



**Shear Bond Strength of Metal Brackets to Zirconia Conditioned with
Various Primer-Adhesive Systems**

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The views expressed in this study are those of the author and do not reflect the official policy of the United States Army, the Department of Defense, or the United States Government. The author does not have any financial interest in the companies whose materials are discussed in this article.

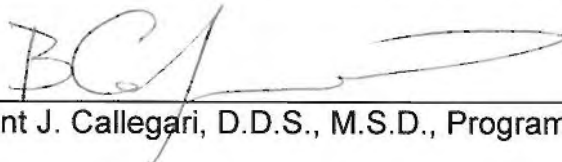
**Shear Bond Strength of Metal Brackets to Zirconia Conditioned with
Various Primer-Adhesive Systems**

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A handwritten signature in black ink, appearing to read "Michael D. Segall".

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DEDICATION

This thesis is dedicated to my family. Without their unwavering support, I wouldn't be where I am today. I cannot thank my beautiful wife enough for making countless sacrifices and exercising patience and understanding during the turbulent times of residency. Her encouragement and love has kept me going as I pursue my dream of becoming an orthodontist. Thank you to my mother for putting my siblings and me first and providing an upbringing full of opportunities and experiences second-to-none. Thank you to my father for showing me the meaning of hard work, perseverance, integrity, and compassion. Together, they have opened so many doors for me. I admire my sister's devotion to teaching and inspiring others and my brother's passion for life and adventure. For their immeasurable influence in my life, I owe them much gratitude. Lastly, it would be unforgiveable not to thank God for His many blessings and fortunes.

ABSTRACT

Purpose: The purpose of this study was to measure the shear bond strength (SBS) of adhesive-coated metal brackets to zirconia conditioned with four different universal primer systems produced by 3M,Ormco, Reliance, and Kuraray. These were compared to a conventional primer system to serve as a control. Additionally, bond failure modes were characterized using the Adhesive Remnant Index (ARI) survey.

Methods: 40mm by 19mm zirconia blocks (BruxZir, Glidewell Laboratories, Newport Beach, CA) were prepared to provide enough substrate surface area for 100 Victory brackets (3M, Monrovia, CA). The samples were equally divided into five groups– a control not containing a universal primer (group 1), and four variable groups possessing universal primers manufactured by 3M,Ormco, Reliance, and Kuraray (groups 2-5, respectively). After bonding the brackets to the zirconia using the designated primer-adhesive system and technique, a single-bladed Instron machine (Norwood, MA) individually sheared the brackets off the zirconia to calculate the SBS. The bracket base corresponding to each sample was further examined under 10x magnification to describe the type of failure by assigning an ARI score.

Results: A significant difference was found among the groups with respect to SBS ($p<0.001$). Group 3 had the highest SBS, and it was significantly greater than all the other groups ($p<0.05$). Groups 2, 4, and 5 exhibited significantly higher SBS than group 1 ($p<0.05$), but they did not differ from each other ($p>0.05$). The control group exhibited adhesive failure modes with all of the

adhesive resin left on the bracket bases. In contrast, experimental groups were associated with mixed failure modes where most of the composite remained on the zirconia.

Conclusions: Pretreating the surface of zirconia with universal primers contributed to an increase in SBS compared to not treating the zirconia with universal primers when bonding metal brackets. Among the four adhesive systems with the universal primer, theOrmco adhesive exhibited a significantly higher SBS to zirconia than 3M, Reliance, and Kuraray adhesives.

TABLE OF CONTENTS

TITLE PAGE.....	i
APPROVAL.....	ii
ACKNOWLEDGEMENTS.....	iii
DEDICATION.....	iv
ABSTRACT.....	v
TABLE OF CONTENTS.....	vii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
I. INTRODUCTION.....	1
II. OBJECTIVES.....	7
III. HYPOTHESIS.....	8
IV. MATERIALS AND METHODS.....	9
A. Zirconia Preparation.....	9
B. Experimental Groups.....	14
C. Bonding the Brackets.....	18
D. Shear Bond Strength Testing.....	22
E. Adhesive Remnant Index Survey.....	26
F. Statistical Management of Data.....	28
V. RESULTS.....	29
VI. DISCUSSION.....	33
VII. CONCLUSIONS.....	38
VIII. REFERENCES.....	39

LIST OF TABLES

Table 1: Composition of Each Group.....	15
Table 2: Bonding Techniques.....	19
Table 3: Criteria for Adhesive Remnant Index Scores.....	26
Table 4: Forces Recorded at Bond Failure and Shear Bond Strength Values....	30
Table 5: Shear Bond Strength Means and Statistical Comparisons.....	30
Table 6: Frequency Distribution of Failure Modes.....	32

LIST OF FIGURES

Figure 1: BruxZir Zirconia Blocks.....	10
Figure 2: Heating of the Zirconia Block's Metal Adapter with a Butane Torch.....	10
Figure 3: Metal Adapter Removal with a Curved Hemostat.....	11
Figure 4: Sanding of the Sample Surfaces with 600-Grit Silicon Carbide Paper.....	11
Figure 5: Vita's Zyrcomat 6000 MS with Zirconia Block in Position for Sintering.....	12
Figure 6: Sintering Temperature Chart.....	13
Figure 7: SandStorm Sandblaster.....	13
Figure 8: Group 1 (Control) - 3M Unitek's Transbond XT Primer and Light Cure Adhesive.....	15
Figure 9: Group 2 - 3M ESPE's Scotchbond Universal Adhesive and 3M Unitek's Transbond XT Light Cure Adhesive.....	16
Figure 10: Group 3 -Ormco's Ortho Solo and Grengloo Two-Way Color Change Adhesive.....	16
Figure 11: Group 4 - Reliance's Assure Plus All Surface Bonding Resin and Quick Cure Adhesive Paste.....	17
Figure 12: Group 5 - Kuraray's Clearfil Ceramic Primer and Transbond XT Light Cure Adhesive.....	17
Figure 13: Group 1's Armamentarium for Bonding Brackets.....	20
Figure 14: Transbond XT Primer Applied to Zirconia Surface and Transbond XT Light Cure Adhesive Buttered into Bracket Base Mesh.....	20
Figure 15: Bracket Placed on Zirconia Surface and Excess Adhesive Resin Removed.....	21
Figure 16: Bracket Light-Cured from All Four Sides.....	21
Figure 17: Instron Model #5943 Setup.....	22
Figure 18: Mounted Substrate Blocks on Jig.....	23
Figure 19: Instron Blade Engaged Brackets Behind the Occlusal Tie Wings.....	24
Figure 20: Increasing Force Applied until Bond Failure.....	25
Figure 21: Leica S4 E Stereo Microscope for ARI Survey.....	27
Figure 22: Shear Bond Strength Box Plot.....	31
Figure 23: Chemical Coupling of Composite Resin to Zirconia.....	34

I. INTRODUCTION

Orthodontic outcomes are predicated not only upon efficient biomechanics but also more critically on precise three-dimensional control of teeth. Historic appliances, such as Fauchard's expansion arch, Harris' vulcanite plates, and Angle's E-arch, were limited in their capabilities because they could only tip teeth into better positions. Innovation in design led to the development of Angle's Edgewise and Andrews' Straight Wire appliances. These systems allowed for complex tooth movements in all three planes of space (Steiner, 1933). The manner in which orthodontists fixate the appliance to the teeth is of equal importance in its evolution. Prior to the latter half of the 20th century, orthodontic therapy involved removable plates, an arch bar and wire slings, or cemented bands and archwires. These methods were difficult to manage for the practitioner and burdensome for the patient.

A breakthrough transpired in 1955 when Buonocore first proposed the basis for adhesion of restorative materials to enamel with the aid of phosphoric acid etching. His work served as the foundation for adhesive techniques in dentistry (Buonocore, 1955). A decade later, Newman used 40% phosphoric acid etch and epoxy resin to directly bond plastic attachments to enamel, which laid the groundwork for modern day bonding in orthodontics (Newman, 1965). In 1977, Gorelick was the first to utilize composite resin in bonding metal brackets to enamel (Gorelick, 1977). He chose composite resin over unfilled acrylic resin due to its superior shear bond strength (SBS) to enamel, which gave rise to lower bracket failure rates in his study. By the 1970s, a handful of studies showcased

the first-rate results of a multitude of bonding systems commercially available (Graber *et al.*, 2011). Given these advances, it was suggested that all teeth could be bonded as opposed to banded (Retief and Sadowsky, 1975). Some key benefits of bonded over banded attachments are increased cleansability, less tissue irritation, better esthetics, and improved manageability. Orthodontics has taken full advantage of adhesive dentistry in almost every facet of treatment from Invisalign composite resin attachments to protective facial surface sealants and anterior bite turbos. Consequently, bonding fixed appliances is standard practice within the orthodontic profession and is critical in delivering a superior level of care.

