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**NiTi SUPERELASTIC ORTHODONTIC ARCHWIRES WITH  
POLYAMIDE COATING.**

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**Key words:** orthodontic archwires, polyamide coating, tribology, nickel ion release, corrosion

## **ABSTRACT**

Twenty orthodontic archwires with 55.2% Ni and 44.8% Ti (% weight) were subjected to a dipping treatment to coat the NiTi surface by a polyamide polymer. It has been selected a Polyamide 11 (PA11) due to its remarkable long lasting performance. The transformation temperatures as well as the transformation stresses of the NiTi alloy were determined in order to know whether the coating process can alter its properties. The adhesive wear tests have been demonstrated that the wear rates as well as the dynamic friction coefficients  $\mu$  of polymer coated wires are much lower than metallic wires. The corrosion studies have shown that the use of this polymer, as coating, seals the NiTi surface to prevent corrosion and the release of nickel ions. The average decrease of Ni ions release due to this coating is around 85%.

## **INTRODUCTION**

The interest in aesthetic orthodontic appliances is increasing: lingually placed brackets, aesthetically polymeric archwires, ceramic brackets are different examples. Besides the aesthetic reasons, another concern is that the oral cavity represents a harsh environment for a metallic orthodontic appliance of any kind [1-2]. Corrosion of orthodontic appliances has been thoroughly studied [3-6]. Two main concerns are directly related to the effects of corrosion: biocompatibility and appliance performance [7]. The most important aspect is the interaction that the appliance may have with the patient in terms of absorption of corrosion products and the systemic reactions that may arise. Attention has been placed on Nickel as an element able to induce allergenic reactions and since it is one of the most used constituents of the alloys commonly used in orthodontics such as Stainless Steel, Nickel-Titanium and Copper-Nickel-Titanium [8-17].

The use of a polymer as coating can provide a wide range of specific surface properties to a biomedical device. A basic application is sealing the surface to prevent corrosion and the release of nickel ions. Orthopaedic clamps of NiTi have been coated with plasma polymerized polytetrafluorethylene (PTFE) for this purpose. PTFE is known for its low friction coefficient; therefore it is suitable as coating on guidewires [18].

Similar or even better corrosion resistance than the one found for PTFE, has been observed for plasma polymerization of hexamethyldisilazane (HMDSN) on a NiTi surface. This coating can withstand 2% strain deformation before failure [19]. Yet the higher elasticity of PTFE and the wide application of that polymer in medicine render PTFE the more attractive polymer coating.

A solution-based elastomeric polycarbonate polyurethane had been applied on vascular stents. The coating with 25-30  $\mu\text{m}$  thickness had been applied to decrease the corrosion from 275 to  $<13$   $\mu\text{m}/\text{year}$ . Crosslinked polyurethane-urea films with Ta particles as radiopaque filler were synthesized directly on NiTi stents [20-21]. The siloxane-based polyurethane copolymer was used for dip-coating of stents. The study did not provide corrosion data, but showed highly improved hemocompatibility concerning coagulation and inflammation [22].

Tetraethyleneglycol dimethyl ether, polyethylene terephthalate,... are other coatings used in order to attain even hemocompatibility characteristics or designed to support the adhesion and proliferation of endothelial cells on the surface.

The aim of this work is to obtain and determine the properties (roughness, transformation temperatures and stresses, friction behaviour, corrosion, nickel ion release) of a new NiTi orthodontic archwire coated with polyamide and to compare its properties with

the conventional NiTi. This new coating presents aesthetic advantages, avoids corrosion and decreases-nickel ion release.

## **MATERIALS AND METHODS.**

Twenty orthodontic archwires with 55.2% Ni and 44.8% Ti in weight have been studied. The archwires were analyzed as received, and ten of these were subjected to a dipping treatment to coat with polyamide PA11 the NiTi surface. Specimens measuring 0.46 mm in diameter and 45 mm in length were cut from the archwires. The treatment was carried out when the NiTi archwires were at 90°C, after the NiTi archwires were immersed in polyamide for 30 seconds. Polyamide at 90°C is in liquid phase and coated all the NiTi surfaces.

