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Influence of various fluoride agents on working properties and surface characteristics of uncoated, rhodium coated and nitrified nickel-titanium orthodontic wires

VIŠNJA KATIC[1], VILKO MANDIC[2], DAMIR JEžEK[3], GORANA BARŠIC[4] & STJEPAN ŠPALJ[1]

[1]*Department of Orthodontics, Faculty of Medicine, University of Rijeka, Rijeka, Croatia,* [2]*Department of Inorganic Chemical Technology and Non-Metals, Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia,* [3]*Department of Process Engineering, Faculty of Food Technology and Biotechnology, University of Zagreb, Zagreb, Croatia, and* [4]*Department of Precise Measurement, Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia*

Abstract

Objective. To analyze the effect of various fluoride formulations in commercially available agents on working properties of various nickel-titanium orthodontic wires. ***Materials and methods.*** Uncoated (NiTi), rhodium coated (RhNiTi) and nitrified (NNiTi) wires were immersed to dH_2O, MiPaste, Elmex and Mirafluor for 1 h. Unloading slope characteristics (average force, bending action of the force and average plateau length) and the percentage of useable constant force during unloading were observed. Surface roughness (R_a) was measured. SEM and EDS were used for observation of the surface. ***Results.*** NiTi had decreased loading and unloading elastic modulus (E) and yield strength (YS) after immersion to MIPaste and Mirafluor. The unloading YS decreased in the RhNiTi by the MIPaste. The loading and unloading YS of the NNiTi increased in Elmex and increased average plateau force. RhNiTi showed higher average plateau length and the percentage of useful constant force during unloading in Mirafluor and the average plateau force lowered after immersion to MIPaste. The unloading slope characteristics for NiTi were affected by all three prophylactic agents, mostly by Mirafluor, and produced significantly lower forces during both loading and unloading, similarly to the NNiTi wires. The RhNiTi had the lowest forces during both loading and unloading in MIPaste. All results were at significance; $p < 0.05$. Difference in R_a was observed for RhNiTi after immersion to the MI Paste ($p < 0.001$; $\eta^2 = 0.761$). ***Conclusion.*** The NiTi and NNiTi wires lose less working force when combined with Elmex. The RhNiTi improve their working properties with Mirafluor and deteriorate when combined with MiPaste.

Key Words: *corrosion, orthodontic appliance, roughness, chemically induced, stress, mechanical*

Introduction

Nickel-titanium (NiTi) shape memory alloys (SMAs) are very useful and widely applicable in orthodontic therapy, because they are very flexible and exhibit excellent recovery, after being submitted to greater deflections [1–3]. The analysis of delivery and duration of forces upon the bending action is of prime interest for orthodontists, as it describes the working properties of the wire and can be well observed in a three-points-bending test curve [2–7]. The nickel content of the SMAs presents potential risk for the patients, with different kinds of hypersensitivity reactions and gingival hyperplasia reported [8,9].

Today on the market there are many various coatings on basic archwires, as they are supposed to improve aesthetics, reduce contact of nickel with oral tissue and saliva, decrease friction, etc. [10–13]. Rhodium coated archwires (RhNiTi) are marketed as High Aesthetic, because rhodium gives high gloss to the wire, making it less visible. It follows current orientation to the use of more biocompatible, stable materials from the noble materials group [14]. Nitrified NiTi archwires (NNiTi) are marketed as IonGuard, implying that nitride ions implanted on the surface reduce wear, corrosion and friction of the wire. During this process, nickel ions on the surface get replaced by nitride and form TiN (titanium nitride). Experimentally-produced TiN coating

Correspondence: Višnja Katić, Krešimirova 40, HR-51000 Rijeka, Croatia. Tel: +385 51 345 636. Fax: +385 51 345 630. E-mail: visnja.katic@medri.uniri.hr

