positive zero current potential, higher breakdown potential, and lower anodic current densities than the uncoated ones. Impedance spectra were interpreted in terms of a duplex film, with corrosion resistance arising mainly due to the thin inner layer as the outer layer being more porous was less sealed. Pseudo-capacitive behaviour and high corrosion resistance were registered for the coated stainless steel alloy, in the medium to low frequency ranges. This paper results are valuable for estimation of coated and uncoated stainless steel orthodontic wires corrosion resistance and for anticipation of their effect upon biochemical events in oral cavity.

Keywords: stainless steel dental alloy, memory shape, polytetrafluoroethylene coatings, tuna fish products, EIS, SEM

Metal alloys are the main materials of orthodontics wires and arch [1]. Formerly, the alloys used in orthodontics were gold-based alloys. Their high costs and low mechanical properties determined their replacement with more economical materials like NiTi alloys and stainless steel. In the actual socio-economical conditions, the dental physician should select with discernment from the rich offer of alternative orthodontic materials existing currently on the market.

Currently, orthodontic materials with the inner ability of transforming between the two phases (austenite/martensite) begin to be of interest for clinical testing, the more so as, the use of metal alloys with shape memory property may reduce the time of treatment in daily practice.

Stainless steels are substantially used in many countries as main materials of orthodontic wires and arches. Among them, AISI 316L stainless steels presented, in vitro, the same corrosion behaviour after immersion in electrochemical media that simulates the inner human body physiological state versus pathological one [2]. However, the performance of an orthodontic wire is conditioned by its corrosion behavior in the oral environment, an aggressive and complex electrolytic medium [3]. Ion leaching and corrosion processes trigger the releasing of the material’s different component particles, depending on solubility, pH, wear induced by biomechanical forces, electrochemical processes at the interface and outer factors. The investigations focusing on the corrosion in different in vitro models may contribute to the selection of an alloy with enhanced properties [4-15], or a special coated layer as coating is one of the most widely used method for reducing biomaterials corrosion. The electrochemical techniques for evaluation of corrosion resistance are rapid, reproducible, reliable, and also provide information about corrosion mechanism involved [22-24].

The increased consumption of refined products derived from fruits, vegetables, milk, meat and fish [16-20], raised the prevalence of orthodontic wires corrosion in the mouth, especially in the last years. However, the paucity of reported studies on the corrosion behaviors of orthodontic wires in refined products, explains the limited information regarding the corrosion behavior of stainless steel orthodontic wires in fish derived products [21].

This work presents the electrochemical study of polytetrafluoroethylene (PTFE) coatings on stainless steels orthodontic wires in contact with derived fish products. The electrochemical behaviour of each stainless steel orthodontic wire was evaluated by potentiodynamic

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polarization and electrochemical impedance spectroscopy (EIS) after different immersion time in derived fish products.

EIS was the major investigative technique, since it has the potential to discover new information on the processes occurring, while not interfering significantly with the mechanism operating. The spectra of uncoated and coated orthodontics stainless steel wires were recorded, and the data were analyzed in order to evaluate the equivalent circuit (EC) parameters and subsequently the degradation characteristics of each material. The corresponding corrosion morphologies after polarization test was also observed using scanning electron microscopy (SEM).

The obtained data are valuable for estimation of coated and uncoated stainless steel orthodontic wires corrosion resistance and for anticipation of their effect upon biochemical events in oral cavity.

Experimental part
Materials and methods
Materials
Two different uncoated and coated with PTFE orthodontics stainless steel, both manufactured by Dentsply Gac International Inc. (Bohemia NY, USA), were considered in this investigation. The chemical compositions has been determined by EDX analysis using a scanning electron microscope (SEM) Quanta 3D Model AL99/D8229 (FEI, Hillsboro, OR, USA) operating with beam energy 30 kV. The chemical compositions of uncoated and coated with PTFE orthodontics stainless steel are presented in figures 1-2.

Differential scanning calorimetry (DSC)
The stainless steel orthodontic wires were examined with DSC technique in order to determine the accompanying transformations with temperature.