### **Roughness**

The roughness of the samples was obtained by white light interferometer microscopy (NT 1100 model, Wyko). The dimensions of the explored zone were 124 X 94  $\mu\text{m}^2$ . Six measurements were done for each group of samples. Roughness, spatial and hybrid parameters were obtained with Vision32 software from direct 3D analysis of the images captured. A correction for curvature and tilt of the sample was also applied.

Height ( $S_a$ ), spacing ( $S_z$ ) and hybrid ( $R_{sk}$ ,  $R_{ku}$ ) parameters, defined according to ISO 4287-1997 and/or ASME B46.1-1995 were obtained.

Sa is also known as the arithmetical mean deviation of the profile and is the most commonly used parameter in surface roughness. The only spacing parameter studied is Sz, and it represents the mean spacing between peaks. The hybrid parameter Rsk is also known as skewness of the profile, and depending on its sign it tells whether the surface is more porous or spiky. Finally, Rsku is also called kurtosis, and it gives an idea of the spikiness of the profile.

### **Calorimetry.**

The transformation temperatures of the alloy obtained were determined by Differential Scanning Calorimetry (DSC, 2920 modulated DSC, TA Instruments) with a heating ramp of 10°C/min and a cooling ramp of 2°C/min. The transformation temperatures and enthalpy determination was made with an appropriate software.  $M_s$  (martensite start) and  $M_f$  (martensite finish) are respectively the starting and finishing temperatures of martensite formation upon cooling from the austenite phase. Similarly,  $A_s$  (austenite start) and  $A_f$  (austenite finish) are respectively the starting and finishing temperatures of austenite formation upon heating from martensite phase.

### **Mechanical tests**

Tensile tests were carried out on a servo-hydraulic testing machine (MTS-Bionix 858), working at a cross-head speed of 10mm/min. The five NiTi specimens tested were cylinders of 0.457 mm in diameter and of 45 mm in length. The critical stresses (austenite to stress-induced martensite) were determined from these tests, which were performed in artificial saliva at 37°C [23]. The chemical composition of the physiological saliva is shown in Table 1.

## **Friction**

Adhesive wear tests were performed in a CSM pin-on-Disk tribometer, in accordance to the ASTM-G99 standard, in salivary medium at 37°C. The underlying principle on this test could be called wire-on-disk because of its analogy with the pin-on-disk test.

As shown in figure 1, the orthodontic archwires were carefully affixed with cyanoacrylate adhesive in a bakelite holder, without adhesive residues, on the wire surface to be tested. The contact wire plane and the disc were in the longitudinal direction to simulate full-arc contact bracket. The tribometer was immersed inside a polymethylmethacrilate container in which artificial saliva solution was circulated with a temperature control at 37°C ( $\pm 1^\circ\text{C}$ ).

An angular velocity of the disks of 0.5236 rad/s and a normal load 10N were used. Ideally, the normal load on the wire should have



been around 1N to simulate the load in service (in which typical values range from 0,196 to 0,98 N load). However, 10N were employed to ensure that there was a full contact between both surfaces that could influence the determination of the coefficients of friction.

The dynamic friction coefficients  $\mu$  (the proportionality constant between the friction force and the normal force) were determined and the wear rates (volume loss) for the orthodontic archwires against the materials commonly used for the brackets (manufactured in 316 Stainless steel and Ti-6Al-4V) were also measured.

As the wear test was being performed, gravimetric measures were controlled in a Sartorius Micro Balance CPA26P, in order to determine the weight loss over time by means of a high-precision set of scales. The sensitivity of these measures was  $\pm 0.001$  mg. With fixed density, the weight lost can be stated as volume loss.

