THE EFFECT OF TOPICAL FLUORIDE AGENTS ON COATED NICKEL-TITANIUM ARCHWIRES

A THESIS IN
Oral and Craniofacial Sciences

Presented to the Faculty of the University
of Missouri – Kansas City in partial fulfillment of
the requirements for the degree

MASTER OF SCIENCE

by
KRISTEN SANDER

B.A., Rockhurst University, 2008
D.D.S., University of Missouri – Kansas City, 2013

Kansas City, Missouri
2015

THE EFFECT OF TOPICAL FLUORIDE AGENTS ON COATED NICKEL-TITANIUM ARCHWIRES

Kristen Sander, Candidate for the Master of Science degree

University of Missouri – Kansas City, 2015

ABSTRACT

This study examined the effect of exposure to topical fluoride agents on the mechanical properties and surface characteristics of esthetic coated nickel-titanium archwires. Two types of coated wires were tested: one with a polymer coating and one with a rhodium ion coating. Wires were divided into treatment groups based on type of fluoride exposure: no treatment (DI water), neutral sodium fluoride gel, neutral sodium fluoride rinse, or acidulated phosphate fluoride (APF) gel. A three-point bend test in DI water at 37±1°C was performed on specimens before and after test solution exposure. Unloading forces at 1, 1.5, and 2mm of deflection were reported, along with unloading elastic modulus and yield strength. Three representative specimens from each treatment group along with untested wires underwent qualitative scanning electron microscopy (SEM) surface topography analysis following test solution exposure.

Results of the present study indicated no significant difference between treatment groups for any mechanical properties measured ($p > 0.05$) after fluoride exposure. However, significant differences were observed between wire types for all measures within all treatment groups ($p < 0.05$). Rhodium-coated wires exhibited significantly lower unloading forces, lower yield strength, and higher elastic modulus than polymer-coated wires. This may

be due to effects of the coatings or due to differences in the underlying nickel-titanium. SEM analysis revealed the polymer coating peeled off in areas of contact with testing apparatus. With polymer-coated wires, exposed underlying nickel-titanium exhibited pitting corrosion after APF gel treatment, which did not occur with other fluoride groups or the DI water group. Similarly, with rhodium-coated wires exposed to APF gel, corrosion pitting appeared to go through the rhodium coating into the underlying NiTi wire, which did not occur with other fluoride groups or the DI water group.

The lack of degradation of mechanical properties of wires exposed to fluoride in this study suggests a potential protective effect of coatings on nickel-titanium. However, polymer coating instability could pose a problem by allowing underlying nickel-titanium to come into contact with fluoride when used in the mouth. Further research is needed to determine whether this protective effect continues even after substantial coating degradation.

APPROVAL PAGE

The faculty listed below, appointed by the Dean of the School of Dentistry, have examined a thesis titled, "The Effect of Topical Fluoride Agents on Coated Nickel-Titanium Archwires," presented by Kristen Sander, candidate for the Master of Science degree, and certify that in their opinion it is worthy of acceptance.

<u>Supervisory Committee</u>

Mary P. Walker, D.D.S., Ph.D., Committee Co-Chair
Department of Oral and Craniofacial Sciences

Jeffrey Nickel, D.D.S., M.Sc., Ph.D., Committee Co-Chair
Departments of Orthodontics and Dentofacial Orthopedics and Oral and Craniofacial Sciences

Jeffrey P. Gorski, Ph.D.
Department of Oral and Craniofacial Sciences

CONTENTS

ABSTRACT iii

LIST OF ILLUSTRATIONS viii

LIST OF TABLES ix

ACKNOWLEDGEMENTS x

Chapter

1. INTRODUCTION 1

Nickel-Titanium Archwires 2

Esthetic Coated Archwires 3

Mechanical Properties of Esthetic Archwires 4

Surface Characteristics and Coating Durability 5

Corrosion Resistance of Coated Archwires 6

Effects of Fluoride Exposure on Mechanical Properties of Nickel-Titanium 7

Effects of Fluoride Exposure on Surface Characteristics of Nickel-Titanium 8

Problem Statement 9

Hypotheses 9

2. MATERIALS AND METHODS 10

Archwires 10

Topical Fluoride 11

Specimen Preparation 12

Mechanical Testing 12

Scanning Electron Microscopy 17

Experimental Design 17

Sample Size 17

Data Analysis 19

3. RESULTS 20

Mechanical Testing 20

Scanning Electron Microscopy 25

4. DISCUSSION 28

Mechanical Testing 28

Surface Characteristics and Corrosion Resistance 31

Clinical Implications 32

Limitations of Study 34

Future Studies 35

5. CONCLUSIONS 36

LITERATURE CITED 37

VITA 39

ILLUSTRATIONS

Figure Page

1. Bend Test Setup 14
2. Representative Load-Deflection Curve 15
3. Representative Stress-Strain Curve 16
4. Unloading Forces at 1, 1.5, and 2mm deflection 22
5. Yield Strength as a function of treatment group 24
6. Modulus of elasticity as a function of treatment group 24
7. Polymer-coated wire SEM images at 50, 1000, and 4000x 26
8. Rhodium-coated wire SEM images at 50, 1000, and 4000x 27

TABLES

Table Page

1. Archwires Used in the Study 10

2. Hybrix White #C57 Composition 11

3. Fluoride Agents Used in the Study 11

4. Study Design Table 18

5. Mean Unloading Forces with Standard Deviation 21

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and special thanks to:

Dr. Mary Walker for her constant guidance and support and for always keeping me on track.

Dr. Jeffrey Nickel for sharing his knowledge and expertise.

Dr. Jeffrey Gorski for his time and input as a committee member.

Mrs. Rachel Reed for her help and patience.

Mr. Jim Thomas for his sharing his time and taking photographs for this thesis.

American Orthodontics for generously donating archwires for this study.

Dentsply/GAC for generously donating archwires for this study.

My husband John for his unfailing love and support, and for always making time.

My son Michael for bringing light and joy to my world, even on the hardest days.

My parents for setting an example and always lending a listening ear.

CHAPTER 1

INTRODUCTION

Orthodontic tooth movement is achieved through forces delivered to the teeth by the bracket-archwire system. The bracket is bonded to the tooth and acts as a handle to which the wire may be ligated. Engaging the archwire in the bracket slot requires a specific amount of loading force depending on variables related to the wire and the tooth position. It is then up to the archwire to apply the forces necessary for tooth movement, which are termed unloading forces. As the wire returns to its original archform, the ligated brackets bring the teeth with it. According to Oltjen and colleagues, minimizing patient discomfort and obtaining the most ideal biological conditions “requires wires of low stiffness to produce gentle forces as the teeth are leveled and aligned” (Oltjen et al. 1997). Ideally, an archwire will possess the following qualities: high strength, low stiffness, high range, and high formability (Proffit et al. 2013). For decades, nickel-titanium archwires have been employed in the practice of orthodontics because they possess many of these useful qualities.

However, with changing demographics in the orthodontic patient population, there is an increasing demand for materials to be as esthetic as possible. Although clinically acceptable and esthetically improved ceramic brackets are now widely in use, traditional nickel-titanium archwires remain unesthetic. Several attempts have been made to develop an esthetic composite archwire, but the properties have proved to be far inferior to nickel-titanium wires. In an effort to maintain the desirable properties of nickel-titanium, but improve esthetics of the appliances, some companies have developed esthetic coatings for their nickel-titanium archwires. As Kusy writes in his 2002 paper, “Orthodontic Biomaterials: From the Past to the Present,” “Practitioners assert that esthetics are desirable but that function is paramount" (Kusy 2002). Thus, it is important to determine whether coating nickel-titanium archwires will change their properties, and whether these coatings maintain stability in the oral environment.

Nickel-Titanium Archwires

Application of nickel-titanium alloy in orthodontics was first proposed in 1971 by Andreasen and Hilleman. They found that nickel-titanium wires could be engaged in brackets on teeth located 1/3 farther out of the arch without undergoing plastic deformation (Andreasen and Hilleman 1971). Further studies have found nickel-titanium archwires to possess lower stiffness than other orthodontic archwires (Oltjen et al. 1997).

Nickel-titanium alloys alternate between two fully-reversible primary crystal structures; the martensitic form exists at lower temperatures and higher stresses while the austenitic form exists at higher temperatures and lower stresses (Proffit et al. 2013). These two forms interchange back and forth through an intermediate rhomboidal (R) phase (Walker et al. 2005). This characteristic is what provides the material with its unique shape memory and superelasticity (Proffit et al. 2013). Shape memory is observed as the alloy changes state as a result of temperature change; superelasticity is observed as the alloy changes state as it releases stress (Laino et al. 2012). When loading force is applied to an orthodontic archwire, stress-induced martensitic transformation causes the amount of stress in the wire to level out (Miura et al. 1986). As the wire is engaged in the bracket, the higher stress induces formation of the martensitic phase; then, as the force is removed and the wire gradually returns to its original shape, transformation to the austenitic phase occurs (Kusy 1997). This transformation is nearly complete, which is what makes the wires superelastic (Kusy 1997).

The wire does not retain any permanent deformation in shape because of the complete return to the austenite phase upon unloading (Miura et al. 1986).