The sample was placed in an aluminum crucible, and sealed. An empty aluminum crucible served as a reference during the DSC measurements with DSC Model 1Mettler Toledo. Nitrogen gas (120 mL/min) was used in order to prevent condensation of water vapors and oxidation of stainless steel orthodontic wires. The temperature of the crucible was scanned from -40 to + 50 °C at 15 °C/min.

Electrochemical media
Electrochemical tests were performed in two different media: the first medium used was the fish paste obtained by mixing (with a blender) the content of a tuna filet in sunflower oil can, that consisted in sliced tuna filet in sunflower oil, having 185g net weight, 140 drained weight, and containing Skipjack tuna (Katsuwonus Pelamis), sunflower oil and salt as ingredients. The pH of the paste obtained from tuna filet in sunflower oil was 5.79.

The second medium, was the paste resulted by mixing (with a blender) the content of tuna filet in brine can, consisting in sliced Skipjack tuna steak (Katsuwonus Pelamis) in brine, having 195g net weight, 150 drained weight, and containing tuna steak, water and salt as ingredients. The pH of the paste obtained from tuna filet in brine was 5.83.

Both types of tuna filet cans (Nixe®, Ecuador) were obtained from supermarket.

Biochemical freshness and proximate composition parameters were determined in order to evaluate the main variations of both electrochemical mediums containing the tuna fish paste (in sunflower oil / in brine), during 8 h storage at room temperature.

The pH was determined on homogeneous solution of sample and distilled water (1:10, w:v), using a InoLab 730 pH metre. Also, moisture, protein, collagen, lipid and salts contents, as the main proximate composition parameters were determined by NIRS Near Infrared Spectrophotometer Food Check Bruins.

Electrochemical measurements
A three-electrode corrosion flow cell kit (C145/170, Radiometer, France) with platinum as counter electrode and saturated calomel reference electrode (SCE) as reference electrode was employed for both electrochemical measurements. The electrochemical cell contained a freely adjustable Luggin capillary that housed the reference electrode. The sample surface of the
uncoated and coated stainless steel orthodontic wires exposed to the electrolyte testing was 0.05 cm². All potentials in this paper are referred to the SCE. All electrochemical measurements were carried out on a Princeton Applied Research potentiostat Model PARSTAT 4000 (Princeton Applied Research, Princeton, NJ, USA). The instrument was controlled by a personal computer and specific software (Versa Studio, PAR, Princeton, NJ, USA).

Electrochemical impedance spectroscopy (EIS) measurements were also performed using the same instrumentation. The perturbation amplitude was 10 mV and the frequency ranged down from 100 kHz to 10 mHz. Five points were recorded for each frequency decade. The EIS spectra were obtained at different times: 1 hour, 2 h, and 8 h after electrode immersion in tuna filet paste in sunflower oil, and in brine. The EIS experimental data were analyzed in terms of equivalent circuits (EC) using ZSimpWin 3.22 software [25]. Measurement of potentiodynamic polarization curves (PPC) was initiated after 8 hours exposure to the test.

Scanning electron microscopy (SEM) of corroded surfaces

In order to observe the surface morphology the polarization tested samples have been analyzed by scanning electron microscopy (SEM) using a HITACHI-SU 1510 microscope.

Results and discussions

DSC analysis of the uncoated and coated stainless steel orthodontic wires

The DSC heating and cooling curves of the uncoated and coated stainless steel orthodontic wires are shown in figures 3 and 4, respectively. The endothermic peaks appear to be constant at 11-12 °C. Such type of endothermic peaks are attributed to the transformation of martensite to austenite due to presence of alloy intermetallic phases. The endothermic peak from the heating curve of the uncoated and coated stainless steel orthodontic wires is the austenite corresponding transformation temperature while the exothermic peak from the cooling curves is considered as the corresponding martensite transformation temperature.

Electrochemical analysis

When an alloy is placed in the oral cavity environment, it takes place an electrochemical interaction (i.e., corrosion process).

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pronounced for the uncoated material. All the spectra exhibit a capacitive loop (open arc). The diameter of the open arc provides an estimation of the polarization resistance. The decrease in diameter indicates a reduction of the corrosion resistance.

Bode plots of the two materials immersed for different periods of time in fish products are shown in figures 7-8.

