Fracture Toughness, Clarity, and Staining of Thermoplastic Orthodontic Retainer Materials

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Fracture Toughness, Clarity, and Staining of Thermoplastic Orthodontic Retainer Materials

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DECLARATION OF INTEREST

None of the authors have any interest, financial or otherwise, in any of the thermoplastic materials involved in this study.

ABSTRACT

Objective: To measure and compare the clarity, essential work of fracture (EWF), and plastic work of fracture (PWF) of six different orthodontic thermoplastic retainer materials before and after prolonged immersion in beverages.

Materials and Methods: Six different materials were studied; three polyethylene copolymers: Ace (Essix, Sarasota, FL), Plus (Essix, Sarasota, FL), and Invisacryl Ultra (Great Lakes Orthodontics, Tonawanda, NY); two polypropylene polymers: C+ (Essix, Sarasota, FL), and Invisacryl C (Great Lakes Orthodontics, Tonawanda, NY), and one polyvinyl chloride polymer, Endure (Great Lakes Orthodontics, Tonawanda, NY). Double-edged-notched-tension specimens were cut from the center of thermoformed discs of the material. The clarity of the materials was measured with a chroma meter using the Commission Internationale de l'Eclairage (CIE) LAB color scale before and after immersion in cola, wine, and coffee for a total of three weeks. The essential work of fracture test was used to measure the EWF and PWF of materials before and after being immersed in the beverages. Color change was calculated using the equation: $\Delta E^*_{ab} = \sqrt{}[(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})]$. ΔE^*_{ab} values were compared between materials using one-way analysis of variance followed by Tukey post-test ($\alpha = 0.05$). Differences in EWF and PWF between materials were compared using an analysis of covariance followed by Tukey post-test ($\alpha = 0.05$).

Results: ΔE^*_{ab} (initial clarity) for the polyethylene copolymers was less than for the polyvinyl chloride polymer, which was less than for the polypropylene polymers. ΔE^*_{ab} (staining) for one of the polypropylene polymers, Essic C+, was greater than all of the other materials. EWF for one of the polypropylene polymers, Essix C+, was

greater than all of the materials; however, it displayed a significant decrease after immersion in beverages. No differences were found between materials' PWF. All reported differences were statistically significant ($P < .05$).

Conclusions: Essix C+ stained more than any other material, and was the only material to display a change in fracture toughness, a decrease in EWF, after immersion in beverages.

Introduction:

Orthodontic relapse is a change in tooth position or arch relationship subsequent to the completion of orthodontic treatment.[1] The four factors most commonly attributed as the cause of orthodontic relapse are: elastic recoil of the periodontal fibers, forces exerted by the facial and oral soft tissues, occlusal forces, and post treatment facial growth and development.[2] Relapse in the form of crowding has been shown to occur even up to 20 years post-retention.[3] The goal of the retention phase of orthodontics is to keep teeth in their corrected positions following treatment.

Several retainer designs have evolved over time. Due to the lack of scientific evidence practitioners currently utilize a specific retainer design based largely on personal preference and nonscientific criteria.[4] A 2010 survey of active members of the American Association of Orthodontists reported that following comprehensive treatment, 30.4% of orthodontists use clear thermoplastic retainers as their most common form of maxillary retention, and 18.2% of orthodontist use them as their most common form of mandibular retention.[5] The most common retainers used by orthodontists in the maxillary and mandibular arches were the Hawley (58.2%) and fixed lingual (40.2%), respectively.[5]

In 1971 Ponitz[6] described the technique for fabrication of clear thermoplastic vacuum formed retainers (VFRs). A machine adapts heat-softened thermoplastic by either negative or positive pressure, and either pulls or pushes the thermoplastic

onto a working study model. The two most common thermoplastics used for fabricating VFRs are polyethylene copolymers and polypropylene polymers.[7]

Documented benefits of VFR's are: simplicity of construction, significant reduction in laboratory time, limited materials and skill needed for fabrication, ease of delivery, and low cost.[8-10] These benefits of VFRs are a consequence of their fabrication, which requires no technical proficiency in wire bending; therefore, auxiliary personnel with only minimal instruction can fabricate the thermoplastic appliance in the orthodontic office.[11]

On the positive side, VFRs have been shown to hold corrections of lower anterior teeth more effectively and be more cost-effective than Hawley retainers.[12] The majority of patients also prefer VFRs to Hawley retainers.[13] VFRs have also been used during retention to produce minor tooth movements[6,8] or as bleaching trays.[14]

On the negative side, Ponitz[6] recognized the shorter life expectancy of the VFRs compared to a standard Hawley appliance. The major drawbacks of VFRs are their tendency to open the bite and their low durability.[9] VFRs have also been shown to inhibit relative vertical tooth eruption, or "settling" of the occlusion.[15] Low durability can result in broken VFRs that have financial cost to replace and may increase the risk of orthodontic relapse if the broken retainer is not replaced in a timely fashion.

VFRs have poor wear resistance along the incisal and occlusal surfaces.[16] Two previous in-vitro wear resistance studies using steatite abraders concluded that the wear resistance of polyethylene copolymers is superior to polypropylene based thermoplastics.[7,11]

Conversations with orthodontists also indicate that retainer fracture[17] and staining are problematic in orthodontic practice; however, there have been no reports of fracture frequency or noncompliance as a result of staining.

The Essential Work of Fracture (EWF) test was developed to evaluate the fracture toughness of ductile, thin, plastic sheets.[18,19] Fracture toughness describes the ability of a material containing a crack to resist fracture. In the double-edge-notched-tension (DENT) specimen EWF test, a series of specimens with equal thicknesses and systematically different internotch distances, or ligament lengths (Ls), are loaded in tension until complete fracture occurs. Integrating the area under the load-elongation curve (Figure 1) yields that specimen's total work of fracture (W_f), representing the energy needed for complete specimen fracture. In EWF theory, W_f is divided into two components: essential work and nonessential work.[17,18] The essential work of fracture (EWF), or W_e, is regarded as a measure of "resistance to crack initiation."[20,21] The nonessential work, known as the plastic work of fracture (PWF) or W_p, is regarded as a measure of "resistance to crack propagation"[20] and an indicator of ductility.[22]

EWF theory predicts that W_f vs L data will be linear. The linearity is described by the equation: $W_f = W_e + \beta W_p L$. Therefore, least square regression can be used to estimate a best fit line for W_f vs L data points (Figure 2). The y-intercept of the best-fit line is the materials EWF, W_e. The slope, βW_p, is the material's PWF. β is a shape factor proportional to the area of the plastic zone of deformation.[23] For the DENT EWF test investigating thin polymer sheets the plastic zone of deformation is considered to be circular, thus $\beta = \pi/4$.[19]

To date there have been no studies that investigated the initial clarity or staining of orthodontic thermoplastic retainer materials. However, conversations with patients indicate that initial clarity, and staining over time, of VCRs is of concern.

The analysis of color in dentistry is generally defined by the Commission Internationale de l 'E´clairage (CIE) L*, a*, b* (LAB) color space.[24] In this three-dimensional color space, with the three axes being L*, a* and b*, the L* refers to the lightness. The L* value ranges from 0 for perfect black to 100 for perfect white. The a* value refers to the chromaticity coordinates in the red–green axis. The b* value corresponds to the chromaticity coordinate in the yellow–blue axis. Total color change is measured in terms of ΔE and is measured by the equation: $\Delta E^*_{ab} = \sqrt{[(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})]}$. E stands for "Empfindung", the German word for "sensation".

The frequently accepted "50:50" clinical perceptibility threshold for color matching

in dentistry is 1 ΔE^*_{ab} units.[25] This is interpreted that given a color difference of 1 ΔE^*_{ab} units, 50% of observers will notice the color difference, and 50 % will see no difference between compared objects. The frequently accepted "50:50" acceptability threshold for color matching in dentistry is approximately 3 ΔE^*_{ab} units.[25] This is interpreted that given a color difference of approximately 3 ΔE^*_{ab} units, 50% of observers will accept the color difference, and 50 % would consider it unacceptable. However, these are not "absolute values", with different lighting conditions having an effect on color perception.[25]

Multiple hypothesizes were tested in this study. First, that orthodontic thermoplastic retainer materials have different initial clarities and work of fracture. Second, that after prolonged immersion in beverages the materials would stain to different degrees and the work of fracture would be affected. Finally, that staining and alteration of work of fracture would be correlated. Thus, this study investigated the initial clarity and staining resistance of six orthodontic thermoplastic materials. Also, the EWF test was used to investigate whether storage in beverages affected the EWF or PWF of the same six materials.

Materials and Methods:

Six thermoplastic materials were chosen for inclusion in the study based on manufactures' recommend use for VFRs. As show in Table 1: three of the materials were polyethylene copolymers: Essix Ace, Essix Plus, and Invisacryl Ultra; two were polypropylene polymers: Essix C+ and Invisacryl C; and one was a polyvinyl chloride polymer, Endure.

The as received thermoplastic sheets were circular discs 1mm in thickness and 125mm in diameter. The thermoplastic discs were formed over an acrylic disc (MED690; Stratasys Ltd., Eden Prairie, MN) measuring 6mm in thickness and 90mm in diameter using a positive pressure machine (Biostar VI; Scheu-Dental, Iserlohn, Germany). The numerical code specified by the manufacture for the material that dictates the amount of heating time was input into the positive pressure machine. A rectangle measuring 25mm by 50mm with bilateral notches, equal in size, was traced from a template and cut from the center of the thermoformed disc (Figure 3) using a band saw. For each material, 10 specimens were fabricated with internotch distances of L = 6, 8, 10, 12, and 14mm; therefore, 50 specimens per material were fabricated.

All specimens were placed on white photo paper (Premium presentation Paper 120g; Hewlett-Packard Company, Palo Alto, CA) and initial color readings were made according to the Commission Internationale de l'Eclairage (CIE) L*, a*, b* (LAB) color scale by a chroma meter (CR-221; Minolta, Osaka, Japan; Figure 4). The

chroma meter was calibrated using a known standard, supplied by the manufacturer, prior to readings. Thirty color readings were made of a clear glass microscope slide 1mm in thickness (Thermo Scientific, Portsmouth, NH) on the white photo paper alone to determine mean L*, a*, and b* values for comparison. The initial readings, VFR material on the white photo paper, were used to calculate the initial clarity of the material by calculating the ΔE^*_{ab} from the clear slide.

Half of the specimens for each material were stored separately in the dark at room temperature for 1-2 weeks, the other half stored in beverages. The specimens stored in the dark will be referred to as the "controls", the specimens stored in beverages as "experimental". The experimental specimens were immersed in each of the following for one week at 37 degrees Celsius in the dark, in this order: soda pop (Diet Coke; The Coca-Cola Company, Atlanta, Georgia), red wine (Charles Shaw Merlot; Bronco Wine Company, Ceres, California), and regular black coffee (Folgers Black Silk; The Folger Coffee Company, Orrville, OH). The coffee was brewed in a drip coffeemaker (Mr. Coffee TF Series 5-Cup Switch Coffeemaker, Jarden Consumer Solutions, Boca Raton, FL) with a ratio of 4 rounded tablespoons of coffee grounds per 5 cups of water. The specimens spent a total of three weeks immersed in beverages.

The experimental specimens had a second color reading made using the previously described chroma meter experimental set-up after the three weeks immersed in beverages. The ΔE^*_{ab} due to staining was determined to be the change in the initial

color readings to this second round of readings.

$$\Delta E^*_{ab} \text{ (Initial Clarity)} = \sqrt{} [(L^*_{\text{slide mean}} - L^*_{\text{initial specimen}})^2 + (a^*_{\text{slide mean}} - a^*_{\text{initial specimen}})^2 + (b^*_{\text{slide mean}} - b^*_{\text{initial specimen}})^2]$$

$$\Delta E^*_{ab} \text{ (Staining)} = \sqrt{} [(L^*_{\text{after staining}} - L^*_{\text{initial specimen}})^2 + (a^*_{\text{after staining}} - a^*_{\text{initial specimen}})^2 + (b^*_{\text{after staining}} - b^*_{\text{initial specimen}})^2]$$

For the essential work of fracture test all specimens, both control and experimental, were tightly gripped with friction grips (Figure 5) and loaded in tension (Figure 6) to fracture at 10mm/min using a QTEST machine (MTS Systems Corporation, Research Triangle Park, NC). Areas under the load-elongation curves were calculated to determine each specimens total work of fracture, W_f, using numerical integration (TestWorks QT V 2.0; MTS Systems Corporation, Cary, NC).