Proffit defines superelasticity as an “extremely desirable” characteristic. He also describes an unusual characteristic of superelastic materials – the fact that the unloading curve differs from the loading curve. This means that the force that is applied to activate the wire is different from the force the wire will apply to the teeth. Some energy is lost in the process, which is termed hysteresis (Proffit et al. 2013). Thus, superelastic wires are capable of sustaining large deflections, and still return to their original shape while delivering low and almost constant forces to the teeth (Parvizi and Rock 2003) (Oltjen et al. 1997). Another way of saying this is that the stress level remains constant despite changes in strain on the wire, at least up to a certain point (Miura et al. 1986). If this constant force level remains above the minimum that is required to instigate tooth movement until the wire is almost totally deactivated, then conceivably one can reduce the number of archwire changes which are necessary in early orthodontic treatment to level and align the teeth because one archwire can be used over a wide range of activation (Segner and Ibe 1995).

Esthetic Coated Archwires

The first esthetic archwires were polymer-based. While they had excellent appearance, they have never taken off in the market due to their poor mechanical properties and brittle nature (Iijima et al. 2012). In order to find an esthetic option that still has the desirable properties of nickel-titanium, manufacturers have begun to use esthetic coatings on their nickel-titanium archwires. Several types of coatings are currently being used to make nickel-titanium wires more esthetic. These include Teflon, various polymers, and metal alloys. Little has been studied in regards to the behavior of these coated archwires, and no studies have reported the effects of fluoride on these coatings.

Mechanical Properties of Esthetic Archwires

A study by Lim and colleagues in 1994 examined the properties of two types of esthetic archwires: one with a silicon dioxide core coated in silicon resin and nylon, and a stainless steel wire coated in Teflon. The study found that the silicon dioxide wire had the lowest stiffness, as well as low springback and tended to have greater amounts of plastic deformation after activation. Springback was found to be acceptable for both the coated and non-coated stainless steel wires. It should also be mentioned that all wires were found to produce unloading forces that were above the minimum required to move teeth in a clinical setting (Lim et al. 1994).

In 2010, Elayyan and colleagues tested the mechanical properties of epoxy-coated superelastic nickel-titanium archwires. A three-point bend test was carried out on these wires as well as non-coated superelastic wires in the as-received condition. The results indicated that coated wires delivered lower forces during both loading and unloading. The authors speculated that this was due to the decreased diameter of the nickel-titanium archwire core in order to compensate for the additional thickness of the coating. For this reason, the authors recommend using larger diameter wires than would normally be selected when using coated superelastic wires clinically (Elayyan et al. 2010).

Epoxy-coated and polymer-coated nickel titanium archwires were compared to traditional non-coated nickel-titanium archwires in a 2012 study by Alavi and Hosseini. In this study, the wires were incubated in artificial saliva at 37°C for 3 weeks and then subjected to a three-point bend test. The findings indicated that epoxy-coated archwires produced significantly lower forces compared to both polymer-coated and traditional nickel-titanium archwires. Forces produced by polymer-coated and non-coated wires were not found to be significantly different. The authors of this study also propose that the lower forces generated by the epoxy-coated wires are due to the thickness of the epoxy coating resulting in a lower core nickel-titanium wire diameter. Thus, Alavi and Hosseini recommend not only using larger epoxy-coated archwires, but also using these wires in .022 slot brackets due to the need for increasing wire diameter to obtain the same forces applied to the teeth (Alavi and Hosseini 2012).

In a study by Iijima and colleagues (2012), a three-point bend test was carried out on both polymer-coated and rhodium-coated nickel-titanium archwires, with the wires being tested as-received and at room temperature. This study found that the polymer-coated archwires had a higher mean unloading force than their non-coated counterpart, while the rhodium-coated archwires had a lower mean unloading force than the same wires without coating. The study did find that all the archwires tested exhibited superelastic properties during testing (Iijima et al. 2012). Another study on rhodium-treated archwires found that the rhodium treatment did not influence the unloading properties of the wire, but that the rhodium treated wires had increased stiffness and produced higher loading forces (Katic et al. 2014). In this study wires were again tested in the as-received condition but at body temperature of 37°C.

Surface Characteristics and Coating Durability

Surface characteristics have also been examined among coated archwires. In a 2012 study, rhodium-coated nickel-titanium wires were found to have the highest surface roughness among nickel-titanium archwires. Stainless steel wires were found to be the smoothest, followed by Teflon-coated nickel-titanium wires (D'Anto et al. 2012). The increase in surface roughness in rhodium treated archwires has been confirmed by a subsequent study, which also found that rhodium wires had the highest surface roughness compared to traditional and other coated nickel-titanium wires (Katic et al. 2014).

Another study found that epoxy-coated archwires exhibited greater surface roughness after retrieval from use in the mouth. This study also found that the coating showed large areas of delamination and discoloration. The authors noted ditching and cracking of the coating, with a 25% loss of coating over the course of 4-6 weeks of use in vivo (Elayyan et al. 2008). The findings of the study by Alavi and Hosseini are in agreement with these findings, as they found that both the epoxy and the polymer coatings demonstrated tearing and peeling away from the wire surface, indicating lack of durability of the coating. Coating loss was greater in the polymer-coated group, which the authors attribute to the epoxy coating being thicker and therefore possibly stronger or having higher bond strength to the underlying metal (Alavi and Hosseini 2012).

Corrosion Resistance of Coated Archwires

A study on corrosion of nickel-titanium archwires found that epoxy-coated nickel-titanium archwires exhibited less corrosion than traditional nickel-titanium upon exposure to a sodium chloride solution (Kim and Johnson 1999). Another study on corrosion found that Teflon coatings completely prevented corrosion, and ion-implanted and polyethylene coated wires also exhibited less corrosion than non-coated wires. However, it was noted in this study that Teflon coatings exhibited more defects after cyclic mechanical loading. This would indicate that the coating may not hold up under stresses induced in a clinical situation (Neumann et al. 2002).

The results of all the previously mentioned studies seem to indicate that the surface coating applied to archwires has a tendency to deteriorate, exposing the underlying metal wire. This has an impact on not only the esthetics of the wire, but also the resulting irregular surfaces may contribute to plaque accumulation as well as entrapment of brackets in the defects leading to unsatisfactory tooth movement (Elayyan et al. 2008).

While the polymer and epoxy-coated wires seem to exhibit less corrosion, rhodium-treated wires have been shown to undergo increased corrosion. A study using electrochemical testing showed rhodium-treated wires to have the lowest corrosion resistance and increased susceptibility to pitting corrosion (Katic et al. 2014). The authors of this study suggest this increase in corrosion is due to galvanic coupling between the noble rhodium coating and the base alloy of the archwire.

Effects of Fluoride Exposure on Mechanical Properties of Nickel-Titanium

Topical fluoride agents are commonly used during orthodontic treatment when oral hygiene is not sufficient to prevent white spot demineralization and increased risk of caries. They have been shown to be more effective at preventing white spot lesions following orthodontic treatment than fluoridated toothpaste alone (Alexander and Ripa 2000). While the fluoride has beneficial effects in caries prevention, it has been shown to have harmful effects on the properties of orthodontic materials. In a previous study, fluoride was shown to produce a significant decrease in the unloading modulus of nickel titanium archwires. This was the case for wires stored in both neutral sodium fluoride and acidulated phosphate fluoride (Walker et al. 2005). Another study showed that exposure to fluoride gel was associated with a significant decrease in the modulus of elasticity of nickel-titanium archwires (Ramalingam et al. 2008).

Researchers propose that the destruction of titanium alloy properties in the presence of fluoride is related to the release of acids such as hydrofluoric acid (HF), which is produced during exposure of titanium to fluoride, and contributes to dissolution of the protective titanium oxide layer on the surface of titanium alloys (Walker et al. 2005). The loss of the oxide layer can lead to the alloy absorbing hydrogen ions from the solution because titanium has a high affinity for hydrogen (Yokoyama et al. 2003). This is confirmed in a study showing that concentrations of hydrogen in superelastic nickel-titanium archwires increased with increasing time spent in acidulated phosphate fluoride solution. The authors of this study also found that the tensile strength of the wire was reduced after fluoride exposure to the extent that martensitic transformation occurred (Yokoyama et al. 2003).

On the other hand, several studies have also shown no significant effects of fluoride on the load-deflection characteristics of nickel-titanium archwires (Srivastava et al. 2012). It also should be mentioned that the concentration and pH of the fluoride solutions used, as well as the time the wire is immersed in the solution, can all change the effects of fluoride on the archwires. The 2012 study used fluoride solutions that were commercially available and therefore lower in fluoride concentration (Srivastava et al. 2012).

Effects of Fluoride Exposure on Surface Characteristics of Nickel-Titanium

Surface characteristics of nickel-titanium archwires have also been examined following exposure to fluoride solutions. One study found that wires exposed to fluoride solutions exhibited increased pitting corrosion. This was greater in wires exposed to acidulated fluoride as opposed to neutral sodium fluoride (Walker et al. 2005). Similar results were found in a study by Ramalingam and colleagues in 2008. Nickel-titanium wires exposed to fluoride were found to have more areas of corrosion than control wires, with more corrosion found in archwires exposed to fluoride gel as opposed to rinse (Ramalingam et al. 2008).

Problem Statement

To date, a limited number of studies have been done to determine the mechanical and surface characteristics of coated nickel-titanium archwires. Most of the studies that have been done tested the wires in the as-received condition, without taking into consideration the effects of the oral environment. No studies have been carried out to determine the effects of fluoride exposure on the loading and unloading mechanical properties of coated nickel-titanium archwires. Therefore, the purpose of the present study will be to examine the effects of fluoride exposure on the mechanical properties and surface characteristics of coated nickel-titanium archwires.