The advantage of the Bode plot is that the data for all measured frequencies are shown and also a wide range of impedance values are displayed.

The frequency dependence of the phase angle indicates the number of time constants present in the system and can be used to determine the parameters values in the equivalent circuit. Two peaks were observed in the Bode-phase plots determined for the coated stainless steel orthodontic wires, whereas only one was observed for the uncoated stainless steel orthodontic wires. This indicates the involvement of two time constants in the open circuit potential for the coated stainless steel orthodontic wires immersed in both type fish products. The rather high impedance values (of the order of 10⁴ Ω cm²), registered in the medium to low frequencies domain, revealed the presence of the corrosion resistance of the coated stainless steel orthodontic wires in the fish products used as electrochemical medium.

The impedance modulus (|Z|) of stainless steel orthodontic wires slowly decreased with the time of sample immersion. All the spectra showed that in the higher frequency region, log |Z| tends to become constant. This is a typical response for the resistive behavior and corresponds to the solution resistance, Rₛₒḷ. In the medium frequency range, a linear relationship between log |Z| and log f was observed in all cases, though with different slopes (always less than -1), whereas the maxima in the phase

Fig. 6. Nyquist plots of the impedance spectra measured for: (a) coated and (b) uncoated stainless steel orthodontic wires as a function of immersion time in the paste of tuna filet in brine

Fig. 7. Bode plots of the impedance spectra measured for: (a) coated and (b) uncoated stainless steel orthodontic wires as a function of immersion time in the paste of tuna filet in sunflower oil

Fig. 8. Bode plots of the impedance spectra measured for: (a) coated and (b) uncoated stainless steel orthodontic wires as a function of immersion time in the paste of tuna filet in brine
angle plots are smaller than –90°, indicating that the stainless steel orthodontic wires were not completely capacitive.

For the interpretation of the electrochemical behavior of a system from EIS spectra, an appropriate physical model of the electrochemical reactions occurring on the electrodes is necessary. The electrochemical system may be represented by an equivalent circuit (EC). In the case of the uncoated stainless steel orthodontic wires, the spectra could be satisfactorily simulated using the simplified EC circuit shown in figure 9a. The occurrence of a second overlapping wave in the phase shift response of the stainless steel orthodontic wires indicated that the spectra cannot be explained by the simple equivalent circuit based on a single parallel combination of a resistance and a constant phase element, as shown in figure 9a. Therefore, fitting of the impedance was done with the EC depicted in figure 9b using a series combination of the solution resistance, $R_{\text{sol}}$ ($75 \pm 10 \ \Omega \ \text{cm}^2$), with two $RQ$ parallel combinations: $R_{\text{sol}} (R_1Q_1) (R_2Q_2)$. The proposed EC gives the electrical representation of two-layer surface films consisting of a barrier-type inner layer and a relatively porous coated outer layer [26 – 28].

Very good agreement between the simulated and experimental data was obtained. The values of the impedance parameters determined from the fits are presented in tables 1 and 2 for the uncoated and coated stainless steel orthodontic wires, respectively.

For the uncoated and coated stainless steel orthodontic wires, the parameters $R_1$ and $Q_1$ account for the reactions at the stainless steel orthodontic wires layer/solution interface and determine the impedance behavior in the high frequency range of the spectrum. The constant phase element $Q_1$ represents the double layer pseudo-capacitance of the stainless steel layer, as shown by the high value of the $n_1$ exponent [29].

Corrosion may occur in pores as the result of the directly metal exposed to the aggressive attack of the electrolyte. Pores in the coating layer may act as paths for the electrolyte attack to the substrate. Therefore for coated stainless steel orthodontic wires, the parameters $R_2$ and $Q_2$ describe the properties of the PTFE layer.

