

## Effect of Fluoride Released from Fluoride-containing Dental Restoratives on NiTi Orthodontic Wires

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Received June 28, 2007/Accepted September 4, 2007

The present study investigated the effect of fluoride released from dental restoratives on orthodontic NiTi wires. Five different restoratives (four fluoride-containing and one non-fluoride-containing) and four different NiTi wires were examined in this study. The pH of artificial saliva (AS) was adjusted to 2.5 and 6. Content of released fluoride was determined daily for 10 days. The morphology of wires was observed using a scanning electron microscope. After immersion for 10 days, the initial microhardness of the wires decreased by 0.3–5.6% depending on the test solution. Dyract AP (DA) and F2000 (F2) (compomers) released significantly more fluoride than the other resin products (composite resins) regardless of the test solution. In pH 2.5 solution, both DA and F2 released 40–45 ppm/day fluoride for five to six days. As for the wires in contact, they did not show any visible modification in surface morphology. Therefore, despite the released fluoride, wires in contact with the fluoride-containing restoratives were not damaged regardless of the pH value of test solution.

Keywords: Fluoride, Composite resins, NiTi wires

### INTRODUCTION

For purposes of oral hygiene and caries prevention, fluoride-containing products such as toothpastes, dental gels, and rinses which contain fluoride at a level of 100–10000 ppm are commonly in use at home. In addition to these over-the-counter (OTC) products, many fluoride-containing dental restorative materials such as glass ionomer cements, compomers (polyacid-modified composite resins), and composite resins are widely in use in dentistry. These restorative materials are non-aqueous systems that cure by free radical photopolymerization of monomers. They also contain fluoride in forms of inorganic salts, leachable glasses, or organic fluoride. In an aqueous oral environment, there is an initial high burst of fluoride release and then in a steady diffusion from the bulk<sup>1–5</sup>.

Fluoride is present in the oral fluids and in plaque on the tooth surface. Fluoride also has a bactericidal effect by diffusing into the oral bacteria as hydrogen fluoride (HF) molecules when plaque is acidified<sup>6</sup>. This is because some oral bacteria such as *S. mutans* and *L. Casei* on the film of dental plaque produce acids when they metabolize fermentable carbohydrates<sup>7</sup>. The pH of human saliva generally ranges from 6 to 8<sup>8</sup>. This range of pH can change from 2 to 11 depending on the foods and beverages consumed<sup>9</sup>. Locally, acids produced by oral bacteria can affect the pH range.

NiTi alloys are stoichiometric compounds of 55 wt% Ni and 45 wt% Ti. These near- equiatomic NiTi alloys have many excellent properties such as adequate springback, low stiffness, superelasticity,

and shape memory which are essential for orthodontic purposes<sup>10–13</sup>. NiTi alloys also have excellent biocompatibility with living tissue and corrosion resistance in various simulated body fluids and NaCl solutions<sup>14–16</sup>. These properties originate from the spontaneously formed oxide passivation layer. However, NiTi alloys have shown an increased corrosion rate in solutions containing chloride ions such as HCl and FeCl<sub>3</sub><sup>12</sup>. Additionally, titanium and NiTi alloys lost corrosion resistance in solutions containing fluoride<sup>17–21</sup>. Furthermore, allergic reactions have been reported after insertion of NiTi orthodontic wires<sup>22,23</sup>.

Due to the complex oral environment in the presence of fluoride released from fluoride-containing dental restoratives, NiTi alloys can confront complex situations. The purpose of the present study, therefore, was to investigate the effect of fluoride released from fluoride-containing dental restoratives on NiTi orthodontic wires under acidic artificial saliva conditions.

### MATERIALS AND METHODS

#### *Specimens and artificial saliva*

For this study, five different fluoride-containing dental restoratives (Surefil (SF), Tetric Ceram (TC), Dyract AP (DA), F2000 (F2), and Z250) and four different orthodontic wires (Neo Sentalloy (NS), Nitinol SE (SE), Ni-Ti (NT), and Copper Ni-Ti (CU)) were used. Their characteristics are listed in Tables 1 and 2 respectively. Z250 was chosen as a reference material because it did not contain fluoride. The composition of artificial saliva (AS) prepared for this study was KSCN (0.517 g/L), NaHCO<sub>3</sub> (1.253 g/L), KCl