The protocol described by Pascual et al[17] was followed to determine the EWF and PWF for each material. For each thermoplastic material, 50 W_f vs L data points, 25 control and 25 experimental, were plotted. From these plots, least-square regression was used to estimate a best-fit line (GraphPad Prism V 5.0; GraphPad Software, Inc., La Jolla, CA). The y-intercept of the best-fit line is the material's EWF, W_e. The slope, βW_p, is the material's PWF (Figure 2).

Data analysis was carried using a statistical software package (Prism version 5.0; GraphPad Software, La Jolla, CA). Unparied t-tests were used to compare the mean L*, a*, and b* values of the clear slide to the initial L*, a*, and b* values of the test specimens. Paired t-tests were used to compare the initial L*, a*, and b* values of the test specimens to those after being immersed in beverages for 3 weeks. Mean ΔE^*_{ab} values were compared across the materials using one-way ANOVA for both initial clarity and staining. For the t-tests and one-way ANOVA $\alpha = 0.05$ was considered statistically significant. Where significance was found, further comparisons between materials were conducted using Tukey post-test with $\alpha = 0.05$.

The y-intercept, EWF, and slope, PWF, of the best-fit line were compared using the programmed analysis in the statistical software package for this purpose. This analysis follows a method described by Zar[26], and is equivalent to ANCOVA with $\alpha = .05$. Where significance was found, further comparisons between materials were conducted using Tukey post-test with $\alpha = 0.05$.

Results:

Thirty L*, a*, and b* readings were taken of the clear slide on the white photo paper used in the initial clarity portion of this study. The mean and standard deviation for these readings were: L* = 89.32 +/- .06, a* = 0.5363 +/- .03, and b* = -3.68 +/- .04. Table 2 reports the descriptive statistics and t-test results for the chromaticity data.

When measured through the VFR material onto the white photo paper, all initial clarity L*, a*, and b* values were statistically different from the clear slide, except for the a* value for Ace. All measurements made after the staining exposure showed L*, a*, and b* values that were statistically different from the initial clarity readings, except for the L* values of Plus, Invisacryl C, and Ultra.

ΔE^*_{ab} for initial clarity for the six materials is shown in Figure 7. ΔE^*_{ab} for initial clarity ranged from 5.06 to 14.97, and was statistically different for all materials except between Ace and Plus, and Plus and Ultra.

ΔE^*_{ab} for staining for the six materials is shown in Figure 8. ΔE^*_{ab} for staining ranged from 0.54 to 1.92, and was statistically greater for Essix C+ than all other materials.

The Invisacryl C material, both controls and experimentals, demonstrated spontaneous brittle fracture before (Figure 9A) and after (Figure 9B) full ligament yielding . Partial spontaneous brittle fractures (Figure 9C) were also seen. The

discontinuity in the curve in Figure 9A is due to slack being taken up in the grips and fixtures, this was seen on multiple specimens at approximately the same extension. When plotted (Figure 10), this resulted in data that could not be analyzed using the EWF test. Therefore, this material was omitted from the fracture toughness portion of this study.

The estimates and 95% confidence intervals of the essential work of fracture for each material are shown in Figure 11. The EWF ranged from 48.52 to 210 kJ/m^2. Essix C+ control had an EWF significantly higher than any other materials. The EWF for Essix C+ experimental was significantly higher than all other materials except Essix C+ control, which it was significantly less than. No other EWF values were significantly different.

The estimates and 95% confidence intervals of the plastic work of fracture for each material are shown in Figure 12. The PWF ranged from 1.82 to 7.15 MJ/m^3. No materials demonstrated statistically significant different PWFs.

Discussion:

No previous study that we are aware of had investigated the initial clarity or staining of VFR thermoplastic materials. This study found that the polyethylene copolymers (Ace, Plus and Ultra) had significantly better initial clarity than the polyvinyl chloride polymer (Endure) and the polypropylene polymers (Essix C+ and Invisacryl C).

For intrinsic polymers, without additives and impurities, the degree of translucency is influenced primarily by the extent of crystallinity. Some scattering of light occurs at the boundaries between crystalline and amorphous regions as a result of different indices of refraction.[27] For highly crystalline specimens, this degree of scattering is extensive, which leads to translucency, and in some cases even opacity. Highly amorphous polymers are completely transparent.[27] The polypropylene polymers are semicrystalline; therefore, one would expect them to be less transparent than the amorphous polyvinyl chloride and polyethylene copolymers.[28] This is reflected in this study as inferior initial clarity of the polypropylene polymers largely attributed to a decrease in the L* value relative to the clear slide on the white photo paper.

Essix C+, a polypropylene polymer, had significantly more staining than any of the other materials, even the other polypropylene polymer Invisacryl C. The ΔE^*_{ab} for staining in Essix C+ was 1.92 units. This is above the accepted "50:50" perceptibility threshold of 1 unit, indicating that the majority of people would recognize a color

difference after the staining protocol. Given that the basic polymeric structure of Essix C+ and Invisacryl C are the same, this difference in staining may be attributable to differences in the two manufacturers processes or additives. The ΔE^*_{ab} for staining in all other materials was below 1 unit, suggesting that the majority of people would not perceive any color change after the staining protocol.

The staining protocol used in this study is likely not representative of how orthodontic thermoplastic retainers stain in the clinical environment. In clinical use the plastics are subjected to two major elements that were not simulated in the current study: oral bacteria and their byproducts, and abrasive forces. Both of these elements likley contribute to the staining seen clinically. The staining protocol used in this study was designed to gauge a materials relative resistance to staining.

The laboratory study by Pascual et al [17] is the only published study we found that has investigated the fracture toughness of VFR materials. The authors tested two different thermoplastic retainer materials, Essix C+ (polypropylene polymer) and Tru-Tain Splint (polyethylene copolymer) after dry storage, and storage in different solutions, using a similar EWF test as used in this study. In the Pascual et al [17] study the materials were stored in the solutions for 160 hours at 25 degrees Celsius versus the 504 hours and 37 degrees Celsius in this study.

Pascual et al [17] reported a mean EWF for Essix C+ of 33.1 kJ/m^2 after dry storage, and 25.6 kJ/m^2 after storage in distilled water. The current study reported mean

EWFs for Essix C+ of 210 kJ/m^2 after dry storage and 141.87 kJ/m^2 after storage in beverages for three weeks. This study found EWF values approximately seven times greater for Essix C+ than the Pascual study. Both Pascual and this study found a decrease in EWF for Essix C+ after storage in aqueous solutions.

Pascual et al [17] reported a mean PWF for Essix C+ of 8.2 MJ/m^3 after dry storage, and 8.4 MJ/m^3 after storage in distilled water. The current study reported mean PWFs of 2.09 MJ/m^3 after dry storage and 7.15 MJ/m^3 after storage in beverages for three weeks. The PWF in this study for Essix C+ after dry storage was approximately 25% of that found by Pascual et al.

Pascual et al [17] did not directly report the mean EWF for Tru-Tain splint after dry storage, or storage in distilled water. However, according to a figure in the article the EWFs after dry storage and storage in distilled water reported were approximately 30 kJ/m^2 and 22 kJ/m^2, respectively. The current study reported mean EWFs after dry storage for Ace, Plus, and Ultra, also polyethylene copolymers, of 61.34, 54.1, and 57.43 kJ/m^2, respectively. The reported mean EWFs after storage in beverages for three weeks for Ace, Plus, and Ultra were 72.72, 63.31, and 48.52 kJ/m^2, respectively. The EWFs reported in this study were higher than those previously reported for a polyethylene copolymer.

Pascual et al [17] reported a mean PWF for Tru-Tain splint of 5.2 MJ/m^3 after dry storage, and 5.7 MJ/m^3 after storage in distilled water. The current study reported

mean PWFs after dry storage for Ace, Plus, and Ultra of 4.91, 3.19, and 2.22 MJ/m^3, respectively. The reported mean PWFs after storage in beverages for threes weeks for Ace, Plus, and Ultra were 3.73, 2.33, and 4.45 MJ/m^3, respectively.

The EWF and PWF of polyvinyl chloride polymer has been reported in the engineering literature as 50 kJ/m^2 and 2-4 MJ/m^3, respectively.[27,29] The current study reported mean EWFs for Endure of 70.08 kJ/m^2 after dry storage, and 59.05 after storage in beverages for three weeks, and the PWFs as 1.82 MJ/m^3 after dry storage and 3.20 MJ/m^3 after storage in beverages for three weeks.

The EWF values in this study were all higher than that of the previous Pascual et al [17] study for similar polymers. Differences in specimen preparation were likely the cause of higher EWFs found in this study. This is supported by Williams [19] who proposed that a blunter notch in the DENT EWF test would result in higher EWF values. In this study the notches in the specimens were cut using a band saw, in the Pascual et al [17] study razor blades were used. Razor blades may have created finer notches with a smaller area for stress concentration versus the band saw, which may have created blunter notches with more area for stress concentration. This would have resulted in earlier crack propagation in the Pascual et al [17] study reflected in lower EWF values.

The data collected from the Invisacryl C EWF test was not usable because it did not meet the requirements of the EWF test. For the data to be applicable to the EWF

test, full ligament yielding must occur just prior to crack onset at the notch tips and the shapes of the load-elongation curves in the series must be similar [30], the data for Invisacryl C did not meet either of these requirements. Invisacryl C exhibited a quasi-brittle mode of fracture.

For thermoplastic polymers both types of fracture modes are possible: ductile and brittle. Classification is based on the ability of a material to experience plastic deformation. Ductile materials typically exhibit substantial plastic deformation with high-energy absorption before fracture. However, many thermoplastics are capable of exhibiting a ductile to brittle transition. Factors that favor brittle fracture are a reduction in temperature, an increase in strain rate, the presence of a sharp notch, increased specimen thickness, and a modification of the polymer structure (chemical, molecular and/or microstructural). [27]

Invisacryl C may have exhibited a quasi-brittle mode of fracture due to being more susceptible than the other materials to one more of the following: strain rate, the presence of the notches, or modifications made by the manufacturer in the polymeric structure.

The EWF of Essix C+ Control was significantly higher than any other material; however, the EWF for Essix C+ did significantly decrease after 3 weeks in beverages. This differs from the Pascual et al [17] study that did not find a significant change in the EWF of Essix C+ after storage in distilled water. On the other hand, the present

study is consistant with Ryokawa et al [28] who found that the elastic modulus and tensile yield stress of Essix C+ significantly decreased after immersion in water at 37 degrees Celsius after 24 hours.

If absorption of water into the polymer is the reason for the decrease in EWF it is surprising to find that Essix C+, a polypropylene polymer, had a significant decrease while the polyethylene copolymers did not. Ryokawa et al [28] showed that after 2 weeks of immersion in water a polyethylene copolymer absorbed more water than two polypropylene polymers. This would lead one to expect that the EWF for a polyethylene copolymer would decrease significantly, while it may not for a polypropylene polymer, after storage in aqueous solutions. Neither this study, nor that of Pascual et al [17] found this to be true.

Water plasticizes polymers by interfering with secondary bonds between polymer molecules and thereby facilitates the untangling of the polymer in response to stress. [17] Polypropylene is a semicrystalline thermoplastic; therefore, it will have a higher density than an amorphous polymer such as a polyethylene copolymer or polyvinyl chloride polymer. The lower free volume of the semicrystalline polymer should inhibit water absorption.

In theory the same mechanism should apply to staining. The more crystalline the polymer, the less free space, and the less impurities can be absorbed. However, this study did not find this to be true. The semicrystalline polypropylene polymer

stained more than the amorphous polyethylene copolymers and polyvinyl chloride polymer.

In the current study no significant differences were found between the PWFs of any of the materials or conditions. For both a polypropylene polymer and polyethylene copolymer Pascual et al [17] found no significant differences in PWF after storage in distilled water. However, they did find that the PWF was significantly higher for the polypropylene polymer than the polyethylene copolymer when stored dry and stored in distilled water. [17]

Why did Invisacryl C behave so differently from Essix C+? The initial clarity of the materials was similar, but Invisacryl C stained significantly less and displayed a quasi-brittle mode of fracture. Given that the basic polymeric molecules of these two materials is the same, it likely is related to a difference in the manufacturers' processing, and/or additives in the polymers, that modified the polymers structure.