As immersion time increases from 1 hour to 8 h, the resistance ($R_2$) of the PTFE coated layer decreases slowly. However, the values of $R_2$ are about 10 times bigger than those of $R_1$ for all time exposures, which revealing that PTFE coated layer provides most of the corrosion protection to the stainless steel orthodontic wires. Therefore, the performance of the PTFE coated stainless steel orthodontic

<table>
<thead>
<tr>
<th>Samples</th>
<th>Immersion time</th>
<th>$10^9 Q_1$, S cm$^{-2}$ g$^{-a}$</th>
<th>$10^9 R_1$, $\Omega$ cm$^2$</th>
<th>$10^9 Q_2$, S cm$^{-2}$ g$^{-a}$</th>
<th>$10^9 R_2$, $\Omega$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated stainless steel orthodontic wires</td>
<td>1 hour</td>
<td>2.1</td>
<td>0.82</td>
<td>2.8</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>2 hours</td>
<td>2.2</td>
<td>0.81</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>8 hours</td>
<td>2.2</td>
<td>0.80</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Uncoated stainless steel orthodontic wires</td>
<td>1 hour</td>
<td>2.1</td>
<td>0.81</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>2 hours</td>
<td>2.2</td>
<td>0.81</td>
<td>1.2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>8 hours</td>
<td>2.4</td>
<td>0.80</td>
<td>0.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition Parameters</th>
<th>Paste of tuna fish in sunflower oil</th>
<th>Paste of tuna fish in brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial</td>
<td>after 8 hours</td>
</tr>
<tr>
<td>pH</td>
<td>5.79</td>
<td>5.80</td>
</tr>
<tr>
<td>Moisture %</td>
<td>64.8</td>
<td>64.1</td>
</tr>
<tr>
<td>Protein %</td>
<td>18.8</td>
<td>18.6</td>
</tr>
<tr>
<td>Colagen %</td>
<td>17.0</td>
<td>16.8</td>
</tr>
<tr>
<td>Fat %</td>
<td>15.5</td>
<td>16.4</td>
</tr>
<tr>
<td>Salts %</td>
<td>0.9</td>
<td>0.9</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>pH and proximate composition values of the paste from tuna fish meat cans samples during 8 hours storage</th>
</tr>
</thead>
</table>

Table 3
wires in the both fish products was superior to that of the uncoated material. Therefore, both type (coated and uncoated) of stainless steel orthodontic wires presented higher corrosion resistance values in the paste of tuna filet in sunflower oil. In the case of fish product containing tuna meat and sunflower oil, the formation (hypothetically) of a fully covered oil film would prevent corrosion [30-31] of the stainless steel surface by separating the water phase, salt and the others main biochemical compounds of the tuna fish meat (table 3). Practically, when the paste of tuna fish in oil was prepared by well blending the can's content, the water phase was embedded into the oil phase, and the resulted stable emulsion, that showed non significant changes of the proximate composition during 8 hours storage (table 3) exerted an inhibitory effect on the corrosion process [32-33].

In the case of the paste of tuna filet in brine, the smaller corrosion resistance values registered for both type of stainless steel orthodontic wires can be explained by the enhanced corrosive effect of sodium chloride [34] and citric acid from the brine aqueous solution [30]. Semi-logarithmic plots between -1000 mV and 1000 mV vs. SCE of the uncoated stainless steel wires in both tunafish derived products are displayed in figures 10-11. The zero current potential (ZCP) and corrosion current ($i_{corr}$) values were determined by Tafel analysis of both the anodic and cathodic branches of the polarization plots. The ZCP is defined as the potential at which the current reaches a minimum during the forward potentiodynamic polarization scan. As a result of the coated samples, the zero-current potential of the uncoated stainless steel orthodontic wires was shifted towards a more noble value in both paste of tuna filet products.

The corrosion current is representative for the degradation degree of each sample. The average values of ZCP and $i_{corr}$ determined from the polarization curves are presented in tables 4 and 5. Corrosion may occur in pores as the result of the metal being directly exposed to the aggressive attack of the electrolyte. Data from figures 10-11 reveals an evident decrease of the anodic current for the coated stainless steel orthodontic wires as compared with the uncoated ones. This fact proves that the coated sample has a greater corrosion resistance compared to uncoated sample, which determine the correspondently smaller measured values of the corrosion current densities. Low corrosion current density values were obtained from the potentiodynamic polarization curves of investigated samples in the paste of the tuna filet in sunflower oil. These results are in agreement with EIS data.

