Effect of Fluoride Prophylactic Agents on the Mechanical Properties of Nickel-Titanium Wires: An in vitro Study

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ABSTRACT

Titanium-based alloys have high corrosion resistance because they form a thin, stable oxide layer. Nevertheless, fluoride prophylactic agents can cause corrosion and associated discoloration of titanium-based orthodontic wires.

Objective: The purpose of this investigation was to study the effects of fluoride prophylactic agents on the mechanical properties of nickel-titanium (NiTi) and copper-nickel-titanium (Cu-NiTi) orthodontic archwires.

Materials and methods: Preformed rectangular NiTi and Cu-NiTi wires were immersed in either an acidulated fluoride agent, a neutral fluoride agent, or distilled water (control) for 1.5 hours at 37°C. After immersion, the loading and unloading elastic modulus and yield strength of the wires were measured with a 3-point bend test in a water bath at 37°C, in accordance with the criteria in the current American National Standard/American Dental Association Specification No. 32 for Orthodontic Wires (2000). Scanning electron microscopy was also used to characterize the effects of the fluoride treatment on the wire topography.

Results: The results showed that unloading mechanical properties of both the NiTi orthodontic wires were significantly decreased after exposure to both fluoride agents [one-way analysis of variance (ANOVA) and Dunnett’s post-hoc, \( \alpha = 0.05 \)]; corrosive changes in surface topography were observed for both wires, with Phos-Flur gel creating more detrimental effects.

Conclusion: The results suggest that using topical fluoride agents with NiTi wire could decrease the functional unloading mechanical properties of the wire and contribute to prolonged orthodontic treatment.

Keywords: Corrosion, NiTi, Fluorides, Modulus of elasticity, Yield strength, Instron.


INTRODUCTION

The direct application of orthodontic attachments to tooth surface evolved when Buonocore \(^1\) introduced the acid etch technique in 1955. Direct bonding orthodontic adhesives, such as composites, possess a polymeric matrix that host a variety of microorganisms acting alone or in consortia. Although most microbes are specific to the oral environment, others are ‘opportunistic’. Their accumulation leads to weakening of the bond strength. \(^2\) This led to the evolution of fluorides which are used as a preventive regime during the course of orthodontic treatment. \(^3\)

The nickel-titanium alloys introduced in the 1970s showed some remarkable properties of superelasticity and shape memory, although these properties were not exploited clinically at that time. \(^4\) The wires had limited formability, but were still used in traditional edgewise appliance. Nickel-titanium (NiTi) orthodontic wires, allow clinicians to increase their efficiency by decreasing the number of wire changes needed for each patient. A full-size archwire can be engaged during the early stage of orthodontic treatment and continued for up to 12 months, allowing longer periods between visits. \(^5\) The unique properties of NiTi-based wires are attributed to phase transformation of the crystal structure from austenitic to martensitic form. \(^4\) This transformation occurs as a result of temperature change or the application and removal of stress. When the wire is loaded, an anatomic shift occurs from the austenitic body-centered cubic lattice structure through an intermediate rhomboïdal phase (R-phase) to the martensitic hexagonal close-packed lattice structure. Upon unloading, the martensitic wire will return to the austenitic lattice, passing again through the R-phase. \(^5\)

A lot of research is done on the bonding materials, bond strength and efficacy of the nitinol wires. But the deleterious effects of such materials and fluorides on orthodontic wires have been least documented.
MATERIALS AND METHODS

Source of Data

The rectangular orthodontic wires were NiTi preformed archwires (54% titanium, 45% nickel, <1% others). These wires were chosen because of their popularity of use. The wires were obtained from the 3M Company. The fluoride agents obtained were Phos-Flur gel (1.1% sodium fluoride acidulated phosphate, APF, 0.5% w/v fluoride, pH = 5.1; Colgate Oral Pharmaceuticals) and Prevident 5000 (1.1% sodium fluoride neutral agent, 0.5% w/v fluoride, pH = 7; Colgate Oral Pharmaceuticals). These fluoride agents were chosen because of their availability, similarity in the method of application and fluoride ion concentrations. However, there is a variation in pH value of both these fluoride agents.

