Differential Scanning Calorimetry (dsc) Analyses Of Esthetic Nickel-Titanium Wires As-Received And After Clinical Use

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DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSES OF ESTHETIC NICKEL-TITANIUM WIRES AS-RECEIVED AND AFTER CLINICAL USE

by

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ABSTRACT
DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSES OF ESTHETIC NICKEL-TITANIUM WIRES AS-RECEIVED AND AFTER CLINICAL USE

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Introduction: The demand for esthetic orthodontics has increased rapidly over the past few decades, and much progress has been made in the development of esthetic clear and translucent brackets for labial orthodontics. However, the majority of wires used with these clear brackets are still the traditional alloys. Recently, American Orthodontics (Sheboygan, WI) and Opal (Ultradent; South Jordan, UT) have released epoxy resin coated nickel-titanium archwires that give a tooth-colored appearance. American Orthodontics has released EverWhite and Opal has released Via Pearl. The goal of this study was to compare the thermal properties of these new archwires with their uncoated counterparts before and after clinical use via differential scanning calorimetry (DSC).

Materials and Methods: Four types of nickel-titanium orthodontic archwires were evaluated in this study. The four types consisted of two epoxy coated wires and two comparable control wires of the same .016 x 0.022 inch dimension. The transformation temperatures and phase transformations of these wires were determined in the as-received condition and after 4 to 12 weeks in the oral cavity by differential scanning calorimetry. In addition, the amount of coating lost for each coated archwire after clinical use was determined using a scanned image of the wire and matlab software.

Results: There were no statistically significant differences in thermal properties when comparing archwires before and after clinical use. However, significant differences were observed between the as-received uncoated and coated counterparts from both manufacturers. Both wire types lost a significant amount of esthetic coating after use, but the Opal Via Pearl wire maintained significantly more coating compared to the EverWhite type.

Conclusions: The significant differences between as-received uncoated and coated wires from the same manufacturer indicate that these wires may perform differently in clinical situations contrary to the manufacturers' claims. In addition, improvements to the coating processes or alternative wires are needed to provide a more esthetic archwire with limited coating loss.

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CHAPTER 1
INTRODUCTION

The demand for esthetic orthodontics has increased rapidly over the past few decades, and progress has been made in the development of esthetic clear and translucent brackets for labial orthodontics (Karamouzos, Athanasiou, & Papadopoulos, 1997). However, the majority of wires used with these clear brackets are still the traditional alloys (Burstone, Libler, & Goldberg, 2001). Recently, American Orthodontics (Sheboygan, WI) and Opal (Ultradent; South Jordan, UT) have released coated nickel-titanium wires that give a tooth-colored appearance to a nickel-titanium alloy wire (NiTi). American Orthodontics has released EverWhite and Opal has released Via Pearl nickel-titanium wires coated in an epoxy covering. Differing manufacturing processes may lead to differing physical and chemical properties of each type of wire, and research is limited on each individual type of wire, specifically in relation to thermal analysis.

In nickel-titanium, nickel and titanium exist in a near one-to-one atomic ratio, and the alloy can exist in various crystallographic forms. Nickel-titanium has the inherent ability to modify the type of atomic bonding which causes unique and significant changes in the mechanical properties and crystallographic arrangement of the alloy (Thompson, 2000). The changes in atomic structure occur as a function of temperature and stress. Nickel-titanium alloys exist in two forms: austenite and martensite. The austenite structure is a body-centered cubic lattice and exists at high temperatures and in low stress situations. Alternatively, martensite is a monoclinic, triclinic, or hexagonal crystal structure that exists at low temperatures and higher stress situations. Both shape memory and superelasticity are related to phase transformations within the nickel-titanium wire between the martensitic and austenitic forms that occur at relatively low temperatures (Proffit, Fields, & Sarver, 2007). Additionally, an intermediate R-phase was identified. The R-phase has a rhombohedral crystal structure and may form between the reversible transformation of martensite to austenite (Thompson, 2000).

Each type of wire has different austenite-martensite transformation temperature ranges and differential scanning calorimetry (DSC) has been frequently utilized to detect these transformations (Bradley, Brantley, & Culbertson, 1996; Biermann, Berzins, and Bradley, 2007; Berzins & Roberts, 2010). Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a wire sample and a blank reference is measured as a function of temperature. The wire and the blank reference are heated and subsequently cooled, and thermograms are fabricated by the associated software.

Start, finish, and peak temperatures, along with change in enthalpy for each sample are calculated for both heating and cooling by analyzing the thermogram (Figure 1). The first peak (H1) on the heating DSC curve represents the transformation from martensite to the intermediate R-phase, and the second peak (H2) represents the transformation from R-phase to austenite. On cooling, the only peak (C1) represents the direct transformation from austenite to martensite. The R Phase may or may not appear on heating and cooling curves. The areas confined within the peaks on the heating and cooling curves represent the change in heating and cooling enthalpies respectively. The downward peak on heating corresponds to an endothermic reaction, while the upward peak on cooling represents an exothermic reaction. The start temperature on heating (R_s) is the temperature at which the transformation of martensite to R-phase begins, and the finish temperature on heating (A_f) is the temperature at which the transformation from R-phase to austenite is complete. On cooling the start temperature (M_s) indicates the temperature at which austenite begins its transformation to martensite, and the finish temperature (M_f) represents the complete transformation to martensite. The transformation ranges for each wire can give a more detailed analysis of the physical properties of the wires and how they will perform in clinical situations.