Table 1 Characteristics of the materials tested in this study

Code	Composition	Filler type	Filler (wt%)*	Batch	Company
SF	Urethane modified Bis-GMA	Ba-Al-F-borosilicate glass, silica	82	020227	Dentsply/Detrey
TC	Bis-GMA, UDMA, TEGDMA	Ba-Al-F-silicateglass, Ba glass, YbF <sub>3</sub>	78	MF542	Vivadent
DA	TCB, UDMA	Sr-F-silicate glass, SrF <sub>2</sub>	73	03060 01925	Dentsply/Detrey
F2	CDMA, GDMA	Al-F-silicate glass	84	200601	3M ESPE
Z250	Bis-GMA, UDMA, Bis-EMA	Zirconia, silica	82	4LNJ	3M ESPE

SF: Surefil, TC: Tetric Ceram, DA: Dyract AP, F2: F2000

\*: According to the manufacturers

Table 2 Compositions of the as-received wires tested in this study

Code	Composition	Size (mm <sup>2</sup> )	Company
NS	50.7%Ni, 49.3%Ti (wt%)	0.46×0.64	GAC
	45.6%Ni, 54.4%Ti (at%)		International
SE	Not known	0.46×0.64	3M
NT	54.9%Ni, 44.9%Ti, 0.2%Cr (wt%)	0.46×0.64	Ormco
	49.8%Ni, 50.0%Ti, 0.2%Cr (at%)		
CU	49.1%Ni, 45.7%Ti, 0.2%Cr, 5%Cu (wt%)	0.48×0.64	Ormco
	44.6%Ni, 50.9%Ti, 0.2%Cr, 4.2%Cu (at%)		

NS: Neo Sentalloy, SE: Nitinol SE, NT: Ni-Ti, CU: Copper Ni-Ti

(1.471 g/L), NaH<sub>2</sub>PO<sub>4</sub>H<sub>2</sub>O (0.188 g/L), and lactic acid (0.90 g/L). The pH of artificial saliva was adjusted to 2.5 and 6 by adding more lactic acid than that of the assigned content.

#### Microhardness measurement

To measure the surface microhardness of the wires, a Vickers hardness tester (MVK-H1, Akashi Co., Japan) was used. The straight part of the arch wire was cut, polished using SiC paper (#1200) and alumina paste (1 μm) to get a fine surface, and ultrasonicated using distilled water. The polished wires were then cut into 5-mm-long pieces.

Resin specimens were prepared by placing the resin into an acrylic ring mold (7 mm in diameter and 2 mm in depth) and covering it with a thin glass slide. Specimens were light-cured (CuringLight XL3000, 3M, St. Paul, USA) for 40 seconds with 700 mW/cm<sup>2</sup> light intensity, as measured using a radiometer. Polymerized specimens were kept in a dark container for 24 hours prior to measurement taking.

After 24 hours, microhardness of the wires was

measured using a hardness tester before immersion. Microindentations (n=15) were made on the surface using a 300-gf load for a dwell time of 10 seconds. After which, the measured surface was made to be in contact with the resin specimen surface and immersed in the artificial saliva for 10 days. The second measurement was done on day 10 of immersion in each designated solution near the previously measured position to maintain consistency. Test solutions were maintained at 37°C throughout the experiments and replaced every two days.

#### Fluoride measurement

To measure the fluoride content, specimens were prepared as discussed above, light-cured, aged for 24 hours (n=15 for each resin product: five for distilled water (pH 7.8), five for artificial saliva of pH 6, and five for artificial saliva of pH 2.5), and then placed in plastic test tubes containing 1 ml of each test solution. Concentrations of the fluoride released from the specimens were measured daily for a total of 10 days using a fluoride-specific electrode (model 96-09BN, Thermo Electron Corp., Beverly, USA) attached to an ion meter (model 720A+, Thermo Electron Corp., Beverly, USA). The instrument was calibrated daily with three standard fluoride solutions containing 1, 5, and 10 ppm F<sup>-</sup>. Before measurement, 1 ml of TISAB II was added to each solution and fully shaken. TISAB is usually added to provide constant background ionic strength, decomplex fluoride, and adjust solution pH. The instrument gave a direct readout of the concentration (ppm) of each solution on the display panel. After measurement, each specimen was cleaned with distilled water and the solution in the test tube was replaced with a new one.