Hypotheses

1. There will be a difference in unloading mechanical properties between coated NiTi wires exposed to fluoride agents, deonized water (positive control) or no treatment (negative control).
2. There will be a qualitative difference in surface characteristics and corrosion-resistance between NiTi coated wires exposed to fluoride agents, deionized water (positive control), and no treatment (negative control).

CHAPTER 2

MATERIALS AND METHODS

Archwires

Two types of preformed archwires were selected for use in this study: two different types of esthetic nickel-titanium archwires[1,2]. Descriptions of the archwires are listed in Table 1. The polymer-coated nickel-titanium wires from American Orthodontics are 55% nickel and 45% titanium, with a coating of Hybrix White #C57 around the entire archwire surface. The composition of this coating can be seen in Table 2. Nickel-titanium "Sentalloy" archwires from GAC contain 51% nickel and 49% titanium. The "High-Aesthetic Sentalloy" wires are the same composition of nickel and titanium with a treatment consisting of 100% rhodium applied via ion beam assisted deposition. Round wires in size .016 inch diameter were chosen because this was the only size available in both types of esthetic nickel-titanium archwires.

TABLE 1

ARCHWIRES USED IN THE STUDY

Archwire Type	**Manufacturer**	**Composition**	**Lot Number**
Everwhite NiTi Wire	American Orthodontics	55% Nickel, 45% Titanium, Hybrix White #C57 coating	B24944 B64288
Sentalloy High-Aesthetic Wire	Dentsply/GAC International, Inc.	51% Nickel, 49% Titanium, 100% Rhodium treatment	D3Z2

[1] Everwhite Ni-Ti Wire, American Orthodontics, 3524 Washington Avenue, Sheboygan, WI 53081
[2] Sentalloy High-Aesthetic Wire, Dentsply/GAC International, One CA Plaza, Suite 100, Islandia, NY 11749

TABLE 2

HYPBRIX WHITE #C57 COMPOSITION

Ingredient	Percentage
1-methoxypropan-2-ol	20-25%
n-butyl acetate	23-28%
toluene	20-25%
aluminum oxide	3-5%
silicon dioxide	15-20%
methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate copolymer	10-15%

Topical Fluoride

Three types of prescription-strength topical fluoride products were selected for use in this study: a prescription neutral sodium fluoride gel[3] (NaF gel), an in-office acidulated phosphate fluoride gel[4] (APF gel), and a prescription neutral sodium fluoride rinse[5] (NaF rinse). See Table 3 for a description of these fluoride agents.

TABLE 3

FLUORIDE AGENTS USED IN THE STUDY

Fluoride Type	Active Agent	[Fl]-concentration	pH	Lot Number
PreviDent Gel	NaF Gel	1.1% (w/v)	6.35	3302USC11A
Acclean 60 S Gel	APF Gel	1.23% (w/v)	4.01	43285
PreviDent Rinse	NaF Gel	0.2% (w/v)	6.00	3217USC11M

[3] PreviDent Brush-on Gel, Colgate Oral Pharmaceuticals, 300 Park Avenue, New York, NY 10022
[4] Acclean 1.23% APF 60S Gel, Henry Schein, Inc., 135 Duryea Road, Melville, NY 11747
[5] PreviDent Dental Rinse, Colgate Oral Pharmaceuticals, 300 Park Avenue, New York, NY 10022

Specimen Preparation

Each archwire produced two specimens, by means of cutting each posterior section away from the manufactured arch form. These ends were cut to 30mm in length. Specimens were randomly assigned to treatment groups based on fluoride exposure status: no exposure/deionized water (DI water), exposure to NaF gel, NaF rinse, or APF gel. Each specimen had diameter measured with a digital caliper at three points and averaged. This was recorded before and after treatment. A three-point bend test was performed in a DI water bath at 37±1 ºC before and after test solution exposure. Data collected prior to test solution exposure served as a negative control. Each specimen was then incubated at 37±1 ºC in a vial containing 3 ml of test gel or DI water for 1.5 hours. This time period was chosen to approximate the exposure achieved by 3 months of daily fluoride applications. Specimens were then rinsed with DI water and subjected immediately to the post-exposure bend test.

Mechanical Testing

The three-point bend test was carried out according the protocol described by ADA Specification No. 32 ((ADA) 2006). This method of testing simulates conditions encountered clinically during orthodontic treatment. Testing was performed using a universal testing machine[6]. Specimens were placed on a fixture with a support span of 10mm, with the radii of each support and the striker being 0.10 ±0.05 mm (See Figure 1). The fixture was placed in a deionized water bath at 37 ± 1ºC for all testing, both before and after test solution exposure, to simulate the aqueous oral environment. Specimens were placed so that arch curvature was concave toward the striker. A preload of 0.1N was applied. Then each specimen was bent to

[6] Model 5967, Instron Industrial Products, 100 Royal Street, Canton, MA 02021

a deflection of 2.5mm at a crosshead speed of 10mm/min. Unloading force at 2.0, 1.5, and 1.0 mm of deflection were reported (Figure 2). Elastic modulus and yield strength were determined from the stress-strain curve. Figure 3 shows the best fit slope line that determined elastic modulus for the unloading section of the curve, as well as the peak from which unloading yield strength was determined.

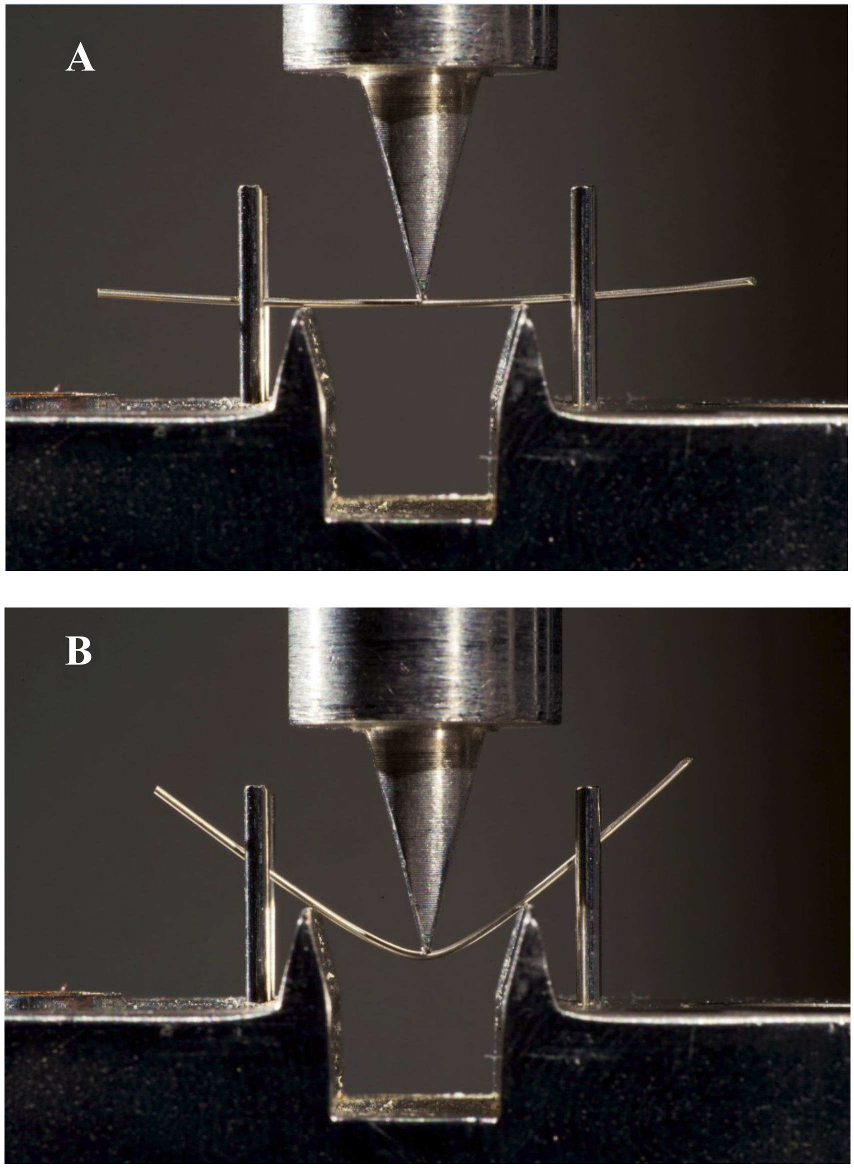

Figure 1. A) Bend Test Setup.   B) 2.5mm deflection.