### **Corrosion tests**

Archwires were sectioned in order to yield corrosion testing samples. A 25 mm length of each archwire was cut with sterile orthodontic pliers and isolated with wax (Paraffin wax Sigma Aldrich) at the interphase between the testing solution and air. The corrosion tests

were performed following the ISO-standard 10993-15:2000 "Biological evaluation of medical devices. Part 15: Identification and quantification of degradation products from metals and alloys".

The tests were carried out with a Voltalab PGZ 301 potentiostat (Radiometer, Copenhagen, Denmark) controlled by Voltmaster 4 software (Radiometer Analytical, Villeurbanne Cedex, France). The testing solution was artificial saliva and artificial saliva with fluoride solution kept at a controlled constant temperature of 37°C. The reference electrode was an Ag/AgCl/KCl electrode ( $E^{\circ}=0.222V$ ). The auxiliary electrode used was a platinum electrode with a surface of 240 mm<sup>2</sup> (Radiometer Analytical, Villeurbanne, France).

In the corrosion tests we defined the following: (a) *Open circuit potential* ( $E_{OCP}$ ), the potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from the material; (b) *Corrosion Potential* ( $E_{CORR}$ ), the potential calculated at the intersection where the total oxidation rate is equal to the total reduction rate; and (c) *Corrosion current density* ( $i_{CORR}$ ), the current divided by the surface of the electrode. It is the size of the anodic component of the current which flows at the corrosion potential  $E_{CORR}$ .

The Open Circuit Potential ( $E_{ocp}$ ) was monitored for three hours in order to allow leveling-off of the value before the polarization resistance test. The Cyclic Voltammetry assay was performed by

scanning the potential of the alloy of the sample at 0.25 mV/s with the minimum current set at -1 A and the maximum at +1 A, with a minimum range set at 100  $\mu$ A between -300 mV and +2000 mV around the OCP value. The Open Circuit Potentials ( $E_{ocp}$ ), Corrosion Potentials ( $E_{corr}$ ) and Corrosion Currents ( $i_{corr}$ ) were recorded for the different samples tested.

### **Nickel ion release**

An ion release experiment was carried out with untreated samples, thermally oxidized samples and samples thermally oxidized and boiled in water for 1 hour. The samples were immersed in 6 ml of saliva artificial at pH=7.4, 37°C for 30 days. At day 5, saliva was renewed to avoid saturation of the medium.

The Ni released was quantified by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) using an UNICAM 939 spectrometer at 1, 2, 5, 15 and 30 days. The results were normalized by the real surface area of each sample and were mean values of three measurements.

### **Statistical analysis**

The data were statistically analysed using t-Student tests and one-way ANOVA tables with Tuckey's multiple comparison in order to evaluate statistically significant differences between sample groups. The differences were considered to be significant when p-value < 0.05.

All statistical analyses were performed with Minitab software (Minitab release 13.0).

## **RESULTS AND DISCUSSION.**

For all the roughness parameters, the differences between untreated and coated surfaces are statistically significant ( $p < 0.05$ ). Polyamide coating decreases  $S_a$  from 21.8 to 13.5 nm (Table 2), and  $S_z$  from 373.4 to 303.2 nm.  $S_{sk}$  is slightly negative (-0.5) for the untreated surfaces, and is -0.7 nm for the coated samples. The kurtosis parameter is much higher than 3 for untreated surfaces and close to 3 for coated surfaces.

The transformation temperatures were measured during the first heating and cooling cycle. However, the results at different cooling/heating cycles do not shown differences with significance. R-phase peaks were not observed in the different calorimetric plots; only one peak was detected in each cooling/heating cycle. Table 3

shows the transformation temperatures for as-received Ni-Ti and with polyamide coating. From these results, it can be observed that the coating treatment does not change the transformation temperatures. The heating produced in the coating treatment at 90°C is insufficient to produce precipitates or grain growth which could change its transformation temperatures [24].