#### Surface morphology observation

To observe the surface morphology of wires, wires were prepared following the same procedures described in the section on microhardness measure-

ment. The polished surface of the wire was made to be in contact with the resin surface and then immersed in the designated test solution for 10 days. Test solutions were kept in a 37°C chamber and replaced every two days. After 10 days, wires were removed from the solution and cleaned. Surface observation was performed using a scanning electron microscope (SEM) (S-4200, Hitachi Co., Tokyo, Japan).

*Statistical analysis*

Results of fluoride content measurements (for different resin products and pH values) were analyzed by two-way ANOVA. This was followed by Tukey's multiple comparison test. All results were analyzed at a significance level of 5%.

RESULTS

*Microhardness*

Tables 3 and 4 show the microhardness values of wires immersed in artificial saliva of different

Table 3 Microhardness (HV) values of NS and SE during immersion in artificial saliva

	pH	NS		SE	
		0	10 Days	0 Days	10 Days
Z250	6	278.6±5.0	263.8±4.4	398.6±13.1	392.5±5.1
	2.5	278.8±5.2	267.2±5.6	398.2±8.7	395.5±5.5
SF	6	281.8±6.2	265.9±4.9	399.6±7.7	389.2±7.8
	2.5	277.4±3.8	266.2±6.4	409.5±8.1	400.5±9.5
TC	6	274.7±8.8	268.5±7.6	393.5±27.3	383.5±7.7
	2.5	276.7±7.4	261.3±7.9	398.6±13.8	387.2±9.3
DA	6	278.5±4.2	268.3±5.2	402.6±7.6	389.9±7.0
	2.5	281.9±4.7	268.7±6.8	399.5±11.1	397.0±9.8
F2	6	280.3±5.4	265.1±3.6	402.8±7.8	386.4±5.8
	2.5	276.8±4.6	270.9±5.4	402.5±7.1	390.9±8.8

Table 4 Microhardness (HV) values of NT and CU during immersion in artificial saliva

	pH	NS		SE	
		0	10 Days	0 Days	10 Days
Z250	6	334.0±5.4	326.7±8.4	300.2±11.6	294.6±9.1
	2.5	333.2±8.3	321.4±6.0	299.6±9.6	296.6±8.0
SF	6	329.9±5.4	328.3±8.3	303.7±8.3	291.8±7.1
	2.5	328.3±5.4	327.3±4.6	306.8±6.9	292.8±5.2
TC	6	338.0±6.2	329.2±7.8	301.9±11.2	297.7±7.4
	2.5	337.7±4.5	328.2±5.1	300.8±9.1	295.4±3.9
DA	6	327.2±9.7	323.9±5.7	306.1±13.1	293.5±8.6
	2.5	327.9±7.0	324.5±5.6	302.6±8.3	295.7±5.0
F2	6	330.8±5.9	322.1±7.0	306.4±5.8	290.6±5.1
	2.5	330.6±5.1	328.2±7.2	308.6±4.1	293.5±5.5

pH values for 10 days after being in contact with the resin specimens. Before immersion, SE and NS showed the highest (approximately 394–410 HV) and lowest (approximately 275–282 HV) values respectively. After immersion for 10 days, the original microhardness of each wire decreased by approximately 0.3–5.6%, depending on the contacted resin product and the pH value of the artificial saliva. NS and NT showed the greatest (2.1–