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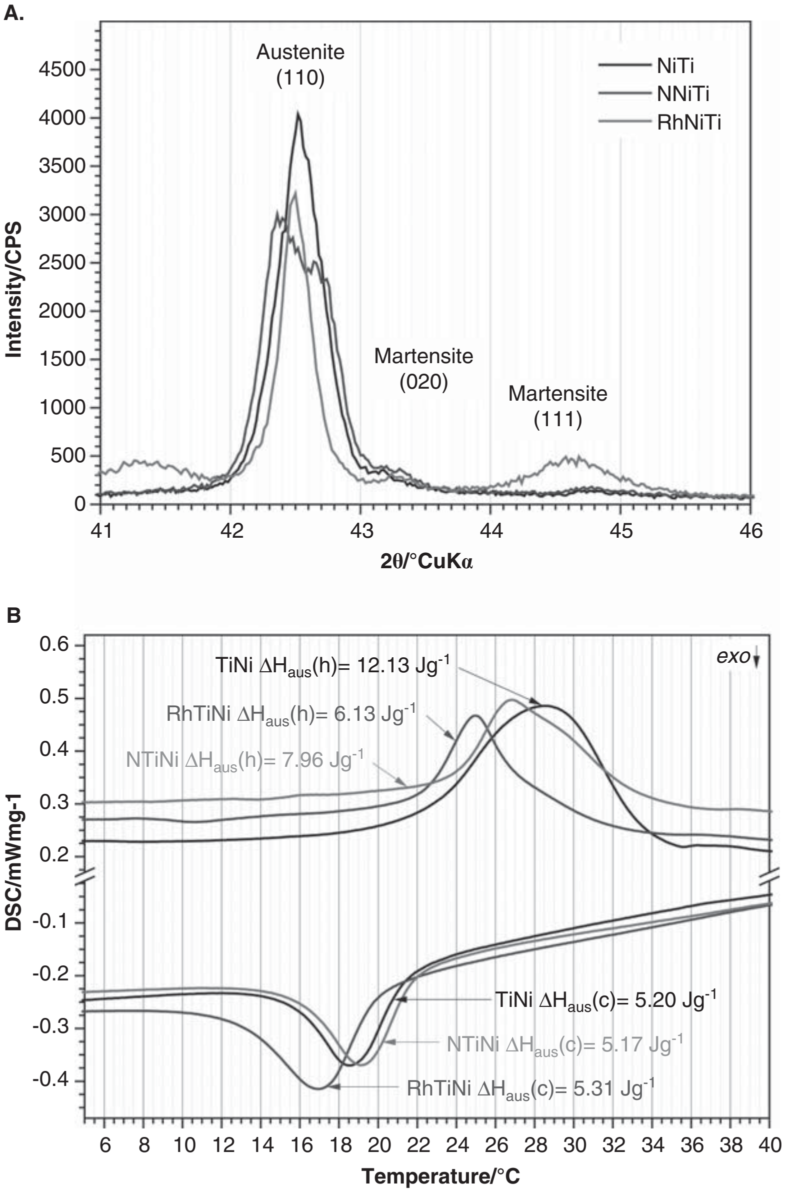

Figure 1. The XRD (A) and DSC (B) curves of the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium wire samples.

showed improvement in wear resistance, surface hardness, resistance to chemical attack, reduced friction and improved biocompatibility [15–17], but commercially available wires with coatings were not yet sufficiently investigated in interaction with additional dental remedies. Our previous research of the NiTi wires with various coatings showed that coatings influence the wires' properties in as-received state, as well as after immersion to the artificial saliva [18,19].

Increased incidence of the white spot lesions and caries was observed in patients from the early start of the orthodontic therapy with fixed appliances [20,21]. This side-effect often requires adjuvant fluoride prophylactic agents, because of the protective role of fluoride on the teeth surface [22–24]. Therefore, the preventive measures should start from the beginning of the tooth alignment; at this time the NiTi wires are engaged [1,2,4] and concurrently also exposed to the prophylactic agents. The source of fluoride dictates its bioavailability in saliva: sodium fluoride (NaF) dissipates instantly in saliva throughout the oral cavity; amine fluoride binds to organic constituents in saliva and plaque and progressively release the fluoride to the adjacent areas; and the metastable supersaturated mixture of casein phosphopeptides (CPP)-amorphous calcium phosphate (ACP)-NaF prevents fast dissipation of calcium, phosphate and fluoride ions from the area of application; according to the manufacturers' statements. The sticky consistency of all three fluoride agents enables prolonged contact of the remedies to the teeth, but also to the orthodontic appliance. Fluoride ions have been considered as the cause of the