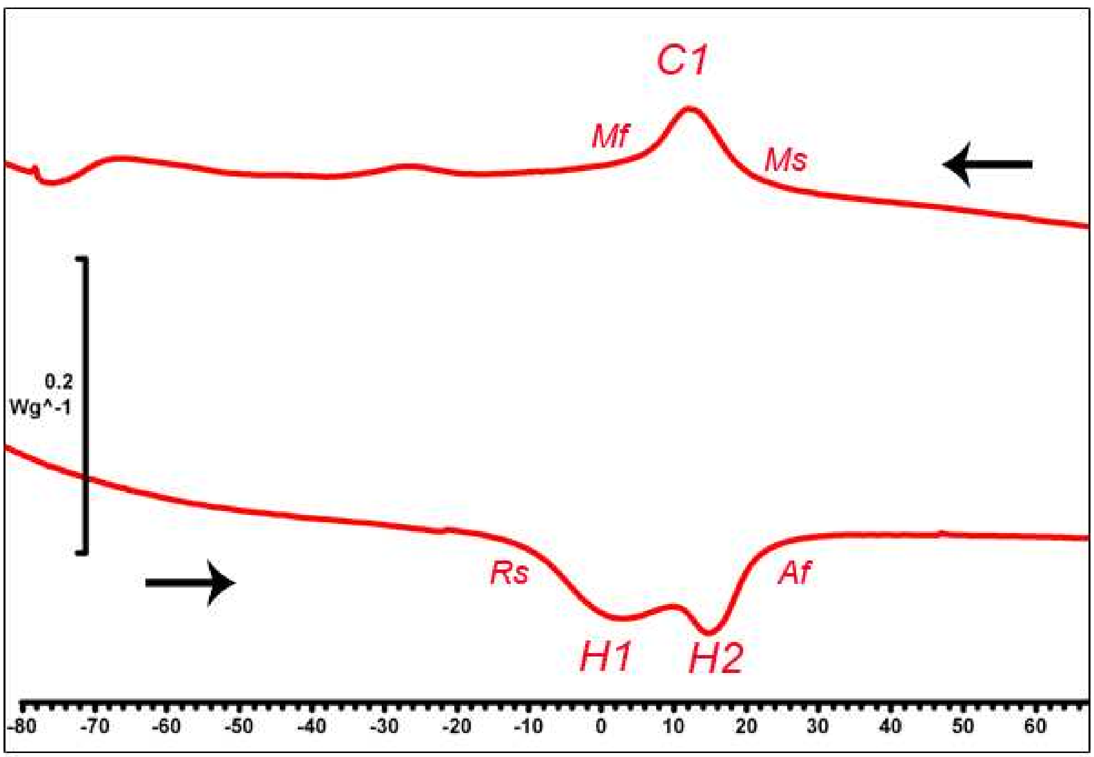

Figure 1: DSC thermogram for heating and cooling of wire samples.

While a previous study has determined that clinical use of NiTi wires have resulted in few differences when compared with as-received wires analyzed by DSC (Biermann et al., 2007), no study has examined the phase transformations of clinically used and as-received esthetic epoxy coated archwires. Therefore, the purpose of this study was to perform a thermal analysis on tooth-colored NiTi archwires in order to better understand their physical and chemical properties before and after use.

CHAPTER 2
LITERATURE REVIEW

History of Nickel-titanium

Nickel-titanium alloy was first developed by W.F. Buehler and the U.S. Naval Ordinance Laboratory in the 1960s for use in the space program due to its shape memory effect. The alloy was named nitinol, which is an acronym for its composition: ni for nickel, ti for titanium, and nol for the Naval Ordinance Laboratory (Buelher, Gilfrich, & Wiley, 1963). While the alloy offered many beneficial properties for the space program, it was not used as an orthodontic archwire until 1971 (Andreasen & Hilleman, 1971).

Dr. George Andreasen recognized the shape memory potential of the nickel-titanium alloy in orthodontics and worked with the Unitek Company (Monrovia, CA) to develop the alloy Nitinol for dentistry (Andreason & Hilleman, 1971). These nickel-titanium wires were seen as ideal for orthodontics in that they provided light, continuous forces with an outstanding range, low stiffness, and high springback. Andreasen soon documented the use of nitinol wires in clinical situations, and determined that nickel-titanium archwires were quite different from stainless steel archwires in that they require less archwire changes, less chair time, and may reduce treatment time through more efficient leveling and rotation control, and reduce patient discomfort (Andreasen & Morrow, 1978; Wang et al., 2010). While early nickel-titanium wires were marketed as having shape memory, the shape memory effect was ultimately suppressed by cold working during manufacturing (Kusy, 1997). Cold working caused the nickel-titanium wire to become passive in the martensitic stabilized structure and lose the ability for shape memory.

Burstone, Qin, and Morton (1997) introduced superelastic Chinese NiTi to the orthodontic community in the 1980s. These wires were developed in Beijing, China and differed from Nitinol wires in that they were fabricated with little work hardening and had an active austenitic grain structure. The wires were deemed to be superelastic due to stress remaining fairly constant on wire deformation as well as when the wire deformation rebounded, and this led to an uncommon deactivation curve. The superelastic wires offered relatively constant forces over a long range of action which is considered physiologically desirable for tooth movement. Unlike Nitinol, the Chinese wires were not dependent on shape memory and transformed from austenitic NiTi to martensitic NiTi during activation. Miura, Mogi, Ohura, and Hamanaka (1991) examined a similar superelastic Japanese NiTi alloy developed around the same time as the Chinese NiTi and came to the similar conclusion that many new possibilities exist in orthodontic tooth movement with superelastic NiTi wires, and they had the potential to be extremely useful in clinical situations with significant crowding.

True shape memory or heat activated NiTi wires were popularized in 1994 with the addition of copper to the alloy by Ormco and are termed martensitic active. These wires undergo phase transformations from the flexible martensitic active phase to the shape-retaining austenite phase when the wires are exposed to higher oral temperatures. The wire is pliable out of the mouth at room temperature, but returns to its original shape once it is heated above the austenite transformation temperature in the oral cavity. These CuNiTi wires routinely come in 27°C, 35°C, and 40°C transformation temperature variants and the 35°C and 40°C wires offer an alternative to superelastic wires (Kusy, 1997). The variable transformation temperatures of the CuNiTi wires are manufactured by altering the amount of copper and chromium in each wire type.

GAC (Dentsply; Islandia, NY) introduced the BioForce archwire that provides gradually increasing forces from the anterior to posterior segments of the archwire. These BioForce archwires are not heat treated in the most posterior segments of the wire but are progressively heat treated for longer periods of time towards the anterior portion of the wire (Kuftinec, n.d). This allows the wires to provide lower force levels to the single rooted anterior teeth and larger force levels to the multi-rooted posterior teeth, and these forces are seen as biologically desirable.

Differential Scanning Calorimetry (DSC) and X-ray Diffraction

Differential scanning calorimetry (DSC) is a thermoanalytical technique that measures the difference in heat needed to increase the temperature of a sample and an inert reference at the same rate. Phase transformations of a material are accompanied by exothermic or endothermic reactions, and the transformations are represented as peaks on a DSC thermogram. The thermograms can be analyzed by computer software to determine phase transformation temperature ranges and enthalpy for heating and cooling processes.

Leu, Fournelle, Brantley, and Ehlert (1990) first utilized DSC to analyze the austenitic-martensitic transformations of superelastic NiTi wires. Transformation temperatures were determined for early superelastic nickel-titanium and an intermediate rhomboidal phase or R-phase was discovered as the wire transformed from martensite to austenite. Bradley et al. (1996) examined the three different types of as-received NiTi wires (superelastic, nonsuperelastic, and shape-memory) through differential scanning calorimetry to determine the transformation temperatures for the austenitic, martensitic, and R structure phases of each. They concluded that superelastic NiTi (Nitinol SE and NiTi) alloys undergo the transformation to austenite below 0^{o}C and the NiTi wire is almost entirely austenite in the oral cavity. An intermediate R phase was also evident in the superelastic wires. In addition, nonsuperelastic wires (Nitinol) were almost entirely martensite at room temperature and only contain small amounts of austenite intraorally. Finally, the shape-memory wires (Neo Sentalloy and Titanal LT) were reported to be entirely austenite intraorally, and their phase transformation temperatures were consistent with their advertised temperatures.

