Thermal Properties of Commonly Used Clear Aligner Systems As-Received and After Clinical Use

Louis Wenger
Marquette University

Recommended Citation
Wenger, Louis, "Thermal Properties of Commonly Used Clear Aligner Systems As-Received and After Clinical Use" (2017). *Master's Theses (2009 -)*. 431.
http://epublications.marquette.edu/theses_open/431

THERMAL PROPERTIES OF COMMONLY USED CLEAR ALIGNER SYSTEMS AS-RECEIVED AND AFTER CLINICAL USE

by

Louis Wenger, D.M.D.

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science

Milwaukee, Wisconsin

August 2017

ABSTRACT
THERMAL PROPERTIES OF COMMONLY USED CLEAR ALIGNER SYSTEMS AS-RECEIVED AND AFTER CLINICAL USE

Louis Wenger, D.M.D.

Marquette University, 2017

Background/Objectives: The purpose of this study was to investigate the thermal properties, particularly glass transition temperature, of the polymers that are used to fabricate three different types of modern orthodontic aligners. Invisalign, (Align Technology, Inc, Santa Clara, CA, USA), Simpli5 (Allesee Orthodontic Appliances, Sturtevant, WI, USA), and ClearCorrect (ClearCorrect, Round Rock, TX, USA) were examined both as-received and after clinical use to determine if any differences were present both between and within aligners.

Materials/Methods: Orthodontic aligners were collected from three different patients using the systems under investigation after two weeks of intraoral use. Duplicate, un-used samples were obtained from the manufacturers for direct comparison. The aligners were then sectioned into sizes that were compatible with the instrumentation being used to analyze them. Differential Scanning Calorimetry (DSC) was used to individually analyze the thermal properties of each sample. The resulting thermograms were then compared to investigate potential differences between brands and conditions. Of particular interest was the temperature at which each polymer went through the glass transition phase. Enthalpy relaxation, recrystallization temperature, and melting point were also analyzed.

Results: There was no statistical difference in glass transition temperature between as-received and after use Invisalign, ClearCorrect, or Simpli5 aligners ($p>0.05$). In addition, there was no significant difference in recrystallization peak and recrystallization enthalpy between as-received and after use Simpli5 aligners ($p>0.05$). There was a significant decrease in melting peak and melting enthalpy between as-received and after use Simpli5 aligners ($p<0.05$). A lack of recrystallization and melting peaks indicates that Invisalign and ClearCorrect are a thermoset material while the presence of these peaks indicates that Simpli5 is thermoplastic. All materials possessed a glass transition temperature above the maximum temperature that is found intraorally.

Conclusions: Glass transition temperature did not significantly change after clinical use in the tested orthodontic aligners, indicating the stability of this property throughout normal treatment. All three types have a glass transition temperature above the maximum temperature that is found intraorally, which has been shown to be a benefit to an aligner's mechanical properties. Melting peak and melting enthalpy showed a small decrease after use in Simpli5, indicating some structural aging intraorally.

ACKNOWLEDGMENTS

Louis Wenger, D.M.D.

I would like to sincerely thank my advisor Dr. David Berzins for his continued help and support throughout this project. I would also like to thank my thesis committee members Dr. Dawei Liu, Dr. Bhoomika Ahuja, and Dr. Ghada Nimeri for their assistance, direction, and encouragement. Lastly, I want to thank Kate Sherman for performing my statistical analysis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1
INTRODUCTION

The perceived unattractive nature of traditional metal orthodontic brackets has long been one of the main drawbacks to orthodontic treatment. The social stigma that it carries is well-known and documented in many studies. In a recent survey, it was found that the public has a lower perception of intellectual ability for those wearing metal braces when compared to clear aligners (Jeremiah et al. 2011). In another study of 200 people, it was found that clear aligners are considered to be more attractive than both metal and ceramic brackets (Ziuchkovski et al. 2008). It was again confirmed in a patient-profiling study that the primary reason that patients pursue clear aligner therapy is for improved esthetics during treatment (Meier et al. 2003). To appeal to these concerns, there has recently been an increase in the implementation of clear orthodontic aligners to meet the esthetic demands of the modern orthodontic patient.

Orthodontic aligner therapy consists of a series of custom-fit, thermoformed plastic trays that each sequentially moves teeth in a desired direction. Recent advances in technology have made the mass production of aligners more predictable and customizable (Kuo and Miller 2003). Being a relatively new treatment modality, there is considerable research being conducted on the efficacy of aligner treatment and the properties of the materials they are composed of (Kravitz et al. 2009, Bradley et al. 2016, Lombardo et al. 2016). Of particular interest is the effect that intraoral use has on the integrity of the aligner material. It has already been shown that used aligners become more brittle, undergo a decrease in creep resistance, and undergo composition changes after oral exposure (Ahn et al. 2015, Bradley et al. 2016, Schuster et al. 2004). Aligners also undergo physical changes such as cracking and wear due to the harsh conditions of the oral cavity (Gracco et al. 2009). These changes in mechanical and chemical properties of aligners have been shown to have an impact on the level of forces that are applied to teeth during treatment, an understanding of which is critical in seeking the ideal material for this type of treatment (Kohda et. al. 2007).

What has not been extensively researched is how this intraoral aging process may affect the thermal properties of the aligners. Past studies have demonstrated that clear aligner therapy has its limitations, particularly in torqueing and extrusive movements (Kravitz et al. 2009, Rossini et al. 2015). For the advancement of this treatment technique it is important to investigate and measure all properties of the materials being used so they may be improved upon. This study investigated thermal properties including glass transition, enthalpy relaxation, and recrystallization temperature of aligners before and after clinical use.

In this study, the thermal properties of Invisalign (Align Technology, Inc, Santa Clara, CA, USA), Simpli5 (Allesee Orthodontic Appliances, Sturtevant, WI, USA), and ClearCorrect (ClearCorrect, Round Rock, TX, USA) were investigated before and after clinical use. Differential scanning calorimetry (DSC) was used to analyze samples from each type of aligner material. DSC has previously been used to identify the glass transition temperature of aligner materials, but that study used blank, unprocessed material and used in vitro thermocycling as opposed to clinical use (Iijima et al. 2015). There are very few studies available that demonstrate the usefulness and repeatability of DSC for determining thermal properties of orthodontic aligners. This is the first study to employ DSC to investigate thermal properties of these particular brands of aligners both before and after intraoral use.

CHAPTER 2
LITERATURE REVIEW

Esthetic Orthodontic Treatment

Due to the current availability of esthetic options for orthodontic treatment, there has been an increase in the desire for and perception of these appliances when compared to traditional metal brackets. Several studies have confirmed what many would intuitively assume regarding the preference for esthetic appliances. One such study of 200 American adult subjects using standardized digital images and a visual analog scale found that there is a significantly higher perception of attractiveness when comparing aligners to both ceramic and stainless steel brackets (Ziuchkovski et al. 2008). Other such surveys have confirmed the above and also found that there is often an increased perception of intellectual ability with those wearing aligners vs. metal brackets (Jeremiah et al. 2011). Some evidence even indicates that certain demographics (in this case patients ages 17-26 with higher socio-economic status) are willing to pay more for aligners when compared to metal brackets (Feu et al. 2012, Rosvall et al. 2009). These reports are indicative of a preference shift in orthodontics from traditional metal brackets towards more esthetic appliances such as aligners.

Due to limitations in dental materials, stainless steel brackets were the only option for several decades once direct bonding became effective enough to replace banding each tooth. Stainless steel is a very suitable biomaterial and continues to perform well today for bracket fabrication and clinical use. However, as esthetic demands in patients grew, the search for an esthetic option became a primary concern among manufacturers. In the 1970s, the first clear brackets became available. These brackets were polycarbonate plastic brackets which seemed at the time to be a drastic improvement over their metal counterparts. However clinical use quickly caused these brackets to lose favor with clinicians due to their tendency to become discolored and distort due to their water absorption (Jena et al. 2007).