Precise repositioning of teeth is impossible without a stable point of force application. Throughout the duration of treatment, the connection between the bracket and tooth must be durable and reliable enough to withstand the harsh oral environment, functional and parafunctional forces, and orthodontic loads placed on the attachment interface (Knox *et al.*, 2001). Low bond strengths may result in unintentional debonding during therapy. Failure of attachment entails potential treatment delay, hard or soft tissue damage, hazard to the airway, and costs in resources and time (Zachrisson *et al.*, 1996). Alternatively, too strong of a bond is undesirable due to the transient nature of orthodontic therapy. At the conclusion of treatment, the appliance must be removed without any damage to enamel, restorations, or any other tissues (Graber *et al.*, 2011). Excessive debonding force is uncomfortable for the patient as well. Retief demonstrated enamel fracture could occur with bond strengths beyond 14.5 megapascals

(MPa), which was reported as enamel's linear tensile strength (Retief, 1974). In a more recent study, forces applied transversely to enamel rods caused them to fracture at 11.5MPa (Giannini *et al.*, 2004). It seems logical to conclude that bond strengths above these levels pose an increased chance of damaging tooth structure during debond. To avoid bond failures during the course of treatment and unwanted side effects during debonding, the bond strength between bracket and tooth should fall within a desired range of clinical acceptability. Multiple studies have proposed minimally sufficient bond strengths of 6-8MPa, 10MPa, and 8-12MPa (Bishara *et al.*, 1999; Jost-Brinkmann and Böhme, 1999; Karan *et al.*, 2007; Pannes and Bailey, 2003; Reynolds, 1979). Bonding orthodontic brackets to ceramic restorative materials poses a unique challenge. Abu et al. measured the strength between metal brackets and three ceramic crowns using standard glass ceramic bonding techniques. In-Ceram, IPS-Impress, and conventional ceramo-metal crowns all tested in the acceptable range indicating brackets can be bonded to ceramic restorations (Abu Alhaija and Al-Wahadni, 2007). Increased bracket adhesion to ceramic crowns through chemical bonding presents a risk of prosthesis surface damage at debond (Falkensammer *et al.*, 2013). When bonding brackets to ceramic restorative materials, the current consensus is the bond strength should be approximately the same value as if bonding to enamel.

Traditional protocol associated with attaching brackets to enamel must be altered for ceramic crowns due to the dissimilarity in composition. The ceramic surface first must be roughened in some capacity to allow for infiltration and

retention of the bonding agent and adhesive resin. Glass ceramics, such as lithium disilicate or feldspathic porcelain, contain glass particles that can be chemically etched with 9.6% hydrofluoric acid. This creates a more coarse and porous superficial layer for adhesion. Other common surface pretreatment methods include mechanical roughening via diamond burs, sandblasting with aluminum oxide particles, and tribochemical silica coating (Grewal Bach *et al.*, 2014; Huang and Kao, 2001; Saraç *et al.*, 2011; Schmage *et al.*, 2003). Next, a silane coupling agent is applied to the roughened ceramic crown to promote a chemical linkage to the bracket resin. Polycrystalline ceramics, including the metal oxide zirconia, do not have glass particles that can be etched with hydrofluoric acid and silanated to facilitate a sufficient chemical bond with bracket resin (DiMatteo and Reynolds, 2013; Kelly and Benetti, 2011). Conditioning zirconia involves air particle abrasion and priming with a phosphate monomer such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) to enable a chemical bond to form between the bracket resin and zirconia (Attia and Kern, 2011; Azimian *et al.*, 2012; Lehmann and Kern, 2009). SBS ranging from 10-20MPa between resin cements and zirconia substrates have been yielded using various primers (Kobes and Vandewalle, 2013). Other studies reveal bond strengths as high as 40-50MPa (Attia and Kern, 2011; Azimian *et al.*, 2012; Lehmann and Kern, 2009). Chemical bonding to zirconia has been investigated primarily for prosthodontic purposes. It is imperative to explore bonding orthodontic attachments to zirconia as these restorations become ubiquitous.

Orthodontic treatment has gained popularity among adults. In fact, they

now represent approximately 25-30% of the total patient population, and older adults (40 and over) are the fastest growing demographic in the specialty (Proffit *et al.*, 2013). Orthodontists face new challenges in managing more aged, restored, and periodontally vulnerable dentitions. They must be prepared to adequately bond to crowns, and fortunately, the materials exist to accomplish this feat as alluded to earlier. The prevalence of porcelain-fused-to-metal (PFM) and full metal crowns is decreasing while the use of all-ceramic options is increasing. Zirconia-based ceramics have evolved and risen to prominence in the dental field over the last 15 years (Bielen *et al.*, 2015). Monolithic, also known as full contour zirconia, was originally known for its strength and fracture toughness and was used primarily for posterior restorative cases (Aboushelib *et al.*, 2008). It exhibits excellent mechanical features including compression resistance of roughly 2,000MPa, resistance to traction as high as 900-1,200MPa, and flexural resistance of 1,000MPa (Manicone *et al.*, 2007; Piconi and Maccauro, 1999). Transformation toughening is a distinctive capability of Yttrium stabilized tetragonal zirconia polycrystals (Y-TZP) through which it can impede crack propagation by transforming from a tetragonal to a monoclinic phase (Magne *et al.*, 2010). Recent improvements in its esthetic characteristics and optical properties now make it a viable ceramic restoration choice for any tooth in the mouth. Of all the crowns Glidewell Labs fabricated in December 2013, BruxZir solid zirconia was the most popular, comprising more than 60% of their business. Furthermore, 46% of all anterior crowns fabricated by Glidewell were made of zirconia, and it is their fastest-growing product since its introduction in 2009

(DiTolla, 2014).

One of the major challenges for orthodontists regarding the increased use of zirconia restorations is the struggle to adhere to this material (Magne *et al.*, 2010). The ideal scenario is where the bracket is bonded well enough to withstand orthodontic forces and the rigors of the oral environment while simultaneously being weak enough to be easily removed when desired without damaging the zirconia. The key in avoiding harm to the patient during debond is through deformation of the bracket, thus breaking the bond at the bracket-adhesive interface or by stressing the adhesive to its ultimate strength causing cohesive failure within the composite resin (Bishara and Fehr, 1997; Karamouzou *et al.*, 1997). In order to improve clinical techniques and outcomes, materials used to bond brackets to zirconia need to be scrutinized. The purpose of this research was to measure the SBS of adhesive-coated metal brackets to zirconia conditioned with four different universal primer systems produced by 3M,Ormco, Reliance, and Kuraray. These were compared to a conventional primer system to serve as a control. The Adhesive Remnant Index (ARI) scoring system was also used to describe the quality and location of bond failure (Artun and Bergland, 1984; Montasser and Drummond, 2009).

II. OBJECTIVES

The purpose of this study was to measure the SBS of adhesive-coated metal brackets to zirconia conditioned with four different universal primer systems produced by 3M,Ormco, Reliance, and Kuraray. These were compared to a conventional primer system to serve as a control. Additionally, bond failure patterns were characterized using the ARI survey.

III. HYPOTHESIS

Hypothesis: There is a significant difference in SBS of the adhesive-coated metal brackets to zirconia amongst the different bonding systems.

Null Hypothesis: There is no difference in SBS of the adhesive-coated metal brackets to zirconia amongst the different bonding systems.

IV. MATERIALS AND METHODS

A. Zirconia Preparation

Thirty 40mm x 19mm zirconia blocks (BruxZir-16, shade A2, Zahn Dental Laboratory, Reno, NV) were employed to provide enough substrate surface area for 100 bracket samples (Figure 1). BruxZir manufactures these blocks with metal adapters glued on to fit into CAD/CAM milling machines. A superficial transparent coating or sealer protects the fragile zirconia during shipping and handling. Thus, the blocks needed to be modified for experimental testing in an attempt to mimic surface characteristics of a zirconia crown. First, the metal attachment's tip was minimally heated with a butane torch and then removed with a curved hemostat (Figures 2 and 3). The surface coating of the blocks' two rectangular sides with the smaller surface area was removed with 600-grit silicon carbide paper (Figure 4). The samples were sintered one at a time in the Zyrcomat 6000 MS sintering furnace (Vita, Baldwin Park, CA)(Figure 5). BruxZir's recommended sintering profile, in terms of temperature and time, was followed as closely as possible given the furnace's capabilities (Figure 6). The additional step of hand polishing or glazing was determined to be unnecessary because the superficial zirconia layer is removed chairside prior to bonding in an actual clinical situation. Next, a SandStorm sandblaster (Vaniman, Fallbrook, CA) was used to visibly roughen the zirconia in the same capacity an intraoral sandblaster is utilized to prepare the surface (Figure 7). The portions of the blocks to which the brackets were bonded were sandblasted with 50 μ m aluminum oxide powder for 5 seconds per sample. They were then rinsed and air-dried before the

bonding procedure.