The differences in phase transformations between as-received and clinically retrieved CuNiTi wires after several weeks of clinical use in patients were investigated by Biermann et al. (2007). It was determined that there were no real differences in thermal activity between as-received and clinically retrieved wires tested by DSC; however, the 27^{o}C retrieved wires did have a significant reduction in heating enthalpy. Berzins et al. (2010) studied the phase transformations in thermocycled NiTi wires by testing wires by DSC that were repeatedly heated and cooled between 5^{o}C and 55^{o}C. While there were no differences in Sentaloy and Nitinol HA wires, there were qualitative and quantitative differences in DSC graphs in the 27^{o}C and 35^{o}C CuNiTi wires that received repeated temperature fluctuations. Therefore, fluctuations in oral temperatures from hot or cold beverages could possibly affect mechanical properties, but evidence is minimal.

In addition to differential scanning calorimetry, x-ray diffraction (XRD) can be a valuable instrument to differentiate crystallographic structures of nickel-titanium wires. X-ray diffraction can differentiate between martensitic and austenitic structures by examining the peaks of diffraction scans. When a phase transformation occurs, x-ray diffraction peaks change in position and intensity. A previous XRD study by Thayer, Bagby, Moore, and DeAngelis (1995) examined the peaks for nonsuperelastic wires and determined that these wires were primarily in the austenitic structure at room temperature which contrasts with the DSC study by Bradley et al. (1996). While x-ray diffraction can be utilized to identify crystallographic phases of NiTi, this technique provides information only within a depth of less than 50 μm from the surface whereas DSC provides information about the entire specimen (Brantley, 2001). In addition, DSC is more convenient and can determine the enthalpy changes caused by phase transformations while XRD cannot.

Esthetic Orthodontics

The demand for esthetic orthodontics and the number of adults seeking treatment has dramatically increased over the past few decades. The unesthetic metallic appearance of fixed appliances can reduce self-esteem of some patients and may lead to avoidance of orthodontic treatment (Rossvall, Fields, Ziuchkovski, Rosentiel, & Johnston, 2009). In order to make orthodontics more esthetic, manufactures have introduced tooth colored brackets, clear aligners, and lingual fixed appliances to mask the appearance of orthodontic treatment.

Before the development of direct bonding, fixed appliances consisted of large unesthetic metal bands surrounding each tooth. With the introduction of direct bonding in orthodontics, manufacturers were able to create clear or tooth-colored brackets that greatly improved the esthetics of orthodontics. Initial polymer-based brackets suffered from a high tendency for staining, poor dimensional stability, and excess friction between the bracket and wire (Thompson, 2000; Brantley, 2001). Alumina and zirconia ceramic brackets improved on the deficiencies of polymer-based brackets and had better stain resistance and durability. While ceramic brackets have gained widespread use, they do have the potential to wear opposing teeth and cause enamel fracture upon bracket removal (Karamouzos et al., 1997).

The use of clear aligner therapy began in the 1980s but did not gain widespread use and acceptance until 1998 when Align Technology introduced Invisalign (Align Technology, Santa Clara, Calif.). Invisalign utilizes CAD/CAM techniques to create multiple clear removable polyurethane aligners from a single impression. Each aligner consists of incremental changes to correct a patient's malocclusion. Teeth are moved 0.25 to 0.33 mm every 14 days (Kravits, Kusnoto, Begole, Obrez, & Agran, 2009). The demand for clear aligner therapy has dramatically increased in the last decade due to improved esthetics and an increased number of adults seeking orthodontics. However, clear aligners have multiple shortcomings and have been shown not to be as efficacious as fixed appliances. In a study by Djeu, Shelton, and Maganzini (2005), cases treated by Invisalign were not as efficient at correcting posterior torque, occlusal contacts, anteroposterior occlusal relationships, and overjet as conventional fixed appliances. In addition, cases treated with Invisalign measured by American Board of Orthodontics (ABO) standards achieved a passing rate 27% lower than cases treated with fixed appliances. Other studies have shown that aligners have a higher propensity for relapse and are best utilized for improving anterior alignment (Kunico, Maganzini, Shelton, & Freeman, 2007; Clements et al., 2003). While clear aligners are continuing to modify their biomechanic abilities with bonded attachments, the aligners, with the level of evidence available today, continue to have problems with certain types of movements such as torquing, extrusion and bodily movement.

Another esthetic orthodontic option is the use of lingual fixed appliances. Even though ceramic brackets and aligners have improved esthetics, brackets on the lingual surfaces of the teeth are the only option that provides ultimate esthetics. Lingual appliances were introduced in the 1970s and were used sparingly until quite recently. Although lingual appliances offer essentially the same control as labial appliances, brackets on the lingual surfaces increase the difficulty, duration, and cost of treatment (Thompson, 2000; Brantley, 2001). New generation custom fitted pads and robotically bent wires in appliances such as Incognito (3M Unitek, St. Paul, MN) have improved treatment outcomes; however, lingual appliances are still hampered by increased patient discomfort and reduced speech ability (Canikligoglu & Ozturk, 2004).

Coated Wires

While the advent of clear or tooth-colored brackets has reduced the visibility of fixed appliances, the main hindrance to improving esthetics in orthodontics is the metallic appearance of conventional archwires. Recent advances have been made in coating conventional metallic archwires in tooth-colored polymeric resin materials such as synthetic fluorine-containing resin (polytetrafluoroethylene) or epoxy resin. However, there have been limited studies on the physical and mechanical properties of these newly introduced coated archwires.

Recent studies have determined that the coating properties have significant effects on mechanical properties. The polymer coatings of coated archwires were shown to significantly reduce frictional behavior when compared with non-coated wires from the same manufacturer (Husman, Bourauel, Wessinger, & Jager, 2002). Also, three point bending tests of coated and non-coated archwires have discovered that coated NiTi archwires produced lower loading and unloading forces in conventional ligation than non-coated wires (Elayyan, Silikas, & Bearn, 2008; Iijima et al., 2012). In addition, the presence of self-ligating brackets produced even lower force values in loading and unloading in the coated wires compared to conventional ligation (Elayyan, Silikas, & Bearn, 2010).

The esthetic value of the wires may decrease while in the mouth as the coating is lost due to a variety of factors (Kusy, 1997). Clinical use was shown to tear the coating, significantly increase surface roughness, and result in up to 25 percent coating loss (Elayyan et al., 2008). Further studies have documented the clinically noticeable color changes of esthetic archwires after only 21 days (Silva, Mattos, Arujo, & Ruellas, 2013). These changes in roughness and color can be attributed to forces from mastication and oral enzyme activities (Kusy, 2002). While coated archwires can serve as an esthetic adjunct to clear or tooth-colored brackets, mechanical properties may be altered by the coating process and the degradation and staining of the coating can hinder ultimate esthetics (Iijima et al., 2012; Elayyan et al., 2010).

Alternatives to Coated Wires

The introduction of composite archwires has offered patients and practitioners a new alternative to coated archwires in esthetic orthodontics. While coated archwires have diminished esthetics due to wearing or peeling, the composite wires have a translucent appearance without a coating. The translucency offers the advantage of the wire transmitting the color and shade of the teeth that surround them (Burstone et al., 2001).