Their replacement came in the 1980s when ceramic technologies made precision bracket fabrication a possibility. Today, almost all esthetic brackets are composed of aluminum oxides in different formulations and possess much more ideal properties for orthodontic use. While much more attractive than metal, these brackets suffer from a lower fracture toughness and increased friction between the wire and slot. An additional concern is the high strength to which they bond to enamel surfaces. While designs have improved, there have still been reports of enamel damage upon debonding ceramic brackets (Ansari et al. 2016).

Due to the difficulties of working with plastic and ceramic, there have also been metal appliances developed to be placed on the lingual surface of the teeth. Their first clinical use in the US came about in the 1970s. These lingual appliances still claim a small portion of the orthodontic market but bring with them their own set of complications. By invading the space occupied by the tongue, they can cause lingual irritation, speech impediments, and annoying food traps for patients. Additionally, due to the complex morphology of the lingual surfaces, these brackets are most often manufactured digitally by a lab for a precise, custom fit for each patient. This brings additional cost to the clinician, which then must be passed on to the patient (Saini et al. 2016).

Finally, the current most popular method of esthetic orthodontic treatment is clear aligner therapy. These custom-made aligners are fabricated by a laboratory off of precise impressions or digital scans of patient's teeth. Each sequential aligner has a specific amount of movement built into it to guide the dentition toward a predetermined outcome (Kuo and Miller 2003). Primary benefits of these appliances are a metal-free, clear appearance and better oral hygiene due to their removability. Downsides to this treatment include lack of chairside modification and increased laboratory costs.

Clear Aligner Therapy

Beginning with Align Technology (Santa Clara, CA) in 1998, advances in technology and manufacturing have allowed companies to consistently and accurately make custom-fit appliances for dentists and orthodontists (Kravitz et al. 2009, Kuo and Miller 2003). In addition to Align, ClearCorrect (Round Rock, TX) and Allesee Orthodontic Appliances (Sturvevant, WI) also produce clear aligners that were investigated in this study (See Figure 1). Due to the need for exacting fit, aligners are produced indirectly, most often by companies such as those listed above. The process is initiated by the orthodontist who sends either an impression or digital scan of the patient's teeth to the lab for fabrication. After receiving the patient's information, the laboratory then uses stereolithography (a form of 3D printing that utilizes photopolymerization) to produce a resin model representing each stage of the treatment. A transparent polymeric material is then used to create an aligner over each model (Kuo and Miller 2003). The aligners are then packaged and shipped to the orthodontist and delivered to the patient, who wears each tray for an average of two week intervals (Kravitz et al. 2009).

Figure 1: As-received aligners used in this study. From left to right, Simpli5, ClearCorrect, and Invisalign

Besides the aforementioned esthetic benefits of aligner therapy, reports have also shown that orthodontic treatment with aligners is more comfortable than traditional fixed appliances. In a prospective study of 60 adult orthodontic patients, those receiving clear aligner therapy reported statistically significant fewer negative impacts on overall quality of life. Subgroups of quality of life were also measured and it was found that in functional, psychosocial, and pain categories there were also significantly fewer impacts compared to fixed appliances. Within the first week of treatment, the group wearing traditional braces experienced significantly more pain and took more pain medications on the second and third day (Miller et al. 2007). This study only investigated the first week of treatment, as this has been demonstrated to be the most detrimental period to the patient’s quality of life (Miller et al. 2007). It would be interesting however to extend this study to observe long-term trends.

While it appears that clear aligner systems such as Invisalign are superior in terms of comfort and appearance, the same cannot be said for their clinical performance. A recent systematic review of the clinical performance of clear aligner therapy found that aligners fall short in achieving their intended movements. The most predictable movements were intrusion, leveling, and aligning, but very poor predictability was found in extrusions, rotations, and tipping movements. The least predictable movement was found to be extrusion, with actual outcomes only showing 30% of the virtually predicted movements (Rossini et al. 2015). Conceptually, this makes sense when imagining the poor grip that smooth plastic has on a smooth tooth surface. Improved attachments and superior aligner material are needed to increase the efficacy and predictability of aligner movements (Rossini et al. 2015). This review was corroborated by a different study which also found that the least effective tooth movement is extrusion. Overall, the mean accuracy of movements performed by Invisalign was found to be 41% (Kravitz et al. 2009). It is clear that there is room for improvement regarding the predictability of movements with clear aligners, and an improvement in and a better understanding of aligner materials will be a key part in that process.

Clear aligners are fabricated with clear polymeric sheets, usually composed of a polyurethane resin or polyethylene terephthalate. The aligners in this investigation are polyurethane based (Invisalign and Clear Correct) and an unlisted proprietary material (Simpli5) (Align Technology MSDS, Bay Materials, LLC MSDS). The analysis of these materials should allow comparisons of two polyurethane materials and make predictions regarding the material being used for Simpli5. Since the desired dental movement is a direct result of the properties of the aligner, there have been several studies on their mechanical properties. The material they are made of, as well as their surrounding environment and thickness, affect their ability to apply forces when deflected (Kohda at al. 2013, Schuster et al. 2004).

The two known materials being used in this study are polyurethane based. Polyurethane is a polymeric plastic that is formed by a reaction between an alcohol with two or more hydroxyl groups and an isocyanate that has more than one isocyanate group. The connection between the two forms a urethane linkage which is the most critical portion of the polyurethane molecule. The physical characteristics of polyurethane can vary widely depending on the components used to create the polymer. The number of reactive sites on the polyol used in the reaction ultimately controls the degree of cross-linking in the polyurethane, which dictates the physical properties of the final product (Zhang 2011, Polyurethanes 2015). It is this high degree of cross-linking which gives the thermosetting properties necessary for forming aligners (Lithner 2011). The versatility in polymerization provides the manufacturer the ability to precisely control the stiffness and stress relaxation properties which are important in clear aligner performance. Additional additives are also used in the fabrication in small amounts to further manipulate physical characteristics such as catalysts, cross-linking agents, fillers, and flame retardants (Lithner 2011). In the context of aligner fabrication, the polyurethane is first made into thin sheets which can then be processed into aligners.

Due to the variability within the composition of polyurethane, no two are exactly alike and thus perform differently in orthodontic settings. Studies have been performed to analyze how these properties affect the clinical uses of clear aligners. In one study, single layer polyurethane aligner material, such as those used in Invisalign and ClearCorrect, was compared to single layer polyethylene terephthalate glycol. Both had similar initial yield strength but differed in the manner in which stress was lost during constant load. It was found that the greatest stress relaxation occurs during the first 8 hours followed by a steady plateau. After 24 hours of constant load, the polyurethane aligner lost 54.5% of its initial stress while the polyethylene terephthalate glycol aligner lost 62% (Lombardo et al. 2016). While polyurethane demonstrated less stress relaxation, the amount was still far greater than should be displayed by an ideal orthodontic aligner. This finding was confirmed in a study that attempted to design a more mechanically ideal aligner material through polymer blending. When polyethylene terephthalate glycol was combined with polyurethane, it was found that stress relaxation decreased further as more polyurethane was added to the mixture (Zhang et al. 2011). However it was also found that water absorption increased as further polyurethane was added, which could cause intraoral permanent degradation of the polymer due to hydrolysis (Zhang et al. 2011). Due to the viscoelastic properties of all aligners, some stress relaxation is bound to occur as much as researchers attempt to minimize the effect. Clear aligners have stiff competition with the nickel-titanium and copper-nickel-titanium used in traditional fixed appliances, which display much more desirable load deflection patterns (Lombardo et al. 2016).