Figure 1: BruxZir Zirconia Blocks



Figure 2: Heating of the Zirconia Block's Metal Adapter with a Butane Torch

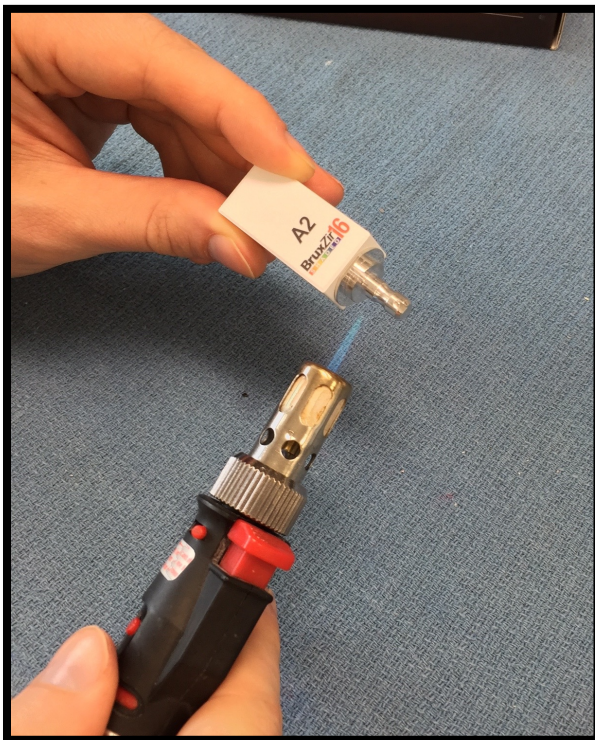


Figure 3: Metal Adapter Removal with a Curved Hemostat

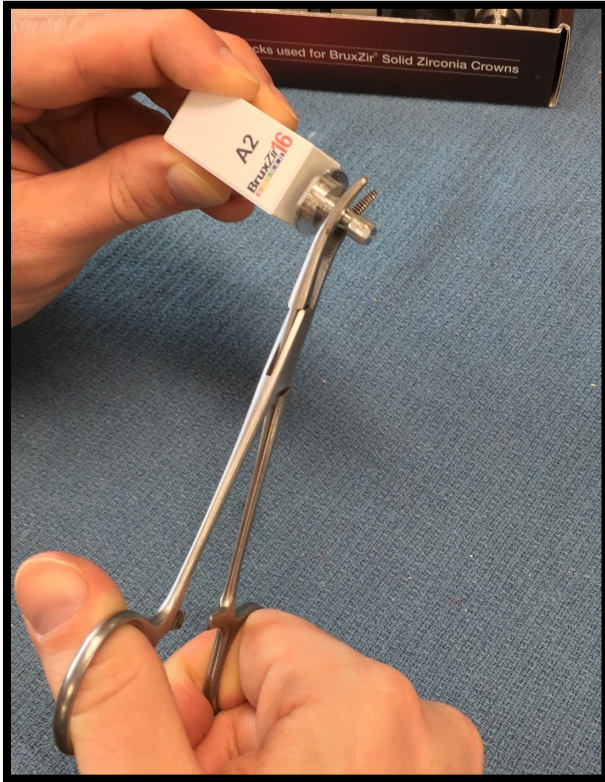


Figure 4: Sanding of the Sample Surfaces with 600-Grit Silicon Carbide Paper



Figure 5: Vita's Zyrcomat 6000 MS with Zirconia Block in Position for Sintering

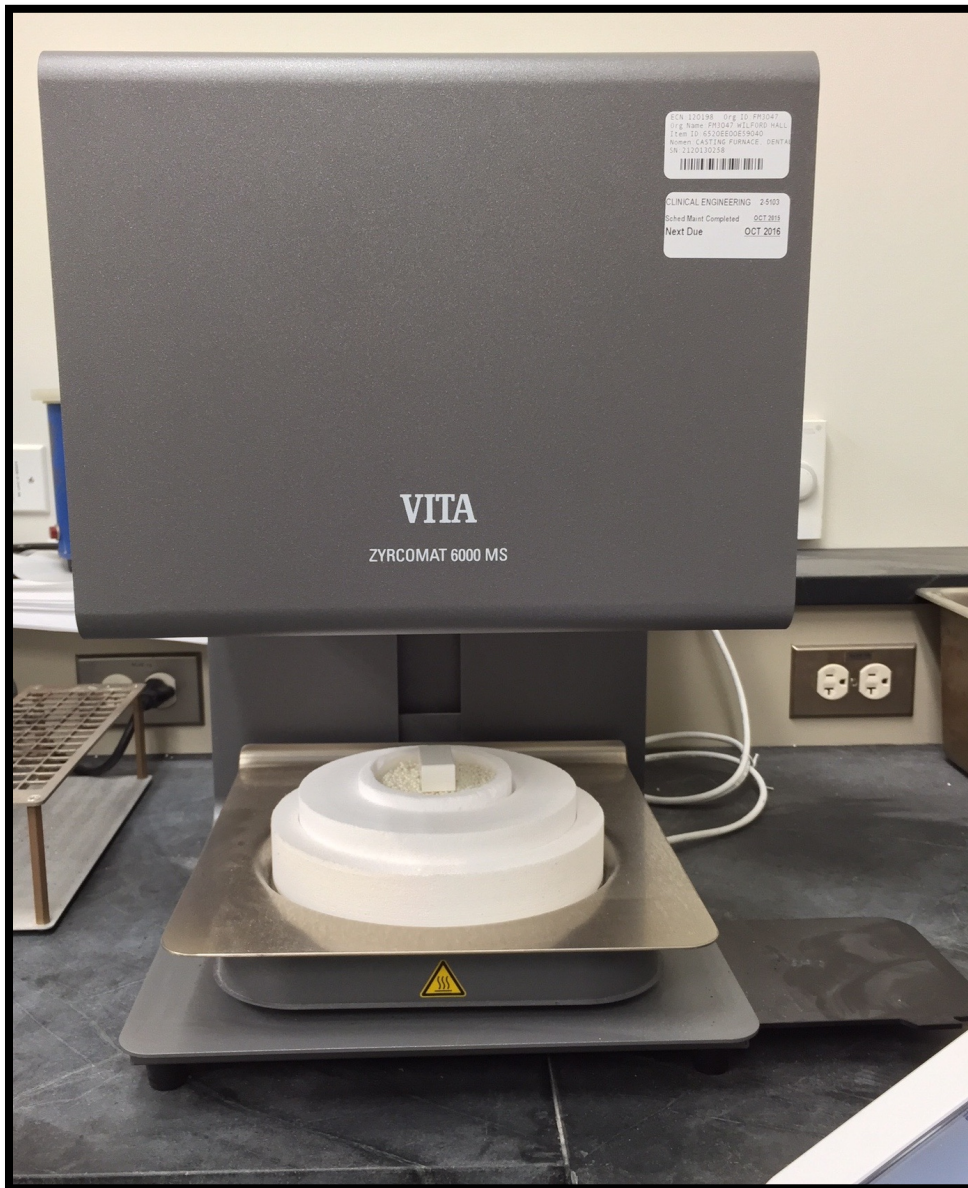


Figure 6: Sintering Temperature Chart



Figure 7: SandStorm Sandblaster



B. Experimental Groups

Five groups of twenty bracket samples were formed (Table 1).

Manufacturer suggestions for primer and adhesive resin paste pairings were followed to most closely resemble what is chosen in a clinical scenario. Group 1, the control, used a conventional primer to bond the bracket resin to zirconia: 3M Unitek's Transbond XT Primer and Light Cure Adhesive (Monrovia, CA)(Figure 8). Variable Groups 2-5 utilized the universal primer and adhesive bonding systems. Group 2 utilized 3M ESPE's Scotchbond Universal Adhesive (St. Paul, MN) and 3M Unitek's Transbond XT Light Cure Adhesive (Figure 9). Group 3 employedOrmco's Ortho Solo and Genglo Two-Way Color Change Adhesive (Orange, CA)(Figure 10). Group 4 involved Reliance's Assure Plus All Surface Bonding Resin and Quick Cure Adhesive Paste (Itasca, IL)(Figure 11). Lastly, Group 5 included Kuraray's Clearfil Ceramic Primer (Houston, TX) and Transbond XT Light Cure Adhesive (Figure 12). Both Group 2's and 3's adhesive primers are traditionally indicated for various restorative and prosthodontic applications. In this study, they were employed in an off-label capacity because of their potential ability to prime zirconia to chemically adhere to adhesive resin. They were paired with the Transbond XT adhesive paste. Scotchbond Universal Adhesive, Ortho Solo, Assure Plus All Surface Bonding Resin, and Clearfil Ceramic Primer all contain a bi-functional phosphate monomer, such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), which allowed for the bracket resin and zirconia to chemically bond to one another.

Table 1: Composition of Each Group

1	3M Unitek's Transbond XT Primer and Light Cure Adhesive (Control)
2	3M ESPE's Scotchbond Universal Adhesive and 3M Unitek's Transbond XT Light Cure Adhesive
3	Ormco's Ortho Solo and Genglool Two-Way Color Change Adhesive
4	Reliance's Assure Plus All Surface Bonding Resin and Quick Cure Adhesive Paste
5	Kuraray's Clearfil Ceramic Primer and Transbond XT Light Cure Adhesive

Figure 8: Group 1 (Control) - 3M Unitek's Transbond XT Primer and Light Cure Adhesive



Figure 9: Group 2 - 3M ESPE's Scotchbond Universal Adhesive and 3M Unitek's Transbond XT Light Cure Adhesive



Figure 10: Group 3 - Ormco's Ortho Solo and Genglool Two-Way Color Change Adhesive



Figure 11: Group 4 - Reliance's Assure Plus All Surface Bonding Resin and Quick Cure Adhesive Paste



Figure 12: Group 5 - Kuraray's Clearfil Ceramic Primer and Transbond XT Light Cure Adhesive



C. Bonding the Brackets

3M Unitek's 0.022 inch Victory Series mini metal #8 bracket with MBT Versatile+ prescription (Monrovia, CA) was the bracket of choice considering its relatively flat bracket base design that interfaced well with the flat zirconia substrate surface. Manufacturer's instructions on bonding technique were followed precisely (Table 2). Figures 13-16 illustrate the experimental setup and steps taken in bonding brackets for Group 1, which can be extrapolated for the remaining groups. Each bracket was cured with Ultradent's VALO™ light (South Jordan, UT) from all four sides on a three second cycle. This light-emitting diode (LED) curing light has variable intensity output settings from 1,000 to 3,200mW/cm² at wavelengths between 395-480nm and was set in plasma mode. A Demetron L.E.D. radiometer (KaVo Kerr, Charlotte, NC) was employed to confirm standardization of the light's intensity above 1,000mW/cm² level.