Conclusions:

- The polyethylene copolymers (Ace, Plus, and Ultra) had the greatest initial clarity, followed by the polyvinyl chloride polymer (Endure), and then the polypropylene polymers (Essix C+ and Invisacryl C).

- Essix C+ exhibited significantly more staining than any other material.

- Essix C+ exhibited greater EWF than any other material; however, this EWF was significantly reduced after 3 weeks in beverages.

- The PWF was unaffected by material type or storage conditions.

- Invisacryl C demonstrated an unexpected quasi-brittle mode of failure.

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Figure Legends:

Figure 1: Load-Elongation curve. Integrating the area under the curve yields the specimen's total work of fracture (W_f).

Figure 2: Linear regression of work of fracture for Essix Ace Experimental (slope = 3.73 MJ/m^3; y-intercept = 72.72 kJ/m^2, $R^2 = .55$)

Figure 3: Specimen geometry

Figure 4: CR-221 chroma meter experimental set-up

Figure 5: Specimen inserted into friction grips in preparation for tensile loading

Figure 6: QTEST loading apparatus

Figure 7: ΔE^*_{ab} for Initial Clarity (means and standard deviations indicated).
a-e indicates $P < .05$

Figure 8: ΔE^*_{ab} for Staining (means and standard deviations indicated).
* indicates $P < .05$

Figure 9: Quasi-brittle mode of fracture demonstrated by Invisacryl C resulted in dissimilar load-elongation curves. (A) Spontaneous brittle fracture of Invisacryl C

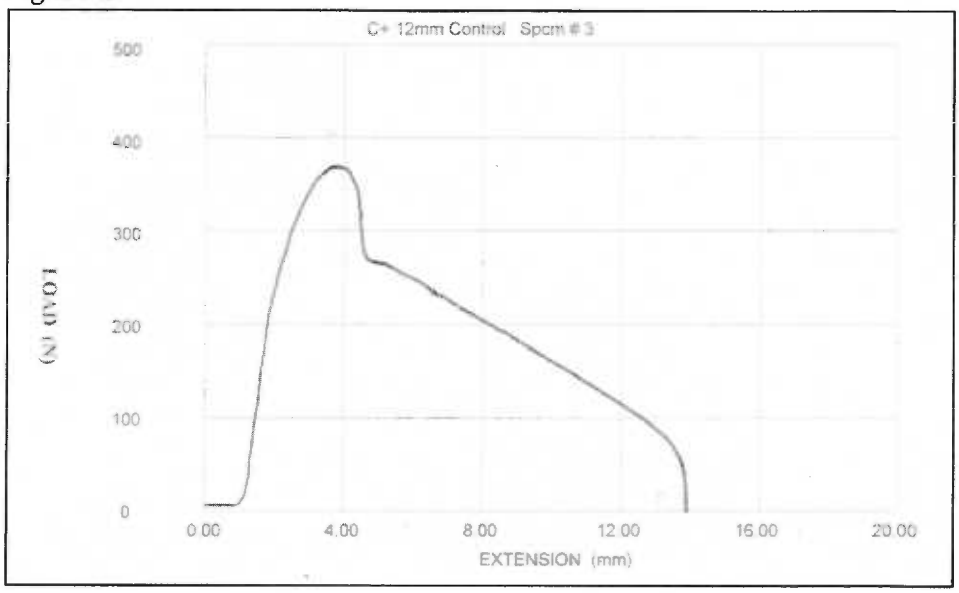
before full ligament yielding. (B) Spontaneous brittle fracture of Invisacryl C after full ligament yielding. (C) Partial spontaneous brittle fracture of Invisacryl C specimen.

Figure 10: Work of Fracture vs. ligament length for Invisacryl C Experimental

Figure 11: Essential work of fracture estimates and 95% confidence intervals. a-c indicates $P < .05$

Figure 12: Plastic work of fracture estimates and 95% confidence intervals. No PWF values were significantly different

Figure 1: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400
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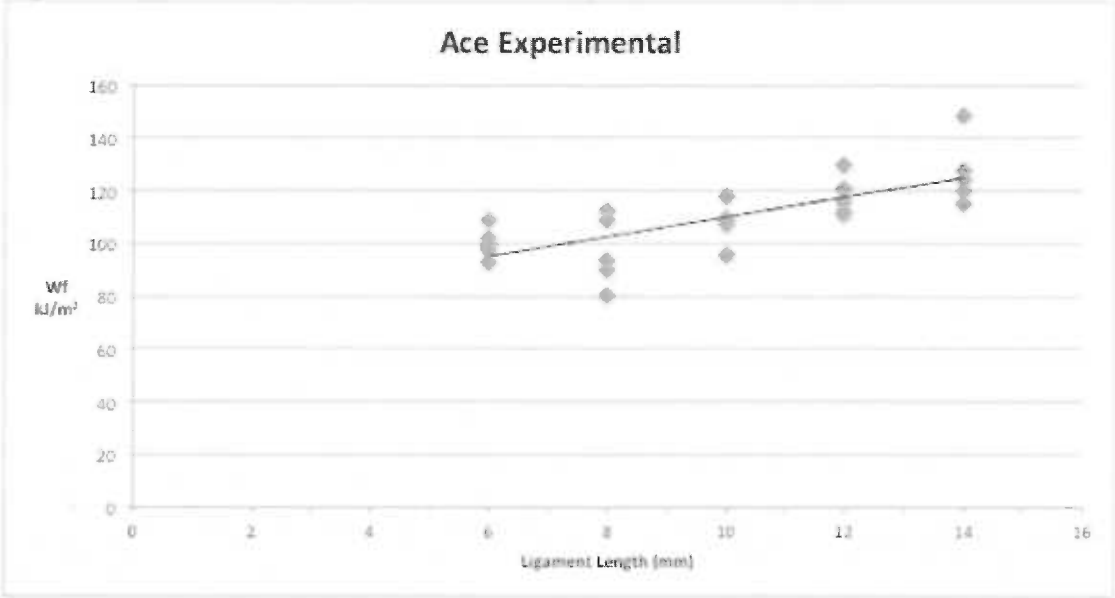
0.00
4.00
8.00
12.00
16.00
20.00
EXTENSION (mm)

Figure 2:


Ace Experimental
160
140
120
100
80
60
40
20
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Wf
kJ/m²
0
2
4
6
8
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14
16
Ligament Length (mm)

Figure 3:

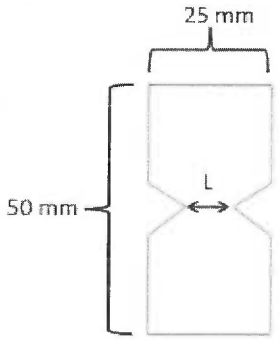
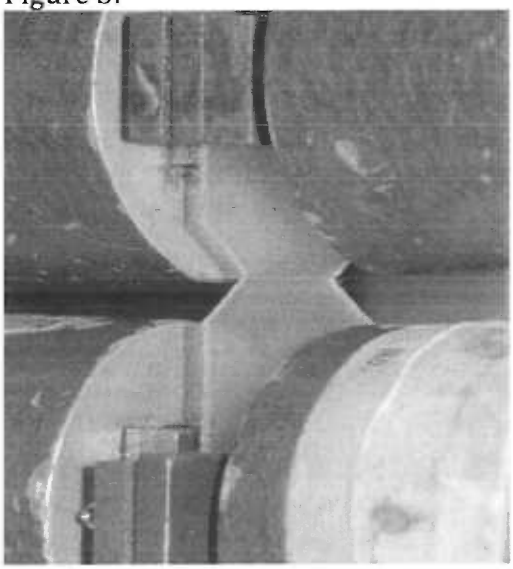


Figure 4:

Figure 5:



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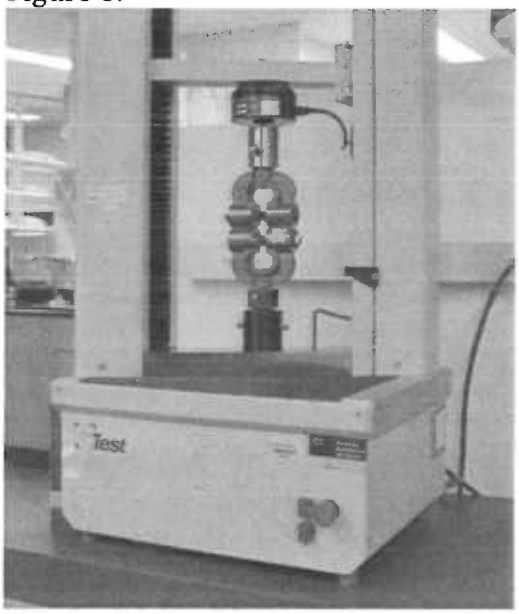

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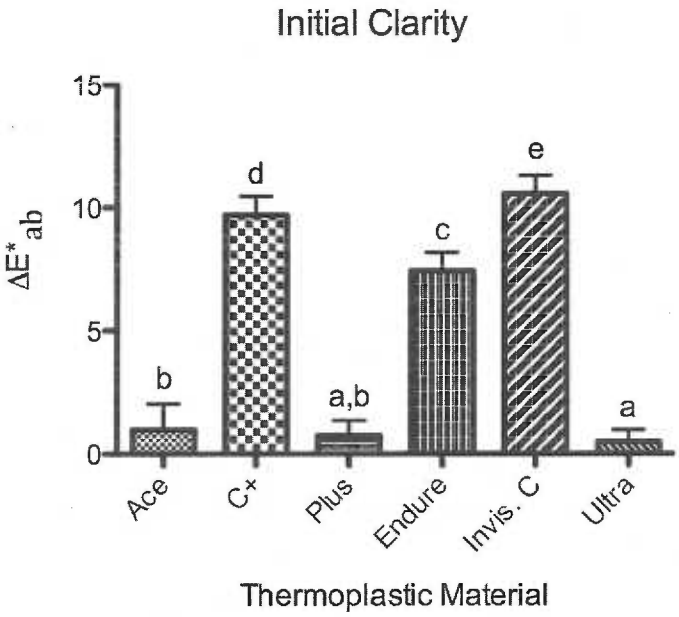

Initial Clarity
15
10
5
0
ΔE*ab
b
d
a,b
c
e
a
Ace
C+
Plus
Endure
Invis. C
Ultra
Thermoplastic Material

Figure 8:

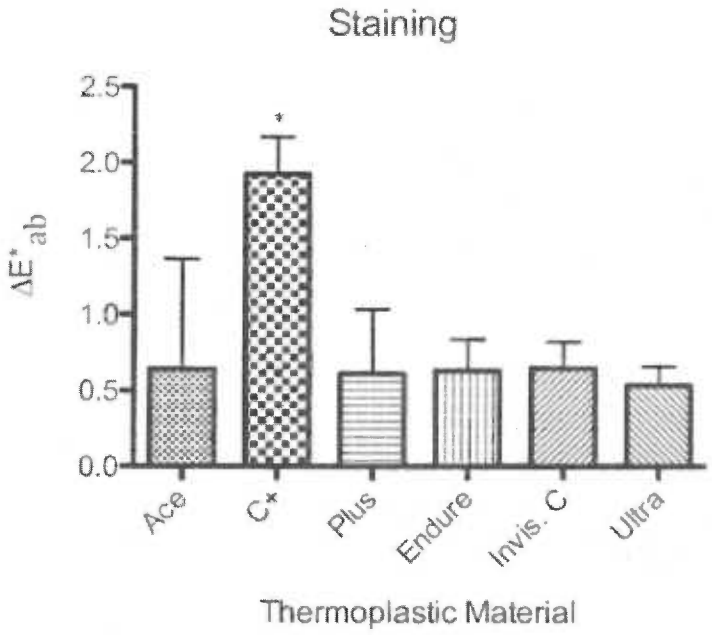
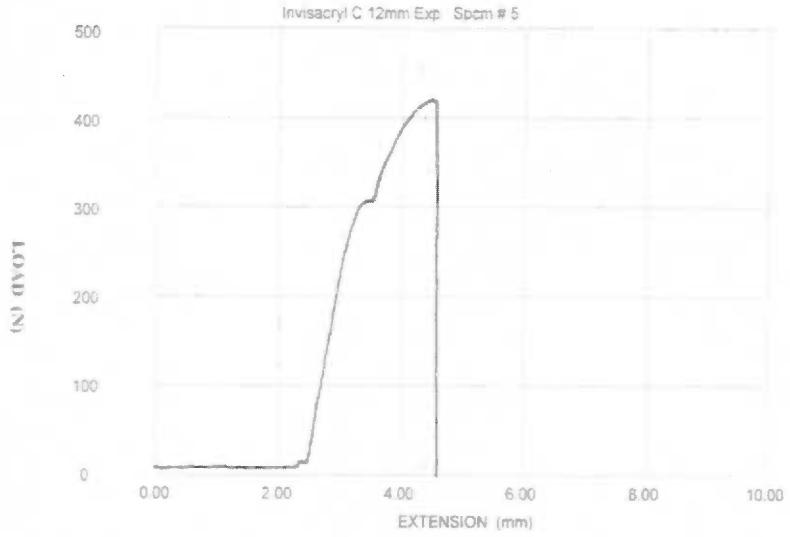

