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SHEAR BOND STRENGTH OF AN ORTHODONTIC ADHESIVE: A COMPARISON OF ETCHED VS UN-ETCHED PORCELAIN

A Thesis
Presented to the Faculty of the Advanced Education in General Dentistry, Two-Year Program,
United States Army Dental Activity, Fort Hood, Texas
And the Uniformed Services University of the Health Sciences – Post Graduate Dental College
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Oral Biology

By

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April 2016

SHEAR BOND STRENGTH OF AN ORTHODONTIC ADHESIVE: A COMPARISON OF ETCHED VS UN-ETCHED PORCELAIN

A REPORT ON
Research project investigating the shear bond strength of an adhesive bonding agent, Assure® Plus, to etched and un-etched lithium disilicate CAD/CAM blocks

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ABSTRACT

Introduction:

Consistent with societal trends, there has been a greater emphasis placed on esthetics in dentistry in recent years. This has perpetuated a rapid evolution of dental products to include adhesives and ceramics. The demand for esthetics has also lead to a greater number of adults seeking orthodontic treatment. Those esthetically driven adults are likely to have a dentition more heavily restored with ceramic restorations, as compared to the traditional adolescent orthodontic patients. Ceramics present a challenge when bonding orthodontic appliances so many adhesive protocols advocate the use of hydrofluoric acid etching to achieve adequate bond strength. The purpose of this study was to compare the shear bond strength to etched versus un-etched e.max.

Methods and Materials:

Samples of e.max were treated with air abrasion and silane. A composite button was bonded to them and sheared off in a universal testing machine. Additional samples of e.max were treated with air abrasion, etched with hydrofluoric acid, and treated with silane. A composite button was bonded to them and sheared off in a universal testing machine.

Results:

A total of 74 samples (37 from the test group and 37 from the control group) were included in this study. In addition to the 60 samples discussed in the materials and methods, seven samples per group from a pilot study were included in the statistical analysis for this study. The mean shear bond strength of Assure® Plus to e.max® without hydrofluoric acid etching was 18.60 MPa with a standard deviation of ±4.74 MPa. The shear bond strength with acid etching was 26.60 MPa with a standard deviation of ±5.03 MPa. According to the Weibull analysis a significant difference between the two groups was found. The statistical difference between the groups was further confirmed by the Oneway Anova, t test and Analysis of Variance.

Conclusion:

One means of bonding to ceramic is to roughen the surface with hydrofluoric acid. Unfortunately, this poses a safety hazard to both patients and clinicians, so eliminating etching from intra-oral bonding protocol could potentially improve patient and provider safety. Eliminating etching protocols that often take several minutes could also save substantial time, a clear advantage for efficient clinicians. In this study we found a statistically significant increase in shear bond strength when acid etching was incorporated into the protocol. We also found that sandblasting without etching provided more than adequate clinical bond strength to porcelain. Therefore, clinicians should consider routinely sandblasting ceramic restorations in preparation for bonding orthodontic appliances, and reserve acid etching for problematic cases that undergo multiple debonds.

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- Dr. Mark McClary of the U.S. Army – Carl R. Darnall Army Medical Center – Advanced Education in General Dentistry for assistance with revisions of thesis.

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Introduction

One needs only to turn on the television or thumb through the glossy pages of a magazine to be inundated with advertisements that typify the emphasis on beauty and esthetics in our modern culture. In alignment with societal norms, dental patients are also becoming increasingly concerned with the appearance of their teeth. The dental profession, by in large, seems to have embraced this obsession with esthetics. According to one author, superior esthetics is what separates good dental care from excellent dental care.[1] In response to a growing emphasis on esthetics, there has been a rapid evolution of dental materials designed to meet the esthetic desires of patients.[2]

Ceramics are dentistry's solution to the need for esthetically pleasing fixed restorations.[1] Dental ceramics were first introduced by a French dentist in 1789 [3] and since then an incredible evolution of the once rudimentary dental ceramic now provides very refined and esthetic solutions for restoring teeth. Not to confuse the reader, ceramic and porcelain will be used interchangeably in this paper; however, there is a technical difference in the definitions of each. Ceramics are "inorganic compounds with nonmetallic properties typically consisting of oxygen and one or more metallic or semi-metallic elements…" [3] to include zirconia. Porcelain is a type of ceramic characterized by infusible elements (crystalline structures) joined by lower fusing materials (amorphous glass). [4] Today there are a wide variety of ceramic restorations available; ranging from traditional porcelain fused to metal, to computer-aided design and computer-aided manufacturing (CAD/CAM) monolithic ceramics (i.e. leucite-reinforced, lithium disilicate, and zirconia) and a myriad of options in between.[3]

In recent decades CAD/CAM technology has become a driving force in the evolution of dental ceramics. Moreover, advances in CAD/CAM technology along with those made in dental materials have made ceramic CAD/CAM restorations the choice for patients and clinician's alike.[5] In fact, all-ceramic restorations are now used more frequently than metal-ceramic, a long standing clinician's choice for esthetic restorations.[3] The technology of CAD/CAM allows a crown to be milled from a solid block of material (usually ceramic), which can be delivered to the patient in the same appointment that the crown preparation is done. Taking full advantage of this technology for single appointment tooth preparation and crown delivery necessitates a material amenable to the milling process with sufficient strength to function as a standalone restorative material. Among the choices for CAD/CAM restoration materials, lithium disilicate ceramic, such as Ivoclar's IPS e.max CAD, stands out for its exceptional esthetics, biocompatibility, strength, and versatility.[6, 7]

Lithium disilicate is classified as a glass-ceramic because it can be formed into the desired shape as a glass (amorphous solid lacking crystalline structure), then heat treated to induce crystalline formation within the material.[3, 8] The crystalline structure functions to prevent crack propagation, giving lithium disilicate one of its most desirable physical properties—strength. Lithium disilicate glass-ceramic is comprised of proprietary compositions of SiO_2-Li_2O-K_2O- P_2O_5-ZrO_2-ZnO-Al_2O_3-MgO combined with coloring oxides [9] to provide a wide variety of shades, opacities and forms.[9, 10] Lithium disilicate restorations can be pressed in a lost wax technique or milled from a solid block of material.[8, 9, 10, 11] To manufacture IPS e.max CAD blocks, a pressure casting technique is used, in which air pressure is used to force the molten ceramic into the cast, rather than relying on gravity to carry the material.[9] Pressure casting minimizes porosities and ensures homogeneity of the material.[9]

IPS e.max CAD is unique in that the CAD blocks are fabricated in an intermediate crystalline phase leading to the formation of lithium metasilicate crystals (Li_2SiO_5).[9] Partial crystallization produces a softer material allowing for rapid machining and prolonged life of milling tools.[8] The microstructure of partially crystallized IPS e.max CAD consists of 40 percent lithium metasilicate crystals embedded in a glassy phase.[9] The platelet-shaped lithium metasilicate crystals have a grain size of 0.2 to 1.0 µm, and in this state IPS e.max CAD has a biaxial strength of 130 ± 30 MPa.[9] In the partial crystallized state, IPS e.max CAD blocks exhibit a blue color because the polyvalent coloring elements show a different oxidation state than found in the fully crystallized lithium disilicate blocks.[9] After milling is complete, the restoration is tempered in a dental furnace at 850 °C to induce lithium disilicate crystallization.[8] The heat treatment that induces final crystallization also changes the oxidation state of coloring elements, thereby changing the material from the blue state and yielding restorations that, with proper staining and shade matching, can closely mimic natural teeth.[9] Fully crystallized IPS e.max CAD has a microstructure consisting of 70 percent fine-grain lithium disilicate crystals ($Li_2Si_2O_5$) embedded in a glassy matrix.[9] The lithium disilicate crystals are reported to have an average length of 1.5 µm.[12] Fully crystallized IPS e.max CAD has a biaxial strength of 360 ± 60 MPa, considerably greater than that of lithium metasilicate[9], and well suited to withstand the forces of mastication placed on posterior restorations.[12,13]

IPS e.max Press lithium disilicate restorations, formed with the lost-wax technique, boast an even greater biaxial strength of 400 ± 40 MPa, attributed to the needle-like crystals ranging from three to six micrometers—a greater length compared to those found in IPS e.max CAD.[14, 10] Unfortunately, what e.max press gains in strength it lacks in achievable bond strength.[12] It is thought that the smaller crystal size found in e.max CAD is more conducive to etching, which facilitates greater penetration of adhesive material, translating to a stronger bond.[12] Due to its high strength, lithium disilicate does not require bonding to a substrate to achieve adequate strength as a restorative material[15], unlike leucite reinforced porcelains that depend on adhesion to the tooth for fracture resistance. Its favorable physical properties and versatility make lithium disilicate a popular choice for ceramic restorations. Due to its widespread use, lithium disilicate was the ceramic material chosen for this study.

Figure 1. Unfired e.max blocks with stem removed.

Figure 2: IPS e.max CAD crown milled in the metasilicate "blue state".

Figure 3: The same IPS e.max CAD crown after staining, glazing and firing. Firing process converts crystalline structure from metasilicate to disilicate and changes oxidation state of coloring elements yielding a stronger more esthetic prosthesis.

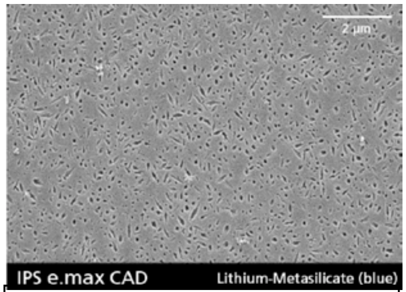


Figure 4. SEM of IPS e.max CAD in lithium metasilicate "blue state".

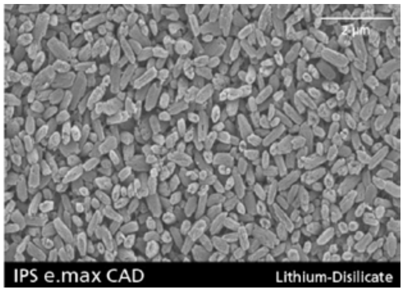


Figure 5. SEM of IPS e.max CAD lithium disilicate.

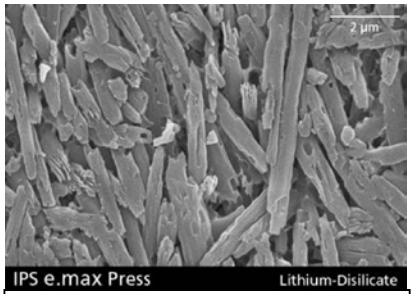


Figure 6. IPS e.max Press lithium disilicate. Note the difference in crystal size and structure.