Table 2: Bonding Techniques

Experimental Groups	Bonding Attachment Protocol
Group 1 - Control	<ol style="list-style-type: none"> 1. Painted Transbond XT Primer uniformly over zirconia surface in a thin film. Gently air-dried. 2. Applied Transbond XT Light Cure Adhesive paste onto bracket base. 3. Firmly seated the bracket on zirconia surface, cleaned excess and light-cured.
Group 2 - 3M ESPE	<ol style="list-style-type: none"> 1. Applied and rubbed Scotchbond Universal Adhesive evenly onto zirconia surface for 20 seconds. Gently air-dried for 5 seconds to evaporate the solvent and light-cured. 2. Applied Transbond XT Light Cure Adhesive paste onto bracket base. 3. Firmly seated the bracket on zirconia surface, cleaned excess and light-cured.
Group 3 -Ormco	<ol style="list-style-type: none"> 1. Applied Ortho Solo to zirconia surface, gently air-dried, and light-cured. 2. Applied Gengloo Two-Way Color Change Adhesive paste onto bracket pad. 3. Firmly seated the bracket on zirconia surface, cleaned excess and light-cured.
Group 4 - Reliance	<ol style="list-style-type: none"> 1. Applied one coat of Assure Plus All Surface Bonding Resin to zirconia surface, gently air-dried, and light-cured. 2. Applied Quick Cure adhesive paste onto bracket base. 3. Firmly seated the bracket on zirconia surface, cleaned excess and light-cured.
Group 5 - Kuraray	<ol style="list-style-type: none"> 1. Painted Clearfil Ceramic Primer on zirconia surface and gently air-dried. 2. Applied Transbond XT Light Cure Adhesive paste onto bracket base. 3. Firmly seated the bracket on zirconia surface, cleaned excess and light-cured.

Figure 13: Group 1's Armamentarium for Bonding Brackets

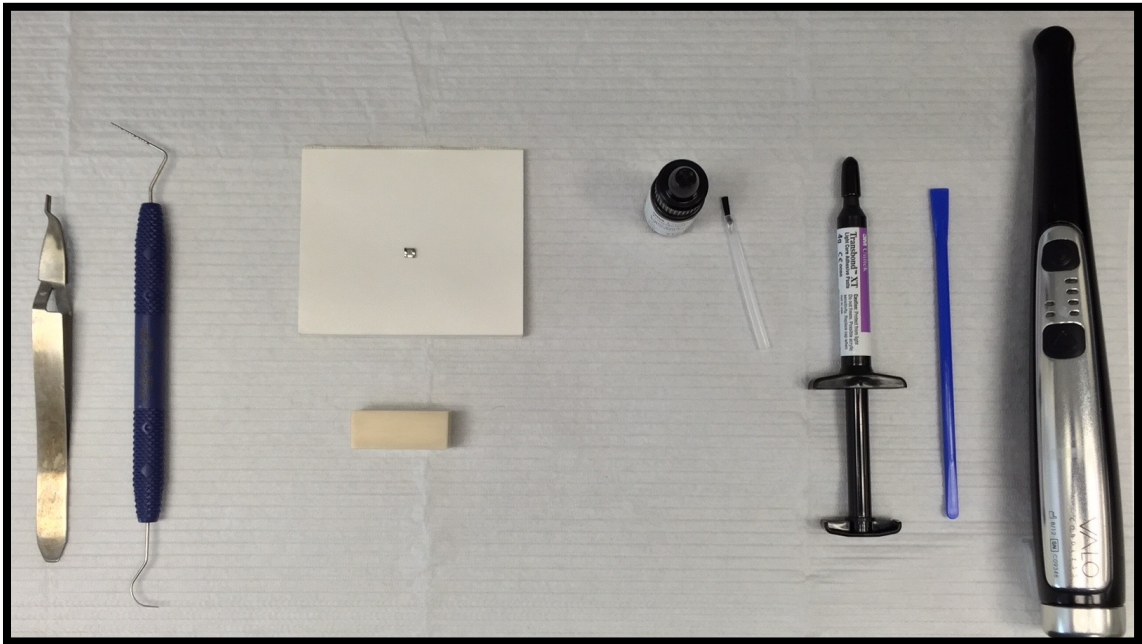


Figure 14: Transbond XT Primer Applied to Zirconia Surface and Transbond XT Light Cure Adhesive Buttered into Bracket Base Mesh

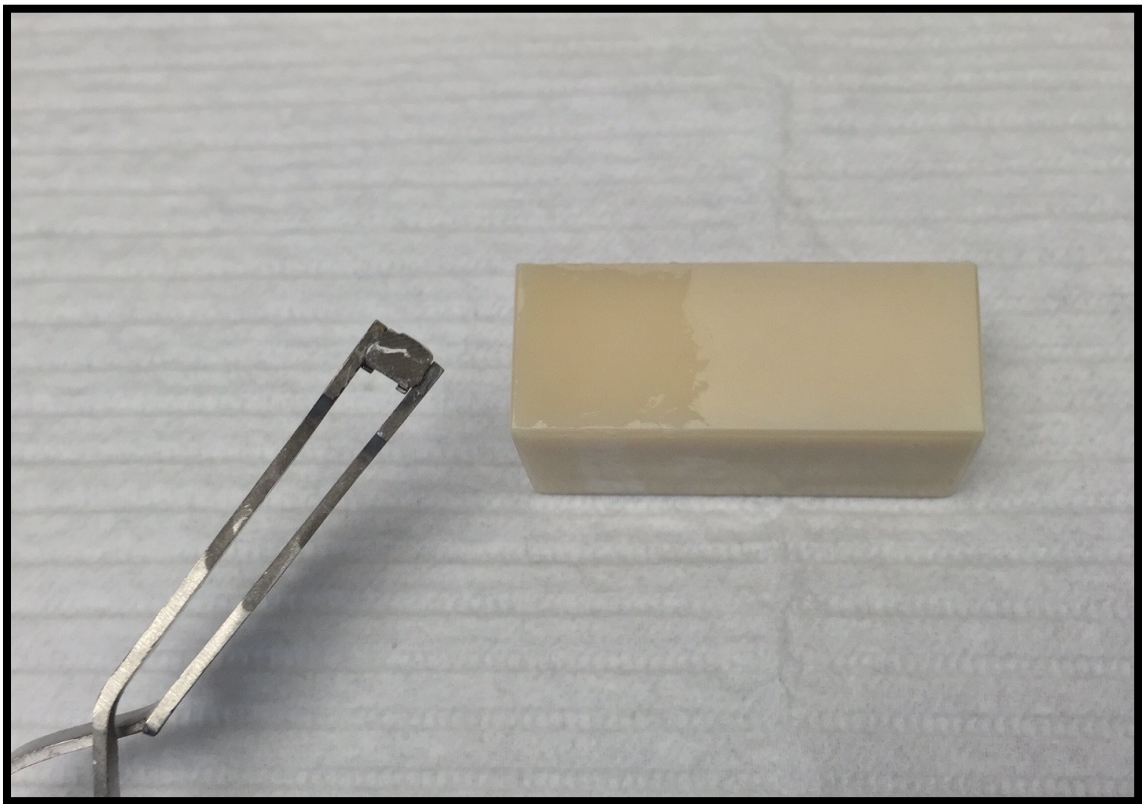
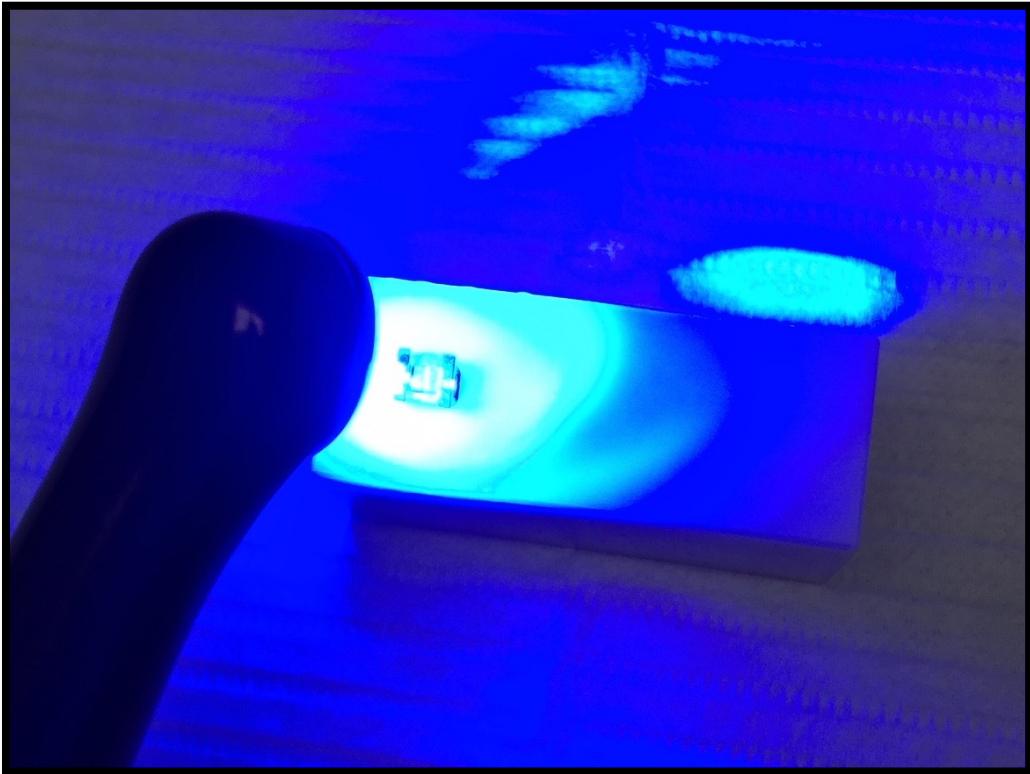