The two main types of composite wires are fiber-reinforced and self-reinforced composites. Fiber-reinforced wires are composite materials with a polymer matrix and glass fibers for reinforcement. These translucent wires have been developed for the initial leveling and aligning stage of orthodontics, and the glass fibers provide the stiffness to straighten the teeth. In addition, the strength and stiffness of the wires can be altered by the manufacturer by adjusting the amount of reinforcement. This maintains the cross-sectional profiles of the wires and can reduce the need to change archwire materials as treatment progresses (Zufal & Kusy, 2000). While fiber-reinforced wires had great potential for esthetic alternatives, they lack ductility, are brittle, and are susceptible to breakage in the mouth. The fiber-reinforced composite wires also have low rigidity and strength in torque control, and the reinforcing fibers can be a hindrance on wire bending (Burstone et al., 2001). Overall, the esthetics of fiber-reinforced wires are impressive; however, the mechanical properties are lacking.

Newly introduced self-reinforced composite wires do not contain fibers and consist solely of polyphenylene polymers. These wires are not currently available but are in the development stage. The self-reinforced polymers possess better strength, hardness, and rigidity compared to previous fiber-reinforced wires while maintaining similar translucency for ideal esthetics (Goldberg, Liebler, & Burstone, 2011). Torque control and formability may be improved in self-reinforced wires with the exclusion of fibers, and the wires even allow the placement of bends. While these wires have similar properties to NiTi and beta-titanium in leveling and aligning, self-reinforced composite wires do exhibit stress relaxation and force loss with use. Composite wires may be promising for esthetic orthodontics but more studies on their mechanical properties will need to be completed once they are available for clinical use.

CHAPTER 3
MATERIALS AND METHODS

Four types of nickel-titanium orthodontic archwires were evaluated in this study. The four types consisted of two epoxy coated wires and two comparable control wires of the same .016 x 0.022 inch dimension: NiTi EverWhite wire and NiTi Memory Wire (American Orthodontics, Sheboygan, WI) and Opal Via Superelastic NiTi and Opal Via Pearl Esthetic Superelastic NiTi (Ultradent, South Jordan, UT). The wires were tested in the as-received state and after clinical use. For the clinical trial, a total of 61 patients were recruited from a private practice and were randomly allocated to receive one of the four types of archwires (n=15); one group had 16 subjects. A written informed consent was signed by each patient and parent. Prior IRB approval (Appendix 1) was received from the Marquette University Institutional Review Board (HR-2347). Sixty wires from the four groups in the as-received condition were also tested (n=15). In total, 121 wires were used. Seven wires from each of the 8 groups were analyzed by differential scanning calorimetry in the as-received state as well as after clinical use for a total of 56 test samples.

Archwires were sectioned into 5 mm segments (Figure 2) from the midline region with a water-cooled diamond saw (Figure 3, Buehler, Lake Bluff, IL). The archwire segments were weighed via an electronic balance (Figure 4, Mettler-Toledo, Columbus, OH) and were sealed into 40 µl aluminum crucibles.

Figure 2: A 5mm segment of clinically retrieved American Orthodontics EverWhite wire.

Figure 3: Water-cooled diamond saw (Buehler, Lake Bluff, IL).

Figure 4: Electronic balance (Mettler-Toledo, Columbus, OH).

An empty 40 µl aluminum crucible served as a reference during testing (Figure 5). Both crucibles were heated from -100°C to 100°C and subsequently cooled from 100°C to -100°C in the differential scanning calorimeter at a rate of 10°C per minute with liquid nitrogen serving as a coolant (Figure 6, Mettler-Toledo, Columbus, OH).

Figure 5: Aluminum crucibles on the sensor of the DSC. The crucible containing the wire sample is on the left and the blank reference crucible is on the right.

Figure 6: DSC equipment and liquid nitrogen.

DSC thermogram plots were constructed by the manufacturer's software and were quantitatively and qualitatively analyzed. Start, finish and peak temperatures along with changes in enthalpy for each sample were calculated for both heating and cooling.

A one way analysis of variance (ANOVA) was performed on each of the measurements to see if there was a difference between wire types. This was utilized instead of a t-test in order to control the Type I error rate. When the ANOVA test returned a significant result, Tukey's HSD test was used to determine which of the variants were significantly different. This also controls the Type I error rate that increases when running multiple t-tests. Eight models were utilized to compare coated and uncoated archwires from the same manufacturer and as-received and clinically retrieved wires from each type.

Additionally, the retrieved esthetic wires were analyzed via a computer program (Matlab, R2011b, The Mathworks, Inc., Natick, Massachusetts) after four to twelve weeks of use to determine the amount of epoxy coating lost while in the oral cavity. Digital scans of each wire on a light green background were taken before and after use, and saved in the TIF format (Figure 7).

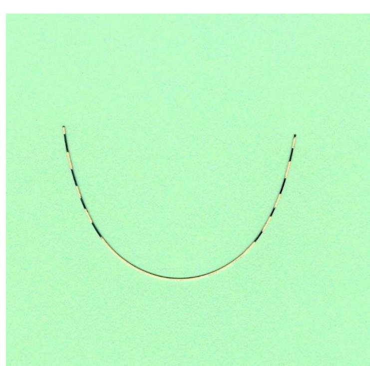

Figure 7: Scan of an Opal Via Pearl wire after clinical use.

The light green background was utilized to provide a contrast between the white wire coating, silver metal wire, and black shadow. Three numerical values were determined for each pixel in each scan – red, green and blue (RGB), and these RGB values were analyzed to determine whether each pixel constituted part of the coating, wire, or background. For the final results, an unused wire was processed as a control for each wire type. The percentage of wire, coating, and background was computed, and an independent t-test was used to compare the percentage in the American Orthodontics EverWhite group to the percentage in the Opal Via Pearl group.

CHAPTER 4
RESULTS

Figure 8 displays a thermogram comparing the as-received American Orthodontics (AO) uncoated wire with the coated EverWhite type, and Figure 9 displays a thermogram comparing the as-received Opal uncoated wire with the coated Via Pearl type. The coated EverWhite American Orthodontics wire has more pronounced peaks on heating and cooling compared to the uncoated version, and this demonstrates that there is a larger change in enthalpy in both the endothermic and exothermic transformations in the esthetic wire. In addition, transformation temperatures for the EverWhite wire are at lower temperatures compared to its uncoated counterpart. Conversely, the as-received esthetic Opal Via Pearl wire has smaller peaks than its uncoated counterpart, and thus has lower changes in enthalpy on heating and cooling. The transformation temperatures on heating and cooling for both Opal types are more similar than the American Orthodontics types, with the coated wires also having slightly lower transformation temperatures.