Staining
2.5
2.0
1.5
1.0
0.5
0.0
ΔE*ab
*
Ace
C*
Plus
Endure
Invis. C
Ultra
Thermoplastic Material

Figure 9a: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400
300
200
100
0
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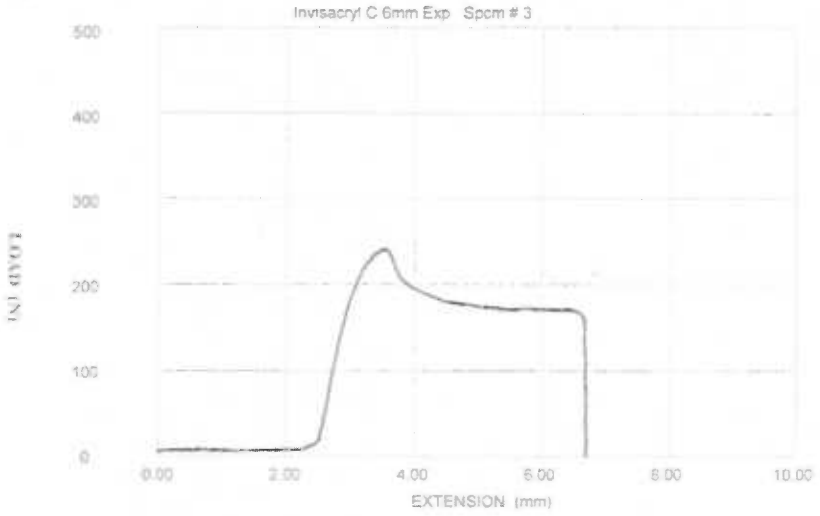
0.00
2.00
4.00
6.00
8.00
10.00
EXTENSION (mm)

Figure 9b:


Invisacryl C 6mm Exp Spcm # 3
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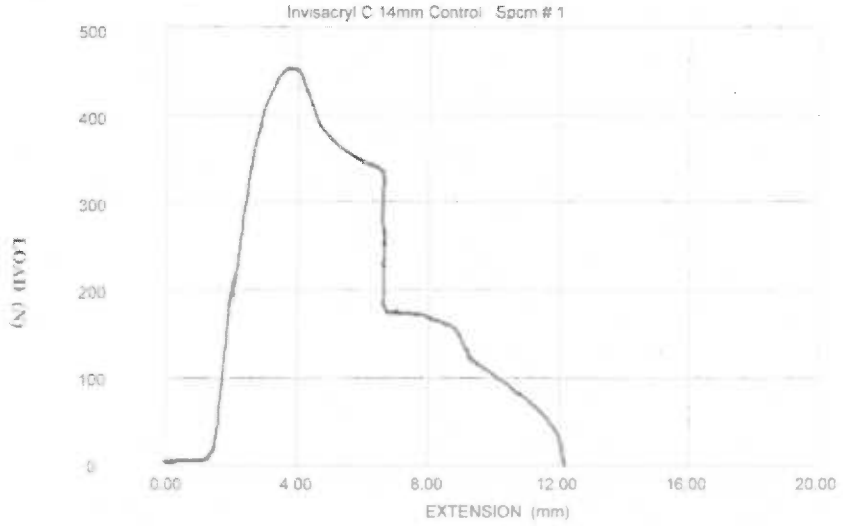
400
300
200
100
0
0.00
2.00
4.00
6.00
8.00
10.00
EXTENSION (mm)

Figure 9c: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400
300
200
100
0
LOAD (N)
0.00
4.00
8.00
12.00
16.00
20.00
EXTENSION (mm)

Figure 10:

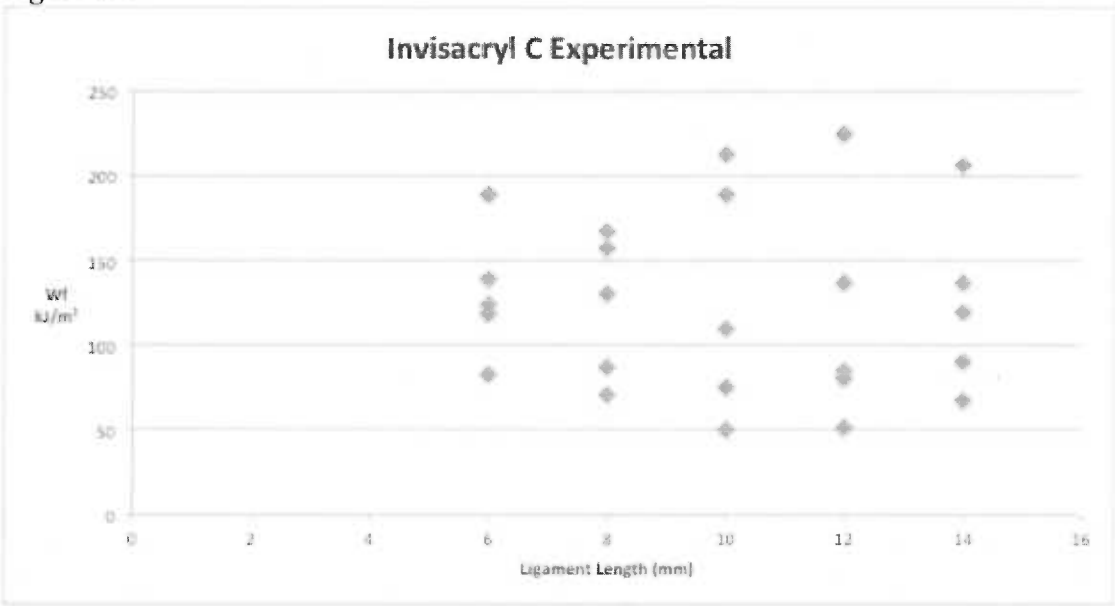
Invisacryl C Experimental
250
200
150
100
50
0
Wf
kJ/m²
0
2
4
6
8
10
12
14
16
Ligament Length (mm)

Figure 11:

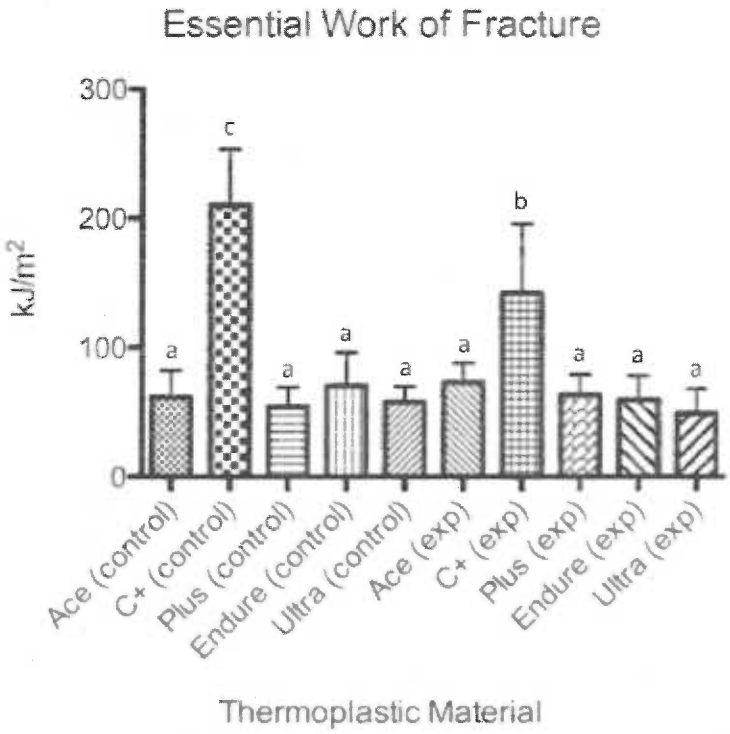
Essential Work of Fracture
300
200
100
0
kJ/m2
a
c
a
a
a
a
b
a
a
a
Ace (control)
C+ (control)
Plus (control)
Endure (control)
Ultra (control)
Ace (exp)
C+ (exp)
Plus (exp)
Endure (exp)
Ultra (exp)
Thermoplastic Material

Figure 12:

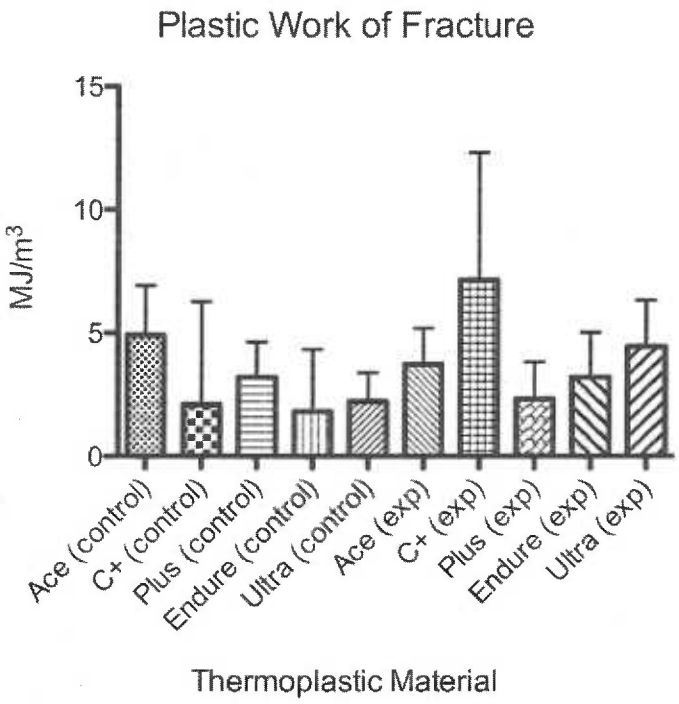
Plastic Work of Fracture
15
10
5
0
MJ/m3
Ace (control)
C+ (control)
Plus (control)
Endure (control)
Ultra (control)
Ace (exp)
C+ (exp)
Plus (exp)
Endure (exp)
Ultra (exp)
Thermoplastic Material

Table Legends

Table 1: VFR Materials used in this study

Table 2: L*, a*, and b* values (mean , SD) for initial clarity and staining

Table 1:

Product Name	Manufacturer	Composition
Essix Ace	Dentsply Raintree Essix, Sarasota, FL	Polyethylene Copolymer
Essix C+	Dentsply Raintree Essix, Sarasota, FL	Polypropylene Polymer
Essix Plus	Dentsply Raintree Essix, Sarasota, FL	Polyethylene Copolymer
Endure	Great Lakes Orthodontics, Ltd., Tonawanda, NY	Polyvinyl Chloride Polymer
Invisacryl C	Great Lakes Orthodontics, Ltd., Tonawanda, NY	Polypropylene Polymer
Invisacryl Ultra	Great Lakes Orthodontics, Ltd., Tonawanda, NY	Polyethylene Copolymer

Table 2:

	Initial Clarity (n=50 per material)				Staining (n=25 per material)		
	L*	a*	b*		L*	a*	b*
Ace	88.43* , 1.10	.50* , .05	-3.48* , .12		88.98* , .61	.47* , .04	-3.26* , .06
C+	80.53* , .79	.88* , .05	.34* , .23		79.66* , .92	.92*, .05	1.97*, .21
Plus	88.64*, .64	.58*, .04	-3.49*, .07		88.78, .89	.46*, .03	-3.15*, .08
Endure	82.12*, 0.77	1.81*, .09	-4.98*, .15		81.73*, .58	1.95*, .06	-4.71*, .18
Invis. C	79.49*, .77	0.91*, .03	.15*, .13		79.35, .72	0.8*, .04	0.7*, .15
Ultra	88.93*, .53	0.48*, .04	-3.53*, .06		88.91, .47	0.45*, .04	-3.07*, .07

* indicates $P < .05$

LITERATURE REVIEW

Retention

Orthodontic relapse is a change in tooth position or arch relationship subsequent to the completion of orthodontic treatment.[1] Without retention there is a tendency for teeth to return to their initial positions.[2] The four factors most commonly attributed as the cause of orthodontic relapse are: elastic recoil of the periodontal fibers, forces exerted by the facial and oral soft tissues, occlusal forces, and post treatment facial growth and development.[3] Relapse in the form of crowding has been shown to occur even up to 20 years post-retention.[4] The goal of the retention phase of orthodontics is to keep teeth in their corrected positions following treatment.