Along with high stress relaxation, clear aligners have also been shown to undergo changes after being worn intraorally, a factor that is taken into account in this study. A 2004 study found that polyurethane aligners were significantly harder and underwent permanent surface distortion after being exposed to the oral environment (Schuster et al. 2004). A second retrieval analysis study found that although no molecular changes occurred in the material after use, every mechanical parameter (indentation modulus, elastic index, Martens hardness, and indentation creep) deteriorated (Bradley et al. 2016). Fang et al. also demonstrated that stress relaxation in aligners increases at body temperature when compared to room temperature (Fang et al. 2013). Orthodontic aligner materials are at risk of mechanical change when subjected to the oral environment and this effect must be evaluated in a study of the properties of these materials. Figure 2 shows the visible changes that aligners undergo after two weeks of intraoral use.

Figure 2: New (left) and used Invisalign trays, demonstrating the visible changes that aligners undergo after two weeks of continuous intraoral use.

The aforementioned mechanical properties of clear aligners have been studied to some length, but thermal analysis of aligners before and after use is far less available. Thermal analysis has however been found to be useful for investigating other dental materials. Differential scanning calorimetry is particularly useful for nickel-titanium products and other such products that possess specific phase transition temperatures. DSC has been found to be useful in the thermal characterization of all types of orthodontic archwires including stainless steel, titanium molybdenum alloy, and nickel-titanium and has also been used to analyze phase transitions found in nickel-titanium endodontic files (Kusy and Whitley 2007, Brantley et al. 2002). DSC has also been used to evaluate for differences between orthodontic archwires before and after clinical use. A study in 2007 that investigated phase transition temperatures in copper-nickel-titanium archwires found very few differences in the transition temperatures when comparing before and after. The only significant difference when comparing used vs. new was found in a wire with a very low martensitic-austenitic phase transition temperature (Biermann et al. 2007). Similarly, a study in 2013 investigating esthetic nickel titanium archwires found no significant differences in phase transition temperature before and after clinical use (Valeri 2013).

One interesting study performed in 2015 did look at orthodontic aligner thermal properties and their relation to mechanical properties before and after simulated use. The mechanical properties of three polyurethane aligner materials, all with different glass transition temperatures, were compared after thermocycling and stress applications. It was discovered that the mechanical properties including hardness, elastic modulus, and yield strength all significantly deteriorated more in the material with the lowest transition temperature (29.6°C). The two materials with transition temperatures (56.5°C and 80.7°C) higher than the upper limit of the thermocycling statistically performed better. The upper limit of the thermocycler was placed at 55°C because this is the upper limit of temperatures found in the oral cavity (Moore et al. 1999). The implication of this study is that aligner materials, particularly polyurethane, may perform clinically better if their glass transition temperature lies above the maximum temperature found intraorally (Iijima et al. 2015). However, this study did not confirm that the transition temperature remained unchanged after simulated clinical use.

Thermal properties of polymers are largely dictated by their molecular structure and branching patterns. Polymers used for orthodontic aligners are semi-crystalline materials meaning they are composed of regions of highly ordered crystalline segments interspersed with amorphous areas. The ratios of the two regions affect both mechanical and thermal properties as a higher proportion of crystallinity will produce a material that is more rigid with a higher glass transition temperature. All polymers have a glass transition temperature which is the point at which the glassy (rigid) state converts to a rubbery state as the increase in temperature allows chains within the amorphous region to become more mobile. Polymers which contain crystalline areas, such as those used in orthodontic aligners, also possess a melting point, which is the temperature at which the crystalline structure breaks down. These two temperatures are affected by the arrangements of polymer chains and how the chains interact with one another. A more orderly, cross-linked polymer will display higher glass transition temperatures and melting temperatures (Balani et al. 2015).

Other points of interest when investigating the thermal properties of polymers are crystallization and enthalpy relaxation. Crystallization peaks are exothermic events that occur when semi-crystalline materials are heated past their glass transition temperatures. The presence of these events is an indication of how rapidly the polymer was cooled. When a liquid polymer is rapidly cooled, a large portion of the polymer is unable to properly form crystals and is trapped in an amorphous phase. When heated to a specific temperature, the polymer chains gain enough mobility to spontaneously form crystalline structures and give off energy as a result of the increasing order of the material. Another characteristic of interest is enthalpy relaxation, which is an indication of the thermal history of a polymer. The longer a polymer sits at temperatures below its glass transition, the greater the structural relaxation that occurs, which is visible as an endothermic peak in the vicinity of the glass transition phase on a DSC thermogram. These temperature points, particularly glass transition, are characteristic for specific materials and can be used in the identification of unknown polymers (Balani et al. 2015, Schick 2009, Mettler Toledo 2013). The basis of this study was the investigation of this temperature point in different clear aligners to make comparisons with each other as well as before and after use.

Glass transition temperature will be measured using differential scanning calorimetry (DSC). This technique measures the heat flow to and from a sample as it is heated at a specific rate and compared to a reference sample. As the samples are heated in a controlled environment, sensitive sensors detect the amount of energy required to maintain a constant increase in temperature within the heating chamber. DSC is particularly useful for investigating thermal events such as glass transition, crystallization, and melting. The energy transfer to and from the sample material is measured in milliwatts, and this output over the course of heating is mapped as a thermogram. These thermograms can function as a form of fingerprint for specific materials, as many thermal properties are characteristic for specific polymers (Schick 2009, Mettler Toledo 2013).

Objective

The objective of this study was to characterize the thermal properties of three types of commonly used clear orthodontic aligners using DSC. The samples obtained were both as-received and clinically used to see if any differences between their thermal transitions of interest differed. The primary point of interest in this investigation is the glass transition temperature, which occurs during heating as the polymers transition from a glassy state to a more mobile rubbery state. Also observed are the peaks representing crystallization and melting point to further characterize the materials. The study should allow identification of the materials under investigation and compare them to one another. As clear aligner therapy becomes increasingly popular, it is important to have a broad understanding of the various properties of the materials they are made from and to know which of these properties may change during use.

CHAPTER 3
MATERIALS AND METHODS

Sample retrieval and preparation

Samples of Invisalign, ClearCorrect, and Simpli5 aligners were obtained from orthodontic patients that were undergoing normal treatment. All three patients had worn their respective aligners for two weeks. As-received, unused aligners of the same brands were also obtained through donation by the three companies.

Testing samples were cut from the facial surfaces of the incisor portions of the aligners. All samples were trimmed to allow placement inside an aluminum crucible used for DSC analysis (Figure 3). Six samples were prepared from the used aligners of each brand, and 9 samples were prepared from the as-received aligners of each brand, with a total of 45 samples. Each sample was individually sealed inside an aluminum crucible.

Figure 3: As-received Simpli5 aligner with a section removed for sampling, cut samples, and a prepared and sealed aluminum crucible ready for testing

Figure 4: Mettler Toledo Model 822 DSC instrument with liquid nitrogen in the background used for thermoregulation

Differential Scanning Calorimetry

DSC measurements were obtained on a Model 822 from Mettler Toledo (Mettler-Toledo Inc, Columbus, Ohio) (Figure 4). All samples were slowly heated at a rate of 10°C per minute. Liquid nitrogen was used for precise temperature modulation and nitrogen gas was used to purge the testing chamber. The resulting output was recorded as a thermogram, the peaks of which were analyzed with the instrument's software. Both new and used samples were analyzed at temperatures ranging between 0°C and approximately 300°C to characterize the glass transition temperature of each material. In addition, three samples of each as-received aligner were run for an extended temperature range up to 600°C. This broader range of analysis allowed the visualization of the entire thermal spectrum of the materials, including their melting and decomposition temperatures at the higher end. See Table 1 for specific analysis parameters for each sample.