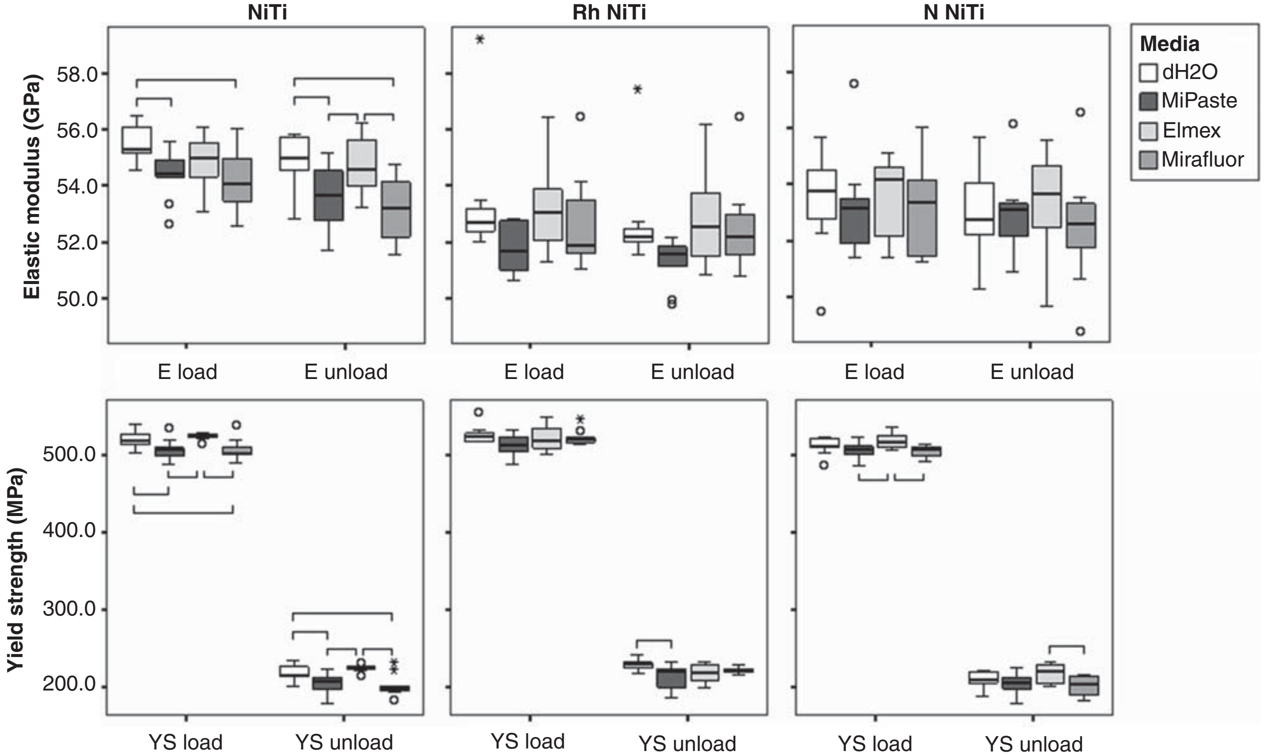

Figure 2. The elastic modulus (E) and yield strength (YS) of the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium wire after immersion to dH$_2$0, Mirafluor, MIPaste and Elmex. Horizontal bars denote significant differences at $p < 0.05$.

corrosion of the orthodontic archwires regarding differences in pH and fluoride ions concentration [25–27], but differences in fluoride formulation and effect on various wire coatings haven't been investigated. The aim of the present study is to explore the effect of various fluoride formulations in commercially available agents on working properties and surface and near-surface characteristics of NiTi wires in relation to their surface coating. Interaction between the new surface coating materials and commercial fluoride agents has not been investigated, yet it presents everyday clinical situation. The hypotheses are that, regardless of surface coating, bigger changes in mechanical and micromorphological properties are caused by:

(1) Higher fluoride concentration and
(2) Lower pH of the prophylactic agent.

Materials and methods

Materials

Three types of preformed rectangular superelastic NiTi alloy orthodontic archwires in dimensions 0.020 × 0.020 inch BioForce Sentalloy (Dentsply GAC Int., New York, USA) were investigated in this study:

- NiTi with untreated surface,
- Rhodium coated NiTi (High Aesthetic) and
- nitrified NiTi (IonGuard).

Chemical composition of the three wire types was determined with atomic absorption spectrometry (AAS) (AA 6800, Shimadzu, Kyoto, Japan) and consisted of nickel (50–51wt%) and titanium (49–50wt%). For rhodium-coated wire our laboratory could not detect rhodium, but detected gold (0.28%) in a 0.123 μm thin layer. The manufacturer stated that rhodium coated Ni-Ti has gold and rhodium in a 0.5 μm thin layer. The detection of nitride also was not possible and the manufacturer described it as 'a fraction of μm' layer of titanium nitride. The manufacturing process for neither coating was revealed.

Structural and thermal analysis methods were applied to observe phase transformations in as-received samples to exclude the possibility that other factors (i.e. the manufacturing procedure) cause greater discrepancies among wires' crystal lattice, thus influencing the functional properties of the wires [28].

The structure types were identified using X-ray diffraction (XRD) on a Shimadzu (Kyoto, Japan) XRD6000 device with CuKα radiation. Data were collected between 5–70° 2θ in a step scan mode with steps of 0.02° and counting time of 0.6 s at 25°C. All samples yield NiTi alloy in austenite structural form as the dominate phase, with more than traces of the martensite structural form found only in RhNiTi (Figure 1A).