Several retainer designs have evolved over time. Due to the lack of scientific evidence practitioners currently utilize a specific retainer design based largely on personal preference and nonscientific criteria.[2] A 2010 survey of active members of the American Association of Orthodontists reported that following comprehensive treatment, 30.4% of orthodontists use clear thermoplastic retainers as their most common form of maxillary retention, and 18.2% of orthodontist use them as their most common form of mandibular retention.[5] The most common retainers used by orthodontists in the maxillary and mandibular arches were the Hawley (58.2%) and fixed lingual (40.2%), respectively.[5]

Retainer History

Retainers used around 1914 by Hawley and others were basically fabricated from gold wire and vulcanite. [6] In about 1937, steel wire and acrylic retainers become the popular materials for retainer fabrication. [6] In 1971 Ponitz[6] described the technique for fabrication of clear thermoplastic vacuum formed retainers (VFRs). A machine adapts heat-softened thermoplastic by either negative or positive pressure, and either pulls or pushes the thermoplastic onto a working study model. The retainers used in the modern orthodontic practice have not progressed since the steel wire and acrylic retainers of 1937 and the VFR of Ponitz in 1971.

Positive Attributes of VFRs

Documented benefits of VFR's are: simplicity of construction, significant reduction in laboratory time, limited materials and skill needed for fabrication, ease of delivery, and low cost. [7-9] These benefits of VFRs are a consequence of their fabrication, which requires no technical proficiency in wire bending; therefore, auxiliary personnel with only minimal instruction can fabricate the thermoplastic appliance in the orthodontic office. [10]

On the positive side, VFRs have been shown to hold corrections of lower anterior teeth more effectively and be more cost-effective than Hawley retainers. [11] The majority of patients also prefer VFRs to Hawley retainers. [12] VFRs have also been used during retention to produce minor tooth movements[6,7] or as bleaching trays.[13]

Negative Attributes of VFRs

On the negative side, Ponitz[6] recognized the shorter life expectancy of the VFRs compared to a standard Hawley appliance. The major drawbacks of VFRs are their tendency to open the bite and their low durability.[8] VFRs have also been shown to inhibit relative vertical tooth eruption, or "settling" of the occlusion.[14] Low durability can result in broken VFRs that have financial cost to replace and may increase the risk of orthodontic relapse if the broken retainer is not replaced in a timely fashion.

VFRs have poor wear resistance along the incisal and occlusal surfaces.[15] Two previous in-vitro wear resistance studies using steatite abraders concluded that the wear resistance of polyethylene copolymers is superior to polypropylene based thermoplastics.[10,16]

Conversations with orthodontists also indicate that retainer fracture[17] and staining are problematic in orthodontic practice; however, there have been no reports of fracture frequency or noncompliance as a result of staining.

Previous Research on VFR Materials

As thermoplastic polymers are highly viscoelastic materials the environment and forming procedures have marked effects on their mechanical properties.[18] The elastic moduli and tensile yield strength stress of thermoplastic materials used for fabrication of invisible retainers are affected by the thermoforming process as well

as immersion in water at 37 degrees for 24 hours.[18] The elastic moduli of amorphous thermoplastics were shown to increase after thermoforming and immersion in water at 37 degrees for 24 hours. The elastic moduli of semi-crystalline thermoplastics were generally shown to decrease after thermoforming and immersion in water at 37 degrees for 24 hours. The tensile yield stress decreased for all the thermoplastic materials tested. The thermoplastics have also been shown to absorb water to different degrees over a 2-week period.[18]

The effect of oral cleansing agents on the essential work of fracture (EWF) and plastic work of fracture (PWF) for two thermoplastic materials has been investigated. Polyethylene copolymer (Tru-Tain Splint) and polypropylene polymer (Essix-C+) sheets were stored in a cleansing agent for 160 hours at 25 degrees and then tested. The polypropylene polymer showed higher EWF after storage in hydrogen peroxide versus storage in distilled water.[17] The polypropylene polymer showed higher EWF after storage in Crest Pro-Health mouth rinse versus the polyethylene copolymer.[17] The polypropylene polymer exhibited lower PWF after storage in hydrogen peroxide than with any other storage conditions.[17] The polypropylene polymer exhibited higher PWF than the polyethylene copolymer after being stored dry, and in distilled water and Original Listerine.[17] The authors concluded that all tested cleansers could be used to clean thermoplastic orthodontic retainers without increasing risk of fracture.[17]

The wear resistance of VFR thermoplastics has been investigated in two previous

studies. Both previous studies, Gardner et al.[10] and Raja et al.[16] used steatite abraders and wear depth to assess wear resistance. Gardner et al.[10] studied three different thermoplastics: Essix C+ (polypropylene), Invisacryl C (polypropylene) and TR (polyethylene co-polymer), and found that the polyethylene co-polymer thermoplastic exhibited greater resistance to wear than two polypropylene based thermoplastics. Raja et al.[16] studied four different thermoplastics: Essix C+ (polypropylene), Essix Ace (polyethylene co-polymer), Duran (polyethylene co-polymer), and Tru-Tain (polyethylene co-polymer), and found that the three polyethylene co-polymers exhibited greater resistance to wear than the polypropylene based thermoplastic. Raja et al.[16] also found that Essix Ace had greater wear resistance than Tru-Tain. These two previous wear resistance studies show similar results indicating that under in-vitro conditions polyethylene co-polymers have superior wear resistance to polypropylene based thermoplastics.[10,16]

To date, no study has investigated the essential work of fracture and plastic work of fracture of numerous thermoplastic orthodontic retainer materials, or the EWF and PWF of these materials after being exposed to a simulated aging process in the oral environment. Initial clarity and staining of the VFR thermoplastics has also not been studied.

Evaluating Fracture Toughness

How VFRs fracture in orthodontic service is unknown.[17] In a previous study by Pascual et al.[17] that tested EWF and PWF of two thermoplastics, moderately fast

monotonic loading, as opposed to slow monotonic, impact, or cyclic loading was used. The essential work of fracture test was developed to evaluate the fracture toughness of ductile, thin, plastic sheets.[19,20] In the most frequently used EWF test, which uses a double-edge-notched-tension (DENT) specimen, a series of specimens with equal thicknesses (t) and systematically different internotch distances, or ligament lengths (Ls), are each loaded in tension until complete fracture occurs. Integrating the area under the load-elongation curve generated during testing of each specimen yields that specimen's total work of fracture (W_f), representing the energy needed for complete specimen fracture. In EWF theory, W_f is divided into two components: essential work and nonessential work.[17,19]

The EWF, or We, is the energy that is "essential" in generating new fracture surfaces. This energy is concentrated near the plane of fracture and crack tip.[20-22] Since EWF depends only on fracture surface area, it is an intrinsic material property. EWF has been regarded as a measure of "resistance to crack initiation."[22,23]

The nonessential work, or Wp, is the energy dissipated plastically throughout the zone surrounding the fracture and is therefore known as the plastic work of fracture. PWF is "nonessential," given that it has no involvement in generating new fracture surface areas but instead depends on specimen volume, geometry, and loading configuration, and is therefore not an intrinsic material property. PWF is regarded as a measure of "resistance to crack propagation"[22] and an indicator of ductility.[24]

Load-elongation curves for a series of specimens with varying L, from which W_f values are measured and plotted on a W_f vs L graph. The data should appear linear, assuming that the two requirements of the EWF test are fulfilled: the full ligament yielding occurs just prior to crack onset at the notch tips, and relative shapes of load-elongation curves in the series are similar.[25] The intercept of the y-axis, w_e, is the evaluated material's EWF. The slope, βw_p, is the material's PWF, where β is a shape factor proportional to the area of the plastic zone. For the DENT EWF test investigating thin polymer sheets the plastic zone of deformation is considered to be circular, thus $\beta = \pi/4$.[20]The linearity of the EWF theory is described by the following equations[26]:

$W_f = W_e + W_p$

$W_f = w_e Lt + \beta w_p L^2 t$

$w_f = W_f/Lt = w_e \beta w_p L$

Evaluating Initial Clarity and Staining

The esthetics of VFRs is considered to be important to both orthodontists and patients. It is assumed that both groups would prefer invisible retainers that can be worn discretely. This requires a material that has optical properties that allow light to easily pass through unaltered. The material must also maintain this ability after exposure to the oral environment for extended periods of time. Thus, companies such as Dentsply have marketing targeted at the superior clarity and staining resistance of their materials.[27]

The investigation of color changes can involve either one or a combination of three tools: spectrophotometers, colorimeters and digital photographic analysis.[28] The analysis of color in dentistry is generally defined by the Commission Internationale de l 'E´clairage (CIE) L*, a*, b* (LAB) color space.[29] In this three-dimensional color space, with the three axes being L*, a* and b*, the L* refers to the lightness. Its value ranges from 0 for perfect black to 100 for perfect white. The a* refers to the chromaticity coordinates in the red–green axis. Positive a* values reflect the red color range and negative values indicate the green color range. The b* corresponds to the chromaticity coordinate yellow–blue axis. Positive b* values indicate a yellow color range while negative values indicate the blue color range. Total color change is measured in terms of ΔE and is measured by the equation: $\Delta E^*_{ab}=(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$. E stands for "Empfindung", the German word for "sensation".

The proposed clinical perceptible limit for color matching with the human eye is 3.7 ΔE units.[30] However, this is not an "absolute value", with different lighting conditions having an effect on color perception and a light source that approximates standard daylight being ideal for color analysis.[28] There are no proposed perceptibility or acceptability thresholds for the changes in transmitted color.[31]

The frequently accepted "50:50" clinical perceptibility threshold for color matching in dentistry is 1 ΔE^*_{ab} units.[28] This is interpreted that given a color difference of 1

ΔE^*_{ab} units, 50% of observers will notice the color difference, and 50 % will see no difference between compared objects. The frequently accepted "50:50" acceptability threshold for color matching in dentistry is approximately 3 ΔE^*_{ab} units. [28] This is interpreted that given a color difference of approximately 3 ΔE^*_{ab} units, 50% of observers will accept the color difference, and 50 % would consider it unacceptable.

Simulated Aging

Thermal cycling has been used extensively in the dental research literature to evaluate the performance of dental restorative materials. Laboratory simulations with thermal cycling are done because clinical trials are often costly and time consuming. Thermal cycling is generally done to accelerate the aging process of materials. The temperatures that are often chosen to cycle between, and the number of cycles are mostly arbitrary; although, the recommendation that 10,000 cycles corresponds to a year of clinical service for a dental restoration has been made.[32]

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8. Wang F. A new thermoplastic retainer. *J Clin Orthod.* 1997;31(11):754-757.

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10. Gardner GD, Dunn WJ, Taloumis L. Wear comparison of thermoplastic materials used for orthodontic retainers. *Am J Orthod Dentofacial Orthop.* 2003;124(3):294-297.

11. Rowland H, Hichens L, Williams A, et al. The effectiveness of hawley and vacuum-formed retainers: A single-center randomized controlled trial. *American Journal of Orthodontics and Dentofacial Orthopedics.* 2007;132(6):730-737.

12. Hichens L, Rowland H, Williams A, et al. *The European Journal of Orthodontics.* 2007;29(4):372-378. doi: 10.1093/ejo/cjm039.