Method of Collection of Data

Each wire specimen of 0.42 × 0.62 × 25 mm, was cut from the straight portion (posterior end) of the preformed archwire and was incubated at 37°C in individual 10 ml plastic vials with either 2 ml of one of the fluoride solutions or distilled de-ionized water (DH2O) (control treatment) for 90 minutes. This exposure time is equivalent to 3 months of 1 minute daily topical fluoride applications. Based on preliminary data and power analysis 12 wire specimens for each experimental condition (3 conditions × 12 wires of each type) were considered to be adequate in order to meet the constraints of $\alpha = 0.05$ and power = 80.

The specimens were removed from their respective solutions, rinsed with DH2O, and placed in new, clean, individually coded vials before mechanical testing. Mechanical testing was based on current American National Standard/American Dental Association Specification No. 32 for Orthodontic Wires (2000). Randomly selected specimens were tested by 3-point bend test on Instron universal testing machine. The configuration of the 3-point fixture was a support span of 12 mm and 0.05 to 0.13 mm radii of each support and the striker. As indicated in the specification, the specimens were submerged and tested in a heated DH2O bath (37 ± 1°C) to simulate the aqueous oral environment. Each specimen was loaded to a deflection of 3.1 mm and then unloaded to zero deflection at a crosshead speed of 1 mm/minute. Load in Newtons (N) and deflection in millimeters (mm) were collected every 100 ms for both loading and unloading of each specimen.

Statistical Analysis

The mechanical property data was analyzed by using a one-way analysis of variance (ANOVA) at 5% level of significance ($\alpha = 0.05$) for both the loading and unloading modulus of elasticity and yield strength for each wire to examine whether any significant differences among the three groups existed. Further, wherever significant results were found through analysis of variance, Dunnett post-hoc test was used to compare the control group with the treatment groups.

RESULTS

The analyzed results are presented in Tables 1 and 2. Analysis was carried out through Fisher’s one-way analysis of variance (ANOVA). It was observed that all the three groups including the control were observed to be the same in case of loading whereas there was a significant difference among them, both with the modulus of elasticity as well as yield strength related to the unloading properties. Hence, a Dunnett’s post-hoc test was carried out which suggested that control group had produced significant difference in the results with Phos-Flur gel and Prevident inferring that both fluoride gels decreased the unloading modulus in NiTi as well as for Cu-NiTi wires.

Representative SEM images of NiTi wires were exposed to DH2O (Fig. 1), Prevident (Fig. 2) and Phos-Flur gel (Fig. 3). The wire surfaces exposed to DH2O appeared to have a numerous dark areas which could be due to the coating of by products on the archwires during the manufacturing process that disappeared after fluoride application. After application of Prevident solution, the wire surface showed a mottled, pitted appearance in addition to dark smudge areas. There was evidence of increased bright white spots, which appeared to be inclusions in the wire that were revealed by the action of fluoride agent. These effects of the fluoride on the NiTi surfaces are demonstrated even more conspicuously in the Phos-Flur specimen with the surface showing globular, pitted, elongated defects, with even greater exposure of white inclusions, indicating a more severe change in the wire surface topography as compared with the control.

Table 1: Loading properties of NiTi and Cu-NiTi wires after exposure DH2O (control T1), Phos-Flur gel (T2) and Prevident (T3)

<table>
<thead>
<tr>
<th>Wire</th>
<th>Treatment</th>
<th>Modulus of Elasticity (Gpa)</th>
<th>Yield Strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>NiTi</td>
<td>DH2O control T1</td>
<td>64.80 (12)</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>Phos-Flur gel T2</td>
<td>65.40 (12)</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>Prevident T3</td>
<td>64.30 (12)</td>
<td>2.21</td>
</tr>
<tr>
<td>Cu-NiTi</td>
<td>DH2O control T1</td>
<td>59.38 (12)</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td>Phos-Flur gel T2</td>
<td>59.63 (12)</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>Prevident T3</td>
<td>58.13 (12)</td>
<td>2.75</td>
</tr>
</tbody>
</table>
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Table 2: Unloading properties of NiTi and Cu-NiTi wires after exposure to DH2O (control T1), Phos-Flur gel (T2) and Prevident (T3)