Figure 15: Bracket Placed on Zirconia Surface and Excess Adhesive Resin Removed



Figure 16: Bracket Light-Cured from All Four Sides



D. SBS Testing

The shear or peel test accurately mimics physiologic forces upon intraoral debonding and was the means by which bond strength was assessed. A universal testing machine, Instron model #5943 (Norwood, MA), was used to carry out this experimental test at 1mm/min crosshead speed. The substrate blocks with bonded brackets were securely mounted on an Instron-compatible jig (Figures 17 and 18). For each sample, the blade was positioned to engage the bracket behind the gingival tie wings (Figure 19). A steadily increasing force was applied to the bracket until it debonded (Figure 20). The shearing force applied at the time of bond failure was recorded in Newtons.

Figure 17: Instron Model #5943 Setup

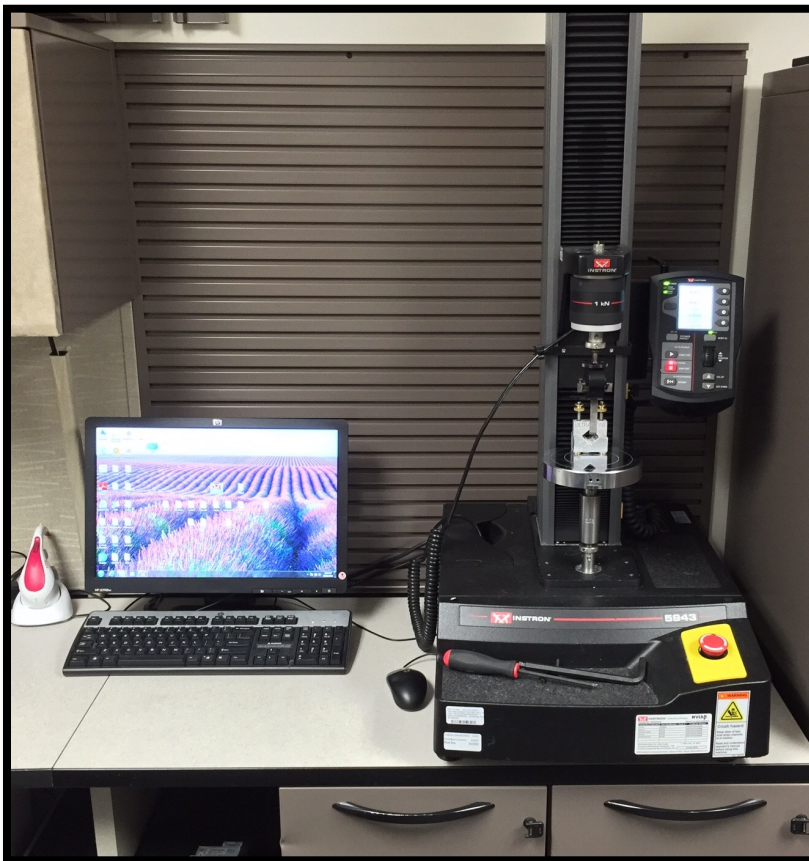


Figure 18: Mounted Substrate Blocks on Jig



Figure 19: Instron Blade Engaged Brackets Behind the Gingival Tie Wings

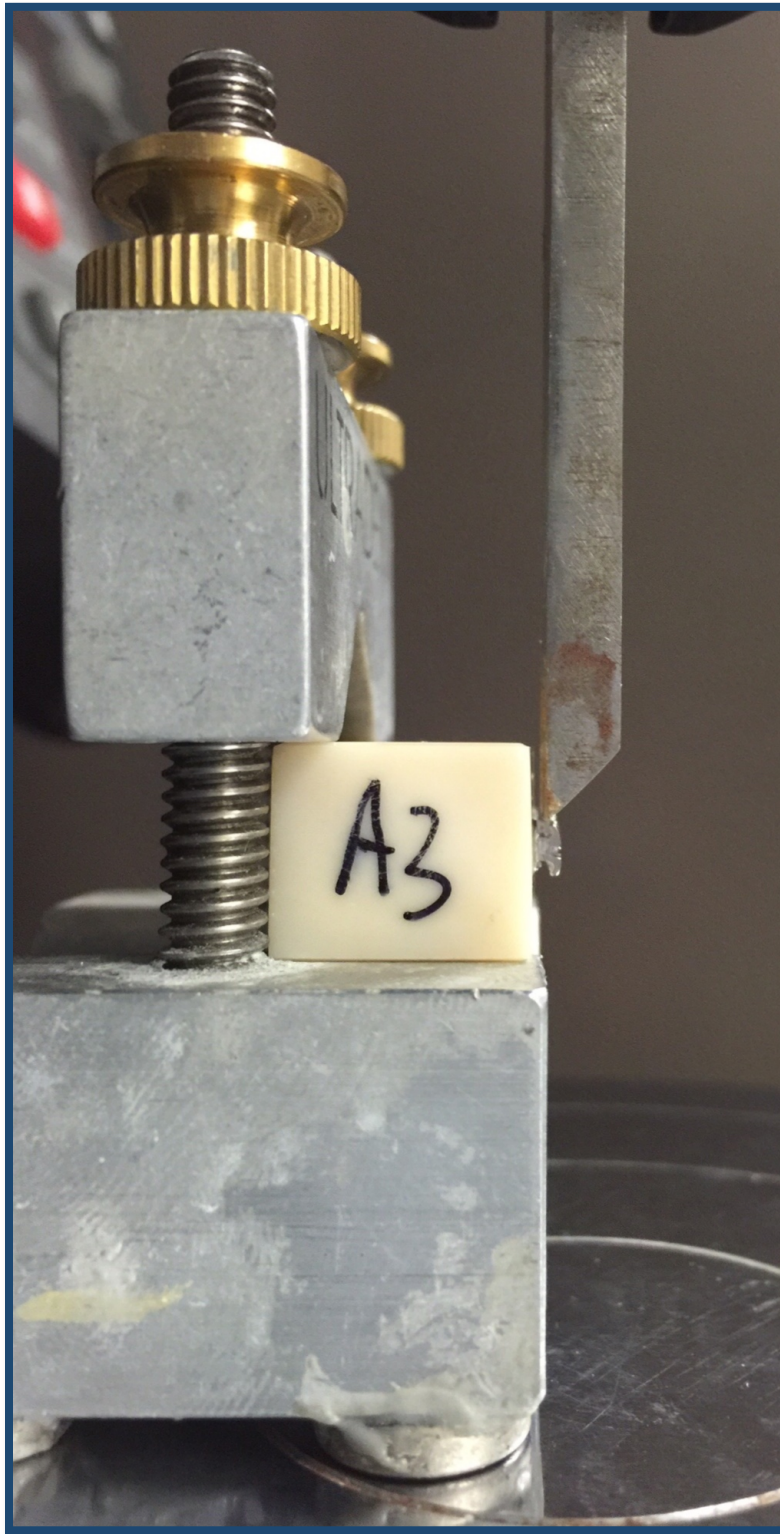
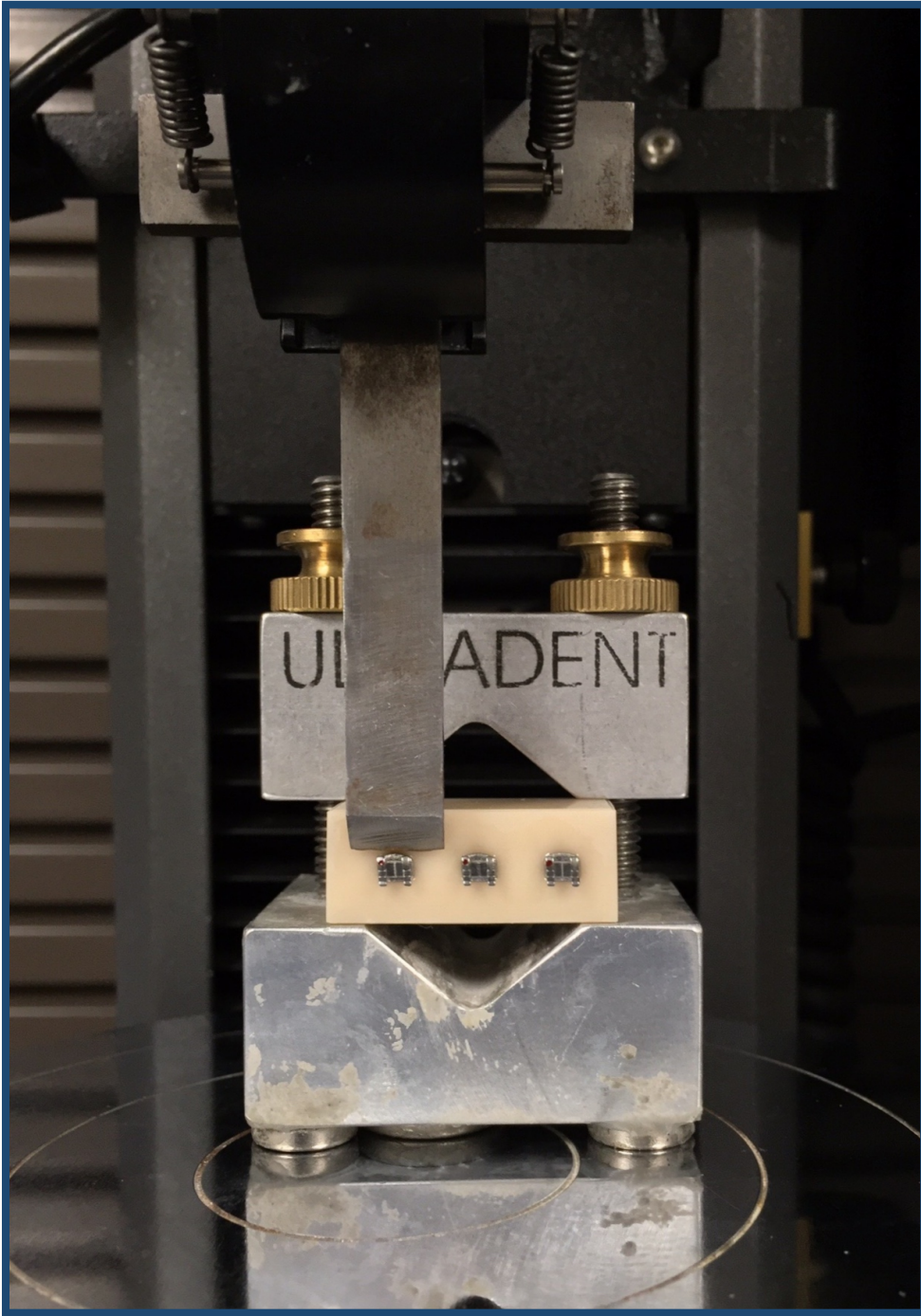