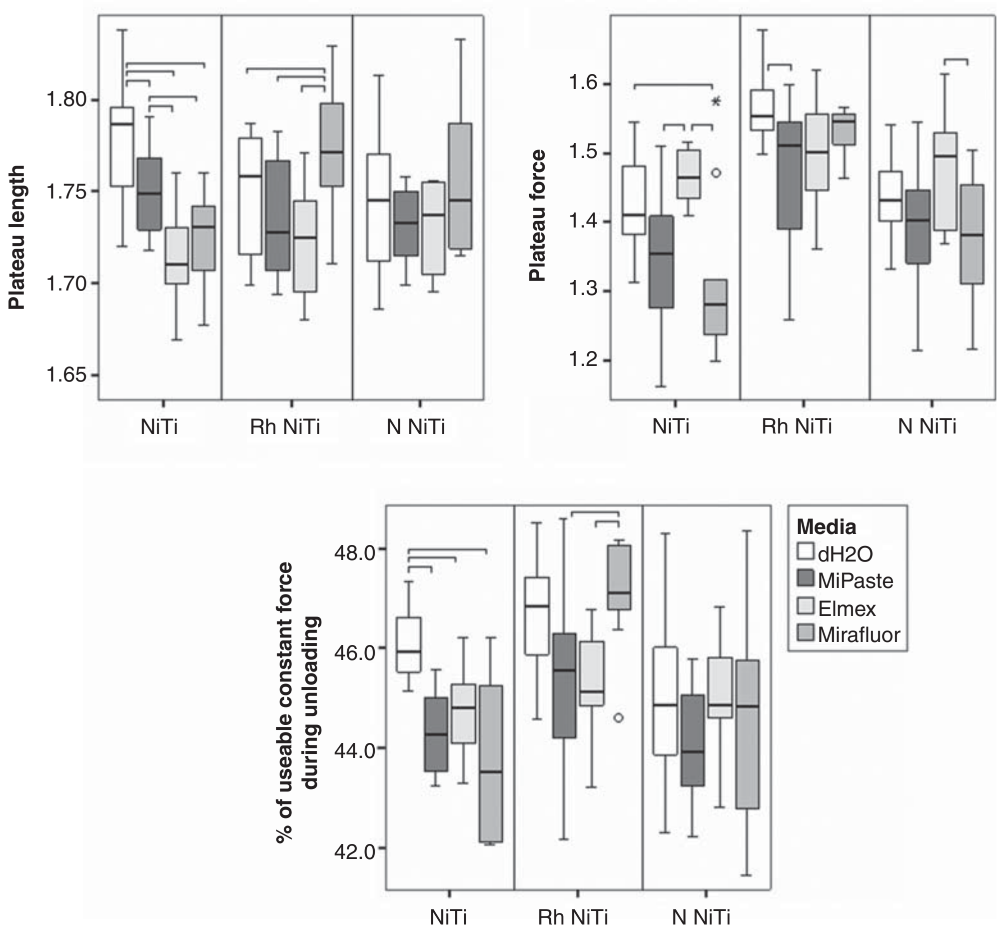

Figure 3. The unloading slope characteristics (average plateau force and average plateau length, the percentage of useful constant force during unloading) of the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium wire after immersion to dH_20, Mirafluor, MIPaste and Elmex. Horizontal bars denote significant differences at $p < 0.05$.

The thermal behavior of the wire samples was characterized using the Netzsch (Selb, Germany) DSC 200 differential scanning calorimetry (DSC) instrument. For the thermal analysis, ~40 mg of wire samples were placed in aluminum crucibles and heated from −15 to 50°C at a rate of 10°C/min in air, then also cooled under the same conditions. An empty aluminum crucible was used as a reference. The DSC scans confirmed that all wire samples consisted of the same austenitic NiTi at oral environment temperature (Figure 1B) and that manufacturing procedures did not induce changes in the crystallization mechanism of the samples.

The following four media were used:

- Elmex gelée (Gaba, Lörrach, Germany)—12,500 ppm of fluoride content in the form of amine fluorides/NaF in a 3/2 ratio,
- Mirafluor-k-gel (Hager&Werken, Duisburg, Germany)—6150 ppm of fluoride in the form of NaF,
- MI Paste Plus (GC, Tokyo, Japan)—900 ppm of fluoride in the form of NaF with casein phosphopeptide-amorphous calcium phosphate (CPP-ACPF) and
- dH_2O—distilled deionized water, with no fluoride ions.

The pH values of tested solutions were recorded at 37°C (pH meter MP 220, Mettler Toledo Int., Greifensee, Switzerland) as follows: Mirafluor-k-gel 5.1; Elmex gelée 5.5; dH_2O 6.1; MI Paste Plus 6.6.