<table>
<thead>
<tr>
<th>Wire</th>
<th>Treatment</th>
<th>Modulus of elasticity (Gpa)</th>
<th>Yield strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>NiTi</td>
<td>DH2O control T1</td>
<td>64.70</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>Phos-Flur gel T2</td>
<td>60.40</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>Prevident T3</td>
<td>62.30</td>
<td>2.16</td>
</tr>
<tr>
<td>Cu-NiTi</td>
<td>DH2O control T1</td>
<td>59.50</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>Phos-Flur gel T2</td>
<td>58.12</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>Prevident T3</td>
<td>52.63</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Fig. 1: SEM specimen depicting treatment with DH2O
Fig. 2: SEM specimen depicting treatment with Prevident gel
Fig. 3: SEM specimen depicting treatment with Phos-Flur gel

DISCUSSION

Orthodontic brackets are predominantly bonded to the teeth by composite resins. Research has shown that plaque accumulates more readily on composite resin adhesive than on enamel. Studies have reported that measurable demineralization occurs around orthodontic bands and brackets as early as in the first month of treatment. This led to the use of various plaque control measures.7 Studies have shown that only 2% of patients on a fluoride regimen developed white spot lesions whereas 58% of patients who did not practice any fluoride regimen developed lesions.8 Studies have also shown that when bacterial species metabolize fermentable carbohydrates in oral environment, they produce lactic, acetic and propionic acids. A small quantity of fluoride in the solution causes hydrogen atoms in these acids to readily dissociate and form hydrogen fluoride 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 oxyfluoride on the surface.9

Ideally arch wires are designed to move teeth with light continuous forces. Such forces may reduce the patient discomfort related to pain and biochemical changes related to tissue hyalinization and undermining resorption.

Studies on the corrosion properties of nitinol wires have seldom been discussed. Nitinol wire has been reported to exhibit
a greater corrosive tendency than stainless steel wires as observed during anodic dissolution.10

Electrolytic or electrochemical corrosion occurs in the oral cavity due to the wet environment. A metal is considered thermodynamically unstable if there is decrease in its energy while changing from a solid state to an ionic form. The direction of energy change is influenced by factors such as the metal itself, surface morphology and phase of the metal, galvanic coupling of dissimilar metals, solution composition, pH and temperature. If the metal is unstable it may undergo corrosion thus releasing metal ions into solution. The surfaces of all the metals react with oxygen to form a surface oxide layer, which inhibits attacking substances such as microbes and chemicals from reaching the metal surface. All metals and alloys that rely on a passive film for corrosion resistance share a common property in that, at sufficiently high potentials the passive layer can be broken down and the metal or alloy will no longer be protected. Metallic materials are non susceptible to corrosion as long as the surface oxide film is intact. But when the breakdown potential of an alloy is reached, the oxide layer dissolves and the onset of surface corrosion and pitting begins.11 This breakdown of the surface oxide layer results in the loss of physical properties of the wire which play a major role in the success of its clinical effectiveness followed by the release of nickel ions resulting in toxicity.12

Embrittlement of hydrogen and fracture susceptibility of titanium-based orthodontic wires in fluoride solutions have been illustrated as a causative factor in corroding the NiTi-based alloys. This is due to diffusion of hydrogen through interstitial sites, dislocations, and grain boundaries reacting with lattice atoms to form titanium hydride. Titanium hydrides have been reported to form a body-centered tetragonal structure which is considered to be the cause for the degradation of the mechanical properties of the alloy.13