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Appendix A: Recommendations and Future Research

The VFR material chosen should be patient specific. The practitioner needs to synthesize the available information about a material's fracture toughness, wear resistance, initial clarity, and staining resistance to choose the most appropriate material to fabricate a patient's VFR. For example, an esthetically conscious adult patient that had severe anterior rotations prior to treatment, indicating full time retention for an extended period of time, would be best suited with a VFR made from a polyethylene copolymer. The polyethylene copolymer would stain less over time and provide superior initial clarity than a polypropylene polymer or polyvinyl chloride polymer. However, if the patient was an adolescent, potentially more abusive of the VFR, which only needed full time wear for one month, the material indicated is a polypropylene polymer due to the superior fracture toughness. Wear resistance is very important for bruxers. Patients with bruxing habits would be better suited with a VFR made from a polyethylene copolymer due to the materials greater wear resistance. Choosing the right material for a patient requires considering the patient's orthodontic retention needs, esthetic demands, and potential causes of retainer breakage.

Material properties yet to be studied, but of importance when choosing a thermoplastic material are formability and creep. Since the thermoplastic materials are heated and pulled or pushed over a working study model, how well the material adapts to the model determines how accurately the teeth will be retained. If the material does not adapt well to the model then the teeth will not be as accurately

retained as a material that adapts very closely to the model. Also, the ability of the material to maintain its shape through the many cycles of being inserted and removed will determine if the initial accuracy of the VFR is maintained. A material that initially adapts well, but doesn't maintain its shape in the clinical environment is not useful as a VFR material.

Smoothing the edges of a VFR to remove any cracks is likely important to longevity of a VFR. In addition to patient comfort, a break in the uniformity of the edge of a VFR is a location for stresses to concentrate. The concentration of stresses can lead to crack initiation and propogation.

Appendix B: Reported values and statistical analysis of ΔE^*_{ab} for initial clarity and staining, EWF, and PWF.

Table B1: ΔE^*_{ab} for initial clarity and staining (mean , SD)

	ΔE^*_{ab} Initial Clarity (n=50 per material)		ΔE^*_{ab} Staining (n=25 per material)
Ace	5.56 , 1.1[b]		0.64 , 0.72
C+	14.03 , 0.8[d]		1.92 , 0.24*
Plus	5.35 , 0.64[a,b]		0.61 , 0.43
Endure	12.02 , 0.76[c]		0.63 , 0.21
Invis. C	14.97 , 0.76[e]		0.65 , 0.18
Ultra	5.06 , 0.53[a]		0.54 , 0.12

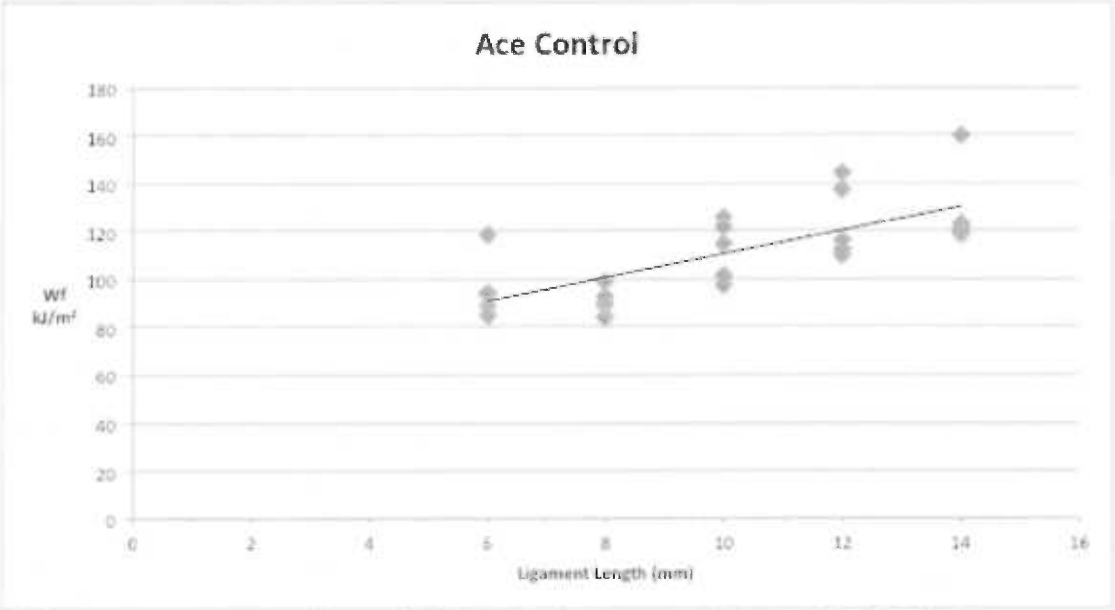
For ΔE^*_{ab} Initial Clarity a-e indicates $P < .05$
For ΔE^*_{ab} Staining * indicates $P < .05$

Table B2: EWF and PWF (estimates, 95% CI)

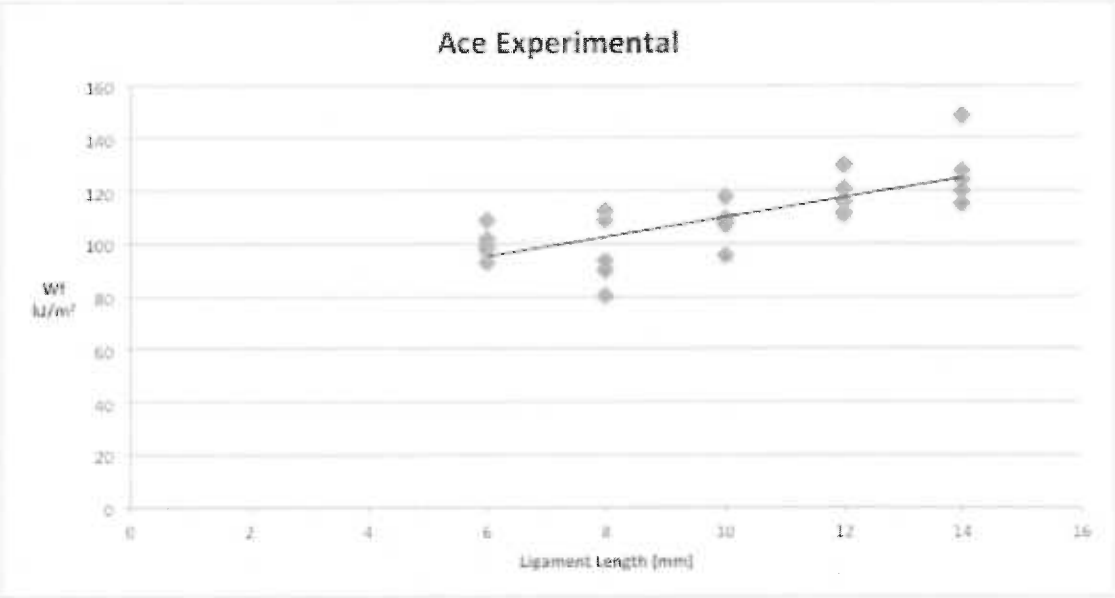
	EWF (kJ/m^2)			PWF (MJ/m^3)	
	Control	Experimental		Control	Experimental
Ace	61.34 , 20.89[a]	72.72 , 15.21[a]		4.91 , 2.01	3.73 , 1.46
C+	210 , 43.4[c]	141.87 , 53.68[b]		2.09 , 4.17	7.15 , 5.17
Plus	54.1 , 14.93[a]	63.31 , 15.5[a]		3.19 , 1.44	2.33 , 1.49
Endure	70.08 , 26.05[a]	59.05 , 18.76[a]		1.82 , 2.51	3.20 , 1.81
Ultra	57.43 , 12.19[a]	48.52 , 19.29[a]		2.22 , 1.17	4.45 , 1.89

For EWF a-c indicates $P < .05$
No PWF values were significantly different

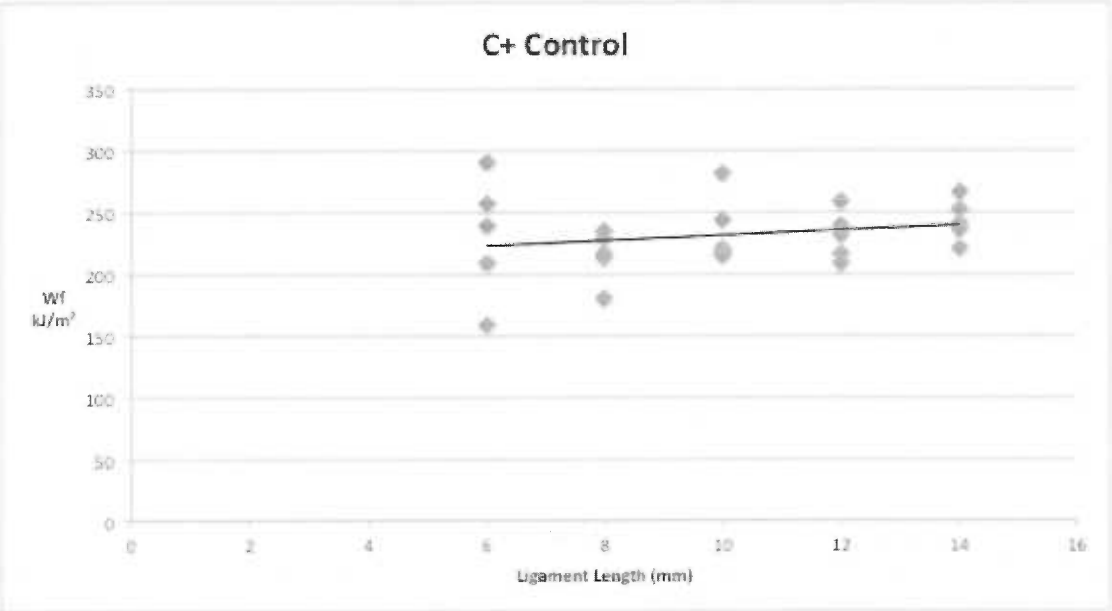
Appendix C: Least-square linear regressions for work of fracture (W_f) vs ligament length (L) for all thermoplastic materials tested.



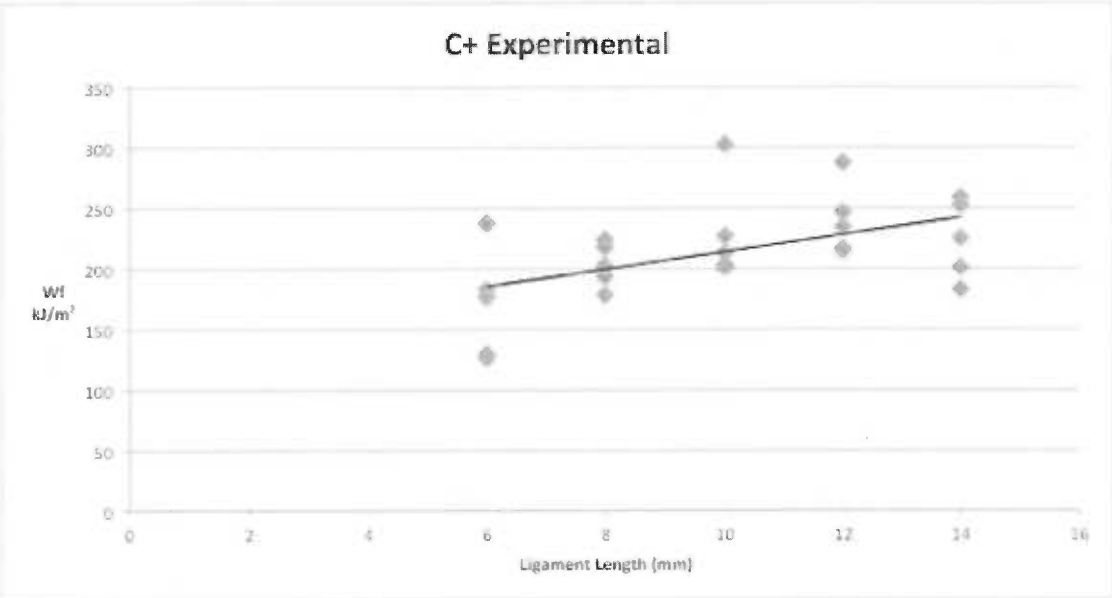
C1: Linear regression of W_f vs L for Essix Ace Control (slope = 4.91 MJ/m^3; y-intercept = 61.34 kJ/m^2, R^2 = .53)