The stress required inducing the formation of stress-induced martensite,  $\sigma^{\beta \rightarrow M}$  and the one required for the reverse transformation  $\sigma^{M \rightarrow \beta}$  at 20°C and 37°C were determined. The transformation stresses ( $\beta \leftrightarrow$  Stress-Induced Martensite) are shown in Table 4. Similar stresses were required to transform the austenite to stress-induced martensite in the coated archwires because the transformation temperatures do not present changes with significance between the original archwires and coated ones.

It is widely known that these critical stresses increase with increasing test temperature [25]. The superelastic behavior is very similar and produces the elastic deformation of an orthodontic wire and the subsequent release of its elastic energy over a period of time, which increases the correcting forces. Generally, it has become an accepted principle in orthodontics that light continuous forces are desirable to achieve physiologic and controlled tooth movement with minimum pathologic repercussions on the teeth and their surrounding tissues. Orthodontic archwires that can deliver such light forces over long

distances would appear to be most useful to clinical professionals during the initial alignment phase of fixed appliance treatment [26].

Frictional force has an important consideration in orthodontic mechanotherapy. The results of the frictional tests performed on the archwires under scrutiny on the two different types of brackets (316L stainless steel and the Ti6Al4V alloy) provided the values for the static and dynamic friction coefficients ( $\mu$ ) as it can be seen in Table 5.

It can be observed that the polymer static and dynamic friction coefficients are lower than beta-Ti and cp-Ti, NiTi and NiTiCu orthodontic archwires in both bracket materials tested. From the results of Table 6, the wear rate of polymeric wires is much lower than metallic wires.

This contribution evaluated static as well as dynamic friction, and the results indicated a lower friction at the archwire-bracket interface when a polymer and Ti-6Al-4V or 316 stainless steel are used in comparison with the other 4 alloy archwires.

Clinically, this means that the net force required for translator movement will be lower for polymer and higher when Ti-based and superelastic alloys (NiTi and NiTiCu) wires are used [27].

The results obtained for the electrochemical corrosion are shown in Table 7. The results of the zero current potential ( $E_{OCP}$ ) defined as

the potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from the material, are positive values, for the original NiTi around +470 mV and for the coated NiTi the value increases up to +870 mV. The results showed that polyamide improved the corrosion behavior and the coated orthodontic archwire remains in its immunity range.

*The corrosion Potential ( $E_{\text{CORR}}$ )* defined as the potential calculated at the intersection where the total oxidation rate is equal to the total reduction rate. In this case, the potential showed negative values from -10 mV for the original NiTi to -75 mV for the coated archwires.

*The corrosion current density ( $i_{\text{CORR}}$ )* is the current divided by the surface of the electrode. It is the size of the anodic component of the current which flows at the corrosion potential  $E_{\text{CORR}}$ . Since by definition the resulting current is equal to zero at that potential, the cathodic component is of equal size, but of opposite sign. The measured resulting current being zero at the corrosion potential, the corrosion current density  $i_{\text{CORR}}$  can only be obtained by indirect methods, e.g. by the Tafel equation. The Tafel equation states that  $a$  and  $b$  are the Tafel proportionality constants for anodic (oxidation) and cathodic (reduction) reactions of a metal. The higher the current density at a given potential, the more prone is the material to corrode. NiTi coated with polyamide had the most passive (-35.1

mA/cm<sup>2</sup>) and the original NiTi had the most active (-5.1mA/cm<sup>2</sup>) critical current density values.

The difference of the current density at a given potential between NiTi is due to the polyamide coating which inhibits the corrosion on the orthodontic archwires. The decrease of the roughness could produce a decrease on the corrosion behavior but this would even be lower.

For the Ni release tests, the highest Ni release occurs within the first day (figure 2). Polyamide coating produces a decrease the Ni release from 120 ng/l to 20 ng/l in 30 days of immersion. Then, the average decrease of Ni release due to the treatment is around 85%. These values do not represent any problem for the human health. The European Union (EU) has accordingly decreed two directives:

- the Ni release from parts in direct and prolonged contact with the skin must be lower than 0.5 microgram/cm<sup>2</sup>/week [28].
- all metallic parts that are inserted into pierced ears and other parts of the human body must not have a Ni release rate greater than 0.2 microgr/cm<sup>2</sup>/week [29-30].