The susceptibility of an alloy to pitting corrosion in a certain medium [35] can be characterized in terms of the breakdown potential ($E_{bd}$) relative to the zero-current potential value (ZCP). The potential range situated between ZCP and $E_{bd}$ represents the passivity zone in which the corrosion rate is low or even insignificant. As the difference between $E_{bd}$ and ZCP becomes smaller, the alloy is expected to become more susceptible to pitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZCP, mV</th>
<th>$i_{corr}$, $\mu A/cm^2$</th>
<th>$E_{bd}$, mV</th>
<th>$E_{bd}$–ZCP, mV</th>
<th>$Q_{corr}$, $\mu C/cm^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated stainless steel orthodontic wires</td>
<td>-221</td>
<td>6.1</td>
<td>594</td>
<td>815</td>
<td>16.9</td>
</tr>
<tr>
<td>Uncoated stainless steel orthodontic wires</td>
<td>-623</td>
<td>14.6</td>
<td>132</td>
<td>755</td>
<td>87.4</td>
</tr>
</tbody>
</table>

**Table 4**
THE MEAN VALUES OF ELECTROCHEMICAL PARAMETERS MEASURED AND CALCULATED FOR THE PASTE OF TUNA FILET IN SUNFLOWER OIL (37 ºC)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZCP, mV</th>
<th>$i_{corr}$, $\mu A/cm^2$</th>
<th>$E_{bd}$, mV</th>
<th>$E_{bd}$–ZCP, mV</th>
<th>$Q_{corr}$, $\mu C/cm^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated stainless steel orthodontic wires</td>
<td>-378</td>
<td>8.9</td>
<td>219</td>
<td>597</td>
<td>18.3</td>
</tr>
<tr>
<td>Uncoated stainless steel orthodontic wires</td>
<td>-256</td>
<td>19.1</td>
<td>217</td>
<td>513</td>
<td>51.8</td>
</tr>
</tbody>
</table>

**Table 5**
THE MEAN VALUES OF ELECTROCHEMICAL PARAMETERS MEASURED AND CALCULATED FOR THE SAMPLES IN TUNA FILET IN BRINE (37 ºC)
corrosion. Also, the area of hysteresis loop ($Q_{hysteresis}$) reflects the susceptibility to localized corrosion.

The analysis of the potentiodynamic polarization curves proved that the uncoated stainless steel alloy exhibited a more area of hysteresis loop and a more negative breakdown potential value than coated stainless steel orthodontic wires. These results indicating that uncoated stainless steel orthodontic wires exhibited a greater susceptibility to localized corrosion, are consistent also with the conclusions derived from $Q_{hysteresis}$ presented above.

A comparison with other published is not applicable in this case, since the corrosion and anodic current densities of stainless steel orthodontic wires depend on potential scanning rate, surface preparation or exposure time. However, our results sustain the recommendation of caution against consumption of products derived from tuna filet in brine for patients with stainless steel orthodontic wires.

The surface morphologies of coated and uncoated stainless steel orthodontic wires polarized at +1 V in the paste of tuna filet in sunflower oil and in brine were examined by scanning electrochemical microscopy (SEM).

The analysis of figures 12-13 indicated the appearance of localized corrosion at the surface of coated and uncoated stainless steel orthodontic wires. The localized corrosion at surface of both coated and uncoated stainless steel orthodontic wires was evident, even the morphology of the electrochemically polarization tests was extremely irregular.

Conclusions

Low corrosion current densities of the potentiodynamic polarization curves for the coated stainless steel orthodontic wires showed more positive zero current (ZCP) and breakdown ($E_{b,\text{d}}$) potentials than the uncoated stainless steel orthodontic wires. However, the PTFE protective layers from the surface of stainless steel orthodontic wires are prone to localized breakdown in both tuna filet products as characterized by the measurement of pitting corrosion potential chloride-containing solutions. The EIS spectra of the coated stainless steel samples in the paste of tuna filet exhibited two time constants: the first accounting for the characteristic reactions at the stainless steel layer/solution interfaces, and the second corresponding to the PTFE coated layer. The experimental potentiodynamic polarization curves, EIS diagrams, and the equivalent circuit parameters showed that the coated stainless steel orthodontic wires in both tuna filet products presented good electrochemical corrosion resistance.

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References


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