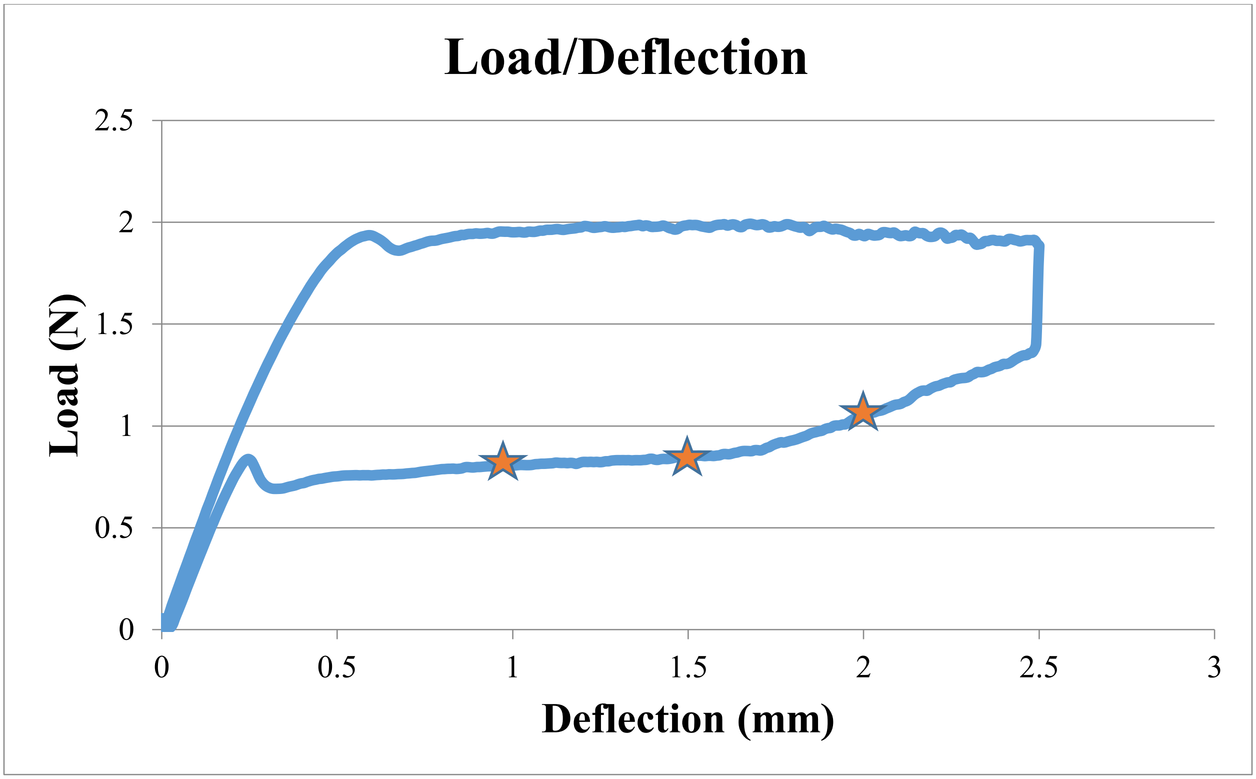

Figure 2. Representative load/deflection curve. Stars indicate points at 1.0, 1.5, and 2.0 mm of deflection where unloading force was reported.

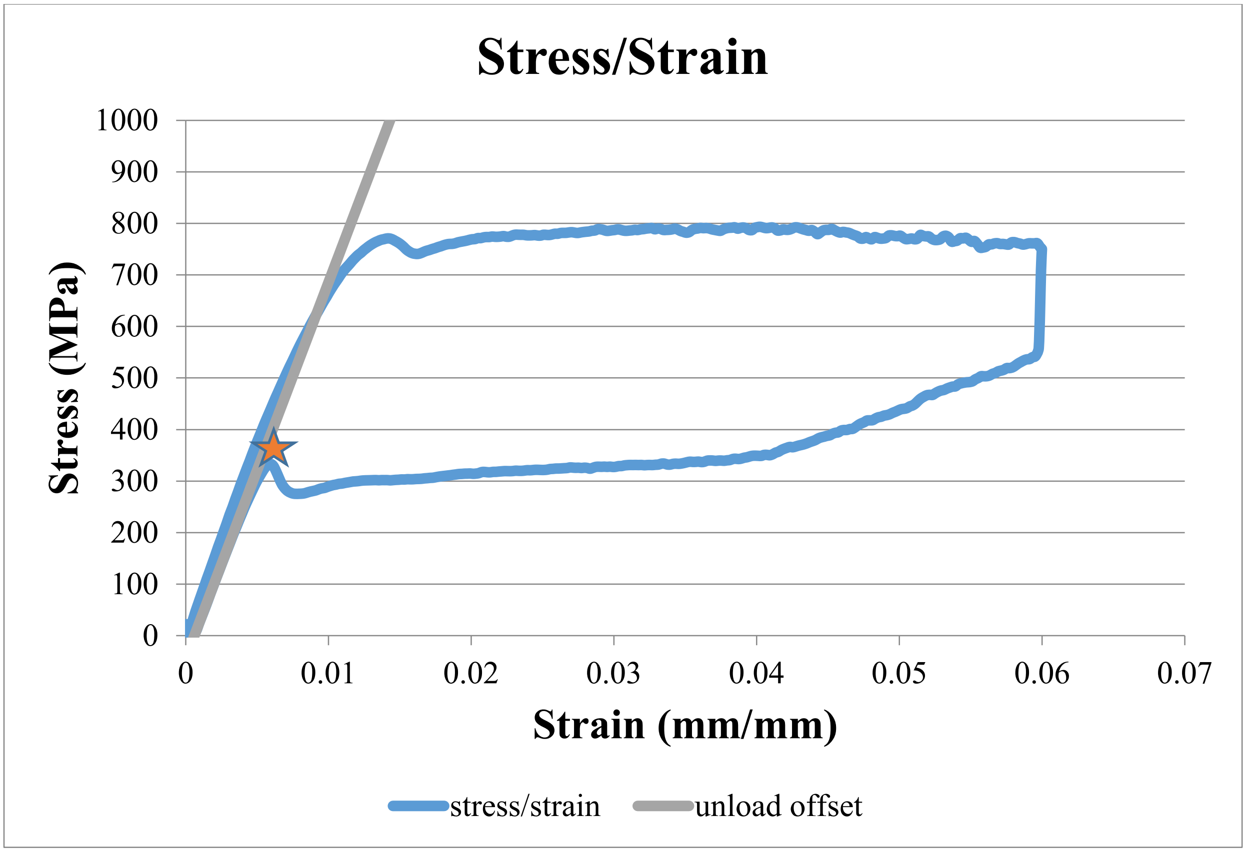

Figure 3. Representative stress/strain curve. Best fit line indicates elastic modulus and star indicates peak from which yield strength was determined.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images of various magnifications were obtained for three representative specimens from each group after mechanical testing. Additionally, images of the same magnifications were obtained on untested (as-received) wires of both types. These images were qualitatively analyzed to determine differences in surface topography and corrosion as a function of treatment group.

Experimental Design

This study used a two-factor, repeated measures design. The independent variables in this study were wire type and treatment. Two coated nickel-titanium archwire types were used: a polymer-coated nickel-titanium wire and a rhodium ion-implanted nickel-titanium wire. Treatment levels administered were as follows: none (DI water), NaF gel, APF gel, or NaF rinse. Dependent variables were unloading force and surface topography/corrosion.

Sample Size

A convenience sample size of 10 wire specimens per treatment group was selected for this study. A total of 40 archwires of each type were obtained from the manufacturers. Each wire produced two specimens by cutting two relatively straight segments from each manufactured arch form. Twenty archwires of each type were required for mechanical testing and SEM. The remaining wires were employed for preliminary testing.

TABLE 4

STUDY DESIGN TABLE

Time Point	Wire	Treatment	Unloading force at 2.0, 1.5, 1.0 mm	Unloading Elastic Modulus	Unloading Yield Strength
Pre-Treatment	Polymer-Coated	NaF Gel			
		NaF Rinse			
		APF Gel			
		DI Water			
	Rhodium-Coated	NaF Gel			
		NaF Rinse			
		APF Gel			
		DI Water			
Post-Treatment	Polymer-Coated	NaF Gel			
		NaF Rinse			
		APF Gel			
		DI Water			
	Rhodium-Coated	NaF Gel			
		NaF Rinse			
		APF Gel			
		DI Water			

Data Analysis

A 2-factor multivariate ANOVA was done to evaluate the effect of treatment and wire type on unloading force, elastic modulus and yield strength. If differences were noted due to treatment group, then one-way ANOVAs and Tukey's post hoc tests would be used within each wire type at each deflection. Statistical analyses were performed using a statistical analysis software program[7] with significance set at $\alpha = 0.05$ for all testing.

[7] SPSS version 21, 233 S. Wacker Dr., Chicago IL 60606

CHAPTER 3

RESULTS

Mechanical Testing

Based on the two-factor ANOVA, there was a significant difference between the wire types ($p < 0.05$), but there was no significant effect ($p > 0.05$) of the fluoride treatment within each wire type on any of the mechanical property measurements.

The unloading force results for each wire type and treatment group including the control can be seen below in Table 5. To more clearly visualize the unloading force comparisons within each wire type, see Figure 4. This figure demonstrates no significant difference as a function of treatment group, but a significant difference between unloading forces for rhodium-coated vs. polymer-coated wires. Results comparing the wire types indicated that for all unloading forces measured, rhodium wires demonstrated significantly lower unloading forces across treatment groups as well the control group.