Sample	Number of Samples Run	Temperature Range
Invisalign, Used	6	0°C to 300°C
Invisalign, As-received	6	0°C to 300°C
Invisalign, As-received	3	-100°C to 600°C
Simpli5, Used	6	0°C to 325°C
Simpli5, As-received	6	0°C to 325°C
Simpli5, As-received	3	-100°C to 600°C
ClearCorrect, Used	6	0°C to 300°C
ClearCorrect, As-received	6	0°C to 300°C
ClearCorrect, As-received	3	-100°C to 600°C

Table 1: Type, sample size, and temperature range for all DSC scans

Glass transition temperature was calculated as the midpoint between the beginning and end of the glass transition phase and averaged between samples of the same category. These values were then used for comparison between the other brands as well as their clinically used counterpart. The presence or absence of enthalpy relaxation, crystallization, and melting peaks was also evaluated if present.

Statistical Analysis

Glass transition temperatures were statistically compared to detect potential differences between as-received and after clinical use samples. In addition to glass transition temperatures, recrystallization peak, recrystallization enthalpy, melting peak, and melting enthalpy were also quantified and compared for Simpli5 due to its unique thermal differences when compared to Invisalign and ClearCorrect. A within-between repeated measures analysis of variance (ANOVA) was performed to detect statistically significant differences in these values before and after clinical use, with p-values of <0.05

representing statistical significance. Tukey’s HSD was used for a post hoc test to compare the change over time and between brands.

CHAPTER 4
RESULTS

After DSC was run on each of the samples, the thermograms that each scan produced were analyzed and compared. Initially, the three types of aligner samples were run over a very wide range of temperature (-100°C to 600°C) to be confident that any and all thermal events were captured. An example of such a wide temperature run can be seen in Figure 5, which uses Simpli5 as an example. An important note for interpreting these thermograms is that exothermic events are recorded as peaks in the upward direction. By setting the temperature endpoints at such extremes, the main points of interest were located to allow a more narrow focus on a specific temperature range. All scans used to quantify glass transition temperature used a shortened temperature range that focused on the main areas of activity (glass transition, recrystallization, melting).

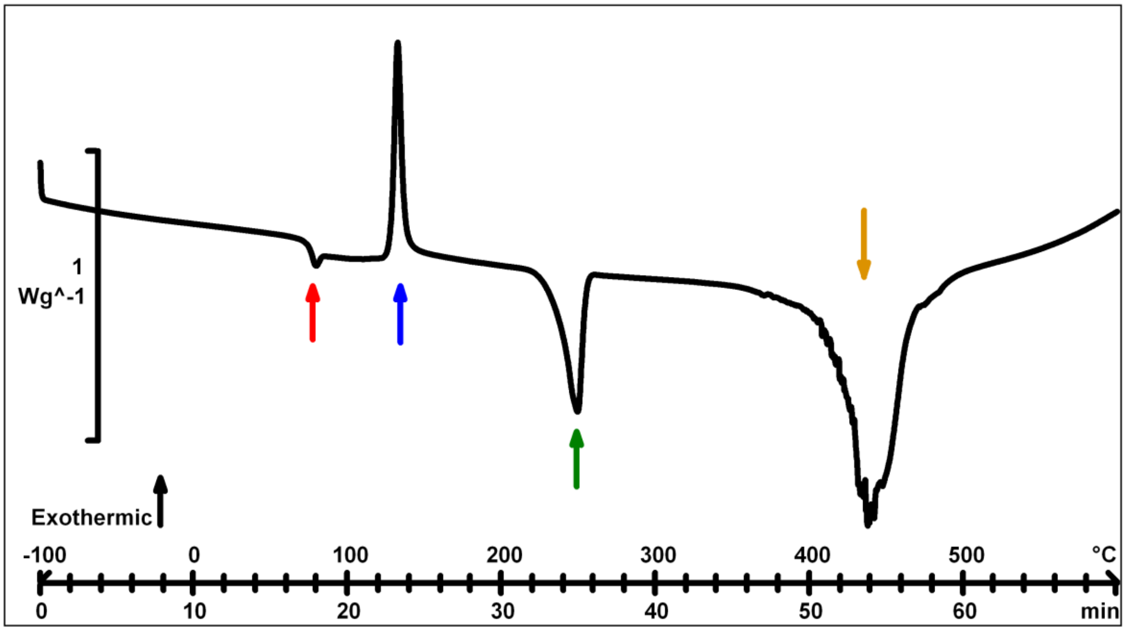

Figure 5: As-received Simpli5, wide temperature scan. Red arrow: glass transition. Blue arrow: recrystallization. Green arrow: melting. Yellow arrow: decomposition

As seen in Figure 5, the wide range analysis of Simpli5 revealed several defined peaks on the thermogram. From left to right, these peaks represent glass transition (primary area of interest), recrystallization, melting, and decomposition. Since the recrystallization and melting peaks were so defined for Simpli5, these values were also quantified in addition to glass transition. The wide temperature range analysis of Invisalign and ClearCorrect also allowed narrowed down search parameters to quantify glass transition, but the other defined peaks as seen with Simpli5 were either missing or not as pronounced (Figures 6 and 7).

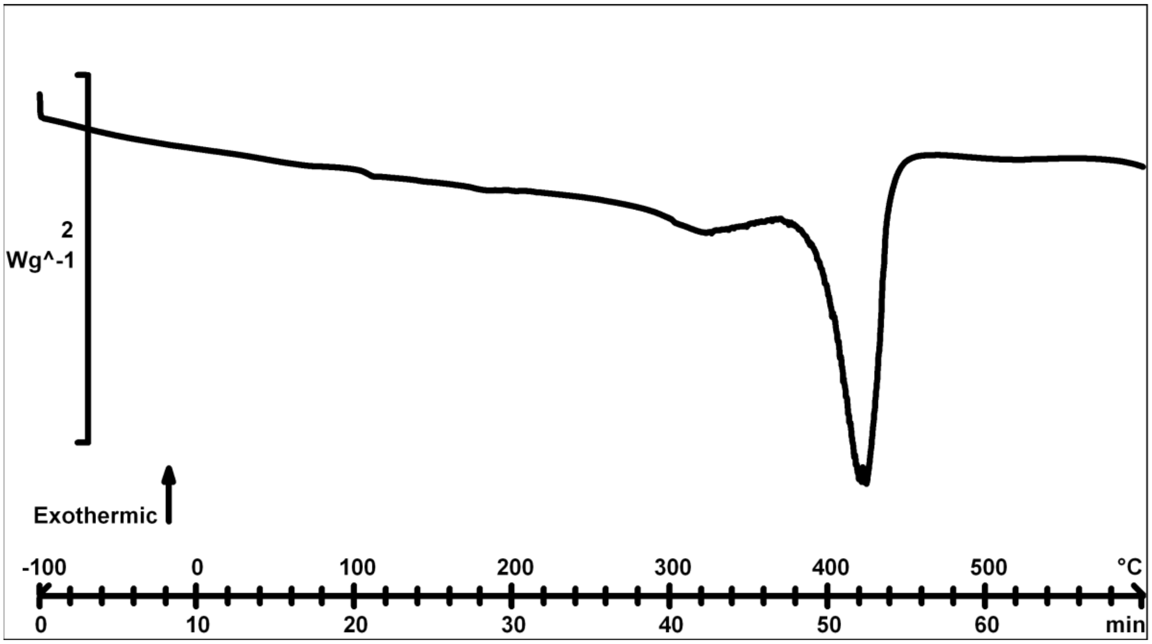

Figure 6: As-received Invisalign, wide temperature scan. Peaks are much more subtle, the small inflection around 100°C represents the glass transition phase. The large endothermic peak near 420°C represents decomposition of the material.