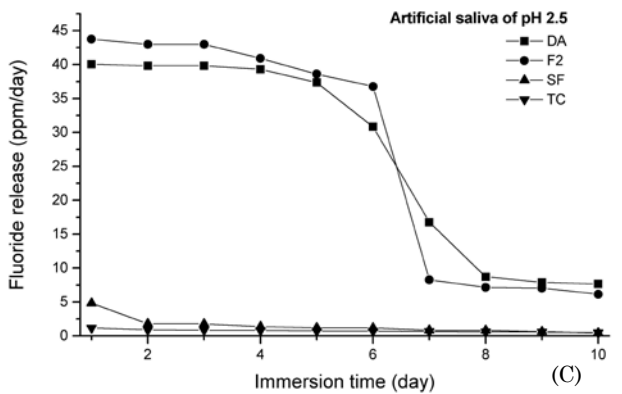
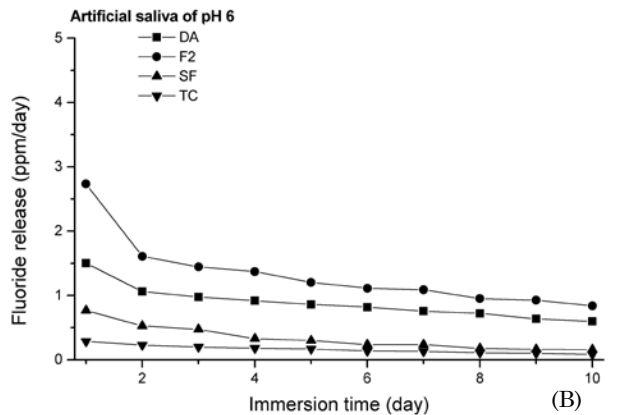
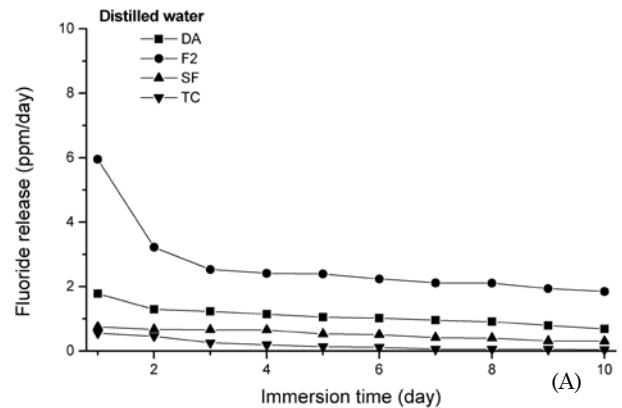


Fig. 1 Daily release of fluoride from specimens immersed in distilled water (A), artificial saliva of pH 6 (B) and pH 2.5 (C).

5.6%) and least (0.3–3.5%) microhardness decrease after immersion for 10 days respectively. However, there was no specific trend in the decrease of microhardness with respect to the pH value and contacted resin product.

#### Fluoride concentration

Figure 1 shows the daily release of fluoride from the resin products which were immersed in different solutions for 10 days. DA and F2 (compomers)

released much more fluoride than SF and TC (composite resins) regardless of the immersion solution. In the case of AS of pH 2.5, both DA and F2 released a similar amount, but at least eight times more fluoride than SF and TC for five days during immersion. After which, the release dropped suddenly to the level of 10 ppm.

Table 5 shows the concentrations (ppm) of the accumulated fluoride released from the resin products for 10 days in different solutions. As shown

Table 5 Accumulated fluoride (ppm) in different solutions for 10 days

	SF <sup>1</sup>	TC <sup>1</sup>	DA <sup>2</sup>	F2 <sup>2</sup>	p-values
Dw <sup>A</sup>	3.37±0.58	1.25±0.27	10.87±1.10	26.75±4.50	$\alpha < 0.001$
AS_pH 6 <sup>A</sup>	3.64±0.56	1.63±0.23	8.85±0.94	13.28±1.66	$\beta < 0.001$
AS_pH 2.5 <sup>B</sup>	14.90±2.20	7.47±1.10	268.26±8.19	274.68±14.33	

Dw: distilled water; AS: artificial saliva

\*Statistically significant difference within rows is shown by superscript letters<sup>A, B</sup>, within columns by superscript numbers<sup>1, 2</sup>. Same letters or numbers are not significantly different ( $p < 0.05$ ).