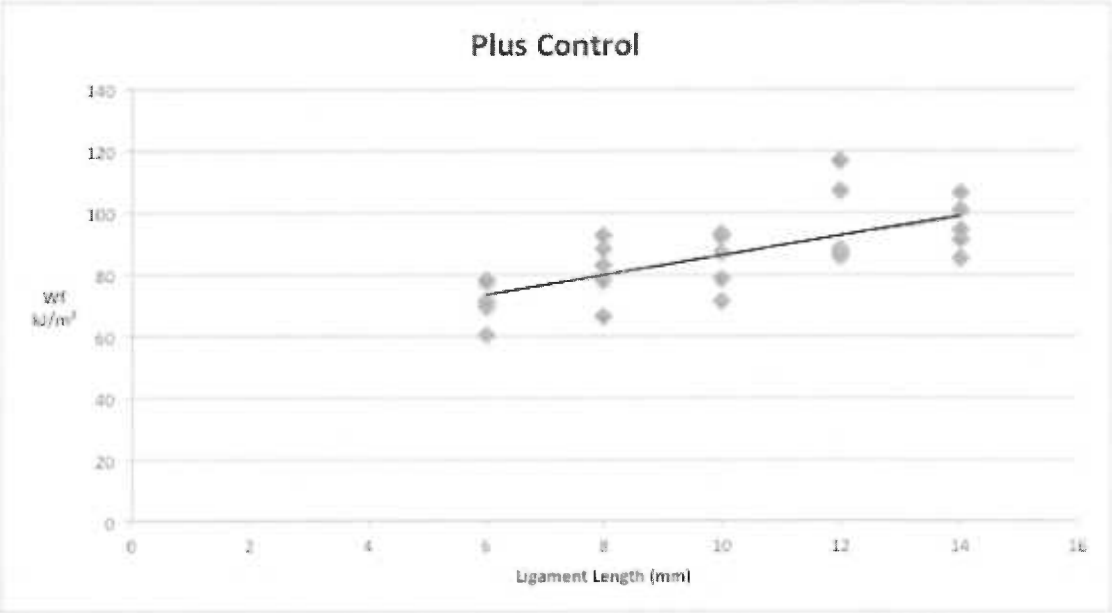
C2: Linear regression of W_f vs L for Essix Ace Experimental (slope = 3.73 MJ/m^3; y-intercept = 72.72 kJ/m^2, R^2 = .55)



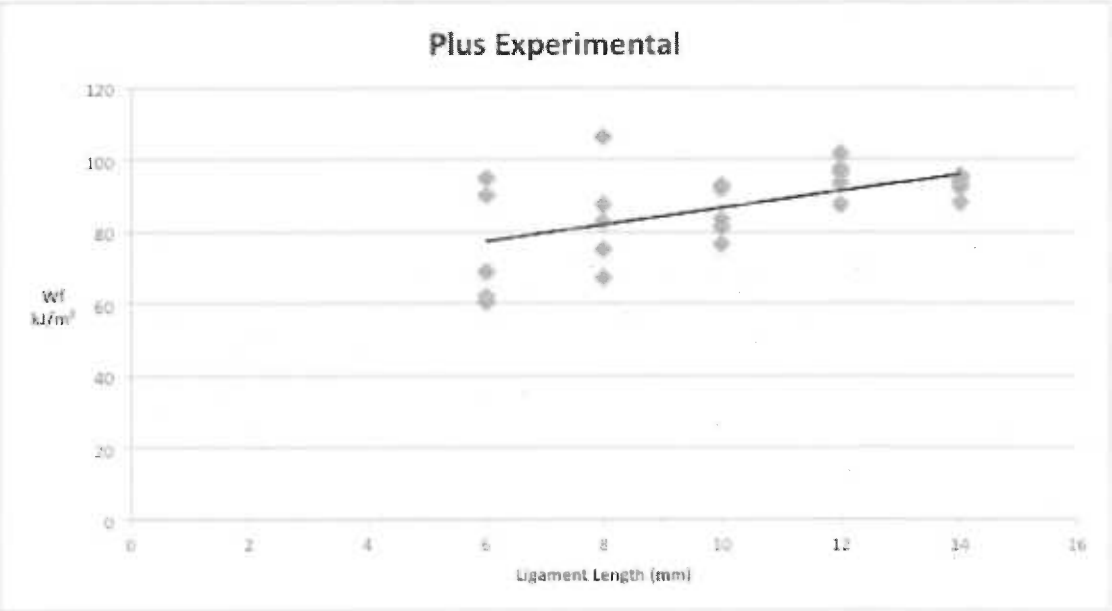
C3: Linear regression of W_f vs L for Essix C+ Control (slope = 2.09 MJ/m^3; y-intercept = 210 kJ/m^2, R^2 = .04)



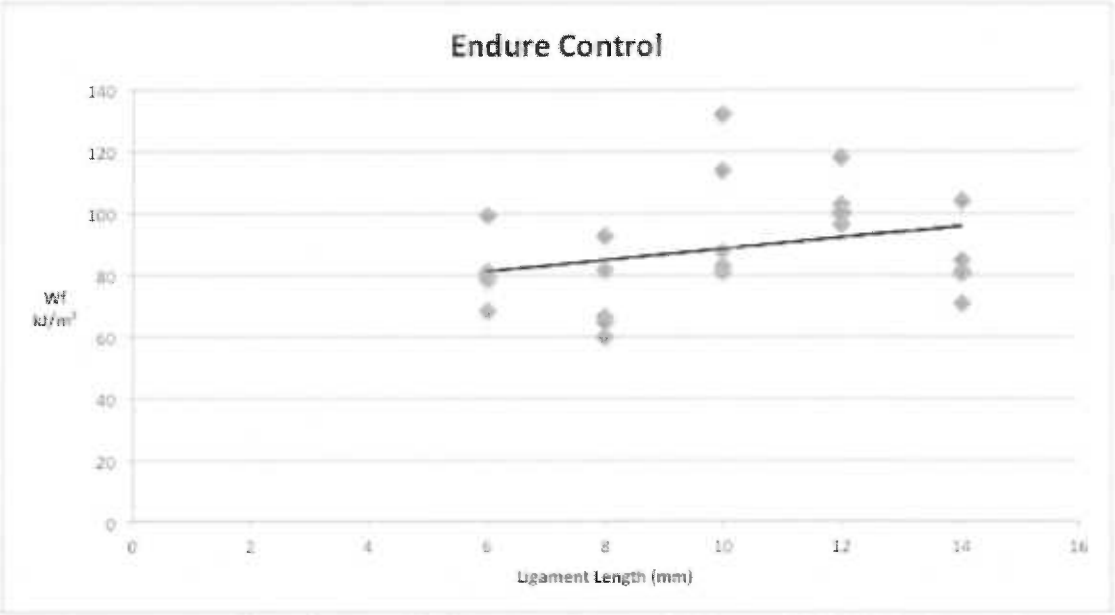
C4: Linear regression of W_f vs L for Essix C+ Experimental (slope = 7.15 MJ/m^3; y-intercept = 141.87 kJ/m^2, R^2 = .26)



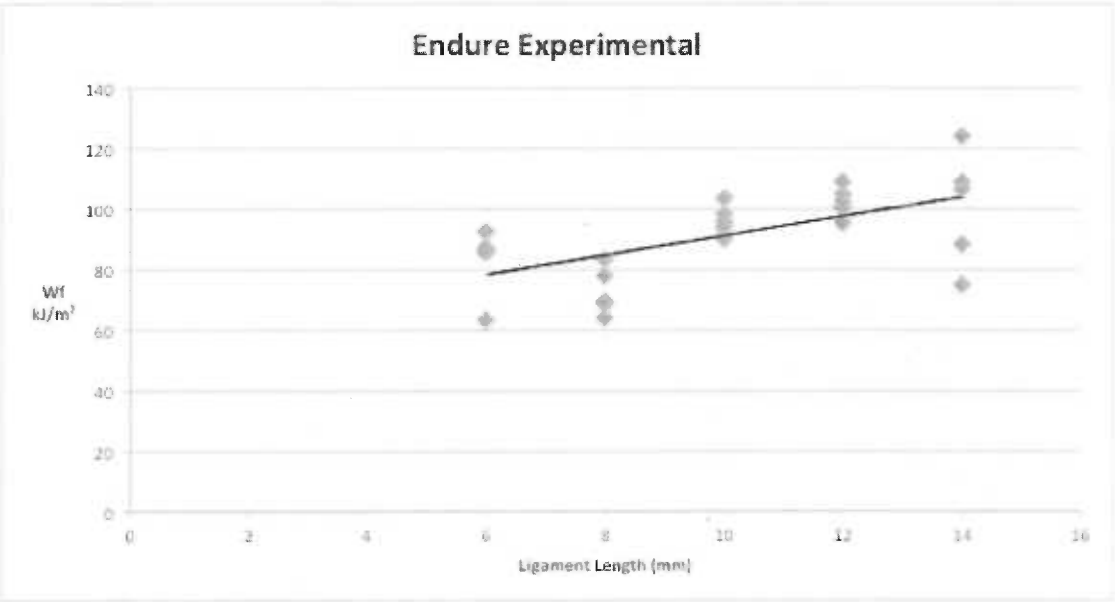
C5: Linear regression of W_f vs L for Essix Plus Control (slope = 3.19 MJ/m^3; y-intercept = 54.1 kJ/m^2, R^2 = .48)



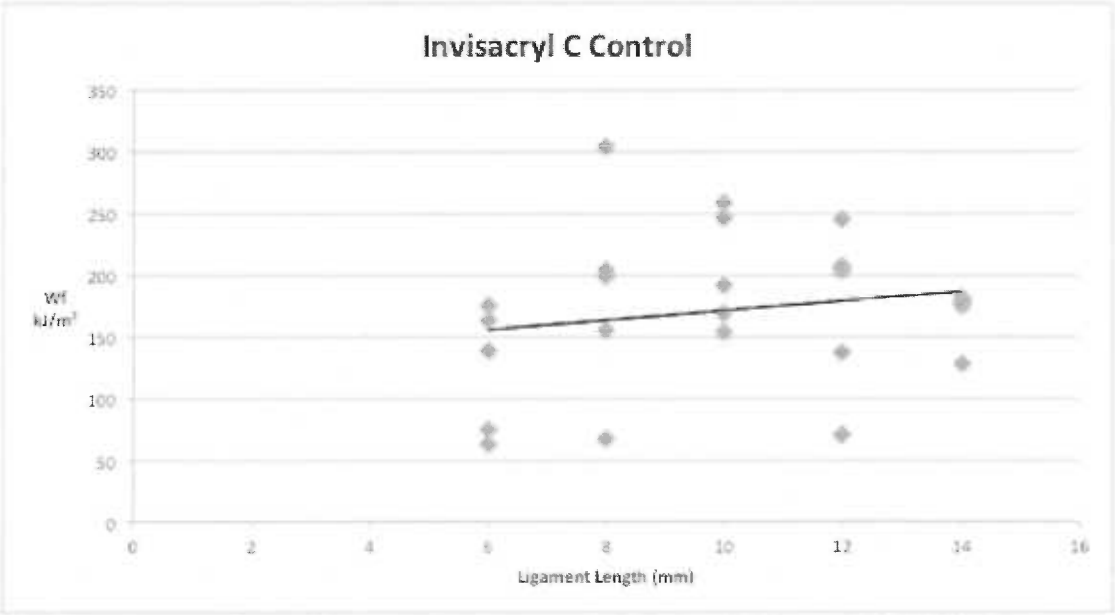
C6: Linear regression of W_f vs L for Essix Plus Experimental (slope = 2.33 MJ/m^3; y-intercept = 63.31 kJ/m^2, R^2 = .31)