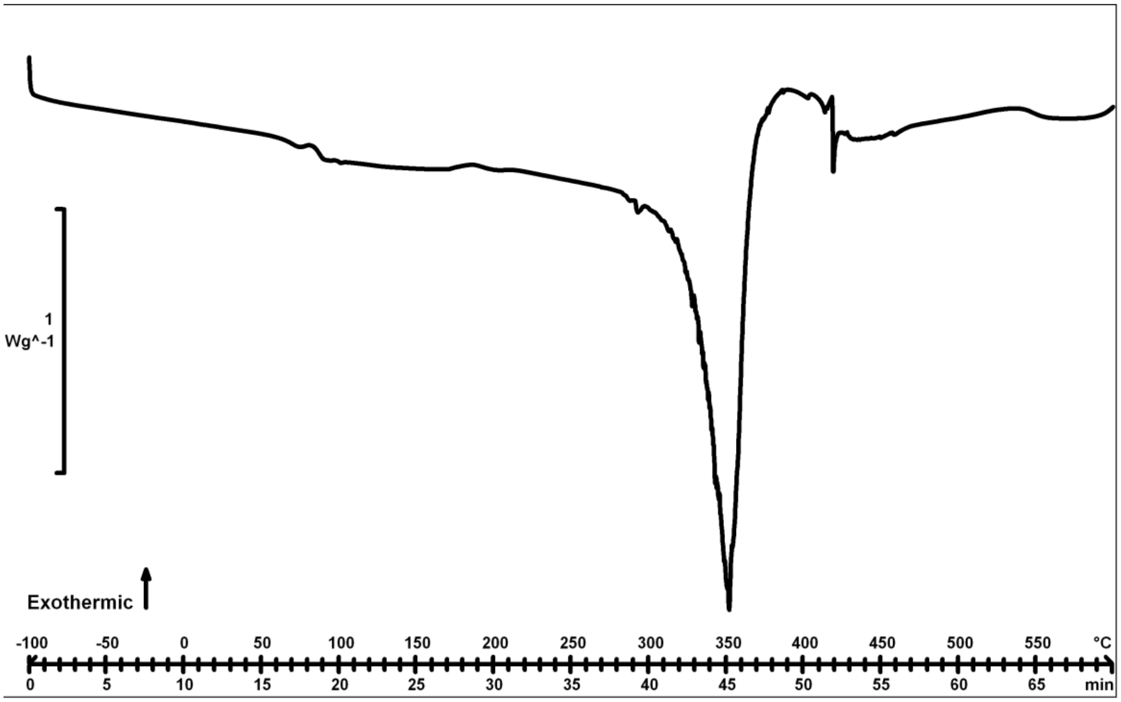

Figure 7: As-received ClearCorrect, wide temperature scan. The sigmoidal event around 80°C represents the glass transition phase. The large endothermic peak near 350°C represents decomposition of the material.

The wide temperature range scans allowed selection of a narrower temperature range to more closely analyze the main areas of interest. This allowed use of the accompanying software to quantify the glass transition temperature for both the new and used samples. In addition, since the recrystallization and melting peaks for Simpli5 were so well defined, they were quantified as well for comparison. An example of the quantification of the thermal events is given in Figure 8, using Simpli5 as an example. Glass transition is calculated as the midpoint of a line connecting two tangent lines that are both before and after the transition phase. Recrystallization and melting point are measured as the most extreme value of their respective peaks. Enthalpy values for both recrystallization and melting are measured as the total area within their respective peaks.

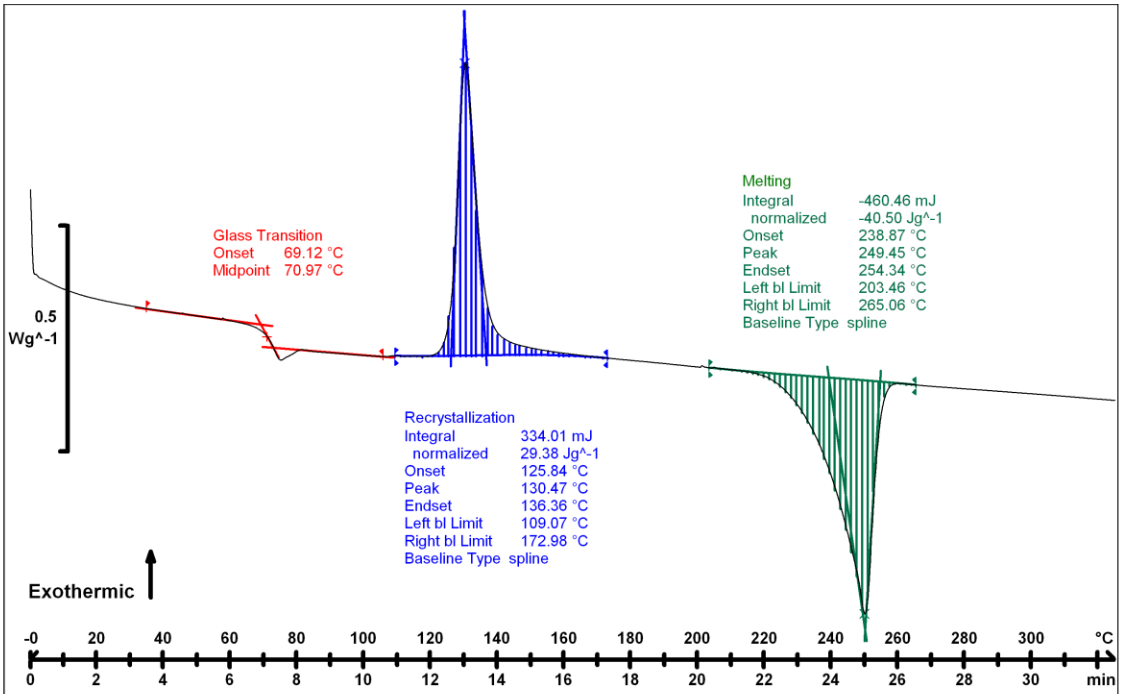

Figure 8: Example of quantifying thermal events in a DSC thermogram

The values that were quantified were compared to detect any significant differences between before and after clinical use. A within-between repeated measures analysis of variance (ANOVA) used with Tukey's HSB for a post hoc test comparison between as-received and after use showed no statistical difference in glass transition temperature when comparing the results for Invisalign with ClearCorrect and Simpli5 (p=0.325). Mauchly's test of sphericity confirmed that the sphericity assumption is not violated, strengthening the finding of no significant difference. Therefore glass transition temperature of all three types of aligners did not significantly change after undergoing prescribed clinical usage. The additional parameters for Simpli5 (Recrystallization peak, recrystallization enthalpy, melting point peak, and melting point enthalpy) were also analyzed with repeated measures ANOVA. There was no significant difference before and after for recrystallization peak and recrystallization enthalpy. However, there was a significant difference in the melting peak and melting enthalpy (p=0.003 and p=0.025, respectively), with the melting peak and enthalpy both being slightly less after use than the as-received product. See Tables 2 and 3 for the descriptive statistics from the measured parameters.