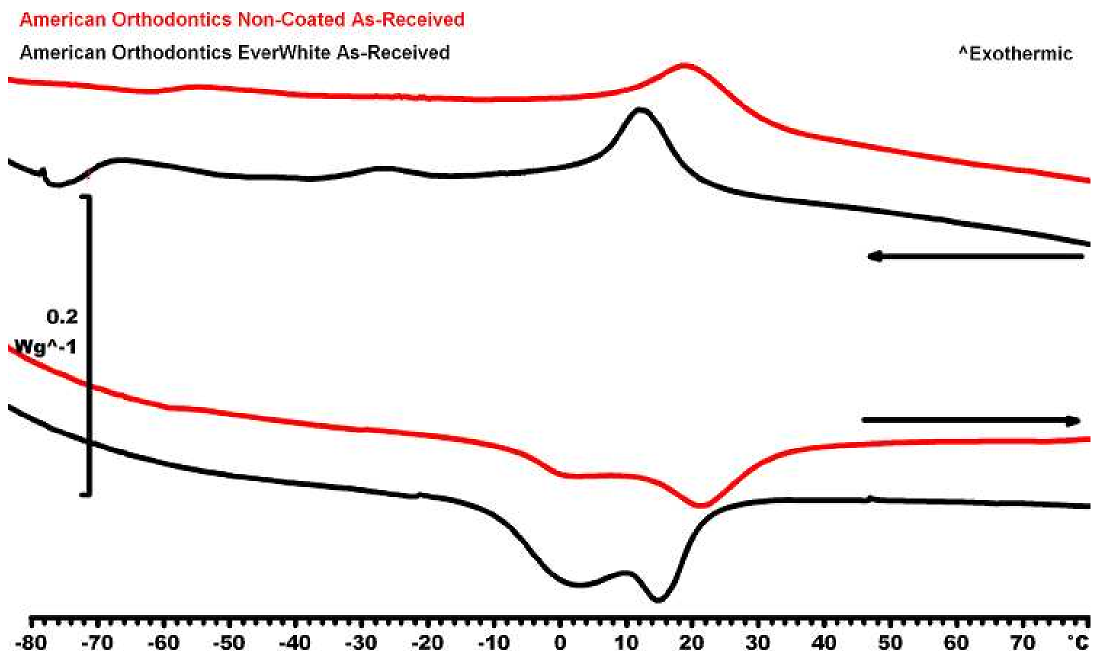

Figure 8: Thermograms of as-received American Orthodontics uncoated and EverWhite wires.

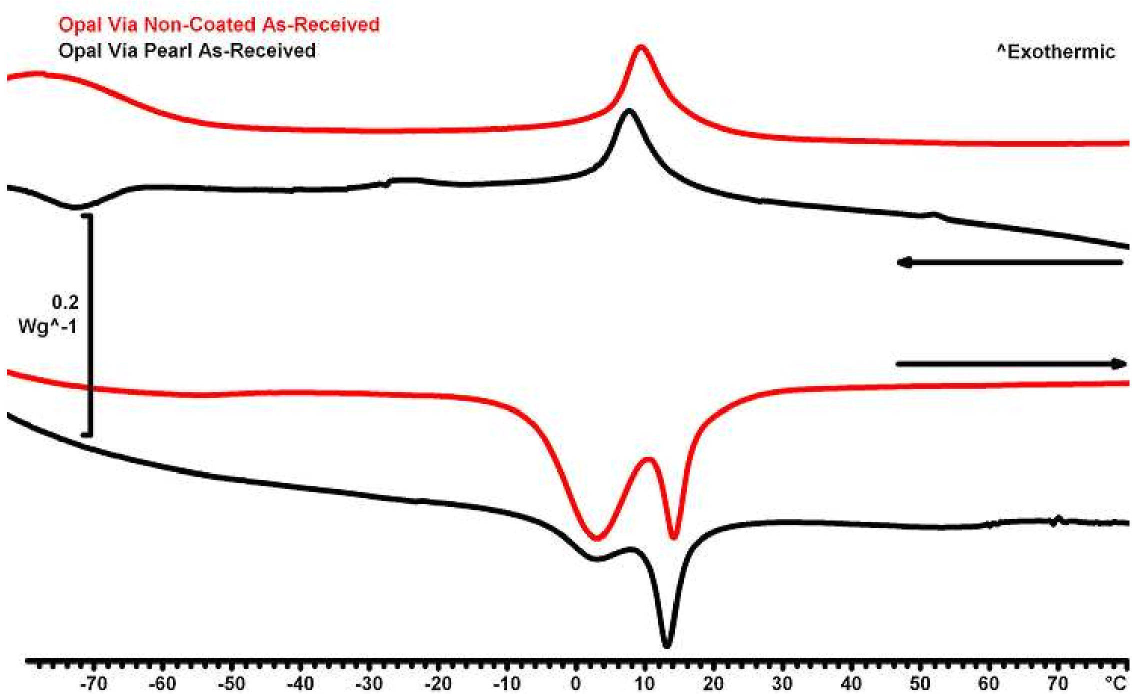

Figure 9: Thermograms of as-received Opal uncoated and esthetic Via Pearl wires.

Figure 10 displays a thermogram comparing the as-received American Orthodontics EverWhite wire with its clinically retrieved counterpart, and Figure 11 displays a thermogram comparing the as-received Opal Via Pearl wire with its clinically retrieved counterpart. There are very minimal visible differences on the thermograms between the as-received and clinically retrieved wires; however, the as-received Opal Via Pearl wire does has a noticeably smaller change in enthalpy compared to its clinically used counterpart.

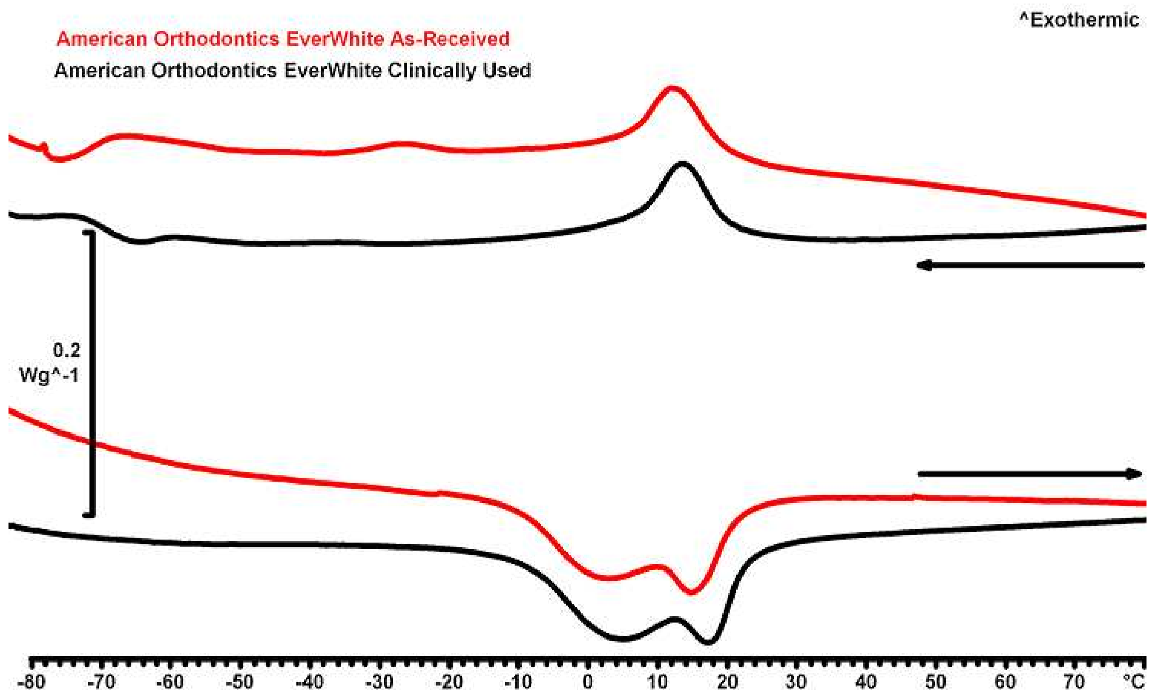

Figure 10: Thermograms of as-received and clinically used American Orthodontics EverWhite wires.