Images in figures 1-6 adapted from: Adapted from: Scientific Documentation IPS e.max® CAD, Ivoclar Vivadent[9]

In addition to the evolution of and demand for dental ceramics, in the recent era there has also been a substantial increase in adult orthodontic patients.[16] According to one author 20-25 percent of orthodontic patients are adults and this number is likely to rise considerably in the future.[17] Modern orthodontics rely heavily on the ability to bond brackets to teeth or the restorations that cover them. The growing number of adult orthodontic patients present a challenge, in that, adults tend to have a more heavily restored dentition compared to adolecesnts.[18] Consequently, clinicians are faced with the dilemma of bonding to a variety of materials to include composite, amalgam, gold and various types of porcelain/ceramic.[18] In the absence of esthetic concerns, bands could be used to avoid bonding issues, however, placing orthodontic bands on anterior teeth restored with ceramic, or any teeth restored with a multi-unit fixed dental prosthesis, is neither practical nor esthetic. This leaves practitioners little choice but to bond brackets to restorations.

Ceramic restorations present a unique challenge due to their smooth glazed surface that impedes penetration of resin adhesives.[19] Moreover, porcelains are inherently brittle so care must be taken that removal of the bracket does not compromise the integrity or esthetics of the restoration.[19] There are three principle means of bonding orthodontic brackets to ceramic restorations: mechanical, chemical or a combination.[20] Mechanical refers to alteration of the porcelain surface by mechanical means in an effort to increase surface topography and hence micromechanical adhesion. Air-particle abrasion (APA) is one method described in the literature for mechanical alteration of porcelain surfaces.[21] Diamond burs or stones can also be used to mechanically enhance surface topography[22], however, this method of surface alteration has been shown to provoke crack initiation in porcelain surfaces.[23] This could be problematic in terms of minimizing damage to restorations that are likely to stay in the patients mouth after orthodontic treatment is complete.

Chemical alteration of porcelain surfaces comes with its own set of problems. Many adhesive systems require hydrofluoric acid (HF) to chemically etch porcelain surfaces, and its use is well supported by the literature.[24-34] Hydrofluoric acid is a very potent inorganic acid that can enter the body through the skin, mucosa, alimentary tract and respiratory tract.[35] It has also been reported that hydrofluoric acid in contact with tooth surfaces could lead to deleterious effects.[36] Upon contact, hydrofluoric acid has severe corrosive effects on tissues and can also lead to systemic toxicity when it enters the body.[37] In concentrations less than 20 percent, pain and erythema produced by hydrofluoric acid may not manifest until as late as 24 hours after exposure.[38] Most hydrofluoric acid solution used in dentistry are less than 10 percent[24-34], a low concentration by National Institutes of Health standards.[24] Due to its relatively lipophilic nature, molecular hydrofluoric acid readily penetrates tissue, even at low concentrations in which it behaves as a weak acid.[35] After tissue penetration, it produces large amounts of fluoride ions that bind to calcium and magnesium ions in tissues, causing increased permeability of cell membranes for potassium ions, nerve polarization, severe pain, and progressive tissue necrosis.[35] The injury mechanism of hydrofluoric acid is illustrated in figure 7 below.

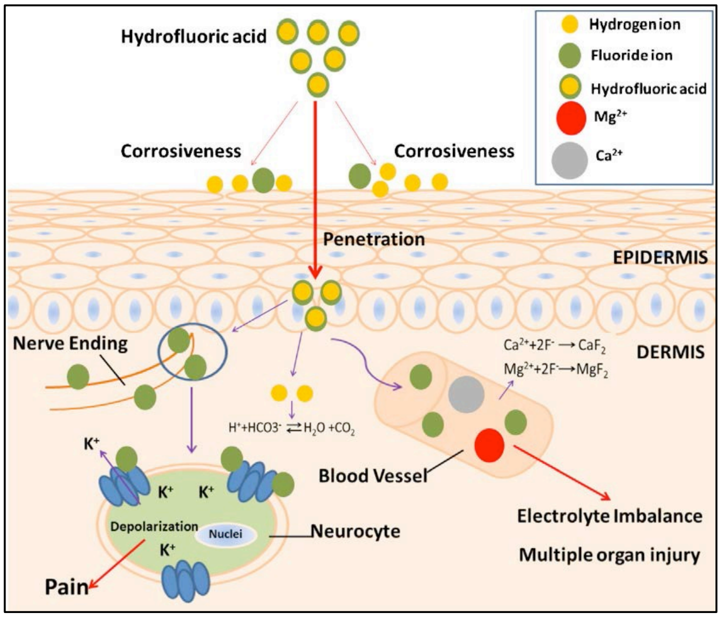


Figure 7: Injury mechanism of hydrofluoric acid that comes into contact with the skin. Adapted from: Bertolini JC: Hydrofluoric acid burns: a review of toxitcity. Journal of Emergency Medicine 1992; 10: 163-168

Not only is the practice of hydrofluoric acid etching potentially dangerous, it can also be time consuming, thus waning on practice efficiency. Etching protocols found in the literature can be four minutes or longer.[24-34] In a modern fast paced orthodontic practice four minutes is a considerable amount of time and an appreciable downfall to etching crowns prior to bracket placement.

Fortunately, just as dental ceramics have rapidly evolved to provide esthetic tooth restorations, so to have dental adhesives, which play a fundamental role in esthetic as well as conservative dentistry.[39] “Minimally invasive” dentistry is made possible by dental adhesives that allow us to place restoration material that is bonded in and does not require the removal of sound tooth structure to facilitate mechanical retention.[39] Dental adhesives are a composition of resin monomers, initiators, and other proprietary ingredients formulated to penetrate the surface of the bonding substrate and provide micromechanical retention and/or chemical bonds with the bonding substrate.[3, 40] Dental adhesives are essentially the "glue" that holds the restorative material to the tooth surface, whether it's a direct composite or an indirect ceramic crown. In the case of orthodontics, dental adhesives form the bond between the tooth or restoration, and the orthodontic bracket.

The basic concept of modern resin adhesives has been around since the 1950's when it was discovered that resin containing glycerophosphoric acid dimethacrylate (GPDM) could bond to the hydrochloric acid etched surface of dentin.[41] The bond strength durability achieved was inadequate for long-term clinical success[41], nonetheless, this paved the way for the development of modern resin adhesives and bonding systems. A brief review of dental adhesives will help the reader understand the mechanism of resin bonding and appreciate its importance in modern dentistry. A general knowledge of resin-adhesives is also fundamental in understanding the premise of this study.

Early resin adhesives were categorized by generation, with the first generation arising with the development of the surface-active co-monomer N-phenylglycine glycidyl methacrylate (NPG-GMA).[41] It was thought that this co-monomer could chelate with calcium on the tooth surface, creating a water resilient chemical bond between the tooth and resin.[4] However, in vitro dentin bond strengths of this material were a meager two to three MPa and further investigation revealed no evidence of ionic bonding between NPG-GMA and hydroxyapatite.[41]

Second generation resin adhesives emerged in 1978 with the introduction of a phosphate-ester material, 2-(Methacryloxy) ethyl phenyl hydrogen phosphate (phenyl-P) and hydroxyethyl methacrylate (HEMA), in ethanol. The premise of this bonding system relied on the polar interaction between negatively charged phosphate groups in the resin and positively charged calcium ions in the smear layer.[41] The smear layer can be defined as the cutting debris from tooth preparation compacted into a layer on the cut surface.[41] Unfortunately, the smear layer proved to be an unreliable substrate, resulting in cohesive failures within the smear layer and dismal bond strengths to dentin, which ranged from one to five MPa, far short of the estimated 10 MPa needed for successful in vivo dentin bonding.[41]

Third generation dentin bonding systems sought to eliminate, or more commonly, modify the smear layer with etchants such as phosphoric acid, acidic primers containing an aqueous solution of 2.5 percent maleic acid, or chelating agents like ethylenediamine tetraacedic acid (EDTA).[41] Removal or modification of the smear layer was done to allow penetration of acidic monomers like phenyl-P or dipentaerythritol pentaacrylate monophosphate (PENTA) into the smear layer and dentinal tubules.[41] The third generation of dentin bonding systems also incorporated a phosphate-based material containing HEMA and 10-Methacryloyoxy decyl dihydrogenphosphate (10-MDP), a molecule with hydrophilic and hydrophobic components.[40] This multifunctional molecule penetrates the hydrophilic environment of the smear layer and dentinal tubules, and provides a bond to hydrophobic resin.[41] The primary function of hydrophilic HEMA molecules was to increase wettability of tooth tissues.[41] Wettability is the ability of a liquid to maintain contact with a solid and is a function of, and measured by, the contact angle—the angle of formed by the liquid at the liquid solid interface.[42]

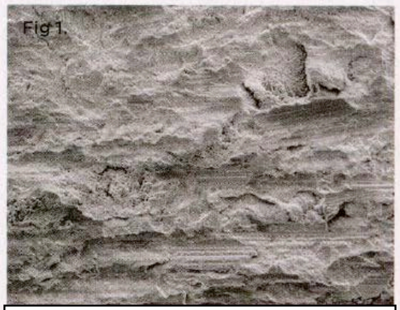


Figure 8: SEM of dentin smear layer.

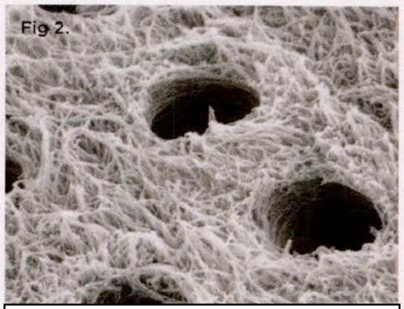


Figure 9: SEM of dentin treated with 37% phosphoric acid to remove smear layer and expose collagen fibrils.

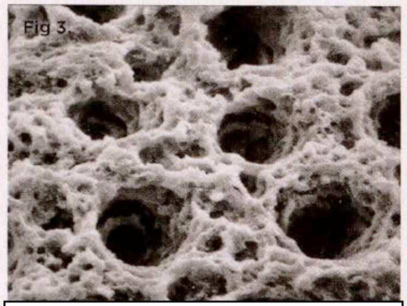


Figure 10: This SEM is the same as Fig. 9 except the collagen seen in Fig 9 has been removed with collagenase enzymes exposing the dentin underneath.