Ken’ichi Yokohama14 et al reported that the reason for the ductility loss and the reduction in the tensile strength of the work hardened NiTi alloy in 2.0% APF solution is the brittle layer formation at the peripheral part of the cross-section associated with rapid absorption of hydrogen. This study is in coherence with our study where the ionizable fluoride compounds activate the surface and can cause rapid corrosion by forming hydrofluoric acid leading to embrittlement of titanium-based alloys. Hydrogen absorption and embrittlement of titanium-based alloys after fluoride exposure have been explained by the fact that, although the surface oxide of titanium is known to be highly effective in reducing hydrogen penetration, ionizable fluoride compounds, such as sodium fluoride and hydrogen fluoride, activate the surface and can cause rapid corrosion.4 When titanium-based orthodontic wires are exposed to acidulated topical fluoride agents, hydrofluoric acid (HF) is produced which dissolves the protective oxide layer on the surface of titanium and its alloys.11

Nakagawa et al15 conducted an anodic polarization and immersion tests in NaF solution of various concentrations and pH values. The concentrations of the dissolved Ti in the test solutions were analyzed by inductively coupled plasma mass spectrometry, which is a type of mass spectrometry that is highly sensitive and capable of the determination of a range of metals and severe nonmetals at concentrations below one part in 1012 part per million. It is based on holding together inductively coupled plasma as a method of producing ions with a mass spectrometer as a method of separating and detecting the ions. Their study suggested that the corrosion behavior of titanium is affected not only by the fluoride concentrations but also by the pH. Corrosion resistance of titanium was lost in the 0.1% NaF solution at pH 4.2. The corrosion of titanium is enhanced in an acidic environment because F ion in the solution combines with H+ ions to form HF, even if the NaF concentration is low. The results of their study coincide with our study where the fluoride solution used were of the pH 5.1 and pH 7 and both the acidulated and the neutral fluoride solutions affected the unloading properties of the NiTi wires. The acidic pH of fluoride agents may be the causative factor for the breakdown of the protective titanium oxide layer resulting in fluoride-related corrosion and embrittlement of hydrogen. However, titanium alloy corrosion resistance also decreases with exposure to neutral sodium fluoride solutions when the fluoride concentration is 0.5% or greater. This suggests that fluoride-related alloy effects depends not only on the pH but also on the fluoride concentration of the prophylactic agent.15 This assertion is confirmed from our study; both the acidulated and the neutral 0.5% fluoride agent produced a significant reduction in the NiTi wire unloading mechanical properties. However, the acidulated fluoride agent produced more degradation of the mechanical properties than the neutral agent.

According to the study conducted by Mary J Walker,13 there was no statistical significance in the Cu-NiTi wires in contrast to our study. This has been attributed to the presence of copper in the NiTi alloy, which acts as a relative inhibitor for the production of acids such as HF.14 The studies also suggested that the oxidation peaks obtained in the fluoride solutions for Cu-NiTi wires seem to indicate that certain additives in the solution must be subjected to oxidation-reduction phenomena, thereby modifying the stability of the electrolyte with repercussions in terms of corrosion of the materials.16

Studies by Nicholas Schiff et al17 have shown that Cu-NiTi wires presented the highest risk of corrosion in Elmex mouthwash. Sodium fluoride and its additives could be the reason for the deterioration of the material. The highest concentration of released nickel ions according to their study was found to occur when the wires were coupled with Fe-Cr-Ni bracket.

Toumelin-Chemla et al18 studied the kinetics of ionization of pure and alloyed titanium in various electrolytic media including commercial dental gels containing fluoride ions. They used an electrochemical device called Solea Polaroprocesseur 220T which is a computerized equipment. Corrosion behavior was studied by determination of linear polarization resistance. According to their study, titanium stability in a corrosive
medium resulted from the formation on the surface of a highly protective passivity film, the thickness of which is between 10 and 20 nm. Pure titanium which is very reactive and extremely oxidizable when perfectly bare could develop several oxides of different stoichiometries among which TiO_2 is the most common. Though the passivation layer does not break down even in cases of aggressive media such as HCl or sulfuric acid, titanium gets easily degraded in acid-fluoridated solutions. This phenomenon is interpreted as being the result of incorporation of F-ions in the oxide layer, whose protective properties are then reduced. Though the results of this study are in accordance with our study, the loading and unloading properties of the nickel-titanium wires have not been tested in their study. In our study, both the fluoride solutions affect the NiTi wire unloading properties. This can be of important clinical relevance because the orthodontic tooth movement occurs during the unloading phase shift of the NiTi wires. When titanium-based orthodontic wires are exposed to acidulated topical fluoride agents, it results in production of hydrofluoric acid (HF) which dissolves the protective oxide layer on the surface of titanium and its alloys.