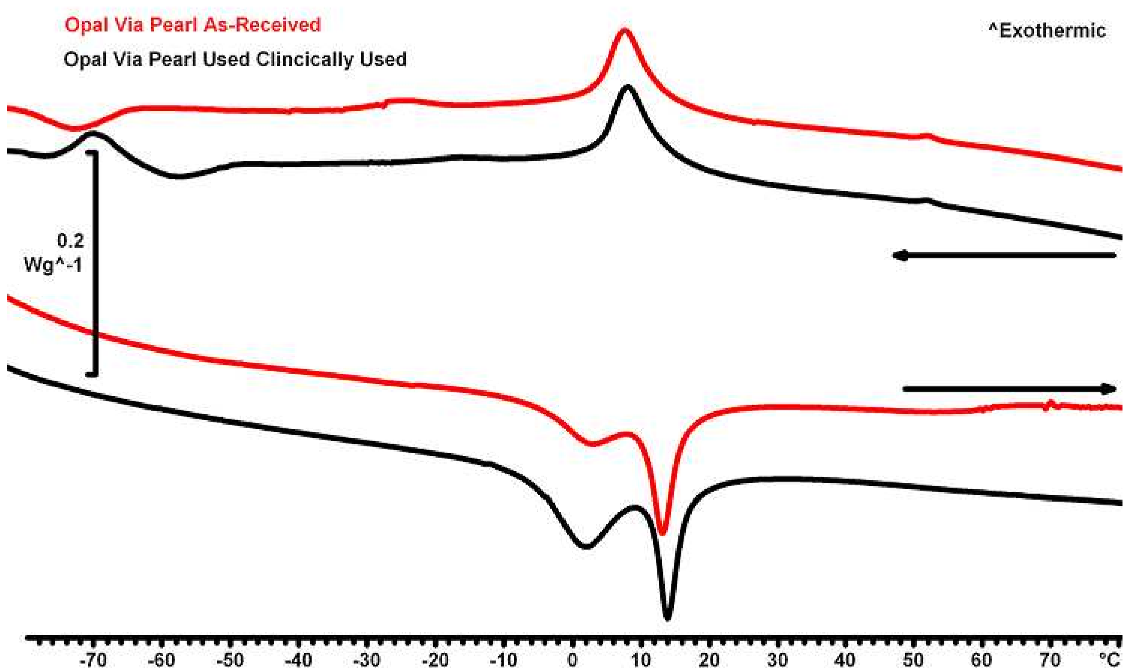

Figure 11: Thermograms of as-received and clinically used Opal Via Pearl wires.

Table 1 and Table 2 list the mean start temperatures, finish temperatures, peak temperatures, and changes in enthalpy for each wire on heating and cooling, and these quantitative findings correlate with the previous qualitative findings.

Wire Variant	Condition	Start temp, °C	1st peak temp, °C	2nd peak temp, °C	Finish temp, °C	Change in enthalpy, J/g
AO uncoated	As-received	-7.3 ± 0.7	3.6 ± 0.8	20.7 ± 0.5	29.8 ± 1.8	4.6 ± 0.5
AO uncoated	Retrieved	-7.1 ± 1.4	3.6 ± 0.8	20.9 ± 0.6	30.2 ± 2.1	4.6 ± 0.6
AO EverWhite	As-received	-10.8 ± 1.0	2.5 ± 2.3	14.5 ± 1.7	20.6 ± 2.2	8.6 ± 1.4
AO EverWhite	Retrieved	-10.8 ± 1.3	2.6 ± 2.2	14.3 ± 1.4	19.9 ± 1.5	9.0 ± 0.8
Opal Via uncoated	As-received	-6.2 ± 0.6	3.5 ± 0.5	14.4 ± 0.4	18.3 ± 0.6	13.0 ± 0.6
Opal Via uncoated	Retrieved	-6.4 ± 0.3	3.4 ± 0.3	14.2 ± 0.3	17.8 ± 0.5	13.1 ± 0.6
Opal Via Pearl	As-received	-6.3 ± 0.7	1.7 ± 0.9	12.5 ± 0.8	15.4 ± 0.8	6.6 ± 1.6
Opal Via Pearl	Retrieved	-7.4 ± 0.5	0.9 ± 0.8	12.0 ± 1.0	14.8 ± 1.2	9.0 ± 1.4

Table 1: DSC measured mean temperature and enthalpy changes for phase transformations during heating.

Wire Variant	Condition	Start temp, °C	Finish temp, °C	Change in enthalpy, J/g
AO uncoated	As-received	27.5 ± 2.0	8.8 ± 0.9	2.0 ± 0.5
AO uncoated	Retrieved	27.5 ± 1.9	8.6 ± 0.4	1.9 ± 0.3
AO EverWhite	As-received	18.5 ± 2.2	5.2 ± 1.5	2.5 ± 0.4
AO EverWhite	Retrieved	17.3 ± 1.8	4.7 ± 1.1	4.7 ± 0.4
Opal Via uncoated	As-received	15.3 ± 0.7	4.9 ± 0.3	3.1 ± 0.4
Opal Via uncoated	Retrieved	15.2 ± 0.5	5.0 ± 0.4	3.1 ± 0.3
Opal Via Pearl	As-received	12.7 ± 1.1	2.8 ± 1.1	2.7 ± 0.2
Opal Via Pearl	Retrieved	11.6 ± 1.1	2.2 ± 0.7	2.4 ± 0.2

Table 2: DSC measured mean temperature and enthalpy changes for phase transformations during cooling.

A one way analysis of variance (ANOVA) and subsequent Tukey HSD tests were performed to compare the coated and uncoated wires before clinical use in addition to all types of wires before and after clinical use. Eight statistical models were analyzed for each of the eight measurements for heating and cooling: start temperature on heating, temperature of the first heating peak, temperature of the second heating peak, finish temperature on heating, change in enthalpy on heating, start temperature on cooling, finish temperature on cooling, and change in enthalpy on cooling (Tables 3-10). The American Orthodontics uncoated wire and the coated EverWhite wire were found to be significantly different in all categories except temperature of the first heating peak. In addition, the Opal Via uncoated wire and Opal Via Pearl coated wire were found to be significantly different in regards to temperature of the second peak, finish temperature on heating, change in enthalpy on heating, and finish temperature on cooling. No other comparisons were found to be significantly different.