Images in figures 8-10 adapted from: Alex G: Universal adhesives: the next evolution in adhesive dentistry?. Compendium 2015; January: 15-26

The fourth generation of dentin bonding agents continued the focus on the smear layer, however, at this point it was considered an obstacle to interlocking resin into the dental tubules; therefore the aim of fourth generation adhesives was to eliminate the smear layer.[41] Elimination of the smear layer was accomplished with the application of an etchant[41]—37% phosphoric acid is commonly used. The process of etching not only removes the smear layer, it also demineralizes the underlying dentin, opening dentinal tubules and exposing a dense filigree of collagen fibers.[41] The process of etching used in fourth generation adhesives is known as the total etch technique because both dentin and enamel surfaces are etched simultaneously with phosphoric acid. In other words, the "total" surface of the tooth to be bonded is etched with the same etchant. Fourth generation dentin bonding systems can be characterized by three primary components: 1) a phosphoric acid etchant that is rinsed off; 2) a primer containing reactive hydrophilic monomers in ethanol, acetone, or water; and 3) filled or unfilled resin bonding agent.[41] In fourth generation systems, each of the three components were applied separately.[41] The three step fourth generation bonding systems provided good in vitro and in vivo bond strengths ranging between 17 and 30 MPa, so the focus of fifth generation systems changed from bond strength to ease of use for the operator.[41]

Fifth generation bonding systems contain all the same components as their predecessors, but the primer and resin-bonding agent are combined into one bottle[43], resulting in a two-step application process instead of three steps. Fifth generation bonding systems were the first of the modern bonding systems to emerge, and they are also referred to as total-etch systems.[44]

The sixth generation of adhesives further simplified the application process by eliminating the rinsing step.[43] This was done by combining the etchant and primer into one, with the use of a multifunctional phosphonated resin molecule that etches and primes dentin and enamel surfaces.[41] In recent literature these systems are referred to as self-etch primer (SEP) systems because the etchant is part of the primer, so a separate etchant, which is required in total-etch systems, is not required in SEP systems.[41] The weaker acids used in SEP systems are not as effective at etching enamel as separate applications of 37% phosphoric acid, so it has been advocated to use a selective-etch technique. In the selective-etch technique, phosphoric acid etchant is carefully placed on the enamel only, and rinsed. Then the SEP is applied to the dentin and enamel, followed by application of the adhesive to both surfaces.

The latest generation (seventh generation) of dental adhesives combines all three components, etch prime and adhesive, into one bottle.[41] They are generally referred to as all-in-one self-etch adhesives.[41] Recent literature has dropped the generation classification system for dentin bonding systems and reclassified them into two categories: total-etch and self-etch. Total etch systems were categorized as fifth generation under the old classification system. Sixth and seventh generation systems both fall under the new category of self-etch systems, which can be further classified as mild (pH >2), intermediate (pH = 1.5) and strong (pH <1) based on their ability to dissolve the smear layer and demineralize the underlying tooth surface.[44, 45] The bonding mechanism of modern bonding systems is micro-mechanical retention with etched tooth surfaces.[44] In enamel, this is achieved by resin adhesive interlocking into the surface irregularities of etched enamel.[41] Whereas, resin interlocks with the hybrid layer and penetrates dentin tubules to form resin tags to form bonds to dentin.[44] The hybrid layer can be described as a resin interdiffusion zone resulting from the penetration of resin into demineralized inter-tubular dentin and exposed collagen fibers.[41]

The most recent trend in adhesive dentistry is universal adhesives, not to be confused with 7th generation “all-in-one” systems.[46] Currently, no official definition has emerged in the literature as to what constitutes a universal adhesive, however, there are some basic features common to universal adhesives. Many currently on the market are one-bottle systems, such as ScotchBond Universal (3M Corp). OptiBond XTR (Kerr Corp.) is an example of a two-bottle system currently marketed as a universal bonding system.[46] According manufacture’s claims, universal adhesives can be used for the placement of both direct and indirect restorations with the ability to be used as self-etch, selective-etch, or total-etch systems depending on the provider preference and the situation.[42] They are also compatible with light-cure, self-cure and dual-cure resin cements.[42] Universal adhesives are purported to have the ability to bond to a wide variety of surfaces including, dentin, enamel, zirconia, noble and non-precious metals, various silica-based ceramics and composites, without the use of additional primers.[42]

The versatility of universal adhesives is made possible by the advanced chemistry found within.[42] To create an ideal universal adhesive the formulation must include multifunctional molecules that function as cross-linking monomers capable of adhesion with tooth surfaces and polymerization with compatible resin-based restorative materials and cements.[42] The formulation must also contain molecules that are hydrophilic enough to wet tooth tissues that have significant water content, but also be hydrophobic when polymerized in order to prevent water sorption that could lead to hydrolytic breakdown.[42] When adhesives are too hydrophilic they have been shown to function as a semi-permeable membranes allowing the detrimental process of water sorption.[42] Water sorption and subsequent hydrolytic breakdown has been reported as one of the primary causes of bond failure.[42] Universal adhesives must have a film thickness thin enough as to not impede seating of restorations. They must be acidic enough to etch tooth surfaces when used in the self-etch mode, yet not so acidic as to cause the breakdown of initiators needed for polymerization.[42] The dissociation and function of acidic monomers requires water, but if too much water remains after air-drying it can lead to hydrolytic breakdown.[42] To combat this, manufactures add ethanol or acetone which enhances wettability and aids in removal of excess water.[54]

To obtain the versatile bonding characteristics, phosphate esters ($R\text{-}O\text{-}PO_3\text{-}H_2$) serve as the backbone of almost all universal adhesives.[42] These multifunctional adhesive molecules provide the ability to bond to metals, zirconia, and tooth structure through formation of non-soluble calcium salts.[42] Moreover, since they are esters of phosphoric acid, they have the ability to demineralize tooth tissues in self-etch systems.[42] Perhaps the most commonly used phosphate ester in dental adhesives is 10-MDP, an amphiphilic molecule with hydrophobic methacrylate group on one side and hydrophilic phosphate on the other side.[42] The methacrylate group enables bonding to methacrylate resins via free radical addition polymerization and the phosphate group is capable of bonding to tooth surfaces, metals and zirconia as described above.[42] 10-MDP is reported to be the most hydrophobic phosphate ester commonly used in dentistry, which is instrumental in inhibition of water sorption.[42] In addition to 10-MDP, most manufactures employ widely used monomers such as hydrophobic bis-GMA to inhibit water sorption and hydrophilic HEMA to enhance wetting of the inherently moist tooth surface. The goal of manufactures is for the blend of monomers to create a highly cross-linked polymer with micromechanical and/or chemical adhesion to the substrates. The bond between dentin and resin-based restorative materials or cement is shown in figure 11.

With certain substrates, silanating agents or primers are necessary to achieve predictable adhesion. Silanes such as 3-methacryloxypropyltrimethoxysilane (shown in figure 12) have a methacrylate group on one side, capable of bonding to resins, and when hydrolyzed, a hydroxyl group on the other side which is capable of chemically bonding to silica-based ceramics. 10-MDP combined with a carboxylic acid monomer, BPDM, is used to prime zirconia. Many universal adhesives contain silanating and priming molecules[42], however, some studies have shown that other molecules within the formulation may inhibit the function of silanes and primers.[42] In addition, silanes and primers may not be stable in the acidic environment of universal adhesives.[42]

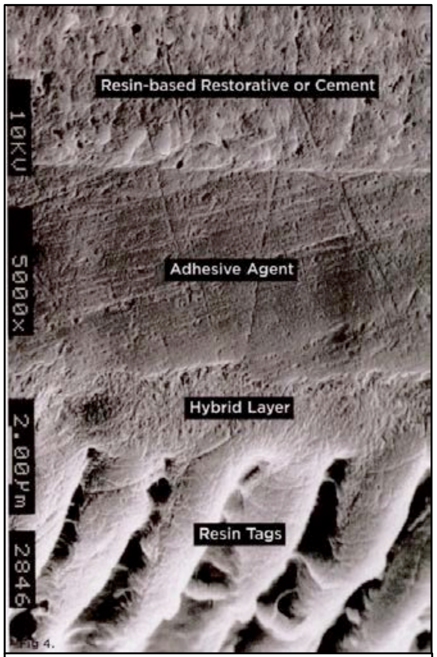


Figure 12: SEM of layers involved in resin adhesive bonding to dentin.

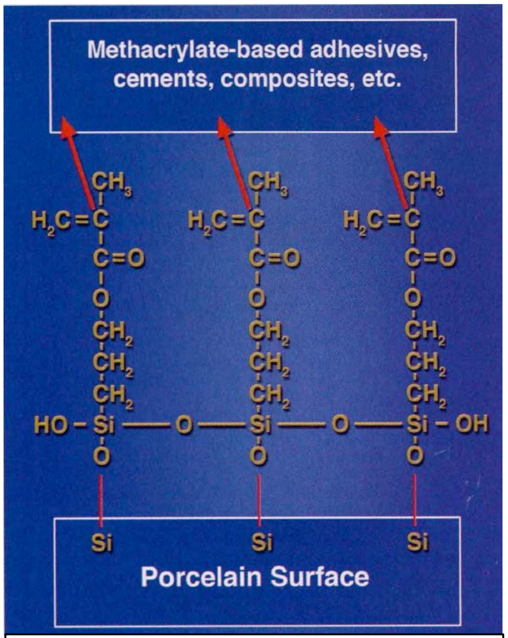


Figure 13: Diagramatic representation of silane bonding to porcelain.

Images in figures 12 and 13 adapted from: Alex G: Universal adhesives: the next evolution in adhesive dentistry?. Compendium 2015; January: 15-26

A new universal adhesive, Assure® Plus (Reliance Orthodontic Products Inc., Itasca, IL) recently came on the market, claiming to eliminate the need for acid etching in order to bond orthodontic appliances to porcelain restorations. This new all-surface adhesive recommends mechanical roughening of ceramic restorations, with no need to chemically alter the surface topography with etchant. A search of the literature revealed studies on the bond of Assure Plus in a moist environment[46, 47], however, published studies that investigated the bond of Assure® Plus to porcelain, without the use of acid etchant, were not found.

The purpose of this study is to begin the investigation into whether or not Assure® Plus can provide a clinically acceptable bond (20 MPa)[56] to porcelain without the need for potentially dangerous surface preparation with hydrofluoric acid. The null hypothesis is that there will be no difference in the bond strength of Assure Plus to porcelain with acid etching the porcelain surface prior to bonding compared to without acid etching.