TABLE 5

MEAN UNLOADING FORCES WITH STANDARD DEVIATION

Wire Type	**Treatment Group**	**Mean Unloading Force (N) at 1.0mm**	**Mean Unloading Force (N) at 1.5mm**	**Mean Unloading Force (N) at 2.0mm**
Rhodium	DI water (control)	0.89 (0.13)	0.92 (0.13)	1.06 (0.13)
	NaF rinse	0.87 (0.12)	0.91 (0.13)	1.06 (0.13)
	NaF gel	0.81 (0.10)	0.84 (0.10)	0.99 (0.09)
	APF gel	0.84 (0.11)	0.87 (0.11)	1.02 (0.11)
Polymer	DI water (control)	1.49 (0.13)	1.43 (0.16)	1.47 (0.19)
	NaF rinse	1.39 (0.11)	1.41 (0.12)	1.37 (0.18)
	NaF gel	1.43 (0.10)	1.41 (0.16)	1.33 (0.13)
	APF gel	1.42 (0.14)	1.45 (0.15)	1.43 (0.17)

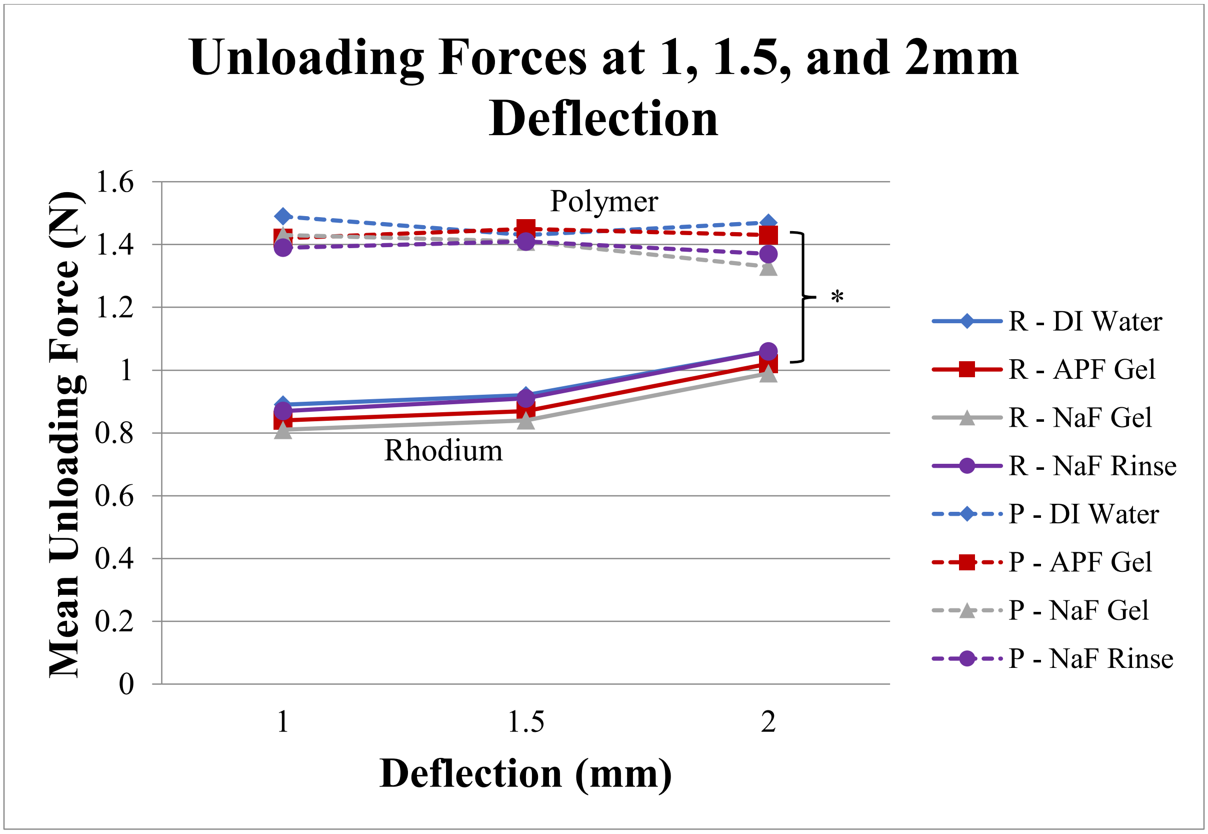

Figure 4. Unloading forces at 1, 1.5, and 2mm deflection. Rhodium-coated wires (denoted by R), produced significantly lower unloading forces than polymer-coated wires (denoted by P) as indicated by *. However, no significant differences were detected between treatment groups within each wire type.

For yield strength and modulus of elasticity, again no significant differences were detected between treatment groups within each wire type. However, significant differences were noted between wire types for all treatment groups, with yield strength being lower and modulus higher in rhodium-coated wires than polymer-coated wires (Figures 5 and 6).

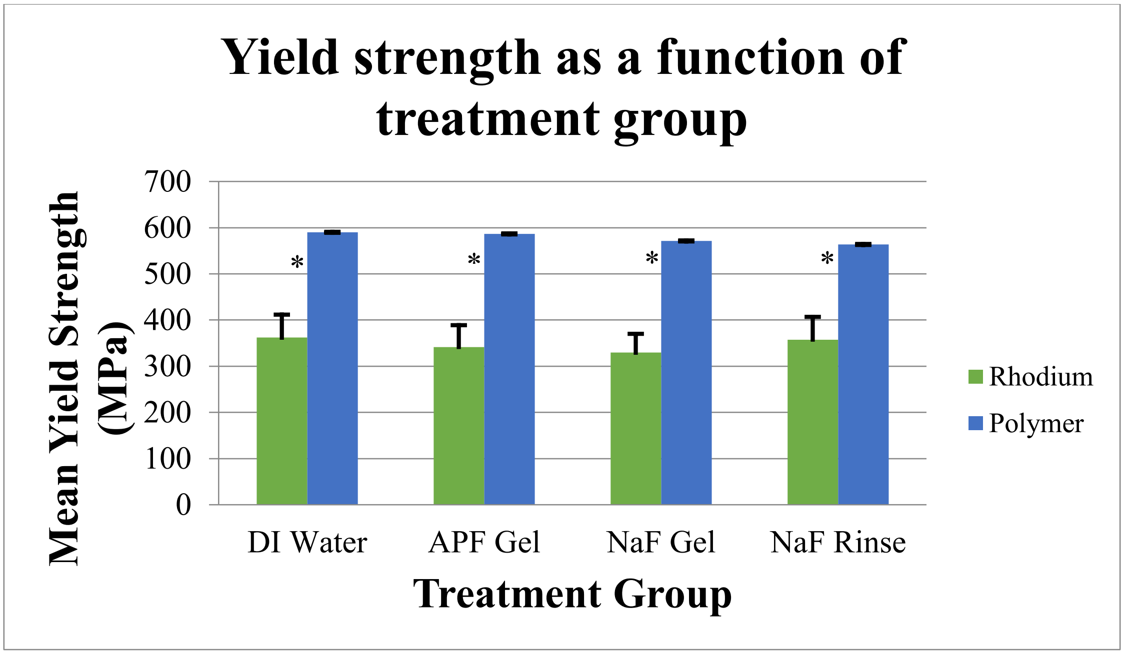

Figure 5. Yield strength as a function of treatment group. Mean values reported with standard deviations for rhodium-coated and polymer-coated wires. No significant differences were found between treatment groups within each wire type, but significant differences were noted between wire types for all treatment groups as indicated by *.

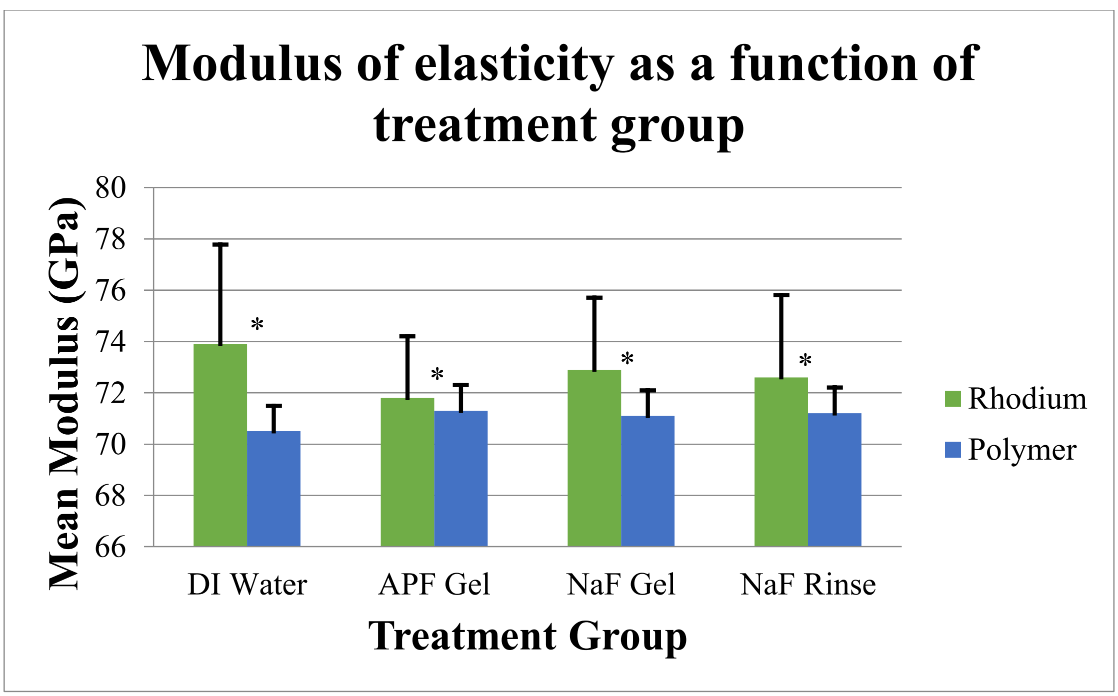

Figure 6. Modulus of elasticity as a function of treatment group. Mean modulus values with standard deviations for rhodium-coated and polymer-coated wires. No significant differences were found between treatment groups within each wire type, but significant differences were found between wire types for all treatment groups as indicated by *.