The prophylactic fluoride agents were chosen because of their commercial availability, identical methods of application, various fluoride ion concentrations, various chemical formulations and differences in pH.

Immersion protocol

Specimens were cut from the straight ends of the preformed archwires for every wire type, each 2.5 cm long. Ten specimens from each wire type were immersed in Elmex gelée (the Elmex group), MI Paste Plus (the MiPaste group), Mirafluor-k-gel (the Mirafluor group) and distilled water (the dH_2O group) as negative control, for 1 h at 37°C. The immersion time was calculated on the average exposure of single orthodontic wire to this type of prophylactic agents (5 min per week ×12 weeks between

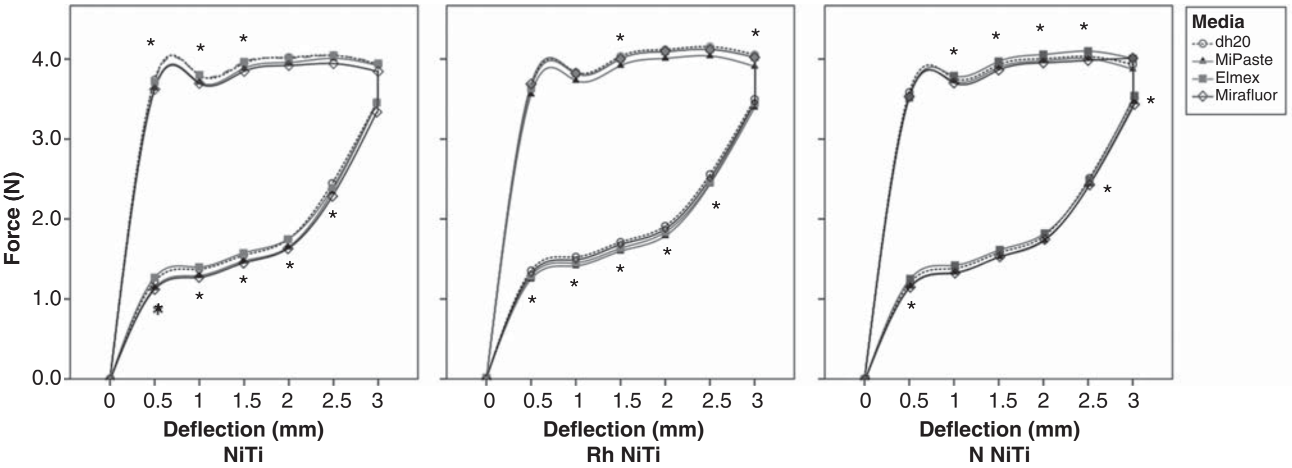

Figure 4. The analysis of forces in distances of 0.5, 1, 1.5, 2, 2.5 and 3 mm during loading and unloading for the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium wire after immersion to dH$_2$0, Mirafluor, MIPaste and Elmex. Horizontal bars denote significant differences at $p < 0.05$.

changes of wires) [5]. After immersion, the specimens were removed from their respective solutions, rinsed with dH$_2$O and placed in new, clean, individually coded protective plastic vials.

The randomized and controlled study design with parallel-groups enabled better control of allocation bias with randomly distributed specimens as well as the control of effect of the prophylactic agents by the use of the dH$_2$O group.

Three-point bending test

The current standards (ASTM; ANSI/ADA) were followed during testing, with parameters described previously [11,18,27]. The support span of testing machine Texture Analyser TA.HD.plus (Stable Micro Systems, Godalming, UK) was set to 12 mm; the factory calibrated 5 kg cell was used for loading; the thermal chamber was automatically regulated to 37°C; deflection was up to 3.1 mm and the unload back to 0 mm; the cross-head speed of 0.0167 mm/s. Data for load (in N) and deflection (in mm) were collected every 5 ms during the whole test and for each specimen and analyzed in the Texture Exponent software program (Stable Micro Systems). The analysis consisted of: the loading and unloading elastic modulus (E) and yield strength (YS); unloading slope characteristics (average plateau force, average plateau length, the percentage of useful constant force during unloading); analysis of the forces in distances of 0.5, 1, 1.5, 2, 2.5 and 3 mm during loading and unloading.

Surface characterization

Surface roughness parameter (R_a) was measured with the Stylus instrument Perthometer S8P (Mahr GmbH, Göttingen, Germany). The two-dimensional tracing of a surface was compliant with the ISO standards ISO 4287, 4288 and 3274, as described previously (diamond stylus with 5 mm radius; measuring force of 1.3 mN; evaluation length of 5.6 mm) [18]. Every specimen was measured on three different profiles and the arithmetic mean of these three measurements was used for further statistical analysis; five random specimens were measured from every experimental group.