Materials and Methods

The metal stems were removed from 30 IPS e.max® CAD blocks (Ivoclar Vivadent, Liechtenstein, Germany) by heating the stem with micro-torch to melt adhesive, allowing manual removal with hemostats. The e.max® blocks were then fired in Programat P510 (Ivoclar Vivadent, Liechtenstein, Germany) porcelain oven for a 22-minute cycle reaching 850˚C for crystallization of lithium disilicate glass-ceramic block. Four sides of each block served as bonding surfaces (totaling 120 surfaces) with two sides counting as a single specimen for the control group and the other two side counting as a single specimen for the test group; this methodology was used for statistical reasons and will be further explained in the results section. In this study four surfaces of 30 lithium disilicate blocks yielded 120 total surfaces and 60 specimens; 30 for the control group and 30 for the test group. All specimens underwent a standard surface preparation as described: Surfaces were cleaned with course laboratory pumice (Henry Schein, Melville, NY) and a rag wheel at 3000 rpm for approximately 5 seconds. Specimens were then rinsed thoroughly with water to remove any residual pumice and air-dried prior to additional surface treatments.

Each specimen was then prepared in accordance with the bonding protocol set forth by Reliance Orthodontics (Itasca, IL). The surfaces of each specimen were roughened with EthchMaster® (Groman Inc., Margate, FL) air abrasion adapter and EtchMaster® single dose 50 μm alumina oxide for 10 seconds. A jig was fabricated from 1/8 inch aluminum to ensure a 3/8 inch diameter area was air abraded in approximately the same location on each of the specimen surfaces. Following air-abrasion, specimens were rinsed to remove any excess debris, and air-dried prior to additional surface treatments. Two surfaces of each block (one specimen) were etched for four minutes with Porc-Etch™ (Reliance Orthodontic, Itasca, IL), a 9% solution of hydrofluoric acid. The other two surfaces on each were not etched and served as the test group. After etching, each specimen was thoroughly rinsed with water.

All 30 specimens (120 surfaces) received a thin coat of Porcelain Conditioner (Reliance Orthodontics, Itasca, IL) and were then allowed to air-dry. After the porcelain conditioner was dry, Assure Plus® (Reliance Orthodontics, Itasca, IL), a universal adhesive, was applied to all 120 surfaces for 10 seconds with a microbrush and air dispersed for 10 seconds.

Filtek Supreme Ultra (3M ESPE Dental, St. Paul, MN) composite buttons, approximately 2.37 mm in diameter, were fabricated and applied to specimen surfaces in accordance with ISO 29022[48] using a button mould and bonding clamp (Ultradent Products Inc., South Jordan, UT) (fig. 14). The composite buttons and Assure® Plus adhesive were light cured simultaneously for 40 seconds with the Maxima® LED curing light (Henry Schein, Melville, NY). One button was applied to each of the four sides of the e.max blocks (two control group and two test group). Each block was counted as a one sample/specimen for the control group and a one sample/specimen for the test group.

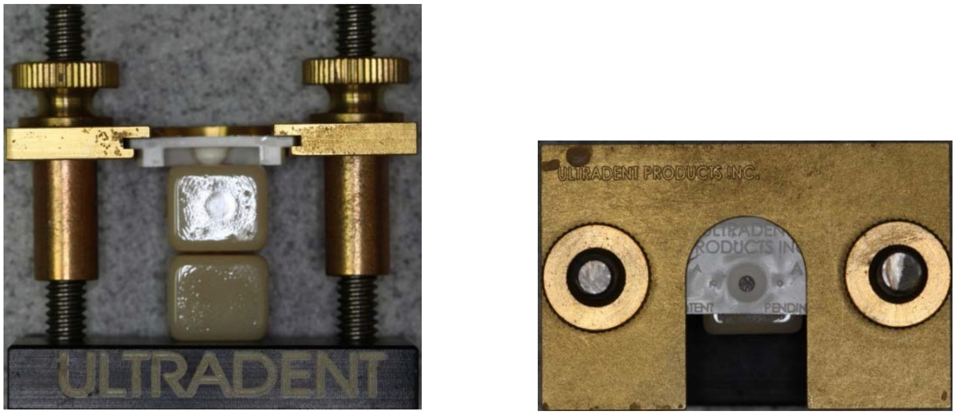


Figure 14: Front view of button forming jig (left) and top view of button forming jig (right).

Each specimen was loaded into an eXpert® 2600 (Admet, Norwood, MA) universal testing machine for notched-edge shear bond strength test in accordance with ISO 29022.[48] Specimens were held in place using a test base clamp (Ultradent Products Inc., South Jordan, UT) with the long axis of the specimen perpendicular to the direction of the applied force. A notched-edge crosshead assembly (Ultradent Products Inc., South Jordan, UT) (fig. 15) was positioned to make contact with the bonded specimen. Bond strength was determined in shear mode at a crosshead speed of 1.0 mm/minute until fracture occurred. Samples were also analyzed microscopically to determine failure mode.

Figure 15: Test base clamp with e.max block (left), crosshead assembly shearing composite button (center) and close-up of crosshead assembly shearing composite button.

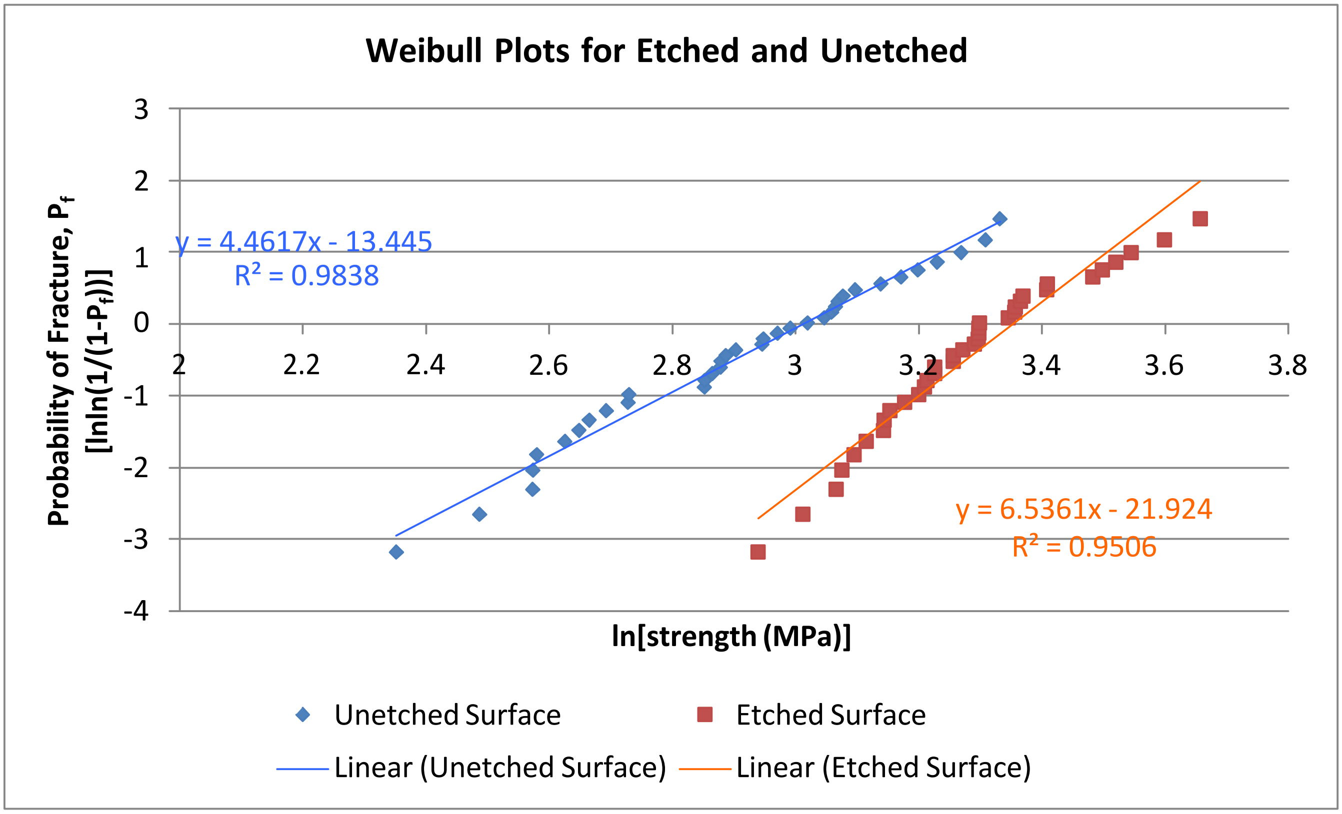
In this study, the independent variable is bonding technique (control: etch and Assure Plus; test group: Assure Plus without etch). The dependent variable is shear strength measured in mega Pascal (MPa). The null hypothesis is that there is no difference in shear strength between bonding techniques. The alternative hypothesis is that there is a difference in shear strength between bonding techniques. A Weibull analysis of the data was completed for comparison of strength values and ranges. Further statistical analysis of the data was done with a two factor ANOVA on shear strength by bonding agent followed by independent sample t-tests corrected for multiple comparisons. If the data were not normally distributed with equal variance, the equivalent non-parametric test would have been used. The failure modes were analyzed statistically.