After clinical use, the American Orthodontics EverWhite coated wire lost an average of 44.31% of its coating while the Opal Via Pearl wire lost an average of 26.44% of its coating (Table 11). The independent t-test was utilized to compare the percentage in the American Orthodontics group to the percentage in the Opal group. Using the t-test, a test statistic of 3.877 ($p < 0.0001$) was calculated. This indicates that there is a significant difference between the clinically retreived American Orthodontics EverWhite and Opal Via Pearl groups.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	-0.39	0.9999
American non-coated before use	**American EverWhite before use**	**7.23**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	0.41	0.9999
Opal Via non-coated before use	Opal Via Pearl before use	0.19	1.0000
American EverWhite before use	American EverWhite before use	0.03	1.0000
Opal Via Pearl before use	Opal Via Pearl after use	2.24	0.3493

Table 3: Model 1: Start temperature (heating) - The ANOVA returned a significant result with a test statistic of F (7,48) = 30.97, p <0.0001. This indicates that at least two of groups are significantly different. Tukey HSD test showed that American Orthodontics uncoated and American Orthodontics EverWhite are significantly different with regards to heating temperature.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	-0.03	1.0000
American non-coated before use	American EverWhite before use	1.57	0.7639
Opal Via non-coated before use	Opal Via non-coated after use	0.25	1.0000
Opal Via non-coated before use	Opal Via Pearl before use	2.69	0.1521
American EverWhite before use	American EverWhite before use	-0.17	1.0000
Opal Via Pearl before use	Opal Via Pearl after use	1.26	0.9088

Table 4: Model 2: Temperature at the first peak (heating) - The overall test statistic of F(7, 48) = 4.36, p = 0.0008. This indicates that at least two of the groups are significantly different so post hoc tests are considered. None of the comparisons that were of interest were significant.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	-0.36	1.0000
American non-coated before use	**American EverWhite before use**	**12.07**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	0.42	0.9999
Opal Via non-coated before use	**Opal Via Pearl before use**	**3.79**	**0.0092**
American EverWhite before use	American EverWhite before use	0.34	1.0000
Opal Via Pearl before use	Opal Via Pearl after use	0.97	0.9763

Table 5: Model 3: Temperature at the second peak (heating) - The overall test statistic of F(7, 48) = 89.29, p < 0.0001. This leads us to conclude that at least two of the groups are different. The American Orthodontics uncoated and American Orthodontics EverWhite wires were found to be significantly different, as were Opal Via uncoated and Opal Via Pearl.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	-0.46	0.9998
American non-coated before use	**American EverWhite before use**	**11.68**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	0.54	0.9993
Opal Via non-coated before use	**Opal Via Pearl before use**	**3.56**	**0.0179**
American EverWhite before use	American EverWhite before use	0.83	0.9905
Opal Via Pearl before use	Opal Via Pearl after use	0.88	0.9868

Table 6: Model 4: Finish temperature (heating) - The overall test statistic of $F(7, 48) = 115.00$, $p < .0001$. Since this tells us that a minimum of two groups are significantly different, we consider the Tukey post hoc tests. Based on these tests, American Orthodontics uncoated and American Orthodontics EverWhite were found to be significantly different, as were Opal Via uncoated and Opal Via Pearl.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	0.01	1.0000
American non-coated before use	**American EverWhite before use**	**-1.35**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	-0.17	1.0000
Opal Via non-coated before use	**Opal Via Pearl before use**	**11.65**	**<.0001**
American EverWhite before use	American EverWhite before use	-0.67	0.9974
Opal Via Pearl before use	Opal Via Pearl after use	-4.41	0.0014

Table 7: Model 5: Enthalpy (heating) - The overall test statistic of $F(7, 48) = 72.40$, $p < .0001$. Based on the Tukey post hoc tests, American Orthodontics uncoated and American Orthodontics EverWhite were found to be significantly different, as were Opal Via uncoated and Opal Via Pearl.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	-0.01	1.0000
American non-coated before use	**American EverWhite before use**	**11.11**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	0.10	1.0000
Opal Via non-coated before use	Opal Via Pearl before use	3.16	0.0515
American EverWhite before use	American EverWhite before use	1.42	0.8425
Opal Via Pearl before use	Opal Via Pearl after use	1.37	0.8678

Table 8: Model 6: Start temperature (cooling) - From the ANOVA model, the test statistic of $F(7,48) = 114.65$, $p < .0001$. Based on the Tukey post hoc tests, American Orthodontics uncoated and American Orthodontics EverWhite were found to be significantly different.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	0.46	0.9998
American non-coated before use	**American EverWhite before use**	**7.25**	**<.0001**
Opal Via non-coated before use	Opal Via non-coated after use	-0.14	1.0000
Opal Via non-coated before use	**Opal Via Pearl before use**	**4.34**	**0.0018**
American EverWhite before use	American EverWhite before use	1.00	0.9728
Opal Via Pearl before use	Opal Via Pearl after use	1.05	0.9633

Table 9: Model 7: Finish temperature (cooling) - The overall test statistic of $F(7, 48) = 44.82$, $p < 0.0001$. From the post hoc tests, we can conclude that American Orthodontics uncoated and American Orthodontics EverWhite were found to be significantly different, as were Opal Via uncoated and Opal Via Pearl.

Group 1	*Group 2*	*t*	*p-value*
American non-coated before use	American non-coated after use	0.23	1.0000
American non-coated before use	**American EverWhite before use**	**-3.25**	**0.0411**
Opal Via non-coated before use	Opal Via non-coated after use	0.29	1.0000
Opal Via non-coated before use	Opal Via Pearl before use	2.52	0.2116
American EverWhite before use	American EverWhite before use	0.09	1.0000
Opal Via Pearl before use	Opal Via Pearl after use	1.59	0.7510

Table 10: Model 8: Enthalpy (cooling) - The overall test statistic for this model is $F(7, 48) = 12.32$, $p < .0001$. American Orthodontics uncoated and American Orthodontics EverWhite were found to be significantly different based on the Tukey HSD test.

Sample	N	Mean days in mouth	Mean coating lost	Std Dev	Std Err	Minimum	Maximum
American Orthodontics EverWhite	15	44.27	44.31	11.60	2.99	28.91	66.38
Opal Via Pearl	16	55.13	26.44	13.94	3.49	5.37	57.09
Difference between esthetic wires			17.87				

Table 11: The mean percentage, mean days intraorally, standard deviation, and maximum and minimum amount of coating lost for both American Orthodontics EverWhite and Opal Via Pearl coated archwires.