Figure 20: Increasing Force Applied Until Bond Failure



E. ARI Survey

Each bracket base was examined under a Leica S4 E stereo microscope (Buffalo Grove, IL) at 10x magnification to pinpoint the primary site of failure (Figure 21). The fracture was described as adhesive where failure occurred at the interface between zirconia and resin or resin and bracket, cohesive where failure occurred within the adhesive resin itself, or mixed when involving a combination of the two. The ARI provided a method of surveying the amount of remaining adhesive on the brackets to ascertain sites of failure (Table 3). In assigning the ARI scores, a single blind method to prevent operator bias was followed. Another orthodontic resident, aside from the principal investigator, independently surveyed the brackets, and his assessment was reported.

Table 3: Criteria for ARI Scores

ARI Score	Criteria
0	All of the adhesive left on the bracket base
1	More than or equal to 50% of adhesive left on the bracket base
2	Less than 50% of adhesive left on the bracket base
3	No adhesive left on the bracket base

Figure 21: Leica S4 E Stereo Microscope for ARI Survey



F. Statistical Management of Data

A power analysis was initially run to determine the study conditions required to correctly find a statistically significant difference. A sample size of 20 per group in 5 groups provided 80% power to detect a moderate effect size of 0.35 or approximately 0.7 standard deviation difference among means when testing with a single factor analysis of variance (ANOVA) at the alpha level of 0.05 (NCSS PASSv11.0.8 2011).

Utilizing the $1\text{N/mm}^2=1\text{MPa}$ conversion equation, the recorded force at bond failure was divided by the bracket base surface area (10.52mm^2) to calculate the SBS in MPa. The mean and standard deviation for the groups were then calculated to describe the collected data set. The ARI data was organized into a table according to predefined ARI scoring categories to present the predominant mode of failure for each group.

One-way ANOVA and Tukey's Post-Hoc tests were used to analyze the effects of primers on the SBS between the adhesive-coated brackets and zirconia. The ANOVA test revealed if a significant difference among groups existed, whereas the Tukey's Post-Hoc tests identified differences when specifically comparing one group to another. To ascertain whether a significant difference existed among the groups for ARI scores, a Kruskal-Wallis test was performed. The Mann-Whitney tests were done for all possible pairs of groups to establish which were significantly different from each other. A Bonferroni correction was applied. Confidence intervals for all statistical tests were set at $p<0.05$.

V. RESULTS

The SBS values for all the groups can be viewed in Table 4. The data is summarized in Table 5 and organized into a box plot (Figure 22). The boxplot uncovered a relatively normal distribution of data with fairly equal variances between groups. A significant difference was found among the groups with respect to SBS ($p < 0.001$). Group 3 had the highest SBS, and it was significantly greater than all the other groups ($p < 0.05$). Groups 2, 4, and 5 exhibited significantly higher SBS than group 1 ($p < 0.05$), but they did not differ from each other ($p > 0.05$). Groups 2-5 with universal primers showed significantly greater SBS than the control group without a universal primer.

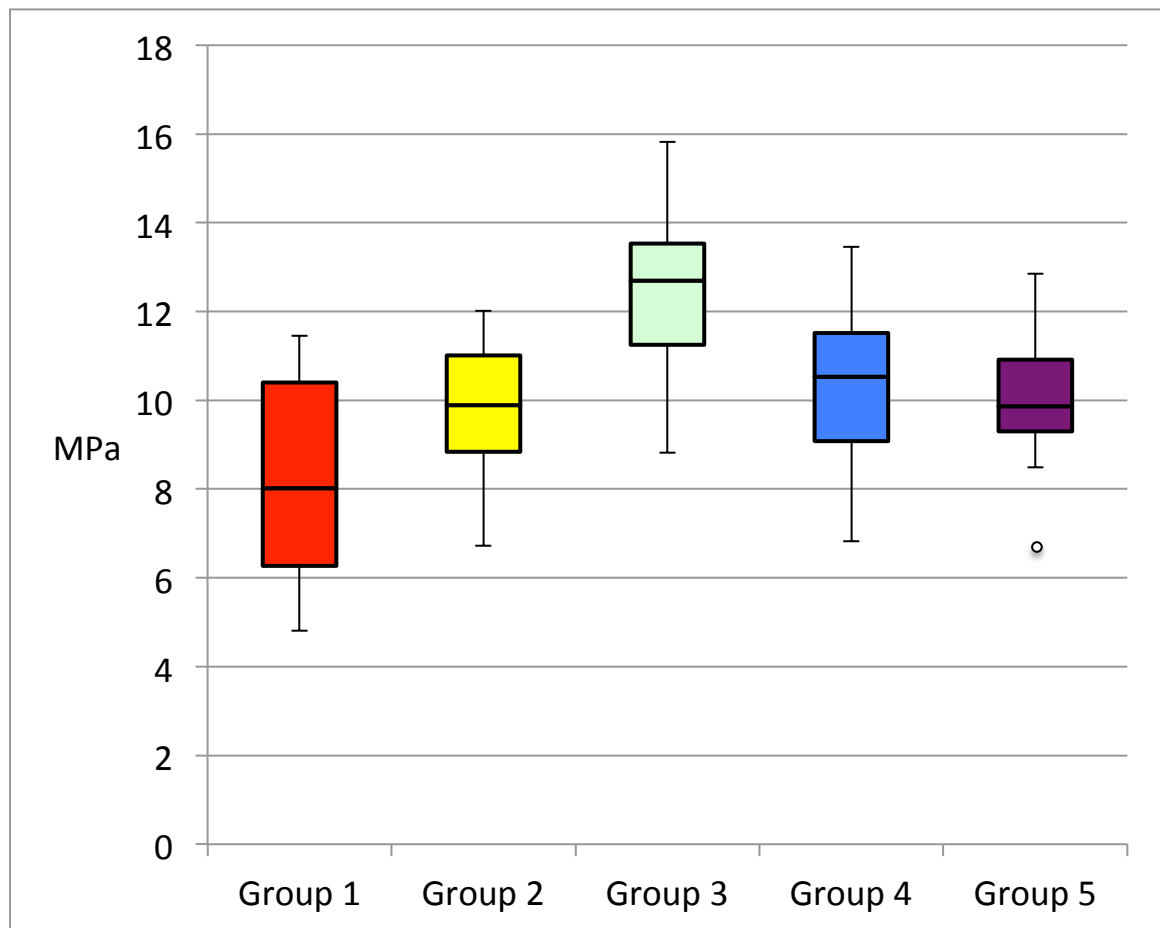
Table 4: Forces Recorded at Bond Failure and SBS Values