Scanning Electron Microscopy

Representative images for polymer wires may be seen in Figure 7. For polymer wires, surface characteristics were found to be different only in the APF gel treatment group. All others were similar to DI water treatment group. Specimens treated with APF gel (Figure 7 B- B'') were found to have pitting evident on the underlying nickel-titanium which was exposed after coating deterioration during testing. Overall, the polymer coating seems to have experienced more deterioration during testing than the rhodium. The polymer coating exhibited rubbing off in the areas of the supports and striker, with the coating around the edges peeling away from the underlying wire (Figure 7A, B, C, D).

Representative images for rhodium wires may be seen below in Figure 8. For rhodium wires, surface characteristics were also found to be different only in the APF gel treatment group. All other groups were similar to the DI water treatment group. In all wires, scratches were noted in the rhodium coating (Figure 8A' and A''). The scratches were most shallow in the untested wires (Figure 8E-E''), and appeared to be much deeper in the APF gel treatment group (Figure 8 B-B''). The APF gel treatment group also exhibited the appearance of breakdown in the coating that was not present in other treatment groups (Figure 8B'').

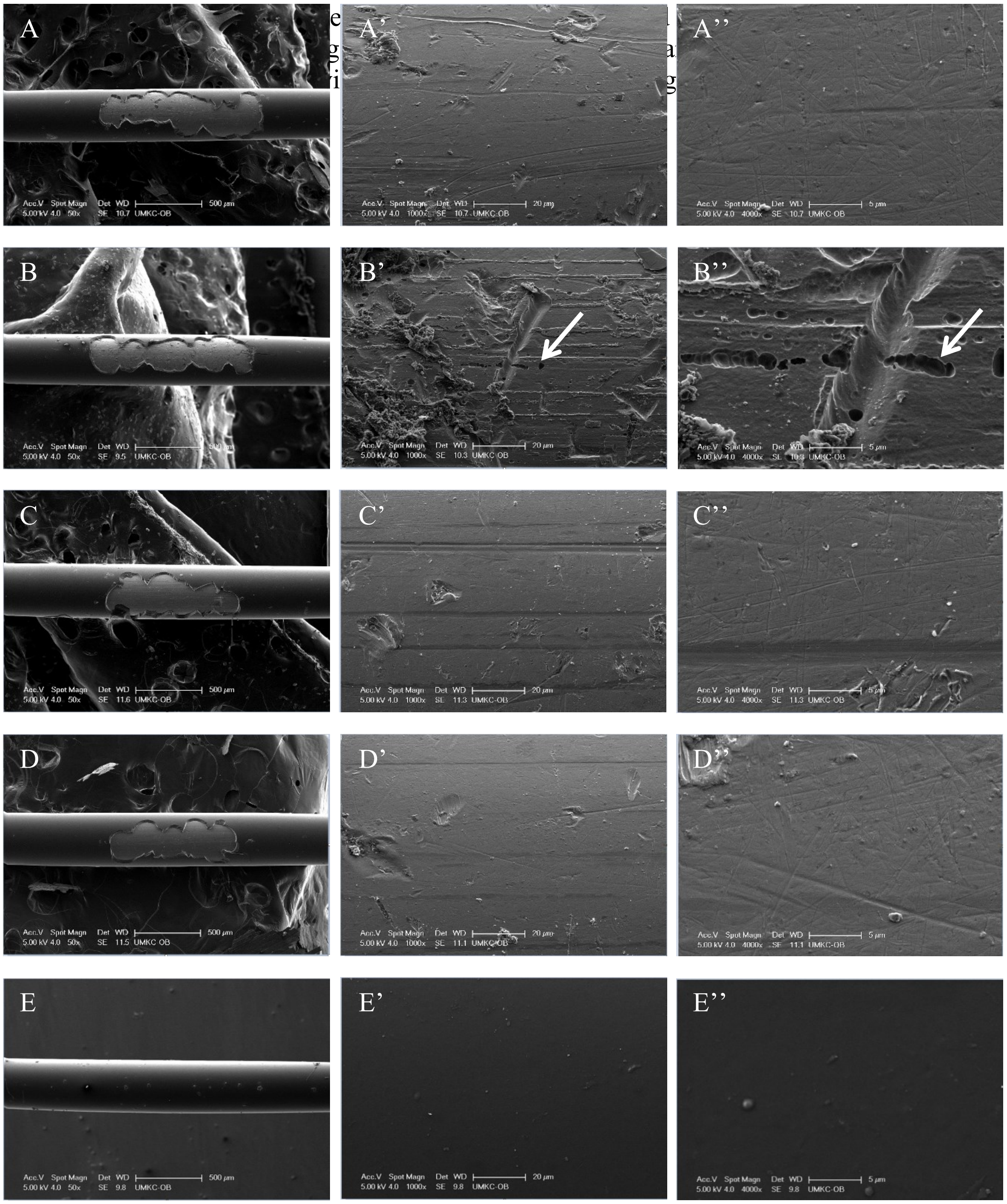

Figure 7. Polymer-coated wire SEM images at 50, 1000, and 4000x.
A-A”. DI water; B-B”. APF gel, pitting noted in B’ and B” arrows; C-C”. NaF gel; D-D”. NaF Rinse; E-E”. Untested wires. Note: Tester striker damage observed in all specimens (A-D) except untested (E).

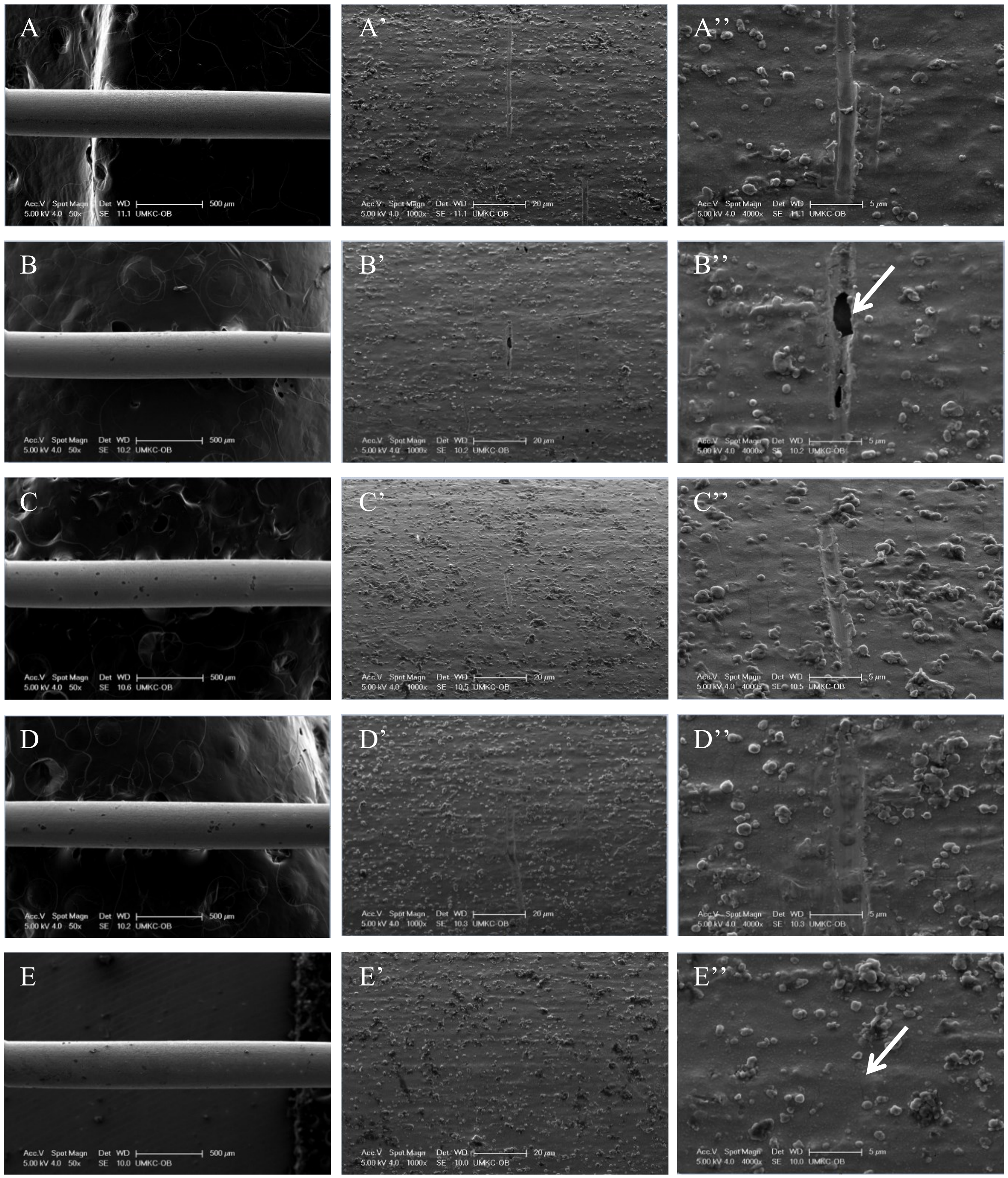

Figure 8. Rhodium-coated wire SEM images at 50x, 1000x, and 4000x.
A-A”. DI water; B-B”. APF Gel, deterioration noted by arrow on B”; C-C”. NaF Gel; D-D”. NaF Rinse; E-E”. Untested wire, faint scratch denoted by arrow on E”. Note: While all wires exhibited some scratching, wires treatment groups had increased depth of scratches, with APF-exposed wires exhibiting deepest breakdown.