Simpli5	N	Mean	Std. Deviation
Recryst. Peak Before (˚C)	6	130.00	0.41
Recryst. Peak After (˚C)	6	130.55	6.16
Recryst. Enthalpy Before (J/g)	6	27.81	1.14
Recryst. Enthalpy After (J/g)	6	28.15	0.44
Melting Peak Before (˚C)	6	249.68	0.15
Melting Peak After (˚C)	6	246.43	1.33
Melting Enthalpy Before (J/g)	6	40.76	0.48
Melting Enthalpy After (J/g)	6	38.58	1.89

Table 2: Descriptive statistics for recrystallization and melting point for Simpli5

Sample	N	Mean (°C)	Std. Deviation
Simpli5 Tg Before	6	72.06	0.69
Simpli5 Tg After	6	73.08	0.29
ClearCorrect Tg Before	6	83.18	0.65
ClearCorrect Tg After	6	82.50	1.29
Invisalign Tg Before	6	105.17	0.81
Invisalign Tg After	6	105.50	0.43

Table 3: Descriptive statistics for Glass transition temperature (Tg) for Simpli5, ClearCorrect, and Invisalign

DSC proved to be a consistent and reproducible method of analyzing thermal properties of orthodontic aligners, as evidenced by the small standard deviation values within samples. The thermograms produced for each separate grouping were extremely similar to one another. For a visual comparison between as-received and used, a representative thermogram was selected for each type of new aligner category and was superimposed with its used counterpart. The curves follow their respective counterpart very closely with only minor deviations, indicating that no major alterations in thermal properties have occurred as a result of orthodontic use (Figures 9, 10, and 11).