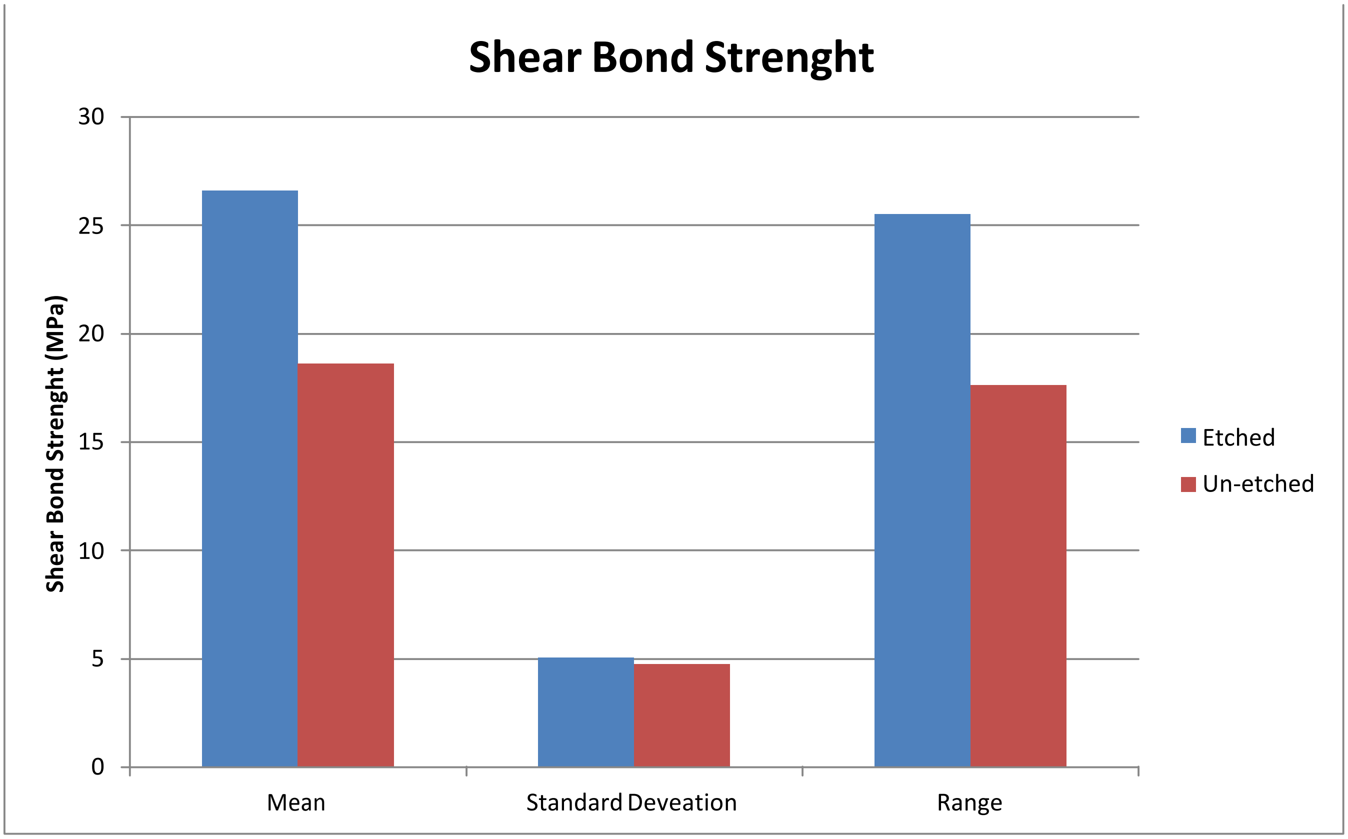
A mean positive standard deviation (SD) for the dependent variable was not estimated, so a general analysis was performed. The on line power analysis program at the University of British Columbia (www.stat.ubc.ca/~rollin/stats/ssize/n2.html) was used to estimate the sample size needed for a power of 80% with a level of confidence of 95%. Four comparisons are appropriate for this design, so a Bonferroni correction of $p = 0.05 / 4 = 0.0125$ was used. With 30 samples per group, we were able to detect an effective size of 0.87 SD.

Results

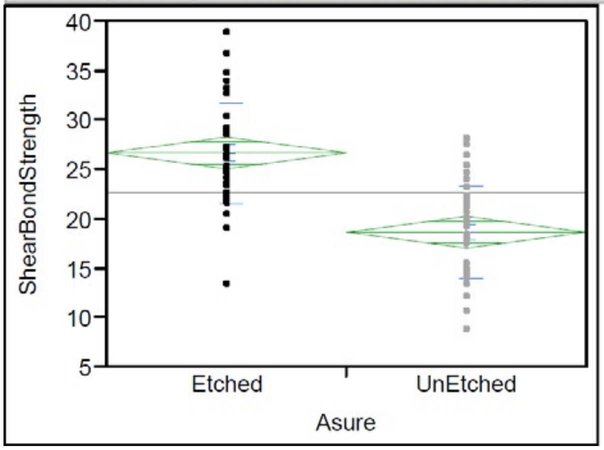
A total of 74 samples (37 from the test group and 37 from the control group) were included in this study. In addition to the 60 samples discussed in the materials and methods, seven samples per group from a pilot study were included in the statistical analysis for this study. The materials and methods used in the pilot study were identical to those used in this study, with the exception of the number of samples tested. Raw data can be found in appendix A.

The mean shear bond strength of Assure® Plus to e.max® without hydrofluoric acid etching was 18.60 MPa with a standard deviation of ±4.74 MPa. Two buttons from the un-etched group debonded prematurely in the testing machine, so no shear bond strength was reported for those two surfaces. However, because each sample was comprised of two surfaces averaged together, the specimens with the debonded buttons were still used—yielding a sample with one surface instead of an average of two. The shear bond strength with acid etching was 26.60 MPa with a standard deviation of ±5.03 MPa. According to the Weibull analysis a significant difference between the two groups was found. The statistical difference between the groups was further confirmed by the Oneway Anova, t test and Analysis of Variance.


Weibull Plots for Etched and Unetched
Probability of Fracture, P_f
[lnln(1/(1-P_f))]
3
2
1
0
-1
-2
-3
-4
2
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
y = 4.4617x - 13.445
R^2 = 0.9838
y = 6.5361x - 21.924
R^2 = 0.9506
ln[strength (MPa)]
◆ Unetched Surface
■ Etched Surface
Linear (Unetched Surface)
Linear (Etched Surface)


Shear Bond Strenght
Shear Bond Strenght (MPa)
30
25
20
15
10
5
0
Mean
Standard Deveation
Range
Etched
Un-etched

Oneway Analysis of ShearBondStrength By Asure



Oneway Anova

Summary of Fit

Rsquare	0.410366
Adj Rsquare	0.402176
Root Mean Square Error	4.889394
Mean of Response	22.6191
Observations (or Sum Wgts)	74

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Etched	37	26.6426	0.80381	25.040	28.245
UnEtched	37	18.5956	0.80381	16.993	20.198

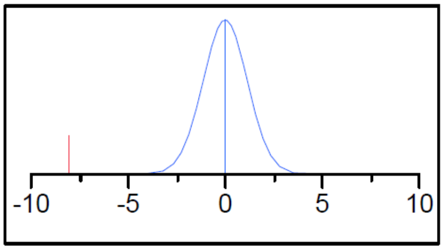
Std Error uses a pooled estimate of error variance

t Test

UnEtched-Etched

Assuming equal variances

Difference	-8.047	t Ratio	-7.07881
Std Err Dif	1.137	DF	72
Upper CL Dif	-5.781	Prob > |t|	<.0001*
Lower CL Dif	-10.313	Prob > t	1.0000
Confidence	0.95	Prob < t	<.0001*



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Asure	1	1197.9286	1197.93	50.1096	<.0001*
Error	72	1721.2442	23.91		
C. Total	73	2919.1728			

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Etched	37	26.6426	5.03191	0.82724	24.965	28.320
UnEtched	37	18.5956	4.74259	0.77968	17.014	20.177

Discussion

The bond strengths achieved in this study have a range of 25.49 MPa and 17.62 MPa for the etched and un-etched groups respectively. Variation of bond strengths is not uncommon for shear bond studies due to the nature of resin adhesive. Moisture, surface preparation, dry time and light cure are all factors that have the potential to alter bond strength. With so many ways to introduce error, the technique sensitivity and subsequent variability of adhesive dentistry becomes obvious. Although a bench-top study allowed for strict control over most variables in the bonding process, it is impossible to eliminate all inconsistency.

It was anticipated that the method of sandblasting used in this study may allow for some variability in surface texture because the technique was dependent on consistent movement of air abrasion tip within the area being sandblasted. This movement was done manually, not with a machine, so the exact movements could not be replicated for each sample. However, the group that was only sandblasted had a lower range of shear bond strength than the group that was sandblasted and etched. This suggests a greater inconsistency in the technique used for etching. Care was taken to ensure equal contact time between etchant and each sample. Perhaps the range of bond strengths could be attributed to inconsistent rinsing. All samples were rinsed with copious water, but no measure was taken to ensure complete removal of the etchant. If varying trace amounts of etchant were left on some of the samples, it would result in variation in surface texture, not to mention acidic residue could interfere with the chemical properties of the adhesive. This could have a great impact on the micromechanical retention achieved and chemical reactions in the bonding process.

In spite of the range of shear bond strengths obtained in this study, there is a statistically significant difference between the shear bond strength of Assure® Plus to etched porcelain compared to un-etched porcelain. Therefore, we can reject the null hypothesis that there would be no difference in the bond strengths achieved with etched and un-etched porcelain. A plausible explanation for the findings of this study is surface topography of the different groups. In other words, the etched samples had a more roughened surface that facilitated micromechanical bonding between the adhesive and substrate. As discussed previously, the actual chemical boding is thought to play only a small role in most dental adhesives; instead, most resin bonding systems rely heavily on macro and micromechanical adhesion. Macro mechanical adhesion is the process by which adhesive material interlocks with surface irregularities in the bonding substrate. Micromechanical adhesion is the exact same thing, but on a microscopic scale. Micromechanical adhesion is demonstrated in fig. 12, which shows dental adhesive interlocking with collagen fibrils and dentin tubules.

After this study was completed, scanning electron microscopy was done on one sample of etched and one sample un-etched e.max. The samples were prepared according to the same protocol used for all the samples in this study, through the point at which the samples were etched, or remained un-etched accordingly. The images below show a substantial difference in surface topography between the etched and un-etched samples, the later having less. A SEM of unprepared e.max is included for perspective.

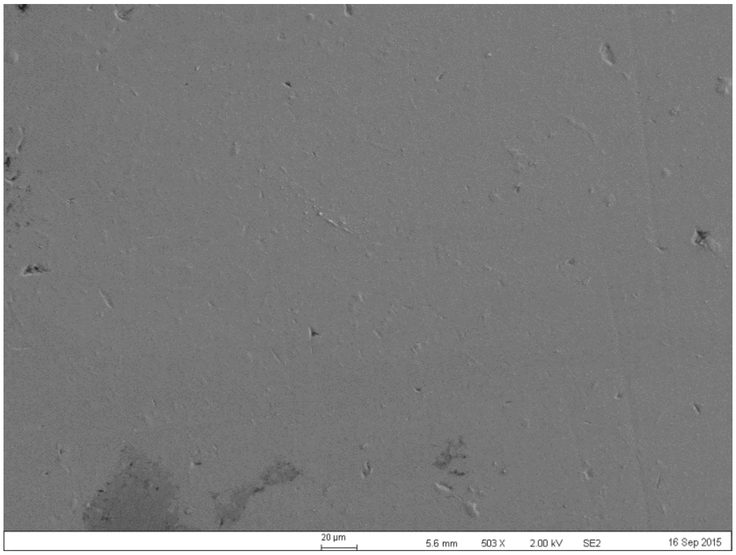


Figure 16: 500x SEM image of unprepared e.max surface.