CHAPTER 4

DISCUSSION

With more orthodontic patients demanding esthetic materials, more manufacturers are producing esthetic materials. It has become increasingly important for the clinician to know what is available and how using it might affect treatment times and outcomes. Esthetic coatings on nickel-titanium wires are increasing in popularity, and little has been done to study the effects of the oral environment on these coatings and the underlying nickel-titanium. The purpose of the present study was to examine the effects of topical fluoride on two types of coated nickel-titanium archwires.

Mechanical Testing

The present study did not detect a significant difference in mechanical properties following fluoride exposure within either coated nickel-titanium wire type. This is in contrast to previous studies which have noted that fluoride exposure produces a decrease in unloading properties of non-coated nickel-titanium archwires. Walker and colleagues found a significant decrease in unloading modulus and unloading yield strength of nickel-titanium archwires after fluoride exposure (Walker et al. 2005). Additionally, Yokoyama and colleagues found that tensile strength of nickel-titanium decreased upon exposure to acidulated fluoride, postulating the cause to be production of hydrofluoric acid (HF) upon exposure of fluoride to titanium. This was shown in their study by increased desorption of hydrogen from solution as it was taken up by the nickel-titanium with increasing immersion time. This leads to acidic dissolution of the protective titanium oxide layer on the surface of the nickel-titanium, which ultimately allows the corrosion and degradation of mechanical properties of the wire by a process termed “Hydrogen Embrittlement” (Yokoyama et al.

2003). The findings of these studies were backed up by Ramalingam and colleagues whose *in vivo* study found a decrease in unloading modulus of nickel-titanium archwires after patients used fluoride gel intraorally for 30 days. They reported a 34% decrease in the unloading elasticity of the wires following fluoride gel use (Ramalingam et al. 2008).

The present study was the first study to look at the effects of topical fluoride on coated nickel-titanium archwires. The present findings indicate no significant effect of prescription fluoride application on the mechanical properties of esthetic coated nickel-titanium archwires. It may be that the coating on these wires has a protective effect, preventing dissolution of the oxide layer on the underlying nickel-titanium. This would prevent hydrogen embrittlement, and therefore preserve the mechanical properties of the wire. Further studies are needed to test this theory, as well as to determine how long this protective effect might last intraorally.

While no significant difference was detected in mechanical properties as a function of fluoride, a significant difference was found between the two wire types. Rhodium-coated wires were found to have significantly lower mean unloading forces (0.8-1.1N as opposed to 1.3-1.5N), lower mean yield strength (300-400MPa as opposed to 550-600MPa), and higher mean elastic modulus (71-74GPa as opposed to 70-72GPa) than polymer wires. Clinically, this could potentially equate to rhodium-coated wires producing lighter forces applied to the teeth, but plastic deformation may occur at lower stresses as compared to polymer-coated wires. There may also be increased difficulty inserting a rhodium-coated wire into brackets on teeth that are significantly out of alignment due to the increased elastic modulus of rhodium-coated wires compared to polymer-coated wires.

The differences between the properties of the two types of coated wires may be due to the coating or they may also be due to the difference in the underlying nickel-titanium manufactured by two different companies. Similar differences between coated wires were reported in a previous study by Iijima and colleagues in 2012. They found that the same rhodium-coated Sentalloy wires had significantly lower unloading forces than the non-coated Sentalloy, while the polymer-coated wires (produced by a different manufacturer; the composition of this polymer was not specified) had significantly higher unloading forces than the paired non-coated wire. The rhodium-coated Sentalloy was found to have even lower unloading forces than in the present study, with a mean of 0.3N (Iijima et al. 2012). The unloading forces in the present study were found to be much closer to what Iijima reported the non-coated Sentalloy to produce. Similarly, Iijima found that the polymer-coated wires produced higher unloading forces (mean of 3.5N) than the polymer wires tested in the present study (Iijima et al. 2012).

The polymer-coated wires in the present study produced unloading forces more similar to the non-coated brand comparison of the Iijima polymer wires. However, the 2012 study used rectangular archwires, a three-point bend test at room temperature, a larger span (12mm) and a much slower crosshead speed (0.5mm/min) than the current study. Without similar testing conditions, differences in outcomes would be expected. To explain the difference in properties between paired coated and non-coated, Iijima proposed that the decrease in unloading forces of the rhodium-coated wires may be due to heat treatment during the process of rhodium ion implantation, and that the increase in unloading forces of the polymer-coated wires may be due to the relatively thick polymer coating (10µm) increasing the wire stiffness (Iijima et al. 2012).

Surface Characteristics and Corrosion Resistance

The present study found that the polymer coating was not stable in the areas of contact with the supports and striker. This left the underlying nickel-titanium exposed in multiple locations, with the coating rubbing off and peeling up along the edges. This is in agreement with previous studies which also noted instability of coatings on nickel-titanium wires. One study of wires using a three-bracket bending test found that an epoxy coating exhibited shrinkage and tearing, while a polymer coating also peeled off of the underlying nickel-titanium, noting that these defects were more noticeable near the bracket interface (Alavi and Hosseini 2012). Another study which was done *ex* vivo found that epoxy-coated nickel-titanium archwires, retrieved after 4-6 weeks in the mouth, had a rougher surface as well as discoloration, ditching, and cracking of the coating, with 25% of the coating lost over the length of the retrieved archwires on average (Elayyan et al. 2008).

Scanning electron microscopy examination of underlying nickel-titanium in areas of polymer coating loss revealed that wires exposed to APF gel had noticeable pitting compared to wires exposed only to DI water. Therefore, although corrosion was noted following acidic fluoride exposure of the exposed nickel-titanium, there was no associated significant effect on mechanical properties. It may be that if more of the coating was lost, exposing a larger area of nickel-titanium surface, there would be a change in mechanical properties of the wire due to a larger area of the wire taking up hydrogen from solution.

In contrast, the rhodium coating appeared to be more stable. There was no distinct loss of the rhodium coating as compared to the polymer loss. However, upon exposure to APF gel, the rhodium did appear to exhibit pitting corrosion defects that were deep and likely extended into the underlying nickel-titanium wire. This would indicate that unlike the polymer, the rhodium coating is susceptible to corrosion, which has also been documented in a previous study. Katic and colleagues found that rhodium-coated nickel-titanium wires corroded with a 3-electrode cell connected to a potentiostat had an increased number and depth of irregularities after corrosion upon SEM examination. There was more evidence of corrosion in the rhodium-coated nickel-titanium than in the traditional nickel-titanium archwires. Katic proposed that this may be due to galvanic coupling between the noble rhodium coating and the base metal of the underlying wire (Katic et al. 2014).

In general in the present study, corrosion effects were noted only with exposure to APF gel. Neither neutral fluoride solution was found to increase corrosion of the tested wires. This is in contrast to previous studies which found that both APF and neutral fluorides lead to pitting corrosion in nickel-titanium (Yokoyama et al. 2003; Walker et al. 2005). It may be that due to protective effects of the coating, a more acidic fluoride solution is required in order to produce a noticeable increase in corrosion of the underlying nickel-titanium or the rhodium coating.

Clinical Implications

Based on the results of the current study it appears that using prescription fluoride in orthodontic patients who have coated nickel-titanium archwires would not have any effect on the mechanical properties of the wires and thus, not negatively impact treatment time or efficiency. These coatings may have a protective effect, preventing hydrogen uptake and embrittlement of the underlying nickel-titanium wires, which has been shown to decrease their performance.

However, polymer coatings are not durable and have a tendency to rub off or deteriorate, leaving the nickel-titanium exposed. If this were to happen over a significant area of the wire, it may lead to increased hydrogen uptake by the nickel-titanium and subsequent alteration of the wire's mechanical properties. This is relevant, given that in the mouth the wires are ligated to an entire arch length of brackets, plus exposed to masticatory forces, which might lead to large amounts of coating deterioration.

In addition to potentially leading to increased hydrogen uptake, deterioration of the polymer coating may also lead to areas of increased friction, which can delay tooth movement. One study found that epoxy-coated nickel-titanium wires retrieved after 4-6 weeks in the mouth had 0 unloading force due to friction at the traditionally ligated bracket-wire interface due to build-up of the damaged coating. Wires in that study were deflected 4mm and exhibited no subsequent elastic return and thus, would potentially produce no tooth movement clinically (Elayyan et al. 2008).

Several studies have also shown that coated nickel-titanium archwires have increased surface roughness compared to traditional nickel-titanium wires (Iijima et al. 2012). One study reported that rhodium-coated nickel-titanium had the highest surface roughness of all wire types tested (Katic et al. 2014). Because surface roughness also can increase friction at the bracket-wire interface, this can subsequently reduce the sliding mechanics necessary for efficient tooth movement.