Microscopic observation was used to depict the effects of the fluoride treatment on the wire topography, regarding the number and size of the dark spots on the wires' surface, and try to establish the

Table I. Surface roughness parameters (R_a) of the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium wire after immersion to dH$_2$0, MiPaste, Mirafluor and Elmex.

	Wire surface roughness (μm) (median (interquartile range))		
Treatment	NiTi	RhNiTi	NNiTi
dH$_2$0	0.160 (0.150–0.160)	0.230 (0.220–0.240)	0.200 (0.190–0.200)
MiPaste	0.170 (0.160–0.180)^a	0.230 (0.230–0.240)^b	0.170 (0.170–0.180)^a
Elmex	0.170 (0.160–0.180)	0.190 (0.170–0.260)	0.190 (0.170–0.200)
Mirafluor	0.170 (0.170–0.170)	0.210 (0.200–0.220)	0.180 (0.170–0.180)

Different superscript letters denote significant differences ($p < 0.001$; $\eta^2 = 0.761$).

correlation between observed surface characteristics and mechanical properties. After the mechanical testing, one specimen from each wire/experimental condition group was taken for the scanning electron microscope (SEM) analysis with the FEG QUANTA 250 (FEI, Eindhoven, The Netherlands) at × 400 magnification.

The chemical composition of the surface and near surface of the wires was analyzed with the energy-dispersive spectroscopy (EDS) QUANTAX EDS (Bruker, Karlsruhe, Germany). Different bright and dark areas on one wire specimen from every experimental group were explored, in order to determine whether those different areas also differ in chemical composition and possibly indicate loss of wire's coating.

Statistical analysis

Power analysis is used for assessment of sample size for laboratory research of materials corrosion. According to previous research [11,12,27], a minimum of four samples of each product type/experimental condition was needed for the detectable differences ($\alpha = 0.05$ and power = 0.80). Kruskal-Wallis and Mann-Whitney tests, with Bonferroni correction for multiple comparisons, were used for analysis of differences in working properties of each wire type exposed to prophylactic agents in relation to exposure to dH_2O. Statistical analysis were carried out using statistics software SPSS 10.0 (SPSS Inc., Chicago, IL), statistical significance was pre-set to $p < 0.05$.

Results

Loading and unloading elastic modulus (E) and yield strength (YS)

Significant differences ($p < 0.05$) were observed for the uncoated NiTi, with decreased E and YS after immersion to MIPaste and Mirafluor, when compared to dH_2O and Elmex, in both loading and unloading (Figure 2). The effect size of the MIPaste and Mirafluor was somewhat lower for the E ($\eta^2 = 0.288$ and 0.341) than for the YS ($\eta^2 = 0.342$ and 0.424).

The E of the both coated wires was unaffected by no media. The unloading YS was affected in the RhNiTi by the MIPaste ($p < 0.05$, $\eta^2 = 0.223$). The loading and unloading YS of the NNiTi was higher under the influence of Elmex, when compared to Mirafluor and MIPaste ($p < 0.05$, $\eta^2 = 0.265$).

Unloading slope characteristics (average plateau force, average plateau length, the percentage of useful constant force during unloading)

The NNiTi wire was least affected by exposure to all experimental conditions, showing a significantly higher average plateau force after immersion to Elmex (Figure 3, $p < 0.05$, $\eta^2 = 0.221$).

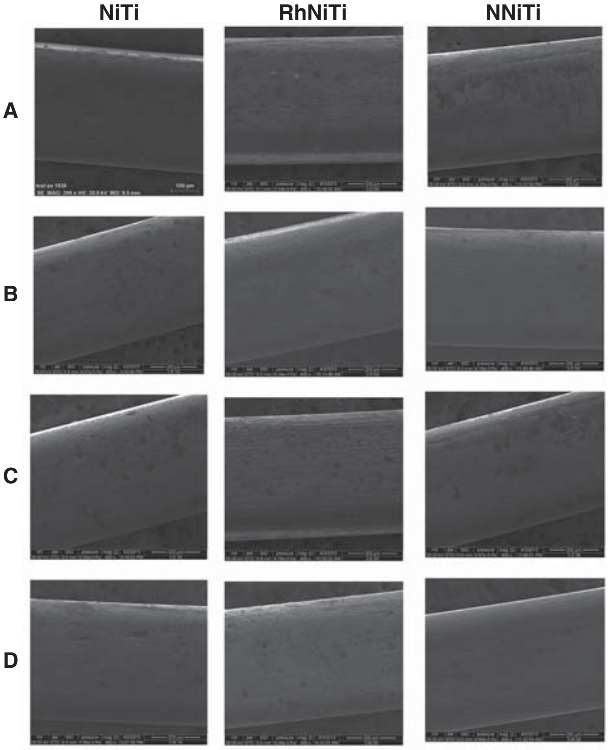

Figure 5. Microscopic observation with ×400 magnification of uncoated (NiTi; left column), rhodium-coated (RhNiTi; middle column) and nitrified (NNiTi; right column) nickel-titanium wire after immersion to dH_20 (A), Mirafluor (B), MIPaste (C) and Elmex (D).