$\alpha$ : resin product,  $\beta$ : pH value

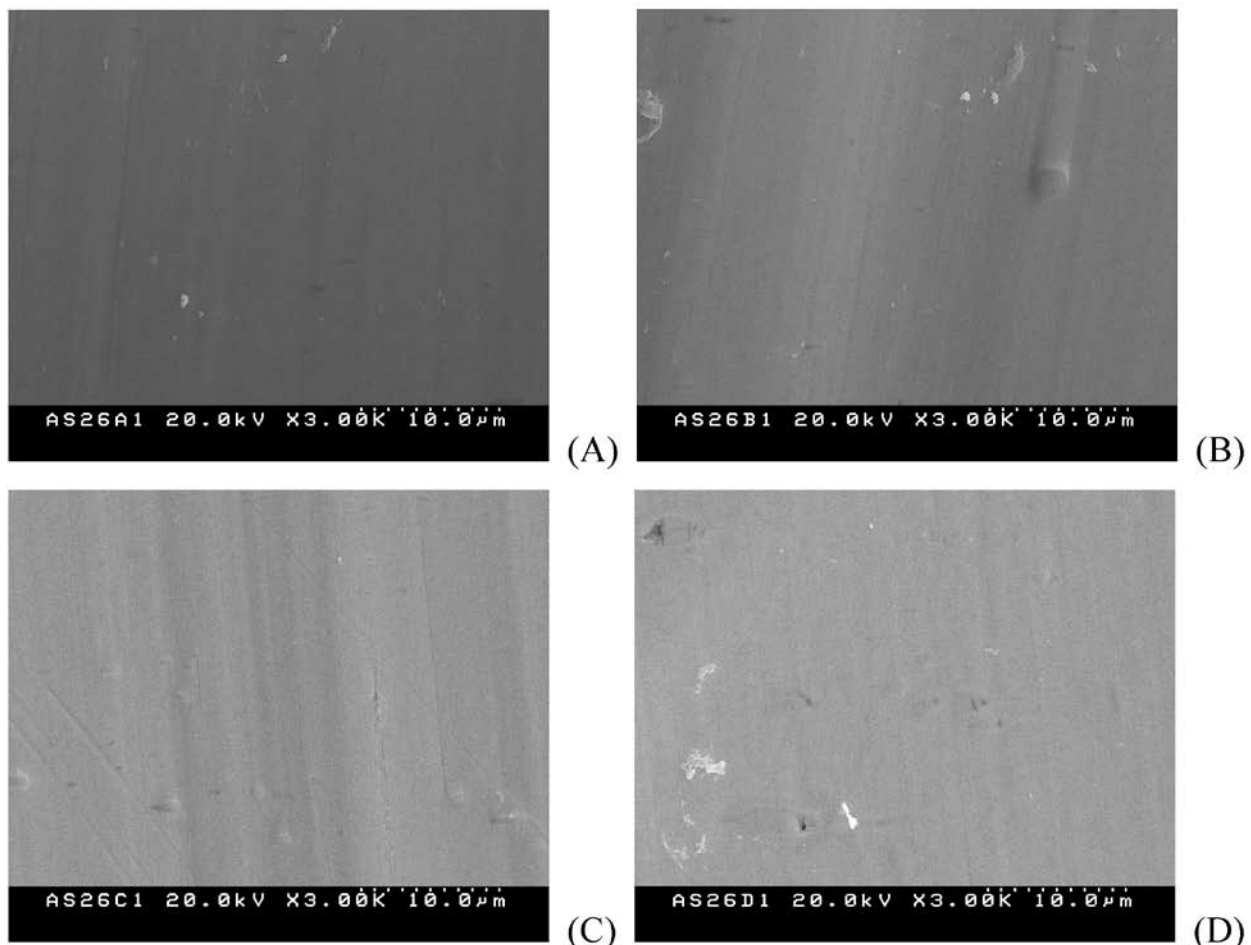


Fig. 2 Surface morphologies of wires in contact with F2 and immersed in artificial saliva of pH 2.5. Wires in contact were NS (A), SE (B), NT (C), and CU (D).

in Fig. 1, both DA and F2 released significantly more fluoride than SF and TC ( $p < 0.05$ ). In pH 2.5 solution, the release of fluoride from DA and F2 was several times greater than in distilled water and pH 6 solution.

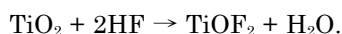
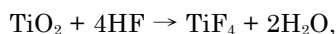
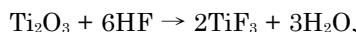
#### Surface morphology

Figure 2 shows the surface morphologies of wires after being in contact with F2 for 10 days in AS of pH 2.5. According to Table 4, F2 released the greatest amount of fluoride among the tested resin products. Nonetheless, the wires did not show any surface modification. Likewise, the same situation occurred in the other immersion solutions (distilled water and AS of pH 6), although all the relevant SEM pictures were not provided here.

## DISCUSSION

The purpose of using fluoride-containing OTC products at home and in dental restorative materials in dental clinics is to inhibit the growth of oral bacteria and caries. OTC products contain fluoride at a level of 100–10,000 ppm. In distilled water, most compomers and composite resins initially release a low level of fluoride (less than  $10 \mu\text{g}/\text{cm}^2/\text{day}$ ), whereby this level of release is sustained for a long time in distilled water<sup>3</sup>. The resin products tested in our study also released a similar level of fluoride in distilled water. However, in AS of pH 2.5, fluoride release was more than 40 ppm for five to six days.