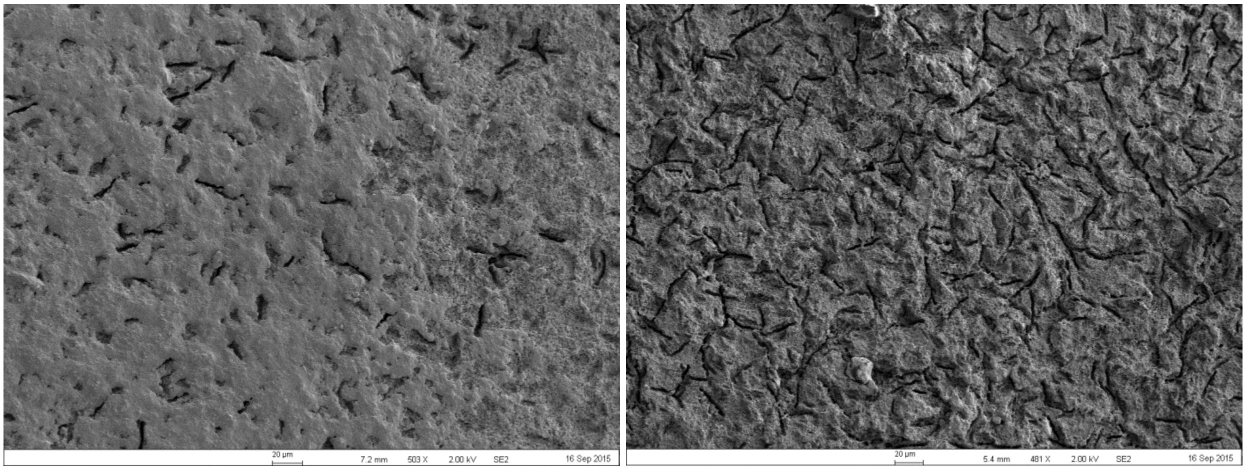


Figure 17: 500x SEM images of etched and un-etched e.max on right and left respectively.

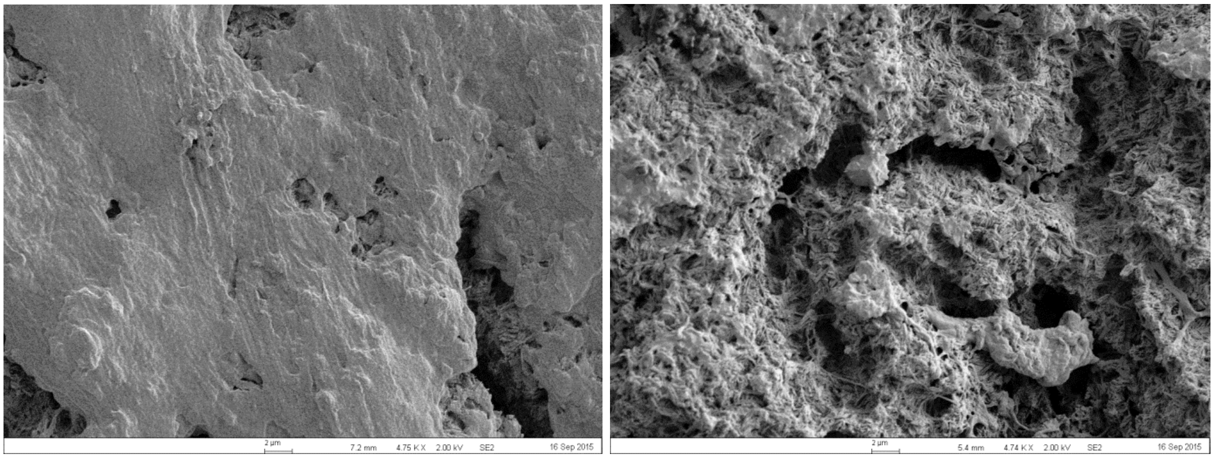


Figure 18: 5000x SEM images of etched and un-etched e.max on right and left respectively.

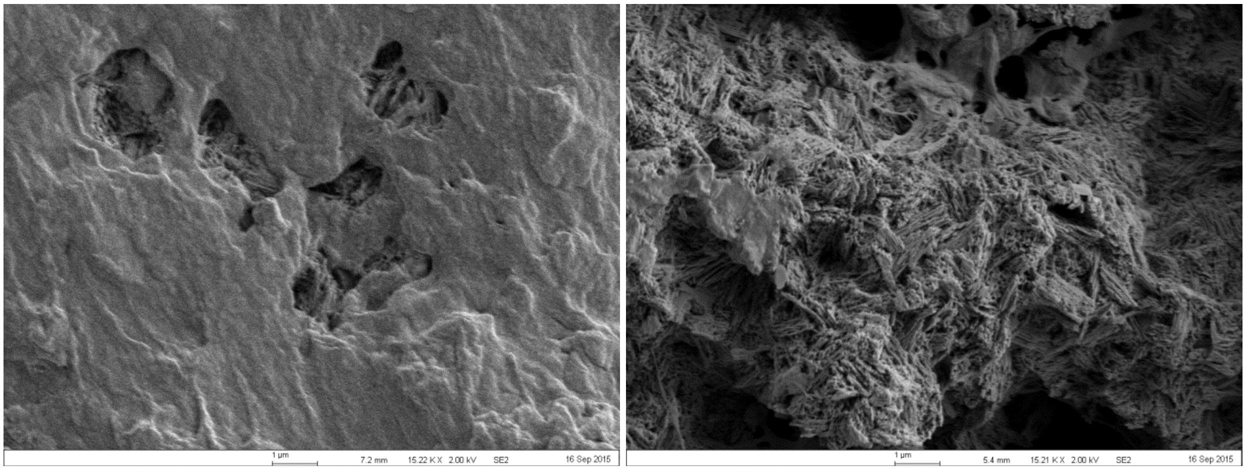


Figure 19: 15000x SEM images of etched and un-etched e.max on right and left respectively.

When acid of sufficient strength is applied to porcelain it creates surface irregularities, as seen above, by the preferential dissolution of the glassy matrix over the crystalline structure on the ceramic surface.[5,26] Addison and colleagues demonstrated this increase in surface topography with profilimetry on porcelain samples etched with hydrofluoric acid. The concept of roughening the porcelain surface prior to bonding is well supported by the literature and numerous studies have examined its effect on bond strength achieved when bonding orthodontic appliances to porcelain.[49] For instance, Huang and Kao, found that etching had the most significant effect on bond strength, when compared to primer application and thermocycling. Stangle et al examined the shear strength of composite bonded to etched porcelain and found that etching with 20% hydrofluoric acid for 2.5 minutes significantly increased the bond strength compared to un-etched porcelain.[24] In another study, Trakyali et al found no statistically significant difference in bond strength when comparing 5% and 9.6% hydrofluoric acid (both for 120 seconds), and in accordance with those findings, they advocated using 5% hydrofluoric acid for intra-oral applications, for safety concerns.[16] Perez and his colleagues found etching with 4.6% hydrofluoric acid to be the most effective when compared to other commonly used time and concentration regimes.[36]

Acids other than hydrofluoric have also been advocated in the literature. In a comparison with other types acid, Nagai et al found etching with hydrofluoric acid facilitated a higher bond strength than etching with 37% phosphoric acid.[50] Other studies have also looked at the effectiveness of phosphoric acid for etching porcelain and found that etching with hydrofluoric acid provided a stronger bond.[27, 28] However, the same studies advocated the use of 37% phosphoric acid, citing easier post-debonding cleanup and safety concerns as compelling reasons for using phosphoric acid.

The use of lasers has even been described in the literature as a means of preparing porcelain surfaces for bonding orthodontic appliances. Yassaei et al found surface preparation with an erbiumdoped yttrium aluminum garnet (Er:YAG) laser yielded similar bond strengths when compared to surface preparation with 9.6% hydrofluoric acid.[33] Tengrungsun and colleagues also found satisfactory results when using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser for surface preparation of porcelain.[32] The laser etches porcelain similar to acid, in that the more susceptible glass phase is selectively removed and crystalline structures in the surface remain, thus increasing the roughness. A unique benefit of etching with certain lasers is that only areas of the restoration pretreated with a laser-initiating material are etched by the laser.[32] This is possible because the very narrow wavelength range of the laser interacts only with materials of certain coloration. This same principle allows lasers to be used in the treatment of periodontal disease with little risk to hard tissues. Despite the advantages of laser etching, it is not likely to become the prominent means of surface treatment due to the expense of lasers and unfamiliarity among practitioners.

More cost effective, mechanical surface roughening has been described in the literature, namely air abrasion and diamond burs. The latter has been shown to initiate cracks in ceramic which may lead to fracture.[28] This could cause irreversible damage compromising the integrity of the restoration. Air abrasion on the other hand, has not been shown to induce cracks in ceramic.[51] According to Chung and colleagues, no significant difference was found in the surface roughness of etched enamel, and that of porcelain, metal and enamel roughened by air abrasion.[51] Chung et al and others advocate intra-oral air abrasion as a viable alternative to intra-oral acid-etching.[51,52] Air abrasion increases surface roughness by partial removal of superficial material, thereby increasing surface energy and bonding surface area.[51] It is also believed that air abrasion removes unfavorable oxides and other surface contaminates.[51] The study by Chung et al compared the surface roughness of enamel etched with 37% phosphoric acid to several air abraded surfaces, but they did not compare the surface of porcelain etched with hydrofluoric acid to that of porcelain roughened with air abrasion.

As shown above in figures 17-20, our study did examine the surfaces of etched and air abraided porcelain. Based on the images obtained in this study, it is apparent that greater surface topography is achieved through etching. That said, air abrasion could offer some benefits in terms of bonding, which etching alone does not afford. For instance, silicate particles can be incorporated into the particulate used for air abrasion. During the process of air abrasion those silicate particles get imbedded into the surface of the restoration and bi-functional molecules such as MDP can form a chemical bond with the silicate particles. This is referred to as tribochemical bonding and is very useful in trying to bond to metal surfaces. Sarac et al found tribochemical bonding was superior to that achieved with sandblasting alone.[20]

Chemical bonding to porcelain surfaces can be achieved through silanes such as 3-methacryloxypropyltrimethoxysilane. Silanes have two functions in terms of increasing bond strength: 1) they form a link between the porcelain surface and resin adhesive, and 2) they increase wettability of the porcelain which allows for more intimate micromechanical contact between the porcelain and adhesive.[53] The importance of silane when bonding to porcelain is demonstrated over and over in the literature. Whether it is done in conjunction with acid etching or some form of mechanical surface alteration, silane increases the bond strength over that achieved with those other surfaces treatment alone.[18,26,27]

Based on the discussion found in much of the literature, one may reach the conclusion that the goal of research concerning adhesive dentistry is to find the material, surface preparation, or combination thereof, that yields the highest bond strength. In many clinical instances, the highest possible bond strength could be the most desirable, however, in orthodontics that may not always be the case. Just as certain surface preparations can be damaging to restorations, excessive bond strength can also lead to restoration damage upon appliance removal.[34] In other words, if the bond strength between an orthodontic bracket and ceramic restoration is too high, removal of the bracket may fracture the porcelain. This could result in an unaesthetic restoration, or in extreme cases, an unserviceable crown that must be replaced. Therefore, the ideal orthodontic bonding system must afford adequate bond strength to prevent appliances from debond during mastication and the application of orthodontic forces, yet also facilitate clean removal without damage to enamel or restorations. According to some studies, the minimum bond strength needed for orthodontic appliances is between six and eight MPa [19, 26]; however, those studies date back to the 1970's when bonding to any teeth posterior to canines was not commonly done. More recent literature reports forces of 20 MPa on posterior teeth during mastication, suggesting a bond strength much greater than 8 MPa is needed for bonding posterior brackets and tubes.[56] Other studies have found that bond strengths as low as nine to eleven MPa can lead to enamel fracture at the time of debond. [55] In this study, bond strengths in excess of 30 MPa were achieved and no adhesive failures within the porcelain occurred. Mixed adhesive/cohesive failures did occur in some of the samples with higher bond strengths, but the adhesive failure occurred within the composite, not the ceramic. Feldspathic porcelain, layered/veneering porcelain applications, and leucite reinforced ceramics are much weaker than lithium disilicate, so it is reasonable to expect a lower threshold of adhesive failure and subsequent fracture for those restorations.