	Group 1		Group 2		Group 3		Group 4		Group 5	
#	N	MPa	N	MPa	N	MPa	N	MPa	N	MPa
1	75.90	7.21	126.47	12.02	147.05	13.98	96.72	9.19	98.45	9.36
2	89.71	8.53	120.02	11.41	149.67	14.23	71.79	6.82	99.97	9.50
3	93.35	8.87	107.34	10.20	129.11	12.27	141.47	13.45	69.18	6.58
4	66.28	6.30	125.29	11.91	114.99	10.93	97.97	9.31	116.64	11.09
5	76.25	7.25	92.26	8.77	152.28	14.48	125.67	11.95	97.22	9.24
6	106.01	10.08	104.15	9.90	135.61	12.89	78.71	7.48	105.69	10.05
7	65.65	6.24	103.63	9.85	120.46	11.45	131.14	12.47	122.84	11.68
8	103.59	9.85	86.44	8.22	166.46	15.82	112.16	10.66	135.18	12.85
9	78.87	7.50	93.72	8.91	134.80	12.81	79.40	7.55	118.90	11.30
10	119.95	11.40	100.18	9.52	116.27	11.05	84.27	8.01	118.06	11.22
11	112.63	10.71	103.96	9.88	137.63	13.08	123.23	11.71	104.19	9.90
12	120.46	11.45	102.93	9.78	123.27	11.72	113.65	10.80	111.03	10.55
13	57.32	5.45	90.58	8.61	128.24	12.19	108.41	10.31	112.99	10.74
14	112.66	10.71	119.57	11.37	104.79	9.96	119.69	11.38	103.36	9.83
15	62.82	5.97	78.03	7.42	151.96	14.44	121.03	11.50	107.84	10.25
16	78.80	7.49	70.66	6.72	92.76	8.82	121.33	11.53	96.90	9.21
17	52.87	5.03	115.79	11.01	134.01	12.74	97.71	9.29	89.33	8.49
18	97.63	9.28	115.59	10.99	115.31	10.96	94.41	8.97	90.71	8.62
19	117.31	11.15	115.80	11.01	135.49	12.88	110.53	10.51	99.97	9.50
20	50.64	4.81	109.54	10.41	133.06	12.65	110.99	10.55	99.04	9.41

Table 5: SBS Means and Statistical Comparisons

Group #	MPa (Standard Deviation)	
1	8.26 (2.23)	c
2	9.90 (1.45)	b
3	12.47 (1.68)	a
4	10.17 (1.80)	b
5	9.97 (1.35)	b

Figure 22: SBS Box Plot



The ARI scores are displayed by frequency distribution of failure modes per group in Table 6. Group 1 exhibited adhesive failure modes with all of the adhesive left on the bracket bases (ARI=0). Groups 2-5 were associated with mostly mixed failure modes with less than 50% of adhesive left on the bracket bases (ARI=2). In fact, only trace amounts or less than 10% of adhesive resin remained on the bracket bases in virtually every sample from groups 2-5.

Table 6: Frequency Distribution of Failure Modes

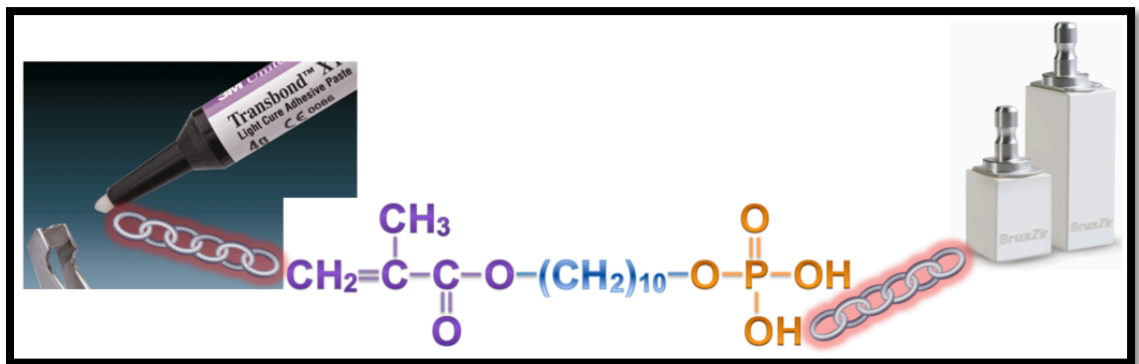
Group #	ARI Scores			
	0	1	2	3
1	20	-	-	-
2	-	-	20	-
3	-	-	20	-
4	-	-	20	-
5	-	-	18	2

VI. DISCUSSION

This laboratory study compared the SBS of metal brackets to zirconia using common orthodontic primer-adhesive systems. The variable groups containing universal primers demonstrated superior SBS ranging from 9.9 to 12.47MPa. The control's SBS was significantly lower at 8.26MPa. The difference in the results can be succinctly elucidated through adhesive chemistry. 3M ESPE's Scotchbond Universal Adhesive,Ormco's Ortho Solo, Reliance's Assure Plus All Surface Bonding Resin, and Kuraray's Clearfil Ceramic Primer all incorporate a phosphate monomer, such as 10-MDP, whereas 3M Unitek's Transbond XT Primer does not. Similar to silane coupling agents, phosphate monomers are bi-functional in that they chemically bond to both the bracket resin and zirconia, thereby forming a linkage between these dissimilar materials. The pertinent moieties of 10-MDP are the methacrylate and phosphoric acid groups, which co-polymerize with composite resin monomers and bond to metal oxides respectively (Figure 23)(Lee *et al.*, 2015; Magne *et al.*, 2010). The universal primers facilitated a chemical bond between adhesive-coated metal brackets to zirconia leading to an increase in bond strength and resistance to bond failure. The brackets utilizing the conventional primer relied solely on micromechanical retention of the bonding agent and adhesive resin to the sandblasted zirconia surface. This accounted for the significantly weaker bond strength. Despite these differences, all primer-adhesive systems and corresponding bonding techniques were considered clinically adequate. Both the control and experimental groups surpassed the minimally sufficient SBS of 6-8MPa as put forth by Reynolds and

others (Reynolds, 1979). The pertinent question is the following: should brackets be chemically bonded to zirconia surfaces or is micromechanical retention of the adhesive paste sufficient for the duration of treatment? Even though both techniques generated outcomes considered sufficient for clinical success, chemically bonding to zirconia may be a better option in this scenario. It substantially improves the durability of the bond and minimizes the risk of accidental bracket debond during treatment. One broken bracket would invalidate the minimal advantage of easier cleanup during braces removal and cost efficiency afforded through traditional bonding methods. As mentioned previously, zirconia possesses exceptional mechanical properties like compression, traction, and flexural resistances beyond 1000MPa (Manicone *et al.*, 2007; Piconi and Maccauro, 1999). Therefore, zirconia's superb strength should negate any risk of damage during debond even with higher bond strengths.

Figure 23: Chemical Coupling of Composite Resin to Zirconia



Ormco's Ortho Solo and Grengloo Two-Way Color Change Adhesive pairing had the highest SBS of 12.47MPa while the other universal adhesive groups were recorded at about 10MPa. This was an unexpected finding because

all universal adhesive groups included the critical molecule to foster the formation of a chemical bond. One plausible reason is the dissimilarity in the primers' proprietary formulations. However, the more likely explanation for this finding lies in the dissimilar adhesive pastes between the groups. For this study, the more probable combinations of primers and adhesive pastes were chosen based on manufacturer recommendations. Grengloo adhesive resin was noticeably less viscous than both Quick Cure and Transbond XT. When buttering the Grengloo onto the bracket bases during sample preparation, it appeared to flow more readily into the 80 gauge woven mesh surface. Since this interface was the predominant site of bond failure in the variable groups, the superior flowability and infiltration of Grengloo into the retentive mesh is hypothesized to be the underlying rationale for its greater SBS.

According to conventional thought, it is desirable for the bond fracture to occur at the bracket-adhesive resin interface with all of the resin remaining on the substrate surface (Proffit *et al.*, 2013). This tends to be the safest debonding method to prevent damage of the substrate, but its disadvantage is the residual composite resin that must be carefully removed. The ARI survey gauged bond failure modes after shearing off brackets. Adhesive resin remained attached to the brackets in the control group. On the other hand, most of the composite remained on the zirconia in the experimental groups. These results were expected given the presence of a chemical bond in the experimental and not the control groups. A crucial point of understanding is the chemical bond between zirconia and adhesive resin was stronger than the mechanical interlocking of the

composite resin into the mesh base. The weakest link or limiting factor in the variable groups was the retentive capacity of the bracket base. Therefore, it can be deduced that the SBS of the various experimental groups are at least greater than those listed in Tables 4 and 5. Multiple dental materials studies have reported bond strengths between adhesive resin and zirconia as high as 40-50MPa (Attia and Kern, 2011; Azimian *et al.*, 2012; Kobes and Vandewalle, 2013; Lehmann and Kern, 2009).

Lee et al. compared the SBS of metal brackets bonded to zirconia surfaces using various bonding techniques. The specimen groups were treated with either Zirconia Liner Premium, Z-PRIME Plus, Monobond Plus, Porcelain Conditioner, or no primer. They were all paired with Transbond XT Paste and subdivided into thermocycled and non-thermocycled subgroups. Similar to the results of this study, the groups with universal primers showed significantly greater SBS than the silane primer and control groups. Thermocycling decreased the SBS of all groups. The no-primer groups displayed adhesive failure modes whereas the universal primer groups showed mixed failure modes (Lee *et al.*, 2015). Yassaei et al. evaluated the effect of four different surface treatment methods on SBS of metal brackets to zirconia. The sample groups were prepared with 9.6% hydrofluoric (HF) acid, 110µm aluminum oxide sandblasting, 1W or 2W Er:YAG laser. Pulpdent silane and Resilience light cured composite resin were utilized with each pretreatment method in bonding brackets to the zirconia. No zirconia-specific primers were used in their investigation. The highest SBS was achieved in the sandblasted group followed by 2W laser, 1W

laser, and HF acid etched groups in a descending order. They concluded sandblasting and Er:YAG laser irradiation were more appropriate alternatives to HF acid etching in preparing the zirconia for bonding brackets (Yassaei *et al.*, 2015).