Several species of oral bacteria reside on the film of dental plaque. Amongst which are *S. mutans* and *L. Casei*, such that when they metabolize fermentable carbohydrates, they produce lactic, acetic, and propionic acids<sup>7</sup>. If there is a small quantity of fluoride in the solution, hydrogen atoms in these acids readily dissociate and form hydrogen fluoride (HF) molecules. Formed HF molecules inactivate oral bacteria and inhibit the occurrence of caries. Additionally, HF can react with the titanium oxide, dissolving the protective oxide layer by forming titanium fluoride or titanium oxide fluoride on the surface<sup>18,19</sup>:



Titanium and titanium alloys have excellent chemical stability and exhibit corrosion resistance in various test solutions such as artificial saliva, Ringer's solution, and physiological saline solution<sup>14-16</sup>. However, such corrosion resistance was lost in solutions which contain fluoride with varying pH

values<sup>17</sup>. The presence of fluoride in a neutral solution (10,000 ppm F<sup>-</sup> at pH 6.75) did not inhibit the formation of a protective layer, but the protective oxide layer degraded in acidic fluoride solutions<sup>20</sup>. For example, titanium alloys were not tarnished in a 30-ppm NaF solution, whereas titanium was not corrosion-resistant in a solution containing 500 ppm of fluoride at pH 4<sup>17,21,24</sup>.

The concentration limit of HF at which the corrosion resistance of titanium could be maintained was 21 ppm<sup>21</sup>. Such an HF concentration can be obtained from a 0.05% NaF solution of pH 4.0 or 0.1% NaF solution of pH 4.3. In our study, solution pH was adjusted using phosphoric acid. It should be borne in mind that the corrosion resistance of titanium is lost in a solution containing more than 30 ppm of HF<sup>21</sup>. Further, HF concentration limit can be changed according to the acid added to adjust the pH value, because each acid has a different acidity.

According to our previous study, wires immersed in acidic NaF solutions were full of micropores and the severity depended on the concentration of HF<sup>25</sup>. However, in the present study, no surface modification was found regardless of wire type and contacting resin product. No modification implied that the concentration of HF formed in the present study might not be over 20–30 ppm.

Maximum daily release of fluoride from DA and F2 in AS of pH 2.5 was approximately 40–45 ppm. This amount of fluoride release was approximately equivalent to the content of fluoride in a 0.01% NaF solution. However, since fluoride was gradually released from the resin product in the test solution, it might require time to reach the maximum (detected) fluoride concentration. To obtain an HF concentration of 21 ppm, 0.1% NaF of pH 4.3 is needed or 0.05% NaF of pH 4.0. In the case of 0.01% NaF, a solution of near pH 2.5 would probably be needed by rough estimation<sup>21</sup>.

In the referred studies thus far, solution pH was adjusted by mixing acid solution (phosphoric acid or acetic acid) into the NaF solution at a fixed concentration. This meant that hydrogen atoms were fully and continuously supplied until an expected pH value was reached. In the present study, however, it should be noted that the pH of AS was fixed — which meant that the available hydrogen atoms were fixed. Therefore, the pH of AS could be increased only when fluoride was released from the resin product and the formation of HF inactivated.

The microhardness of the wires tested had no specific trend in their changes — whether they be in contact with fluoride-containing resin product or not. The decrease in microhardness might be attributable to the degradation of the surface by the acidic solutions. In the present study, HF concentration was not measured when the resin product was

immersed in AS solutions of pH 2.5 and 6. Nevertheless, no surface modification and decrease in microhardness could be related to the very low concentration or complete absence of HF in the solution. Otherwise, the surface should show some pores or some visible modification. According to our previous study, wires immersed in HF-formed (greater than 10 ppm) acidic fluoride solution showed enhanced microhardness and pores after immersion<sup>25</sup>.

### CONCLUSIONS

Fluoride released from fluoride-containing resin products at a level of 40–45 ppm per day for some days did not change the microhardness nor surface morphology of NiTi wires immersed in AS of pH 2.5 and 6 for 10 days. Solution of pH 2.5 represented the worst condition in the current study. Nonetheless, it seemed that the amount of HF formed — if it were formed — was not enough to corrode the wires tested. Based on the results obtained, it thus seemed that further immersion of more than 10 days is needed to elucidate the long-term effect of acidic artificial saliva on NiTi wires.

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