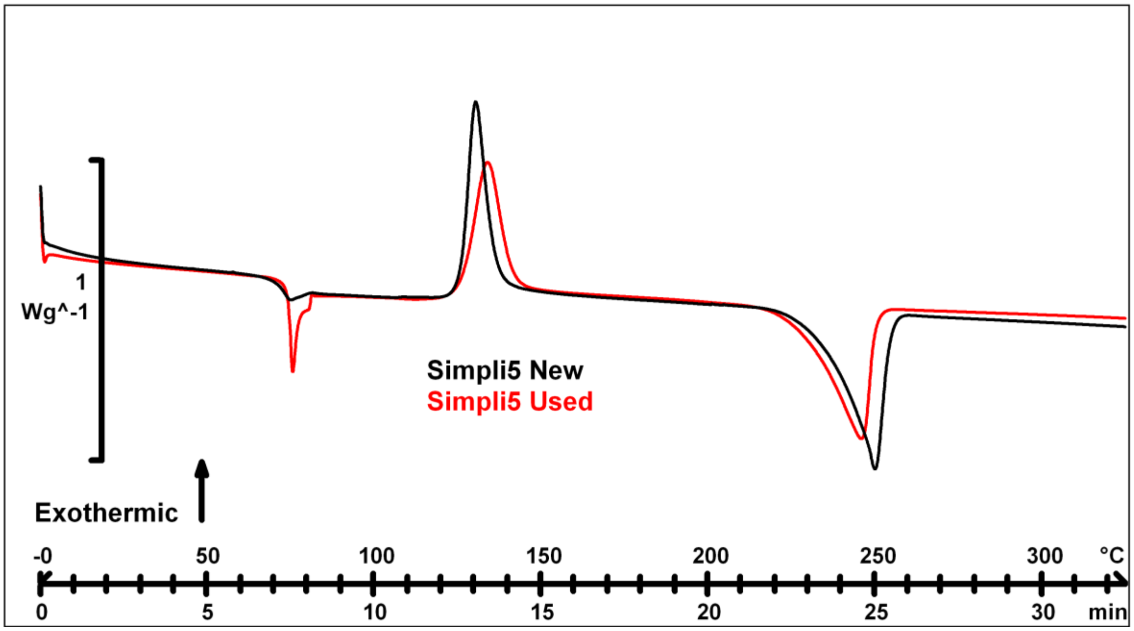

Figure 9: Comparison between as-received and used Simpli5 samples

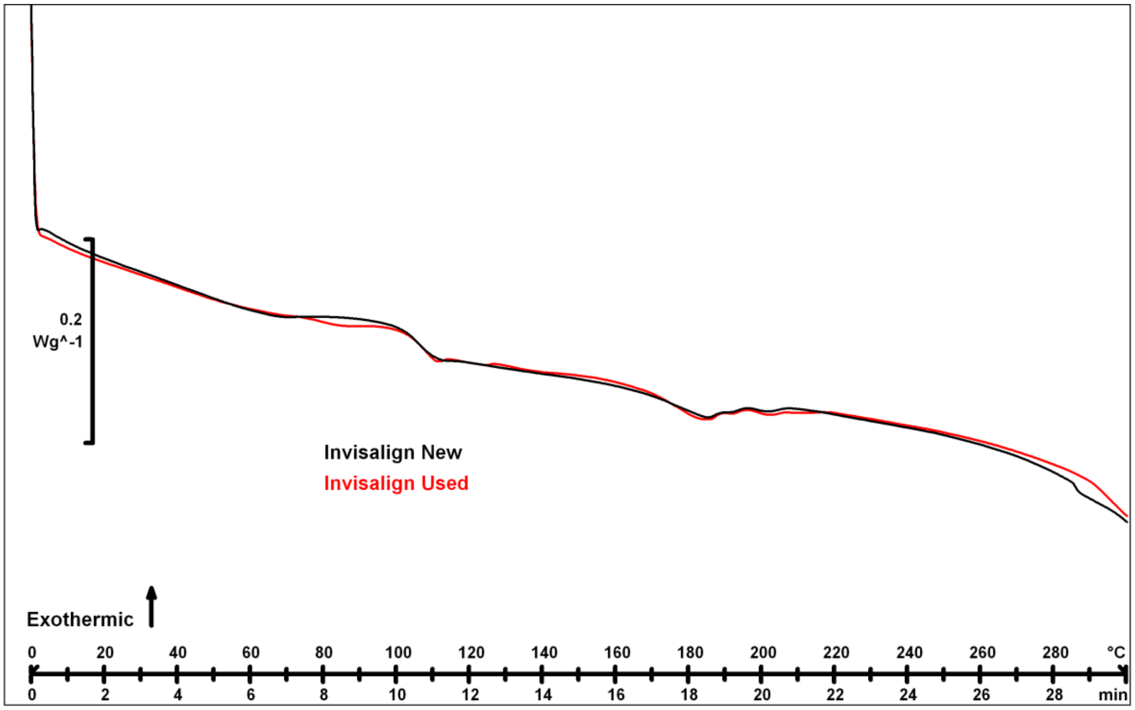

Figure 10: Comparison between as-received and used Invisalign samples

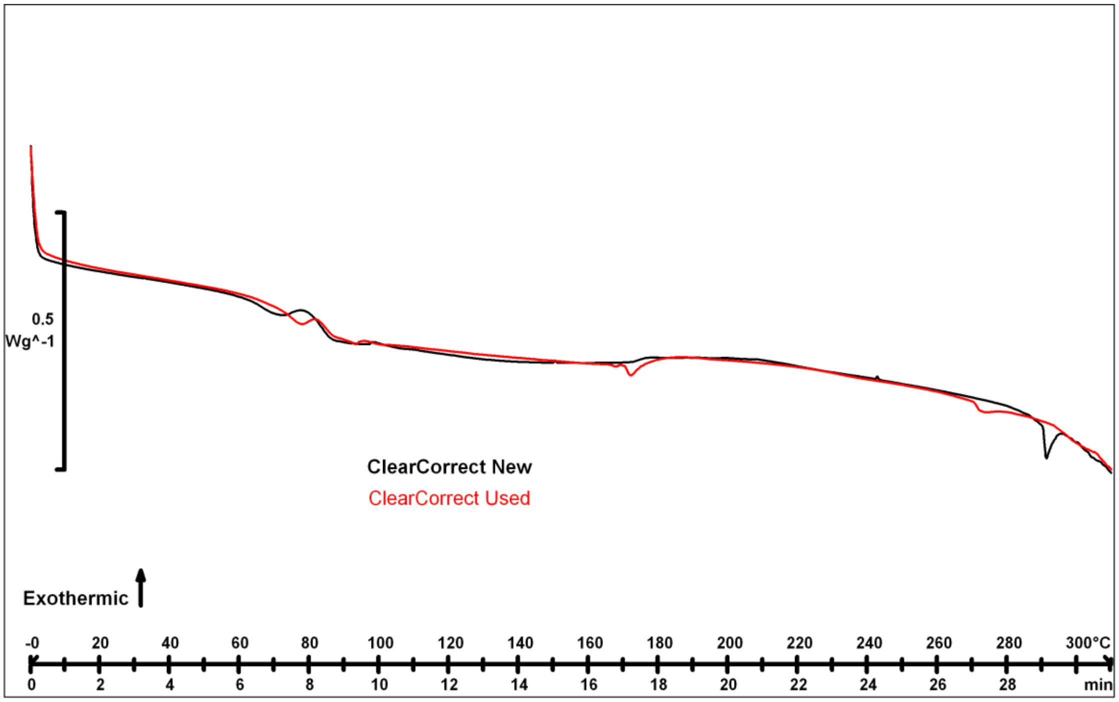

Figure 11: Comparison between as-received and used ClearCorrect samples

CHAPTER 5
DISCUSSION

This study is an extension of a prior study that analyzed the mechanical properties of Invisalign and Simpli5 aligners using dynamic mechanical analysis (DMA) before and after clinical use. The results indicated that there was no statistically significant difference before and after clinical use in any of the parameters under examination, which were storage modulus, loss modulus, tan δ, creep compliance, and strain recovery. The study also attempted to compare glass transition temperature before and after use, but the author was unable to successfully quantify glass transition using DMA (Montoure 2015). In the current study, DSC was selected as an alternative testing modality to specifically measure glass transition temperature. In addition to the previously studied aligners (Invisalign and Simpli5), ClearCorrect was added to this investigation for additional comparison.

The stimulus behind the present study lies in that fact that orthodontic aligners have been shown to undergo various physical and mechanical changes after being subjected to intraoral conditions. Past retrieval analysis studies of used aligners have shown an increased hardness, permanent surface distortion, cracking, wear, increased stress relaxation, and an increased elastic index (Schuster et al. 2004, Bradley et al. 2016, Fang et al. 2013). Among the more visible of changes is the physical appearance of orthodontic aligners after two weeks of intraoral use, indicating these polymers are susceptible to the absorption of exogenous stains (Figure 2). These changes are important because as the popularity of orthodontic aligners rise, it becomes increasingly important to understand which properties are susceptible to distortion and degradation.

An ideal aligner material would display ideal properties that remain static throughout treatment to ensure consistent and uniform forces to the teeth throughout treatment. This study focuses primarily on glass transition temperature because this property has been shown in prior studies to correlate with the resiliency of various mechanical properties of aligners. Polyurethane aligners with glass transition temperatures above the maximum temperature found in the oral cavity displayed superior resiliency of mechanical properties (Iijima et al. 2015). As the aligner material transitions from a glassy to a rubbery state, it is likely that such a significant physical change would have an effect on the aligner's original attributes. Using this logic, it is would be prudent to employ a material that has an initial glass transition temperature above what is found in the oral cavity and also ensure that it does not drop below that temperature during clinical use. There have been no prior studies of the aligners tested in this study to evaluate whether or not the glass transition temperature changes significantly as a result of exposure to the oral environment.

Analysis of the results of this study shows no significant change in glass transition temperature after clinical use for all three brands. Additionally, all three aligner types display transition temperatures that are higher than the accepted extreme maximum oral temperature of 55°C-58.8°C (Iijima et al. 2015, Moore et al. 1999). These results indicate that the aligner material will remain in its glassy state before, during, and after clinical use.

The thermograms produced using DSC showed strong agreement between as-received and after use samples of the same brand. The exception to this observation is the endothermic peak at the tail end of the glass transition phase found in the thermogram for after use Simpli5. This peak represents relaxation enthalpy, which is seen in some polymers and represents physical aging under the material's glass transition temperature (Mettler Toledo 2013). The harsh environment and physical stresses of orthodontic use most likely induced the aging that resulted in the visible relaxation peak. While the presence of the peak does indicate aging, the mean glass transition temperature of the used Simpli5 samples was not different than the temperature of the as-received Simpli5 samples.

It is known that ClearCorrect and Invisalign are constructed from polyurethane based polymers, which helps to explain the similarity in appearance of their respective thermograms (Align Technology MSDS, Bay Materials, LLC MSDS). Glass transition temperature is visible and measurable with DSC, but their remaining curves are largely uneventful until the endothermic peak which represents the material's decomposition. This is characteristic of a polymer with largely thermosetting characteristics. Polymers can either be thermoset or thermoplastic. Thermoset polymers are highly crosslinked and lack the internal mobility to be continually heated, softened, and reshaped. Thermoplastic polymers have higher internal mobility and can be continually softened and reshaped. Polyurethanes are composed of combinations of rigid segments and soft segments, and by varying the molecular weights of these segments, the resulting physical properties can be endless. By increasing the amount of isocyanite reactive sites within the rigid segments, the more crosslinked a polymer will be. The lack of distinct recrystallization and melting peaks in Invisalign and ClearCorrect indicate that they are composed of thermoset polyurethanes that are highly crosslinked with limited mobility even after the glass transition phase is reached (Lithner 2011).

In contrast, the thermogram for Simpli5 is starkly different than those seen with Invisalign and ClearCorrect. Clearly defined recrystallization and melting peaks indicate this is likely a different material entirely. While the material is listed by the company as proprietary, the curve is remarkably similar to published curves for polyethylene terephthalate (PET), which is a polyester formed via a condensation reaction between ethylene glycol and terephthalic acid (Mettler Toledo 2013, Lithner 2011). PET is a commonly produced thermoplastic used for many applications such as plastic bottles. It is PET's thermoplastic properties that make it an attractive material for the fabrication of recyclables, since it can be reshaped many times over (Lithner 2011). PET is also used in other types of orthodontic aligners, giving credibility to the likelihood that Simpli5 is based on PET (Fang 2013). This explains the presence of a recrystallization peak, which demonstrates the formation of crystal structures as the mobility of the polymer increases upon gradual heating.

Since two distinct additional peaks were found after analyzing Simpli5 with DSC, these peaks were also quantified to evaluate for differences before and after clinical use. The recrystallization peak represents exothermic energy given off as portions of the polymer organize into more orderly crystalline structures. The melting peak represents endothermic energy absorbed by the polymer as the material melted into a liquid state. Both the peak and the total enthalpy of recrystallization values were not statistically different after clinical use. However, the peak and total enthalpy of melting values were statistically lower after clinical use. This likely indicates weakened structural integrity as a result of clinical usage, leading to a lower melting point requiring less energy. The absorption of impurities intraorally may also have modified melting behavior. This may have also been seen with Invisalign and ClearCorrect had they possessed a clearly defined melting point.

DSC proved to be an effective means of evaluating glass transition temperatures in orthodontic aligners. As indicated by the small standard deviations within sampling groups, measurements were consistent between separate scans. One shortcoming of this study is the irregularity of the physical size of the samples. Since this study is a retrieval analysis, samples had to be cut from aligners, not from uniform blank material. All sections were taken from the facial surface of incisors to ensure that samples were as flat as possible, but there was no way to make all samples perfectly uniform.