With the rising popularity of zirconia, more orthodontic patients can be expected to present with these restorations. Brackets need to be aptly bonded to the zirconia substrate in order to effectively move teeth, minimize bond failures, and prevent damage to the restorations when the appliance is taken off. The clinical relevance of this study sheds light on viable ways to attach metal brackets to zirconia and provides a benchmark measurement for bond strength between metal brackets and zirconia for a number of primer-adhesive systems. Traditional bonding protocols and materials should be used on a routine basis. When bonding to anything other than enamel, a universal primer containing the components to bond to a variety of restorative materials should reduce chair time, inventory, material cost, and burden on the patient. The biggest limitation of this in vitro investigation is that the results may not fully translate to the clinical setting. Thermocycling, which simulates thermal changes in the oral cavity, was not employed to bridge the gap between in vitro and in vivo conditions. Ceramic surface properties in the oral environment could be affected by temperature, humidity, acidity, and plaque (Zachrisson *et al.*, 1996). Future research should explore orthodontic bonding to zirconia in vivo. Testing other variables like adhesive pastes, other brackets, surface pretreatment methods, and types of forces would bring more clarity to the practice of orthodontics.

VII. CONCLUSIONS

Pretreating the surface of zirconia with universal primers contributed to an increase in SBS compared to not treating the zirconia with universal primers when bonding metal brackets.Ormco had the highest SBS among the universal primer-adhesive bonding systems tested. The control group exhibited adhesive failure modes with the adhesive resin left on the bracket bases. In contrast, experimental groups were associated with mixed failure modes where most of the composite resin remained on the zirconia. The chemical bond between zirconia and adhesive resin was stronger than the mechanical interlocking of the resin into the mesh base.

IX. REFERENCES

- Aboushelib MN, Matinlinna JP, Salameh Z, Ounsi H. Innovations in bonding to zirconia-based materials: Part I. *Dent Mater*. 2008 Sep;24(9):1268-72.
- Abu Alhaija ES, Al-Wahadni AM. Shear bond strength of orthodontic brackets bonded to different ceramic surfaces. *Eur J Orthod*. 2007 Aug;29(4):386-9.
- Artun J, Bergland S. Clinical trials with crystal growth conditioning as an alternative to acid-etch enamel pretreatment. *Am J Orthod*. 1984 Apr;85(4):333-40.
- Attia A, Kern M. Long-term resin bonding to zirconia ceramic with a new universal primer. *J Prosthet Dent*. 2011 Nov;106(5):319-27.
- Azimian F, Klosa K, Kern M. Evaluation of a new universal primer for ceramics and alloys. *J Adhes Dent*. 2012 Jun;14(3):275-82.
- Bielen V, Inokoshi M, Munck JD, Zhang F, Vanmeensel K, et al. Bonding Effectiveness to Differently Sandblasted Dental Zirconia. *J Adhes Dent*. 2015 Jun;17(3):235-42.
- Bishara SE, Fehr DE. Ceramic brackets: something old, something new, a review. *Semin Orthod*. 1997 Sep;3(3):178-88.
- Bishara SE, Gordan VV, VonWald L, Jakobsen JR. Shear bond strength of composite, glass ionomer, and acidic primer adhesive systems. *Am J Orthod Dentofacial Orthop*. 1999 Jan;115(1):24-8.
- Buonocore MG. A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res*. 1955 Dec;34(6):849-53.
- DiMatteo AM, Reynolds TA. Dental ceramics: evolution, advancements and current applications. *Inside Dentistry*. 2013;9(6):52-62.
- DiTolla M. Is the PFM dead?. *Dental Economics*. 2014;104(1):56 and 77.
- Falkensammer F, Jonke E, Bertl M, Freudenthaler J, Bantleon HP. Rebonding performance of different ceramic brackets conditioned with a new silane coupling agent. *Eur J Orthod*. 2013 Feb;35(1):103-9.

- Giannini M, Soares CJ, de Carvalho RM. Ultimate tensile strength of tooth structures. *Dent Mater*. 2004 May;20(4):322-9.
- Gorelick L. Bonding metal brackets with a self-polymerizing sealant-composite: a 12-month assessment. *Am J Orthod*. 1977 May;71(5):542-53.
- Graber T, Vig K, Vanarsdall Jr. R. *Orthodontics: Current Principles and Techniques*. 5th ed. Philadelphia: Mosby;2011. p.728-744.
- Grewal Bach GK, Torrealba Y, Lagravère MO. Orthodontic bonding to porcelain: a systematic review. *Angle Orthod*. 2014 May;84(3):555-60.
- Huang TH, Kao CT. The shear bond strength of composite brackets on porcelain teeth. *Eur J Orthod*. 2001 Aug;23(4):433-9.
- Jost-Brinkmann PG, Böhme A. Shear bond strengths attained in vitro with light-cured glass ionomers vs composite adhesives in bonding ceramic brackets to metal or porcelain. *J Adhes Dent*. 1999 Autumn;1(3):243-53.
- Karamouzios A, Athanasiou AE, Papadopoulos MA. Clinical characteristics and properties of ceramic brackets: A comprehensive review. *Am J Orthod Dentofacial Orthop*. 1997 Jul;112(1):34-40.
- Karan S, Büyükyılmaz T, Toroğlu MS. Orthodontic bonding to several ceramic surfaces: are there acceptable alternatives to conventional methods?. *Am J Orthod Dentofacial Orthop*. 2007 Aug;132(2):144.e7-14.
- Kelly JR, Benetti P. Ceramic materials in dentistry: historical evolution and current practice. *Aust Dent J*. 2011 Jun;56 Suppl 1:84-96.
- Knox J, Kralj B, Hubsch P, Middleton J, Jones ML. An evaluation of the quality of orthodontic attachment offered by single- and double-mesh bracket bases using the finite element method of stress analysis. *Angle Orthod*. 2001 Apr;71(2):149-55.
- Kobes KG, Vandewalle KS. Bond strength of resin cements to zirconia conditioned with primers. *Gen Dent*. 2013 Sep-Oct;61(6):73-6.

- Lee JY, Kim JS, Hwang CJ. Comparison of shear bond strength of orthodontic brackets using various zirconia primers. *Korean J Orthod.* 2015 Jul;45(4):164-70.
- Lehmann F, Kern M. Durability of resin bonding to zirconia ceramic using different primers. *J Adhes Dent.* 2009 Dec;11(6):479-83.
- Manicone PF, Rossi Iommetti P, Raffaelli L. An overview of zirconia ceramics: basic properties and clinical applications. *J Dent.* 2007 Nov;35(11):819-26.
- Magne P, Paranhos MP, Burnett LH Jr. New zirconia primer improves bond strength of resin-based cements. *Dent Mater.* 2010 Apr;26(4):345-52.
- Montasser MA, Drummond JL. Reliability of the Adhesive Remnant Index score system with different magnifications. *Angle Orthod.* 2009 Jul;79(4):773-6.
- Newman GV. Epoxy adhesives for orthodontic attachments: progress report. *Am J Orthod.* 1965 Dec;51(12):901-12.
- Pannes DD, Bailey DK, Thompson JY, Pietz DM. Orthodontic bonding to porcelain: a comparison of bonding systems. *J Prosthet Dent.* 2003 Jan;89(1):66-9.
- Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials.* 1999 Jan;20(1):1-25.
- Proffit WR, Fields HW, Sarver DM. *Contemporary Orthodontics.* 5th ed. St. Louis: Mosby;2013. p.17,364-367.
- Retief DH. Failure at the dental adhesive-etched enamel interface. *J Oral Rehabil.* 1974 Jul;1(3):265-84.
- Retief DH, Sadowsky PL. Clinical experience with the acid-etch technique in orthodontics. *Am J Orthod.* 1975 Dec;68(6):645-54.
- Reynolds IR. A review of direct orthodontic bonding. *Br J Orthod.* 1979;2:171-178.

- Saraç YŞ, Külünk T, Elekdağ-Türk S, Saraç D, Türk T. Effects of surface-conditioning methods on shear bond strength of brackets bonded to different all-ceramic materials. *Eur J Orthod*. 2011 Dec;33(6):667-72.
- Schmage P, Nergiz I, Herrmann W, Ozcan M. Influence of various surface-conditioning methods on the bond strength of metal brackets to ceramic surfaces. *Am J Orthod Dentofacial Orthop*. 2003 May;123(5):540-6.
- Steiner CC. Is there one best orthodontic appliance?. *Angle Orthod*. 1933; 3:277–294.
- Yassaei S, Aghili HA, Davari A, Mostafavi SM. Effect of Four Methods of Surface Treatment on Shear Bond Strength of Orthodontic Brackets to Zirconium. *J Dent (Tehran)*. 2015 Apr;12(4):281-9.
- Zachrisson YØ, Zachrisson BU, Büyükyılmaz T. Surface preparation for orthodontic bonding to porcelain. *Am J Orthod Dentofacial Orthop*. 1996 Apr;109(4):420–430.