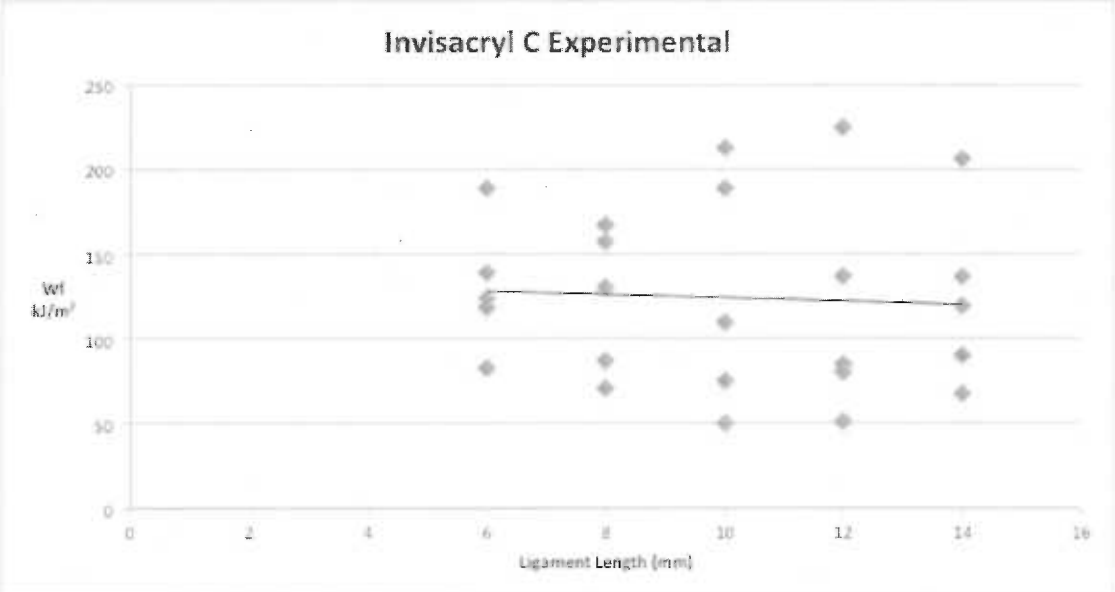
C7: Linear regression of W_f vs L for Endure Control (slope = 1.82 MJ/m^3; y-intercept = 70.08 kJ/m^2, R^2 = .09)



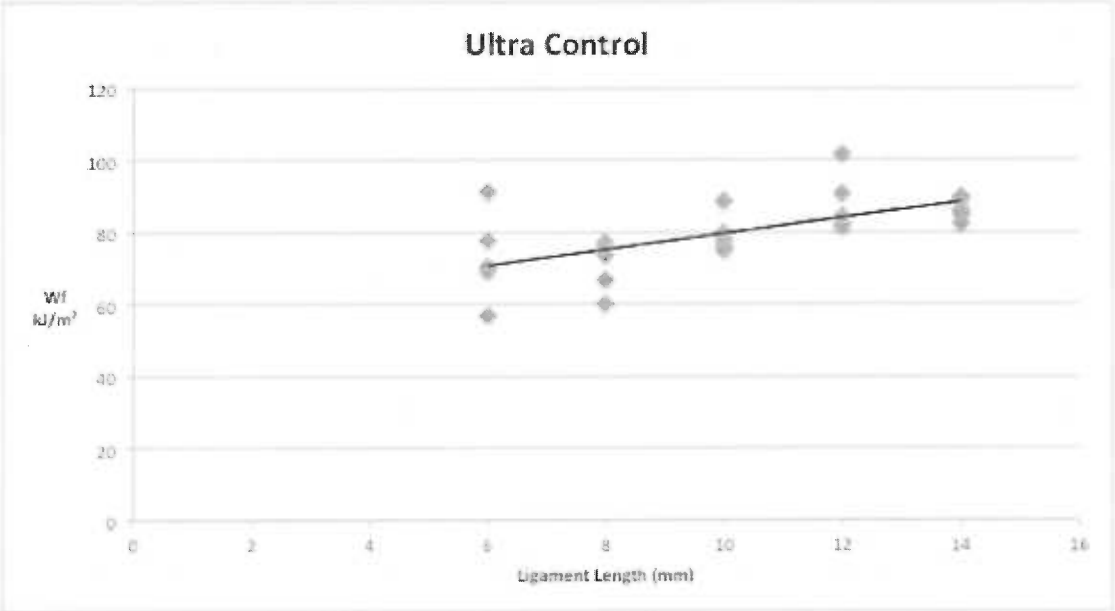
C8: Linear regression of W_f vs L for Endure Experimental (slope = 3.20 MJ/m^3; y-intercept = 59.05 kJ/m^2, R^2 = .37)



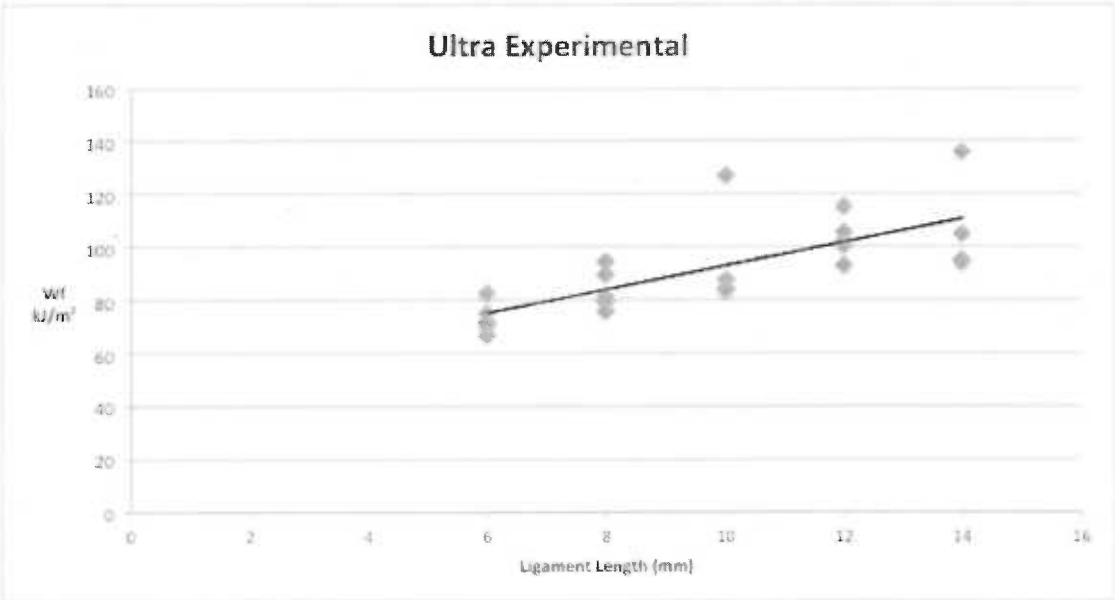
C9: Linear regression of W_f vs L for Invisacryl C Control (slope = 3.88 MJ/m^3; y-intercept = 132.15 kJ/m^2, R^2 = .03). Data was not usable due to requirements of EWF test not being met.



C10: Linear regression of W_f vs L for Invisacryl C Experimental (slope = -1 MJ/m^3; y-intercept = 134.22 kJ/m^2, R^2 = .003). Data was not usable due to requirements of EWF test not being met.

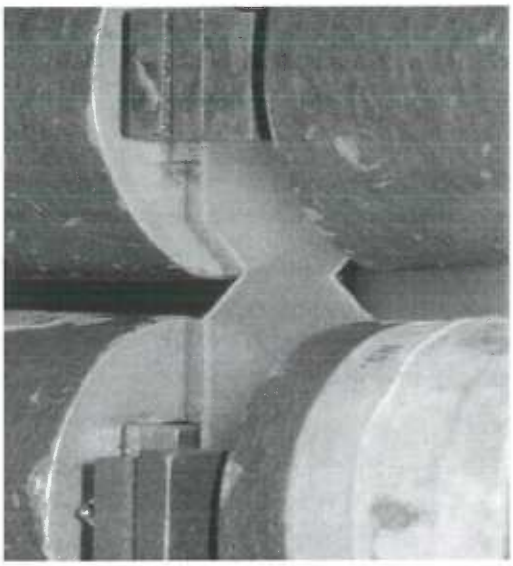


C11: Linear regression of W_f vs L for Invisacryl Ultra Control (slope = 2.22MJ/m^3; y-intercept = 57.43 kJ/m^2, R^2 = .4).

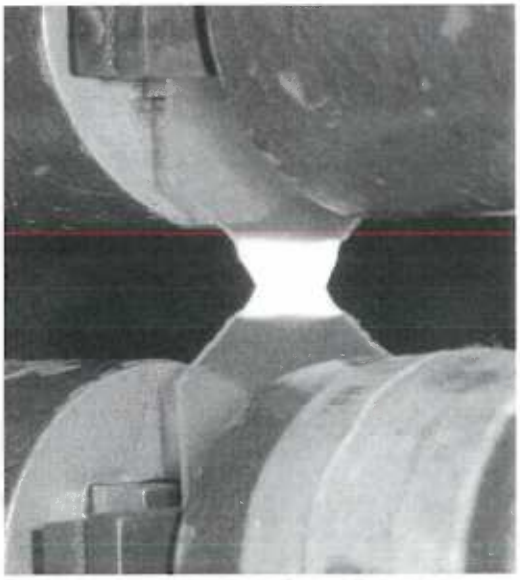


C12: Linear regression of W_f vs L for Invisacryl Ultra Experimental (slope = 4.45MJ/m^3; y-intercept = 48.52 kJ/m^2, R^2 = .53).

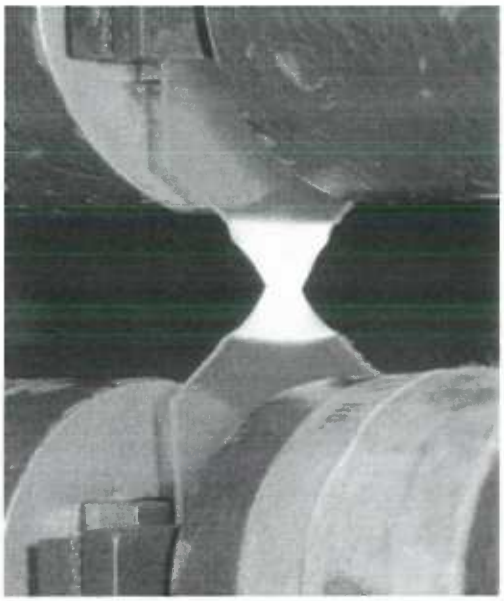
Appendix D: Essix C+ specimen undergoing double-edged notch tension essential work of fracture test.



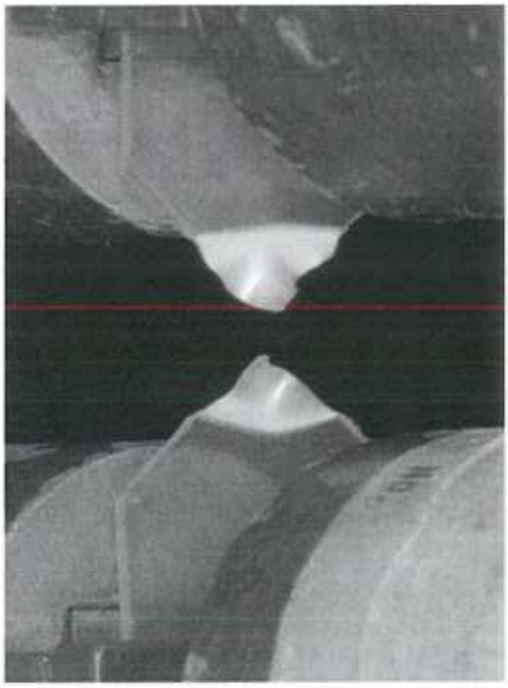
D1: Before initial yielding



D2: After yielding and crack initiation



D3: Crack propagation



D4: After fracture

Appendix E: Biostar material codes and heating times

Material	Biostar Code	Heating Time
Ace	133	35
C+	163	60
Plus	143	40
Endure	132	35
Invis. C	203	70
Ultra	153	45

Appendix F: Summary of researched thermoplastic orthodontic retainer material properties.

Composition	Brand	Initial Clarity	Staining Resistance	Fracture Toughness	Wear Resistance
PE Copolymers	Essix Ace	+	+	–	+
	Essix Plus	+	+	–	
	Invisacryl Ultra	+	+	–	
	TR				+
	Duran				+
	Tru Tain			–	+
PP Polymers	Essix C+	–	–	+	–
	Invisacryl C	–	+	+/-	–
PVC Polymer	Endure	–	+	–	

+ indicates that material displays desirable properties, - indicates that material displays undesirable properties