CHAPTER 5
DISCUSSION

Both manufacturers advertised their esthetic coated wires as having the same properties as their uncoated counterparts, but there were statistically significant differences between the wires. American Orthodontics uncoated Memory NiTi and coated EverWhite wires were significantly different in seven of the eight measurements analyzed in this study, and the temperature of the first heating peak was the only parameter in which there was no statistically significant difference. In addition, the American Orthodontics EverWhite wire had a drastically different austenitic finish temperature, 20.9°C, compared to the uncoated type, 29.8°C. The austenitic finish temperature of the EverWhite wire is considerably below room and oral temperature, and therefore, the wire is in the austenitic form at room temperature and may be superelastic or force dependent. This is in contrast to the uncoated American Orthodontics wire which is not completely transformed to the austenitic form until it reaches a temperature above 29.8°C, such as in the oral environment. Thus, the uncoated wire is characterized as being heat activated or temperature dependent. Therefore, these two wire types with significantly different thermal properties may have differing forces and behaviors that can significantly alter their clinical use.

While there are significant differences between the Opal Via uncoated and the coated Via Pearl wire types, the wires are more similar in comparison to the American Orthodontics coated and uncoated wire types. There are significant differences between the temperature of the second heating peak, the finish heating temperature, and the change in enthalpy on heating; however, differences between the Opal Via uncoated and

Via Pearl transformation temperatures are minimal when compared to the American Orthodontics wire types. Both Opal wires have austenitic finish temperatures below room temperature, and this coincides with the advertised claim of superelasticity in both Opal nickel-titanium wire types. Although both wires are superelastic, there is a 2.9°C difference between austenitic finish temperatures in both wire types. This difference could alter the forces produced by these wires since the force applied depends partially on the austenitic finish temperature and the deviation from the ambient temperature (Iijima, Ohno, Kawashima, Endo, & Mizoguchi, 2002).

The coated Opal Via Pearl wire has a significantly lower change in enthalpy on heating, 6.6 J/g, compared to the uncoated type, 13.0 J/g, and this coating may ultimately act as an insulator. The coating may prevent some heat to transfer from the wire to the differential scanning calorimeter and ultimately reduce the endothermic transformation. In addition, the change in enthalpy for the Via Pearl wire after use was 2.4 J/g higher compared to the as-received type. This coincides with the clinically retrieved wires having significantly less coating after use and demonstrating less of an insulating effect. Although the uncoated American Orthodontics wire has a lower change in enthalpy on heating than the coated type, the EverWhite coated type does have a slightly larger change in enthalpy after use and coating loss which correlates with the findings from the coated Opal Via Pearl wire. While there are some differences between the coated and uncoated types, Opal's advertised claim that both wires possess similar properties appears to be accurate.

The present DSC data for as-received and clinically retrieved nickel-titanium archwires from this study displays that clinical use of uncoated and epoxy resin coated nickel-titanium archwires does not alter their thermal properties. Differences in phase transformation temperatures and changes in enthalpy after clinical use were minimal and were not found to be statistically significant. This finding correlates with the study done by Biermann et al. (2007) in which copper-nickel-titanium archwires in three temperature variants showed minimal thermal property changes after clinical use by differential scanning calorimetry. Three CuNiTi temperature varieties, 27ºC, 35ºC, and 40ºC, were analyzed and there was only a statistically significant change in the heating enthalpy for the clinically retrieved 27ºC wire type. A similar DSC study analyzing superelastic nickel-titanium endodontic files by Brantley, Svec, Iijima, Powers, and Grentzer (2002) found that simulated clinical use of endodontic files had no evident effect on the martensite-asutenite phase transformation as well; however, there was minimal mechanical deformation of the nickel-titanium files during use in that particular study.

The present study included epoxy resin coated nickel-titanium archwires and both of the previous studies mentioned solely examined uncoated nickel-titanium archwires and endodontic files. Even though four to twelve weeks of clinical use resulted in the loss of a significant portion of the epoxy resin coatings in both wire types, the loss of coating did not alter the wire's thermal properties compared to the as-received coated wire counterparts. Therefore, it can be determined that the epoxy resin coating has minimal effect on the phase transformation of the underlying nickel-titanium wires.

Four to twelve weeks of clinical use of epoxy coated archwires resulted in a significant amount of coating removal. The Opal Via Pearl wire had an average of 26.44% of the coating lost while the American Orthodontics EverWhite wire had an average of 44.31% of the epoxy coating lost, and the difference between these two types was statistically significant. This finding correlates with a previous study done by Elayyan et al. in which an alternative epoxy resin coated nickel-titanium archwire lost an average of 25% of their coating after an average of 33 days in the oral environment. In addition, surface roughness of the coated archwires increased after use and surface morphology showed severe deterioration under microscopy in that study (Elayyan et al., 2008). The findings of this study also contradict the advertised claim that the American Orthodontics EverWhite wire has the most durable cosmetic coating available (American Orthodontics Coated Wire, n.d.). Although wire from both companies lost a significant amount of coating, the Opal Via Pearl maintained an average of 17.87% more coating than the EverWhite wire.

While the wires lost a large portion of their coatings, the majority of the coating loss in both sets of wires coincides with where the wire was in intimate contact with the bracket. This would suggest that the mechanical engagement of the wire into the brackets with elastomeric ligation and the forces transferred in normal function appear to have caused the major portion of the coating loss with the remainder of the wire coating being more stable. This is an interesting finding in that the coating may be expected to impact friction as the surface defects are at the edges of the brackets, and this may impede the archwire from sliding.

The American Orthodontics EverWhite wire and Opal Via Pearl wire were used clinically for an average of 48.27 and 55.13 days respectively. While the Opal Via Pearl wire was used for an average of 6.86 days longer than the EverWhite wire, it still maintained more coating than the EverWhite type. In addition, some wires from both manufacturers that were used for the longest period of time showed lower than average coating loss, and conversely some wires that were used for the shortest period of time showed higher than average coating loss. Therefore, it appears that time of clinical use does not directly relate to the amount of coating loss and that coating loss is due to some other mechanical or chemical irritants and could be patient-related.

Although the esthetic appearances of these archwires are limited, the majority of the coating loss was on portions of the wire that are not readily visible. Therefore, both sets of coated wires offer a modest improvement to the uncoated conventional nickel-titanium archwires. To improve esthetics, manufacturers must develop a coating or an alternative material that does not deteriorate under friction or mechanical stress.

CHAPTER 6
CONCLUSIONS

In this study, the following conclusions were demonstrated:

- Comparison of measured DSC parameters showed differences between as-received coated and uncoated archwires from both manufacturers.
- The coated American Orthodontics EverWhite wire may act superelastic while its uncoated counterpart may be heat activated. The wires have significantly different thermal properties, and this may lead to these wires having differing forces and behaviors that can significantly alter their clinical use.
- The difference in austenitic finish temperatures for the Opal coated and uncoated wires may cause the wires to exhibit slight differences in forces.
- There was no statistically significant difference of thermal properties between the archwires from both manufacturers before and after clinical use.
- The amount of epoxy resin coating loss appears to be dictated by archwire engagement and not by the time the wire was present in the oral cavity.
- Both wires lost a significant amount of esthetic coating after four to twelve weeks in the oral cavity, and improvements to coating techniques or alternative wires must be explored for better esthetics.

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