Wiltshire and Noble [31] showed that in dentistry, allergies to metals were also frequently reported. In particular, allergy to Ni in females was reported to vary from 9-20%, and in orthodontic patients with pierced ears, 30% were allergic to Ni, Cu and Cr. Bass et al. [32]



were surprised that only few papers reported about patients reacting adversely to Ni-containing dental restorations and there was little evidence that Ni adsorption intra-orally exacerbated existing dermatitis. Nevertheless, there were authorities that advised dentists against using Ni for those patients known to be sensitive to the metal [33].

## **CONCLUSIONS**

The use of a polyamide polymer (PA11), as coating for NiTi orthodontic archwires, presents excellent properties with great potential for the future.

The calorimetric studies have shown that the polymer coating process does not change the transformation temperatures as well as the transformation stresses ( $\beta \leftrightarrow$  Stress-Induced Martensite) required to transform the austenite to stress-induced martensite. This means that the superelastic behavior is very similar than uncoated archwires.

In comparison with the uncoated NiTi, the adhesive wear tests have been demonstrated that the wear rate of polymeric wires is much lower than metallic wires. Clinically, this means that the net force required for translator movement will be lower than for uncoated archwire.

The corrosion tests as the Ni release tests have shown that the polyamide coating inhibits the corrosion and it produces a decrease in the Ni release ions. This is an important result due to one of the main concerns about orthodontic appliances set in the oral cavity is corrosion. Orthodontic appliances are continually under the corrosive action of saliva, extrinsic fluids coming from food intake or products used for the oral care and hygiene. Furthermore, it is well reported that the Ni ions release could lead to an allergic reaction depending on the severity of the corrosion process.

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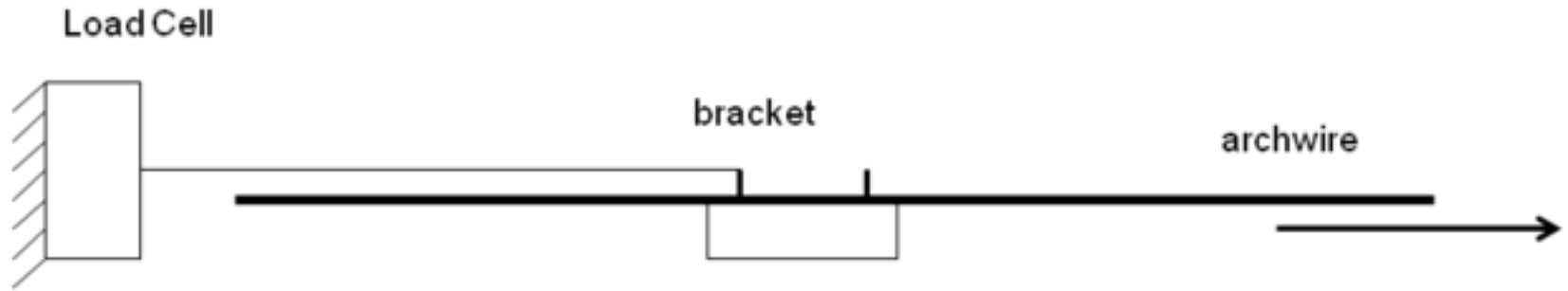
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## FIGURE CAPTIONS

Figure 1. Scheme of the test method to determine the friction coefficient.

Figure 2. Ni ion release at different test times. The area of the samples was 1 cm<sup>2</sup>.