This study indicates that the glass transition temperature of orthodontic aligners remains stable throughout treatment. Future studies should investigate whether or not aligners with differing glass transition temperatures behave differently clinically. Prior studies indicate that polyurethane aligners perform better with a transition temperature above the maximum oral temperature, and it would be useful to continue that research among other commonly used types of aligners.

CHAPTER 6
CONCLUSION

There was no significant difference found when comparing glass transition temperature before and after clinical use for three commonly used orthodontic aligners. ClearCorrect and Invisalign produced thermograms indicative of thermoset polyurethane, while Simpli5 produced thermograms indicative of thermoplastic polyethylene terephthalate. All possessed glass transition temperatures above the accepted oral maximum temperature. Simpli5 displayed additional peaks representing recrystallization and melting point. There was no difference in recrystallization values before and after use, but melting peak and melting enthalpy were significantly lower after clinical use.

BIBLIOGRAPHY

Align Technology, Inc. *SmartTrack aligner material.* [Material safety data sheet]. 2015.

Ahn HW, Ha HR, Lim HN. Effects of aging procedures on the molecular, biochemical, morphological, and mechanical properties of vacuum-formed retainers. *J Mech Behav Biomed Mater*. 2015; 51: 356–366.

Ansari MY, Agarwal DK, Gupta A, Bhattacharya P, Ansar J, Bhandari R. Shear Bond Strength of Ceramic Brackets with Different Base Designs: Comparative In-vitro Study. *J Clin Diagn Res*. 2016;10(11):ZC64-ZC68.

Balani K. Biosurfaces: A Materials Science and Engineering Perspective. John Wiley & Sons Inc.: New Jersey, 2015.

Bay Materials, LLC. *Zendura*. [Material safety data sheet]. 2013.

Biermann MC, Berzins DW, Bradley TG. Thermal analysis of as-received and clinically retrieved copper-nickel-titanium orthodontic archwires. *Angle Orthod*. 2007;77, 449-503.

Bradley TG, Teske L, Eliades G. Do the mechanical and chemical properties of Invisalign appliances change after use? A retrieval analysis. *Eur J Orthod.* 2016; 38(1): 27-31.

Brantley WA, Svec T, Iijima M, Powers J, Grentzer T. Differential scanning calorimetric studies of nickel-titanium rotary endodontic instruments after simulated clinical use. *J Endod*,2002; 28, 774-778.

Fang D, Zhang N, Chen H, Bai Y. Dynamic stress relaxation of orthodontic thermoplastic materials in a simulated oral environment. *Dent Mater J*. 2013;32:946–951.

Feu D, Catharino F, Duplat CB, Capelli Junior J. Esthetic perception and economic value of orthodontic appliances by lay Brazilian adults. *Dental Press Journal of Orthodontics*. 2012;17(5), 102-114.

Gracco A, Mazzoli A, Favoni O, Conti C, Ferraris P, Tosi G, Guarneri MP. Short-term chemical and physical changes in Invisalign appliances. *Aust Orthod J*. 2009;25:34-40.

Iijima M, Kohda N, Kawaguchi K. Effects of temperature changes and stress loading on the mechanical and shape memory properties of thermoplastic materials with different glass transition behaviors and crystal structures. *Eur J Orthod*. 2015;37:665–670.

Jena AK, Duggal R, Mehrotra AK. Physical properties and clinical characteristics of ceramic brackets: a comprehensive review. Trends Biomater Artif Organs 2007; 20: 101–15.

Jeremiah HG, Bister D, Newton JT. Social perceptions of adults wearing orthodontic appliances: a cross-sectional study. *Eur J Orthod*. 2011;34:476-482.

Kohda N, Iijima M, Muguruma T, Brantley WA, Ahluwalia KS, Mizoguchi I. Effects of mechanical properties of thermoplastic materials on the initial force of thermoplastic appliances. *Angle Orthod*. 2013;83:476–483.

Kravitz ND, Kusnoto B, BeGole E. How well does Invisalign work? A prospective clinical study evaluating the efficacy of tooth movement with Invisalign. *Am J Orthod Dentofacial Orthop* 2009; 135(1): 27–35.

Kuo E, Miller RJ. Automated custom-manufacturing technology in orthodontics. Am J Orthod Dentofacial Orthop. 2003;123:578–81.

Kusy RP, Whitley JQ. Thermal and Mechanical Characteristics of Stainless Steel, Titanium-molybdenum, and Nickel-titanium Archwires. *Am J Orthod*, 2007;131, 229-37.

Lithner, D. (2011). Appendix A: Report S1. Thermoplastic and thermosetting polymersSynthesis, chemical substances used and initial hazard assessments. Sweden, Department of Plant and Environmental Sciences- University of Gothenburg.

Lombardo L, Martines E, Mazzanti V. Stress relaxation properties of four orthodontic aligner materials: a 24-hour *in vitro* study. *Angle Orthod.* 2016; doi:10.2319/113015-813.1.

Meier B, Wiemer KB, Miethke RR. Invisalign—patient profiling. Analysis of a prospective survey. *J Orofac Orthop*. 2003;64(5):352–8. doi: 10.1007/s00056-003-0301-z.

Mettler Toledo. (2013). Thermal analysis of polymers. Retrieved from http://us.mt.com/dam/LabDiv/Campaigns/gp/gtap/thermal_analysis_of_polymers_en.pdf.

Miller KB, McGorray SP, Womack R, Quintero JC, Perelmuter M, Gibson J, Dolan TA, Wheeler TT. A comparison of treatment impacts between Invisalign aligner and fixed appliance therapy during the first week of treatment. *Am J Orthod Dentofacial Orthop*. 2007;131:302.e1-302.e9.

Montoure L. (2015) Mechanical Properties and Patient Perceptions of Commonly Used Clear Aligner Systems As-Received and After Clinical Use [Master's thesis]. Milwaukee, Wisconsin: Marquette University.

Moore RJ, Watts JT, Hood JA, Burritt DJ. Intra-oral temperature variation over 24 hours. *Eur J Orthod*. 1999;21:1–13.

"Polyurethanes," The Essential Chemical Industry: Online, 2013, Web. Mar 31, 2015.

Rossini G, Parrini S, Castroflorio T, Deregibus A, Debernardi CL. Efficacy of clear aligners in controlling orthodontic tooth movement: a systematic review. *Angle Orthod*. 2015;85,5, 881–889.

Rosvall MD, Fields HW, Ziuchkovski J, Rosenstiel SF, Johnston WM. Attractiveness, acceptability and value of orthodontic appliances. *Am J Orthod Dentofacial Orthop*. 2009;135:276e1-276e12.

Saini P, Sharma H, Kalha AS, Chandna AK. The current evidence and implications of lingual orthodontics. *J Indian Orthod Soc*. 2016;50, Suppl S1:4-9.

Schick C. Differential scanning calorimetry (DSC) of semicrystalline polymers. *Anal Bioanal Chem*. 2009;395(6):1589–611.

Schuster S, Eliades G, Zinelis S, Eliades T, Bradley TG. Structural conformation and leaching from *in vitro* aged and retrieved Invisalign appliances. *Am J Orthod Dentofacial Orthop.* 2004; 126 (6): 725–728.

Valeri N. (2013) Differential Scanning Calorimetry (DSC) Analyses Of Esthetic Nickel-Titanium Wires As-Received And After Clinical Use [Master's thesis]. Milwaukee, Wisconsin: Marquette University.

Zhang N, Bai Y, Ding X. Preparation and characterization of thermoplastic materials for invisible orthodontics. *Dent Mater J.* 2011; 30 (6): 954–959.

Ziuchkovski JP, Fields HW, Johnston WM, Lindsey DT. Assessment of perceived orthodontic appliance attractiveness. *Am J Orthod Dentofacial Orthop*. 2008;133:S68-78.