The RhNiTi wire showed higher average plateau length and the percentage of useful constant force during unloading in Mirafluor, when compared to the other tested media ($p < 0.05$, $\eta^2 = 0.260$), whereas the average plateau force was lower after immersion to the MIPaste (Figure 3, $p < 0.05$, $\eta^2 = 0.219$).

Every observed parameter of the unloading slope for the uncoated NiTi wire was affected by all three prophylactic agents (Figure 3, $p < 0.05$, $\eta^2 = 0.504$ for average plateau length, $\eta^2 = 0.345$ for average plateau force and $\eta^2 = 0.435$ for percentage of useful constant force during unloading).

Analysis of forces in distances of 0.5, 1, 1.5, 2, 2.5 and 3 mm during loading and unloading

The NiTi were affected most by the Mirafluor and produced significantly lower forces during both loading and unloading (Figure 4, $p < 0.05$, η^2 in a range between 0.258–0.407), when compared to the other tested media, similarly to the NNiTi wires (Figure 4, $p < 0.05$, η^2 in a range between 0.194–0.262). The RhNiTi wires were affected most by the MIPaste, causing the lowest forces during both loading and unloading (Figure 4, $p < 0.05$, η^2 in a range between 0.196–0.373).

Table II. Chemical composition of the surface and near surface of the uncoated (NiTi), rhodium-coated (RhNiTi) and nitrified (NNiTi) nickel-titanium orthodontic wires with the EDS analysis in $dH_{2}0$, Mirafluor, MIPaste and Elmex.

		Chemical composition, wt %					
Wire	Media	Ni	Ti	Rh	Au	O	Dross
NiTi	$dH_{2}0$-B	52.09	46.44	—	—	0.00	1.47
	$dH_{2}0$-D	29.19	26.90	—	—	0.00	43.92
	Mirafluor-B	48.51	42.62	—	—	7.11	1.75
	Mirafluor-D	36.03	32.08	—	—	25.73	6.16
	MIPaste-B	52.19	47.81	—	—	0.00	0.00
	MIPaste-D	41.85	37.59	—	—	17.66	2.89
	Elmex-B	52.34	46.01	—	—	0.00	1.65
	Elmex-D	39.89	36.47	—	—	19.38	4.26
RhNiTi	$dH_{2}0$-B	20.60	18.64	17.30	23.07	16.56	3.83
	$dH_{2}0$-D	14.74	13.38	11.56	18.87	36.02	5.44
	Mirafluor-B	21.35	19.35	19.91	22.70	14.78	1.91
	Mirafluor-D	6.78	8.41	13.69	16.17	46.68	8.26
	MIPaste-B	12.63	10.67	26.33	13.38	16.21	20.78
	MIPaste-D	15.10	9.77	23.66	11.43	34.73	5.30
	Elmex-B	16.05	14.78	16.01	23.13	24.66	5.37
	Elmex-D	22.67	20.22	22.99	33.31	0.00	0.81
NNiTi	$dH_{2}0$-B	43.86	40.29	—	—	15.13	0.71
	$dH_{2}0$-D	39.79	36.65	—	—	20.46	3.10
	Mirafluor-B	51.59	46.95	—	—	0.00	1.46
	Mirafluor-D	40.02	36.51	—	—	20.57	2.90
	MIPaste-B	46.06	41.25	—	—	12.69	0.00
	MIPaste-D	43.54	39.64	—	—	15.25	1.57
	Elmex-B	44.32	39.48	—	—	15.09	1.10
	Elmex-D	37.32	33.15	—	—	25.06	4.48

Analysis in the bright spots is marked (-B), in dark spots marked (-D).

Surface roughness

The rhodium-coated wire showed a tendency to the higher surface roughness, when compared to the other wires tested (Table I). A significant difference was observed only for RhNiTi wire after immersion to the MI Paste ($p < 0.001$; $\eta^2 = 0.761$).

Microscopic observations

Microscopic observations (Figure 5) showed surface irregularities in the form of dark corrosion spots after exposure to all tested media, not showing clear differences between various wires and prophylactic agents.