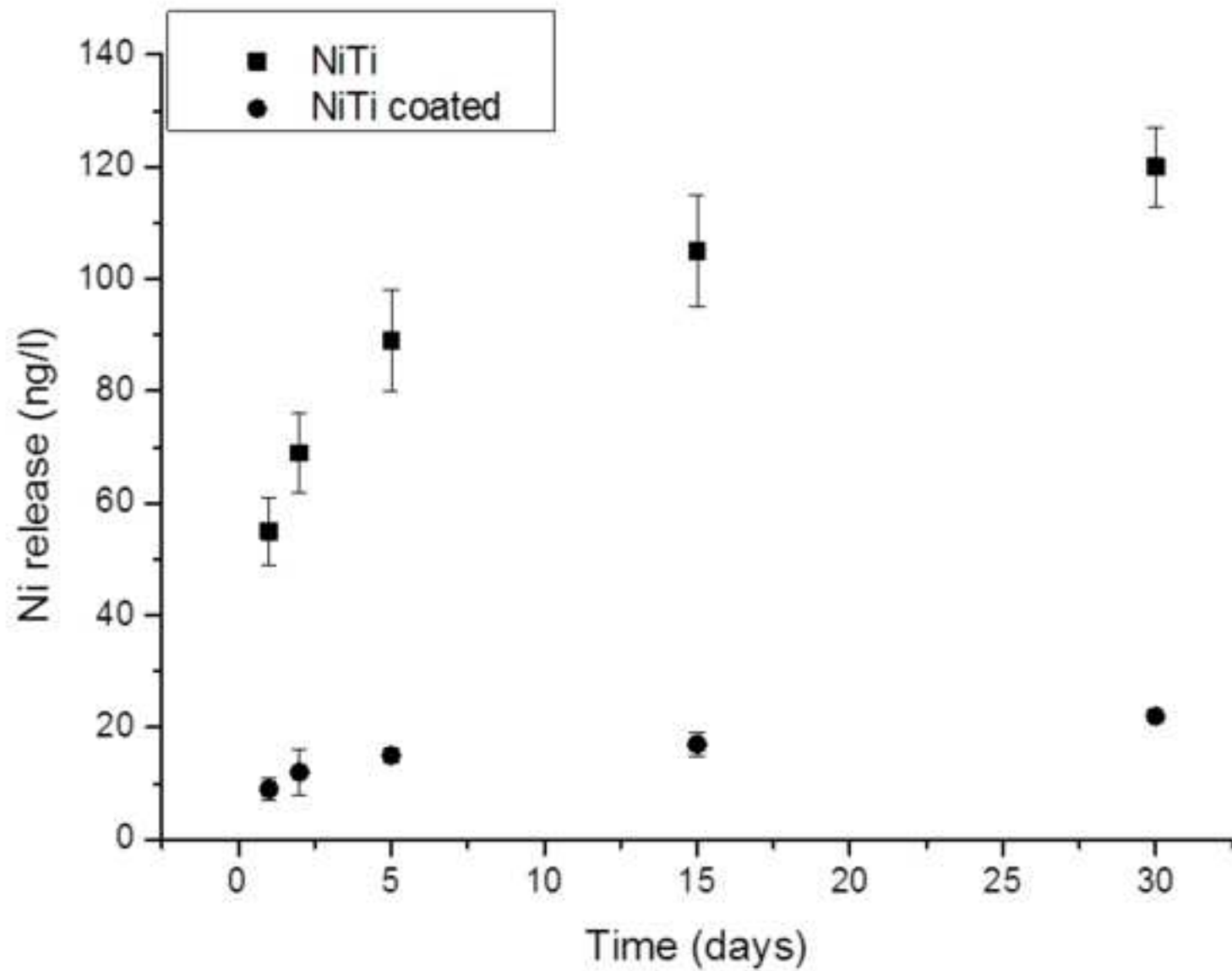


TABLE 1. Chemical composition of artificial saliva.