Given potential effects on the bracket-archwire interface, it may be advisable to limit use of coated nickel-titanium archwires to situations in which sliding mechanics are not as crucial. Using coated wires in situations where the sliding behavior of the bracket along the wire is necessary, as in tooth translation or space closure, could potentially lead to treatment delays due to elevated friction causing a reduction in rate of tooth movement.

In addition to producing higher levels of friction, the increased surface roughness and coating damage of these wires may lead to larger amounts of plaque accumulation, which could make the teeth more susceptible to white-spot decalcification. Finally, the purpose of the coating is to increase the esthetics of the appliances. Coating deterioration and discoloration certainly could have negative impact on the esthetics of these wires when used in the mouth alongside esthetic fixed appliances.

Limitations of Study

The present study was the first to test the question of the effects of fluoride on esthetic coated nickel-titanium archwires. As such, it had multiple limitations including the convenience sample of 10 specimens per group. Also, the 90-minute exposure to the various test solutions was meant to simulate 1-month of fluoride use at home. However, each fluoride type used has different application methods clinically. The Acclean APF gel is meant to be used as a 60-second in-office treatment, while the PreviDent gel is meant to be used once per day at home and the PreviDent rinse is meant to be used once per week by the patient at home. This makes it difficult to compare these materials using a 90-minute single application procedure. However, as a first test of coated wires and fluoride products, it was important to determine if there was any impact of fluoride exposure on the coated wires.

Additionally, wires in this study were stored in solution passively, without any stress applied. This is different from the clinical situation in which the wire would be exposed to fluoride while the wire was ligated into brackets on teeth that were out of alignment. It has been shown in a previous study that nickel-titanium wires subjected to electrochemical corrosion while ligated to a 5-bracket simulation apparatus to deliver stress experienced a significantly increased rate of corrosion compared to non-deflected wires (Segal et al. 2009).

Future Studies

Future research regarding coated nickel-titanium archwires and fluoride is indicated. It would be interesting to see whether increasing amounts of polymer coating loss do in fact lead to alterations in mechanical properties after fluoride exposure. Also, this study only looked at the coated archwires, without considering their non-coated specific counterpart. While it was not the aim of this study to compare wire types, this would be facilitated if the non-coated nickel-titanium archwires were tested as well to be able to more specifically determine whether coatings have a protective effect in preserving mechanical properties of the wire upon fluoride exposure. Also, exposing the wires to fluoride when under load in a simulated bracket set-up could produce an increase in rate of corrosion; future studies to examine this are warranted and would increase clinical relevance. Additionally, looking at these coated nickel-titanium archwires under the influence of simulated intraoral mechanics, such as cyclic loading to simulate the effects of the masticatory system, could help to answer the question of how these coatings stand up to the intraoral environment.

CHAPTER 5

CONCLUSIONS

1. There was no significant difference in unloading mechanical properties between coated NiTi wires exposed to fluoride agents, deionized water (positive control) or no treatment (negative control).

2. There was a qualitative difference in surface characteristics and corrosion-resistance between NiTi coated wires exposed to APF as opposed to other fluoride agents, deionized water (positive control), and no treatment (negative control).

LITERATURE CITED

ADA. ANSI/ADA specification no. 32. Chicago IL: American Dental Association; 2006.

Alavi S, Hosseini N. Load-deflection and surface properties of coated and conventional superelastic orthodontic archwires in conventional and metal-insert ceramic brackets. Dent Res J (Isfahan) 2012;9:133-8.

Alexander SA, Ripa LW. Effects of self-applied topical fluoride preparations in orthodontic patients. Angle Orthod 2000;70:424-30.

Andreasen GF, Hilleman TB. An evaluation of 55 cobalt substituted nitinol wire for use in orthodontics. J Am Dent Assoc 1971;82:1373-5.

D'Anto V, Rongo R, Ametrano G, Spagnuolo G, Manzo P, Martina R, et al. Evaluation of surface roughness of orthodontic wires by means of atomic force microscopy. Angle Orthod 2012;82:922-8.

Elayyan F, Silikas N, Bearn D. Ex vivo surface and mechanical properties of coated orthodontic archwires. Eur J Orthod 2008;30:661-7.

Elayyan F, Silikas N, Bearn D. Mechanical properties of coated superelastic archwires in conventional and self-ligating orthodontic brackets. Am J Orthod Dentofacial Orthop 2010;137:213-7.

Iijima M, Muguruma T, Brantley W, Choe HC, Nakagaki S, Alapati SB, et al. Effect of coating on properties of esthetic orthodontic nickel-titanium wires. Angle Orthod 2012;82:319-25.

Katic V, Curkovic HO, Semenski D, Barsic G, Marusic K, Spalj S. Influence of surface layer on mechanical and corrosion properties of nickel-titanium orthodontic wires. Angle Orthod 2014;84:1041-8.

Kim H, Johnson JW. Corrosion of stainless steel, nickel-titanium, coated nickel-titanium, and titanium orthodontic wires. Angle Orthod 1999;69:39-44.

Kusy RP. A review of contemporary archwires: Their properties and characteristics. Angle Orthod 1997;67:197-207.

Kusy RP. Orthodontic biomaterials: From the past to the present. Angle Orthod 2002;72:501-12.

Laino G, De Santis R, Gloria A, Russo T, Quintanilla DS, Laino A, et al. Calorimetric and thermomechanical properties of titanium-based orthodontic wires: Dsc-dma relationship to predict the elastic modulus. J Biomater Appl 2012;26:829-44.

Lim KF, Lew KK, Toh SL. Bending stiffness of two aesthetic orthodontic archwires: An in vitro comparative study. Clin Mater 1994;16:63-71.

Miura F, Mogi M, Ohura Y, Hamanaka H. The super-elastic property of the japanese niti alloy wire for use in orthodontics. Am J Orthod Dentofacial Orthop 1986;90:1-10.

Neumann P, Bourauel C, Jager A. Corrosion and permanent fracture resistance of coated and conventional orthodontic wires. J Mater Sci Mater Med 2002;13:141-7.

Oltjen JM, Duncanson MG, Jr., Ghosh J, Nanda RS, Currier GF. Stiffness-deflection behavior of selected orthodontic wires. Angle Orthod 1997;67:209-18.

Parvizi F, Rock WP. The load/deflection characteristics of thermally activated orthodontic archwires. Eur J Orthod 2003;25:417-21.

Proffit WR. Mechanical principles in orthodontic force control. In: Contemporary Orthodontics. Proffitt WR, HW Fields and DM Sarver editors. 5th ed. St. Louis, Mo.: Elsevier/Mosby; 2013, pp 312-46.

Ramalingam A, Kailasam V, Padmanabhan S, Chitharanjan A. The effect of topical fluoride agents on the physical and mechanical properties of niti and copper niti archwires. An in vivo study. Aust Orthod J 2008;24:26-31.

Segal N, Hell J, Berzins DW. Influence of stress and phase on corrosion of a superelastic nickel-titanium orthodontic wire. Am J Orthod Dentofacial Orthop 2009;135:764-70.

Segner D, Ibe D. Properties of superelastic wires and their relevance to orthodontic treatment. Eur J Orthod 1995;17:395-402.

Srivastava K, Chandra PK, Kamat N. Effect of fluoride mouth rinses on various orthodontic archwire alloys tested by modified bending test: An in vitro study. Indian J Dent Res 2012;23:433-4.

Walker MP, White RJ, Kula KS. Effect of fluoride prophylactic agents on the mechanical properties of nickel-titanium-based orthodontic wires. Am J Orthod Dentofacial Orthop 2005;127:662-9.

Yokoyama K, Kaneko K, Moriyama K, Asaoka K, Sakai J, Nagumo M. Hydrogen embrittlement of ni-ti superelastic alloy in fluoride solution. J Biomed Mater Res A 2003;65:182-7.

VITA

NAME
Kristen Marie Wellemeyer Sander

DATE AND PLACE OF BIRTH
July 21, 1986, Kansas City, MO

MARITAL STATUS
Married to John Robert Sander

EDUCATION

5/2004	Diploma	Kapaun Mt. Carmel Catholic High School Wichita, KS
5/2008	BA/Psychology	Rockhurst University Kansas City, MO
5/2013	DDS	University of Missouri - Kansas City School of Dentistry Kansas City, MO

PROFESSIONAL ORGANIZATIONS

2013 – Present	Member of American Association of Orthodontists
2013 – Present	Member of American Dental Association
2009 – 2013	Member of American Student Dental Association
2009 – 2013	Member of Kansas Dental Association
2009 – 2013	Member of Missouri Dental Assocation

HONORS

2009-2013	Dean's Academic Honor Roll (UMKC)
2013	Omicron Kappa Upsilon National Dental Honor Society
2012	UMKC Dental Alumni Association Scholarship
2012	Hocott/Munn Scholarship
2012	Dr. Jerry Fankhauser Scholarship
2012	Kansas Dental Association Scholarship
2012	Richard Ackerman Award (OKU Scholarship)
2011, 2012	Zola N. and Lawrence R. Nell Educational Trust Scholarship
2011	UMKC Class of 1977 Scholarship
2010, 2011	Dr. Mike R. and Jerrie Ronie Memorial Scholarship
2011	Kansas Dental Student Silver Lining Scholarship
2010, 2011	UMKC Dental Alumni Association Scholarship
2009	Dr. George Aden Esterly Scholarship
2004-2008	Rockhurst University Trustees' Scholarship