The EDS analysis

Table II shows the average chemical composition (weight percentage), with the differences observed between bright and dark spots on the wire surfaces and more oxides and dross (carbon, sodium, etc.) found in the dark areas. The presence of nickel and titanium was recorded for the both coated wires, indicating the very thin surface layers.

Discussion

Our research showed that deterioration of the working properties is not uniform and proportional neither to the higher fluoride concentration, nor to the lower pH, for all orthodontic NiTi wires. Various coatings on NiTi wires can change response of the wire to the same fluoride agent and various fluoride formulations affect the wires differently. Previous findings on fluoride induced corrosion of NiTi wires [25–27] did not take into account the chemical formulations of various fluoride products on the market and the uprising variety in materials used in the making of orthodontic wires. The coatings on as-received wires were shown to be very thin and unevenly distributed throughout the surface [18,19] and responding differently to corrosion in artificial saliva. The present study revealed that the form of fluoride had more influence on observed changes than the total amount of the fluoride in a specific agent. Significant decrease in stiffness and yield strength of the uncoated wires was caused by Mirafluor and MiPaste, the two prophylactic agents with lower concentrations of fluoride (2× lower fluorides content for Mirafluor, and 14× lower fluorides content for MiPaste, when compared to Elmex). Amine fluorides exhibited less corrosion potential, when compared to the inorganic NaF. Also, the pH value of the remedies was not deciding element for the observed changes (e.g. Mirafluor and MiPaste were on the opposite ends of the pH scale, yet, both of them had substantial impact on the wires). The additional content in the preventive agents should also be considered in the modification of the corrosion processes. Despite its high pH and low fluoride content, MiPaste caused significant changes, probably because of the CPP-ACP formation, which transforms to $CaCO_3$ with CO_2 from the air (or dental plaque within the oral cavity), which promotes corrosion [29].

For further analysis of the working properties of the wires, the influence of various prophylactic agents on the unloading slope characteristics was recorded. Average plateau length defines the duration of the light continuous spring-back forces and the NiTi wire exhibited significant shortening of this segment in all experimental media, which indeed means weakening of the wire's working property. On the contrary, for the RhNiTi wire, prolongation of the unloading horizontal segment was observed after immersion to the Mirafluor, thus prolongs the effective working time in the mouth. The duration of the working time for the NNiTi was unaffected by immersion to neither control nor fluoride-containing media.

The average plateau force in NiTi was affected by MiPaste and Mirafluor, in the RhNiTi by the MiPaste and in the NNiTi wire by the Mirafluor, contributing to the poorer performance of the wires.

Exposure of uncoated NiTi to prophylactic agents lowered the percentage of useful constant force in comparison dH_2O, exhibiting the deterioration of the wire's spring-back potential. In the RhNiTi, deterioration was recorded in MiPaste and Elmex groups, while the NNiTi was least affected in useable constant force by exposure to any media.

The forces in the NiTi and NNiTi were lowered by MiPaste and Mirafluor and in the RhNiTi by the MiPaste, further contributing to the degradation of wires' working properties.

Single influence of the tested prophylactic agents explains in total between 19–41% of the variability of the influence on the working properties of the wires.

The surface roughness parameters are nowadays more often measured by means of the non-invasive optical techniques [30], yet our measurement showed good consistency and the results were comparable to the findings from previous studies, which used similar materials [12,18]. The highest R_a measured for the RhNiTi could be attributed partly to the unevenness of the coating, observed earlier [12,18,19], yet a large proportion of the change in R_a was attributed to the prophylactic agent (76%). Increase in roughness induced by the MiPaste was compliant with earlier in the text observed deterioration of the mechanical properties, also caused by the MiPaste in the RhNiTi wires.

The deterioration of the working properties of the wires after exposure to adjuvant remedies for the prevention of the WSL could be reduced by choosing remedies accordingly to the wires surface composition. The nitride coating protects best the wire's working properties caused by immersion to the fluoride-containing prophylactic agents, followed by the rhodium coating, leaving the uncoated NiTi wire the least protected. Contrary to the NiTi and NNiTi wires, the Mirafluor had a positive effect on the RhNiTi's working properties. Furthermore, the uncoated NiTi wires lose less working force when combined with Elmex; the RhNiTi improve their working properties with Mirafluor and deteriorate when combined with the MiPaste; the NNiTi wire deteriorates least in combination with the Elmex.

The corrosion of the NiTi wires with various coatings is not proportional to the high fluoride content and the low pH value of the prophylactic remedies; rather, it is the result of the chemical reactions between different prophylactic formulations and materials from the wires' coating.

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Declaration of interest: The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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