Chemical product	Composition (g/dm <sup>3</sup> )
K <sub>2</sub> HPO <sub>4</sub>	0.20
KCl	1.20
KSCN	0.33
Na <sub>2</sub> HPO <sub>4</sub>	0.26
NaCl	0.70
NaHCO <sub>3</sub>	1.50
Urea	1.50
Lactic acid	up to pH=6.7

Table 2. Topographical parameters for untreated and coated samples of NiTi

	Sa (nm)	Sz (nm)	Rsk <sup>b</sup>	Rku <sup>b</sup>
Untreated	21.8 ± 4.8	373.4 ± 58.1	-0.5 ± 0.3	10.0 ± 4.2
Coated	13.5 ± 9.7	303.2 ± 93.3	-0.7 ± 0.1	3.1 ± 0.2

<sup>a</sup> mean value of ten measurements ± standard deviation

<sup>b</sup> dimensionless

TABLE 3. Transformation temperatures in Celsius for the different NiTi archwires.

Alloy	$M_s$	$M_f$	$A_s$	$A_f$
NiTi	$34.6 \pm 0.4$	$25.8 \pm 0.5$	$33.9 \pm 0.4$	$42.5 \pm 0.4$
NiTi coated	$33.8 \pm 0.1$	$25.4 \pm 0.2$	$31.5 \pm 0.2$	$41.8 \pm 0.3$

TABLE 4. Critical stresses at different temperatures. The numbers in parentheses are the standard deviation.

Alloy	$\sigma^{\beta \rightarrow \text{SIM}}$ (MPa)		$\sigma^{\text{SIM} \rightarrow \beta}$ (MPa)	
	20°C	37°C	20°C	37°C
NiTi	233 (15)	321 (22)	54 (5)	210 (19)
NiTi coated	244 (12)	354 (23)	45 (12)	209 (23)

**Table 5.** Static and Dynamic friction coefficients of orthodontic archwires obtained against two types of brackets: Ti6Al4V and 316L stainless steel.

**STATIC**

Archwire Bracket	NiTi coated	SS ASI304	TiMo	Ti (cp)	NiTi	NiTiCu
Ti-6Al-4V (353 ± 1 HVN)	0,29 ± 0,08	0,36 ± 0,05	0,38 ± 0,07	0,43 ± 0,11	0,59 ± 0,07	0,49 ± 0,13
SS 316L (435 ± 3 HVN)	0,33 ± 0,10	0,42 ± 0,03	0,45 ± 0,09	0,51 ± 0,13	0,66 ± 0,02	0,57 ± 0,11

**DYNAMIC**

Archwire Bracket	NiTi coated	SS ASI304	TiMo	Ti (cp)	NiTi	NiTiCu
Ti-6Al-4V (353 ± 1 HVN)	0,18 ± 0,02	0,26 ± 0,01	0,31 ± 0,02	0,33 ± 0,01	0,51 ± 0,05	0,44 ± 0,03
SS 316L (435 ± 3 HVN)	0,22 ± 0,08	0,32 ± 0,02	0,39 ± 0,02	0,41 ± 0,03	0,56 ± 0,02	0,47 ± 0,01



**Table 6.** Wear rate of orthodontic archwires (Volume worn in mm<sup>3</sup>/h) obtained against two reference materials Ti6Al4V and 316L stainless steel with its hardness values.

Archwire Bracket	NiTi coated	Stainless Steel	TiMo	Ti (cp)	NiTi	NiTiCu
<b>Ti-6Al-4V</b> (353 ± 1 HVN)	0,0027 ± 0,0002	0,0054 ± 0,0001	0,0086 ± 0,0002	0,0102 ± 0,0006	0,0153 ± 0,0008	0,0120 ± 0,0007
<b>SS 316L</b> (435 ± 3 HVN)	0,0033 ± 0,0009	0,0062 ± 0,0009	0,0093 ± 0,0021	0,0113 ± 0,0009	0,0193 ± 0,0008	0,0131 ± 0,0007

Table 7. Mean values obtained from potentiostatic polarization plot of dental materials studied in artificial saliva solution.

<b>Material</b>	$E_{OCP}$ (mV)	$E_{CORR}$ (mV)	$i_{CORR}$ (A/cm <sup>2</sup> )
NiTi	+478 ± 25	-10 ± 3	-5.1 ± 2.0
NiTi-PA coated	+860 ± 34	-75 ± 9	-35.1 ± 3.0