Corrosion of titanium-based orthodontic wires are reported to be caused due to topical fluorides. This suggests that fluoride might also adversely affect the mechanical properties of titanium-based alloys inspite of having high corrosion resistance due to the formation of a thin stable oxide layer as a result of passivation. Corrosion and associated discoloration of titanium-based orthodontic wires caused by fluoride prophylactic agents is a well-known fact. In our study, both the fluoride agents (Prevident and Phos-Flur gel) produced a statistically significant decrease in the unloading properties in terms of their elastic modulus (E) and the yield strength (YS) of the NiTi and Cu-NiTi orthodontic wires.

In only 90 minutes of fluoride exposure, there was a statistically significant decrease in both the unloading E and YS of the NiTi orthodontic wire. This decrease in mechanical properties is a result of fluoride-related hydrogen embrittlement affecting the NiTi wire unloading-related phase shift. The formation of a titanium hydride due to hydrogen penetration in the lattice of the NiTi structure could interfere with the lattice’s ability to undergo the unloading phase shift from the martensitic form to the austenitic form. This phenomenon may account for the statistically significant differences in the unloading properties of the wire.

The decrease in the NiTi wire unloading mechanical properties in this study might not seem large enough to be clinically significant, but these differences occurred after only 90 minutes of fluoride exposure, which would be equivalent to 3 months of a 1 minute daily topical fluoride application. However, in a clinical situation, the exposure time to fluoride would be longer. For example, although the topical fluoride application time is 1 minute, the actual fluoride exposure during each application would be much longer because patients are instructed not to rinse for 30 minutes after the application. In addition, an archwire can often be used for up to 1 year, also increasing the overall fluoride exposure time.

A qualitative SEM analysis of wire surface topography showed that there was increased disclosure of inclusion bodies and pitting that followed the length of the wire. Both pH and fluoride concentrations appear to be important factors related to surface corrosion of titanium-based alloys. Both the acidulated 0.5% fluoride agent and the neutral 0.5% fluoride treatment produced pitting corrosion in the NiTi and Cu-NiTi wires. However, it was observed that the acidulated fluoride agent caused more aggressive surface degradation than the neutral agent, and consequently the change in topography was more pronounced in the Cu-NiTi specimens. This can be attributed to the presence of metallic copper at the alloy/oxide film interface resulting in increased susceptibility to pitting corrosion.

CONCLUSION

The results of this in vitro study indicate that, after exposure to fluoride prophylactic agents, there was a statistically significant decrease of both the loading and unloading mechanical properties of both the types of NiTi wires. This decrease might be clinically relevant because the unloading forces of the wire produce the required orthodontic tooth movement. Therefore, in patients who are using highly concentrated fluoride topical gels in association with NiTi orthodontic wires, the fluoride-related degradation of unloading mechanical properties could contribute to prolonged orthodontic treatment.

The judicious prescription of fluoride gels during orthodontic treatment is likely to lead to very noticeable side effects, which are strongly prejudicial to the durability of the nickel-titanium orthodontic wires. At present, it would be advisable to prescribe these concentrated fluoride gels very carefully. Dental practitioners should take into account the types of wires used during orthodontic treatment when prescribing mouthwashes. There appears to be a need for a new type of mouthwash, containing both fluoride and corrosion inhibitors which can minimize and counteract the corrosion effect in order to maintain the mechanical properties of such wires at the highest level in patients undergoing orthodontic therapy.

REFERENCES