Given the delicate balance between bond strength and ease of removal, the question becomes: Is the use of hydrofluoric acid, a potentially dangerous substance, warranted for intra-oral bonding of orthodontic appliances? Based on the results of this study, I would argue, no. It is not necessary to always use hydrofluoric acid to bond orthodontic appliances to ceramic restorations. According to the literature, 6-8 MPa may be all that is needed to bond anterior orthodontic appliances. [19, 26] The test group in this study, which did not incorporate acid etching, achieved a mean bond strength of 18.59 MPa, more than double the 6-8 MPa recommended in the literature. Therefore, clinically acceptable bond strength in the anterior can be achieved without the use of acid etching. That is not to say that hydrofluoric acid should never be used for intra-oral bonding of anterior orthodontic appliances. There are certain cases that have a high propensity for debonding, where multiple debonds have occurred and every available way to enhance adhesion is needed to keep the appliance in place. In such cases, the use of hydrofluoric acid is not only appropriate, but necessary for clinical success. Certainly posterior appliances may necessitate the use of acid etching to exceed the 20 MPa of normal masticatory forces.

Conclusion

The purpose of this study was to compare the shear bond strength of an orthodontic adhesive, Assure® Plus (Reliance Orthodontic Products Inc., Itasca, IL), to etched versus un-etched porcelain. In today's esthetically driven dentistry, ceramic restorations are rapidly increasing in popularity. Moreover, esthetically driven adults, who may have multiple ceramic restorations, are also seeking orthodontic treatment. Hence there is a growing need to bond orthodontic appliances to ceramic restorations. One means of bonding to ceramic is to roughen the surface with hydrofluoric acid. Unfortunately, this poses a safety hazard to both patients and clinicians, so eliminating etching from intra-oral bonding protocol could potentially improve patient and provider safety. Eliminating etching protocols that often take several minutes could also save substantial time, a clear advantage for efficient clinicians.

In this study we found a statistically significant increase in shear bond strength when acid etching was incorporated into the protocol. We also found that sandblasting without etching provided more than adequate clinical bond strength to porcelain in the anterior. Although the mean bond strength demonstrated in this study fell slightly below the potential forces on posterior orthodontic appliances, many of the samples tested did exceed 20 MPa. Therefore, clinicians should consider routinely sandblasting ceramic restorations in preparation for bonding orthodontic appliances; reserving acid etching for molars and problematic cases that undergo multiple debonds.

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Appendix A

Assure + (Pilot-Unetched)

Sample #	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stress (Mpa)	Failure Mode
1	2.3798	2.37	4.448061689	4.411502944	86.803	19.5147923	19.67651413	mix
2	2.3798	2.37	4.448061689	4.411502944	95.36	21.43855159	21.61621588	mix
3	2.3798	2.33	4.448061689	4.263848089	58.341	13.11605011	13.68271073	adhesive
4	2.3798	2.34	4.448061689	4.300526183	53.504	12.02861015	12.44126828	adhesive
5	2.3798	2.37	4.448061689	4.411502944	62.886	14.13784349	14.25500579	adhesive
6	2.3798	2.36	4.448061689	4.374353611	58.359	13.12009681	13.34117111	adhesive
7	2.3798	2.37	4.448061689	4.411502944	46.743	10.50862224	10.59570867	adhesive
Average	2.3798	2.358571429	4.448061689	4.369248523	65.99942857	14.83779524	15.08694208	
SD	0	0.016761634	9.59342E-16	0.061913673	18.02081495	4.051386022	4.012024745	

Assure + (Pilot-Etched)

Sample #	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stress (Mpa)	Failure Mode
1a	2.3798	2.37	4.448061689	4.411502944	119.465	26.857766	27.08034008	cohesive
2a	2.3798	2.37	4.448061689	4.411502944	144.806	32.55485425	32.82464091	cohesive
3a	2.3798	2.37	4.448061689	4.411502944	120.453	27.07988522	27.30430004	cohesive
4a	2.3798	2.35	4.448061689	4.337361357	84.134	18.91475566	19.39750762	mix
5a	2.3798	2.37	4.448061689	4.411502944	103.263	23.21528055	23.40766884	cohesive
6a	2.3798	2.38	4.448061689	4.448809357	172.409	38.76047862	38.75396453	cohesive
7a	2.3798	2.36	4.448061689	4.374353611	129.334	29.07648523	29.56642547	cohesive
Average	2.3798	2.367142857	4.448061689	4.400933729	124.8377143	28.06564365	28.33354964	
SD	0	0.009511897	9.59342E-16	0.03532435	28.43802816	6.393352915	6.285193812	

Assure + (Pilot-Unetched-24hr Water)

Sample #	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stress (Mpa)	Failure Mode
1w	2.3798	2.37	4.448061689	4.411502944	86.803	19.5147923	19.67651413	mix
2w	2.3798	2.37	4.448061689	4.411502944	95.36	21.43855159	21.61621588	cohesive
3w	2.3798	2.34	4.448061689	4.300526183	58.341	13.11605011	13.56601437	adhesive
4w	2.3798	2.35	4.448061689	4.337361357	53.504	12.02861015	12.33561043	adhesive
5w	2.3798	2.37	4.448061689	4.411502944	62.886	14.13784349	14.25500579	adhesive
Average	2.3798	2.36	4.448061689	4.374479275	71.3788	16.04716953	16.28987212	
SD	0	0.014142136	0	0.052342754	18.53796277	4.167649657	4.093762008	

Assure + (Pilot-Etched-24hr Water)

Sample #	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stress (Mpa)	Failure Mode
1aw	2.3798	2.36	4.448061689	4.374353611	119.465	26.857766	27.31032071	cohesive
2aw	2.3798	2.38	4.448061689	4.448809357	144.806	32.55485425	32.54938308	cohesive
3aw	2.3798	2.37	4.448061689	4.411502944	179.949	40.455599	40.79086023	cohesive
4aw	2.3798	2.37	4.448061689	4.411502944	120.453	27.07988522	27.30430004	cohesive
5aw	2.3798	2.32	4.448061689	4.227327075	84.134	18.91475566	19.90241079	mix
Average	2.3798	2.36	4.448061689	4.374699186	129.7614	29.17257203	29.57145497	
SD	0	0.023452079	0	0.086487007	35.4247688	7.964091164	7.721499938	

Assure + (Unetched)

Sample	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stess (Mpa)	Failure Mode
1	2.3798	2.29	4.448061689	4.118706509	54.89	12.34020655	13.3269996	mix/adhesive
2	2.3798	2.38	4.448061689	4.448809357	99.346	22.33467226	22.33091869	adhesive
3	2.3798	2.4	4.448061689	4.523893421	117.49	26.41375237	25.97099203	adhesive
4	2.3798	2.37	4.448061689	4.411502944	107.478	24.16288431	24.36312553	adhesive
5	2.3798	2.37	4.448061689	4.411502944	102.429	23.02778315	23.21861762	adhesive
6	2.3798	2.33	4.448061689	4.263848089	79.837	17.9487169	18.72416614	adhesive
7	2.3798	2.37	4.448061689	4.411502944	113.15	25.43804648	25.64885515	adhesive
8	2.3798	2.38	4.448061689	4.448809357	104.936	23.59139943	23.58743466	adhesive
9	2.3798	2.33	4.448061689	4.263848089	89.223	20.0588495	20.92546407	adhesive
10	2.3798	2.32	4.448061689	4.227327075	69.011	15.51484777	16.32497292	adhesive
11	2.3798	2.34	4.448061689	4.300526183	80.24	18.03931816	18.65818195	adhesive
12	2.3798	2.37	4.448061689	4.411502944	97.047	21.81781791	21.99862524	adhesive
13	2.3798	2.37	4.448061689	4.411502944	103.485	23.26518993	23.45799183	adhesive
14	2.3798	2.39	4.448061689	4.486272849	139.923	31.45707272	31.18914179	adhesive
15	2.3798	2.37	4.448061689	4.411502944	92.304	20.75151076	20.92348145	adhesive
16	2.3798	2.37	4.448061689	4.411502944	100.796	22.66065694	22.84844899	adhesive
17	2.3798	2.34	4.448061689	4.300526183	78.196	17.57979216	18.18289127	adhesive
18	2.3798	2.31	4.448061689	4.19096314	44.75	10.06056191	10.67773648	adhesive
19	2.3798	2.37	4.448061689	4.411502944	103.369	23.23911115	23.43169693	adhesive
20	2.3798	2.35	4.448061689	4.337361357	88.151	19.81784565	20.32364674	adhesive
21	2.3798	2.39	4.448061689	4.486272849	126.174	28.36606343	28.12445971	adhesive
22	2.3798	2.37	4.448061689	4.411502944	107.746	24.22313527	24.4238758	adhesive
23	2.3798	2.37	4.448061689	4.411502944	91.561	20.58447171	20.75505812	adhesive
24	2.3798	2.37	4.448061689	4.411502944	95.676	21.50959377	21.6878468	adhesive

25	2.3798	2.37	4.448061689	4.411502944	103.631	23.29801321	23.49108712	mix/adhesive
26	2.3798	2.3	4.448061689	4.154756284	56.054	12.60189357	13.49152541	adhesive
27	2.3798	2.38	4.448061689	4.448809357	129.904	29.20463093	29.1997228	adhesive
28	2.3798	2.37	4.448061689	4.411502944	39.794	8.946368729	9.020508544	adhesive
29	2.3798	2.34	4.448061689	4.300526183	57.497	12.92630454	13.36975931	adhesive
30	2.3798	2.41	4.448061689	4.561671073	154.7	34.77919391	33.91301072	adhesive
31	2.3798	2.37	4.448061689	4.411502944	74.531	16.75583776	16.89469574	adhesive
32	2.3798	2.35	4.448061689	4.337361357	79.729	17.92443666	18.3819132	adhesive
33	2.3798	2.29	4.448061689	4.118706509	29.109	6.544198807	7.067510137	adhesive
34	2.3798	2.35	4.448061689	4.337361357	88.346	19.86168497	20.36860495	adhesive
35	2.3798	2.35	4.448061689	4.337361357	74.904	16.83969451	17.26948571	adhesive
36	2.3798	2.36	4.448061689	4.374353611	81.242	18.26458482	18.57234399	adhesive
37	2.3798	2.37	4.448061689	4.411502944	22.589	5.078391798	5.120477145	adhesive
38	2.3798	2.37	4.448061689	4.411502944	108.897	24.48189967	24.68478461	adhesive
39	2.3798	2.36	4.448061689	4.374353611	80.698	18.14228436	18.44798276	adhesive
40	2.3798	2.37	4.448061689	4.411502944	81.555	18.33495255	18.48689688	adhesive
41	2.3798	2.37	4.448061689	4.411502944				
42	2.3798	2.37	4.448061689	4.411502944	84.655	19.03188533	19.18960524	adhesive
43	2.3798	2.37	4.448061689	4.411502944	84.408	18.97635552	19.13361525	adhesive
44	2.3798	2.34	4.448061689	4.300526183	51.775	11.63990152	12.03922446	mix/adhesive
45	2.3798	2.37	4.448061689	4.411502944	89.421	20.10336327	20.26996267	adhesive
46	2.3798	2.37	4.448061689	4.411502944	100.142	22.51362661	22.7002002	adhesive
47	2.3798	2.37	4.448061689	4.411502944	82.251	18.4914252	18.64466624	adhesive
48	2.3798	2.35	4.448061689	4.337361357	76.216	17.13465445	17.57197377	mix/adhesive
49	2.3798	2.37	4.448061689	4.411502944	102.676	23.08331295	23.27460761	adhesive
50	2.3798	2.37	4.448061689	4.411502944				
51	2.3798	2.31	4.448061689	4.19096314	41.023	9.222668854	9.788442091	adhesive
52	2.3798	2.37	4.448061689	4.411502944	86.901	19.53682437	19.69872878	adhesive
53	2.3798	2.33	4.448061689	4.263848089	64.075	14.40515094	15.02750536	adhesive
54	2.3798	2.37	4.448061689	4.411502944	132.889	29.87570976	30.12329396	adhesive
55	2.3798	2.39	4.448061689	4.486272849	153.496	34.50851421	34.21459308	adhesive
56	2.3798	2.37	4.448061689	4.411502944	95.636	21.50060109	21.67877959	adhesive
57	2.3798	2.35	4.448061689	4.337361357	63.459	14.26666365	14.63078466	adhesive
58	2.3798	2.37	4.448061689	4.411502944	72.988	16.40894509	16.54492832	mix/adhesive
59	2.3798	2.34	4.448061689	4.300526183	52.421	11.78513332	12.18943863	adhesive
60	2.3798	2.37	4.448061689	4.411502944	24.735	5.560849136	5.606932674	adhesive
Ave	2.3798	2.359166667	4.448061689	4.371739544	86.37163793	19.41781476	19.67607278	
SD	4.47775E-16	0.024582627	8.88178E-16	0.090605658	28.71987797	6.456717551	6.274088828	

Assure + (Etched)

Sample	Diameter (mm)	Measured Diameter (mm)	Surface Area (mm^2)	Measured Surface Area (mm^2)	Peak Load (N)	Peak Stress (Mpa)	Measured Peak Stress (Mpa)	Failure Mode
1	2.3798	2.37	4.448061689	4.411502944	135.53	30.46945152	30.72195615	adhesive
2	2.3798	2.37	4.448061689	4.411502944	105.285	23.66986057	23.86601604	adhesive
3	2.3798	2.37	4.448061689	4.411502944	125.261	28.16080548	28.39417804	mix/adhesive
4	2.3798	2.31	4.448061689	4.19096314	98.74	22.19843314	23.56021676	adhesive
5	2.3798	2.37	4.448061689	4.411502944	109.433	24.6024016	24.80628516	adhesive
6	2.3798	2.37	4.448061689	4.411502944	81.464	18.3144942	18.46626899	adhesive
7	2.3798	2.37	4.448061689	4.411502944	119.505	26.86675868	27.08940729	adhesive
8	2.3798	2.35	4.448061689	4.337361357	77.109	17.33541605	17.77785931	adhesive
9	2.3798	2.38	4.448061689	4.448809357	105.261	23.66446496	23.66048791	adhesive
10	2.3798	2.37	4.448061689	4.411502944	113.018	25.40837063	25.61893337	adhesive
11	2.3798	2.35	4.448061689	4.337361357	95.698	21.51453975	22.06364472	mix/adhesive
12	2.3798	2.37	4.448061689	4.411502944	110.597	24.86408861	25.07014081	mix/adhesive
13	2.3798	2.37	4.448061689	4.411502944	109.261	24.56373307	24.76729618	adhesive
14	2.3798	2.37	4.448061689	4.411502944	121.588	27.33505255	27.56158197	adhesive
15	2.3798	2.37	4.448061689	4.411502944	118.203	26.57404691	26.79426978	adhesive
16	2.3798	2.35	4.448061689	4.337361357	103.125	23.1842558	23.77597611	adhesive
17	2.3798	2.37	4.448061689	4.411502944	36.701	8.251009668	8.319386945	adhesive
18	2.3798	2.3	4.448061689	4.154756284	81.382	18.2960592	19.5876712	adhesive
19	2.3798	2.37	4.448061689	4.411502944	93.25	20.96418767	21.13792084	adhesive
20	2.3798	2.37	4.448061689	4.411502944	120.289	27.04301523	27.2671245	adhesive
21	2.3798	2.37	4.448061689	4.411502944	121.284	27.26670817	27.49267121	adhesive
22	2.3798	2.37	4.448061689	4.411502944	133.842	30.08996038	30.33932011	adhesive
23	2.3798	2.37	4.448061689	4.411502944	119.691	26.90857465	27.13156979	adhesive
24	2.3798	2.37	4.448061689	4.411502944	138.019	31.0290211	31.28616296	adhesive
25	2.3798	2.35	4.448061689	4.337361357	91.729	20.62224097	21.14857224	adhesive
26	2.3798	2.31	4.448061689	4.19096314	101.126	22.73484656	24.12953697	adhesive
27	2.3798	2.37	4.448061689	4.411502944	107.694	24.21144479	24.41208844	adhesive
28	2.3798	2.33	4.448061689	4.263848089	73.224	16.46200191	17.1732197	adhesive
29	2.3798	2.37	4.448061689	4.411502944	115.027	25.86002804	26.07433373	adhesive
30	2.3798	2.37	4.448061689	4.411502944	105.329	23.67975252	23.87598996	adhesive
31	2.3798	2.37	4.448061689	4.411502944	172.086	38.68786272	39.00847448	adhesive
32	2.3798	2.38	4.448061689	4.448809357	136.329	30.64908032	30.64392944	adhesive
33	2.3798	2.41	4.448061689	4.561671073	176.657	39.71550135	38.72637838	adhesive
34	2.3798	2.37	4.448061689	4.411502944	117.452	26.40520933	26.62403301	adhesive
35	2.3798	2.36	4.448061689	4.374353611	106.577	23.96032417	24.36405684	adhesive
36	2.3798	2.37	4.448061689	4.411502944	117.528	26.42229542	26.6412607	adhesive
37	2.3798	2.38	4.448061689	4.448809357	168.322	37.84165143	37.83529176	adhesive
38	2.3798	2.37	4.448061689	4.411502944	157.247	35.35180287	35.64476823	adhesive
39	2.3798	2.35	4.448061689	4.337361357	102.677	23.08353777	23.6726875	adhesive
40	2.3798	2.36	4.448061689	4.374353611	105.639	23.7494458	24.14962516	mix/adhesive
41	2.3798	2.38	4.448061689	4.448809357	153.046	34.40734655	34.40156404	adhesive
42	2.3798	2.37	4.448061689	4.411502944	147.584	33.17939595	33.45435827	adhesive
43	2.3798	2.37	4.448061689	4.411502944	125.233	28.15451061	28.38783099	adhesive
44	2.3798	2.37	4.448061689	4.411502944	115.611	25.99132118	26.20671492	adhesive
45	2.3798	2.38	4.448061689	4.448809357	152.626	34.3129234	34.30715676	adhesive

46	2.3798	2.37	4.448061689	4.411502944	116.081	26.09698518	26.31325457	adhesive
47	2.3798	2.37	4.448061689	4.411502944	118.078	26.54594479	26.76593476	adhesive
48	2.3798	2.38	4.448061689	4.448809357	151.013	33.95029353	33.94458784	adhesive
49	2.3798	2.38	4.448061689	4.448809357	149.925	33.70569261	33.70002802	adhesive
50	2.3798	2.36	4.448061689	4.374353611	102.578	23.06128088	23.44986463	adhesive
51	2.3798	2.37	4.448061689	4.411502944	99.569	22.38480645	22.57031249	adhesive
52	2.3798	2.37	4.448061689	4.411502944	100.876	22.67864231	22.8665834	adhesive
53	2.3798	2.37	4.448061689	4.411502944	140.68	31.6272592	31.88935875	mix/adhesive
54	2.3798	2.35	4.448061689	4.337361357	99.717	22.41807937	22.99024494	adhesive
55	2.3798	2.35	4.448061689	4.337361357	108.575	24.40950859	25.03250042	adhesive
56	2.3798	2.37	4.448061689	4.411502944	125.908	28.3062621	28.54084007	adhesive
57	2.3798	2.37	4.448061689	4.411502944	116.483	26.18736163	26.40437998	adhesive
58	2.3798	2.37	4.448061689	4.411502944	114.534	25.74919325	25.96258043	adhesive
59	2.3798	2.37	4.448061689	4.411502944	120.304	27.04638748	27.2705247	adhesive
60	2.3798	2.37	4.448061689	4.411502944	135.246	30.40560349	30.657579	adhesive
Average	2.3798	2.365166667	4.448061689	4.39375949	117.0307667	26.3105089	26.59661319	
SD	8.95674E-16	0.017319693	8.95674E-16	0.063914468	24.84249582	5.585016027	5.433339227	