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BONDS AND CONTACT ANGLES PRODUCED WITH SURFACE ALTERATIONS TO LITHIUM DISILICATE

by

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A THESIS

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MASTER OF SCIENCE - DENTISTRY

ABSTRACT

The success of ceramic restorations depends upon factors like the composite resin cement, the adhesive, cementation procedure and the substrate. With the introduction of newer ceramic and adhesive systems the factors that contribute to the most durable bond strength remains unclear.

The objective of the study was to measure 24 hour and thermocycled shear bond strength of a composite to lithium disilicate glass ceramic with a universal single bottle adhesive. A combination of surface treatments of hydrofluoric acid, silane, salivary contamination and subsequent cleaning were also evaluated. Blocks of lithium disilicate (e.max CAD) were sectioned, polished with a rotational polishing device using a series of SiC disks and finished with 0.5µ Al_2O_3 slurry. All specimens were cleaned in an ultrasonic cleaner and were examined to ensure uniform surface finish.

Surface treatments were done with concentrations of hydrofluoric acid and silane in various combinations followed by a bonding agent, according to the manufacturer’s protocols. A cylinder of composite of diameter (1.5mm) was bonded to the cured adhesive and specimens were stored for 24 hours.

In the next part of the study; saliva, collected from a single participant (2hrs postprandial), was pipetted onto the etched and silanated surfaces. Additionally some surfaces were cleaned using reagent alcohol or 35% phosphoric acid and the bonding agent applied, cured and composite cylinders bonded.

For both the studies, the specimens were tested at 24 hours after bonding and the second group thermocycled for 10,000 cycles (5-50°C/15 sec dwell time) and debonded.

For debonding the specimens were subjected to shear loading until failure using a universal testing machine and the shear bond strength calculated from the peak failure load. Contact angle measurements and scanning electron microscopy were used to analyze the effects of the treatments on the specimen surfaces.

Data were analyzed with ANOVA and Tukey/Kramer post-hoc tests (p=0.005). Data were presented as estimated marginal means (least-square means).

Keywords: lithium disilicate, adhesive, silane, hydrofluoric acid, shear bond strength

DEDICATION

I dedicate this work to my parents for their immeasurable support and faith in my abilities. I also dedicate my work to my faculty and peers for their guidance, their valuable input to help complete the study and encouragement through the whole experience.

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I wish to thank Dr. John O. Burgess, Chair of my graduate committee without his vision and guidance, this work could not have been completed. I thank him for his immense patience, motivation and extraordinary insight that made my research possible.

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LIST OF ABBREVIATIONS

1 SBS - Shear bond strength

2 SBU - Scotchbond Universal

3 C – Celsius

4 ANOVA- Analysis of Variance

5 SEM – Scanning electron microscope

NULL HYPOTHESIS AND AIMS

When composite is bonded to lithium disilicate using Scotchbond Universal, no significant difference in the Shear bond strength will be produced by HF etching, adjuvant silane application (coats and heat), thermocycling and salivary contamination with and without cleaning.

AIMS:

- To measure the shear bond strength (SBS) of composite to lithium disilicate treated with Scotchbond Universal.
- To measure the SBS of composite to lithium disilicate when treated with Scotchbond Universal:

  - With or without HF etching
  - Adjuvant silane application
  - Heating silane
  - Salivary contamination and contamination cleaning protocols

- At :

24 hours

or

10,000 thermocycles

INTRODUCTION

Restorative dentistry and dental materials have progressed from replacing tooth structure lost by disease and trauma to materials which not only meet form and function but are indistinguishable from the surrounding tooth

Historical perspective:

The use of porcelain in dentistry spanning around 200 years, has now become an integral part of most restorative treatment modalities.

In 1723, Pierre Fauchard first described the enameling of metal denture bases. An apothecary, Alexis Duchateau, with assistance from Parisian dentist Nicholas Dubois de Che´mant fabricated the first ceramic complete denture by 1774. In 1808 another Parisian dentist, Giuseppangel Fonzi, significantly improved the versatility of ceramics by firing individual denture teeth, each containing a platinum pin. This invention allowed teeth to be fixed to metal framework. Dr. Charles H. Land was a pioneer in ceramic materials and introduced porcelain jacket crown construction by 1889. Later developments included the use of vacuum firing to reduce porosities and varying compositions of ceramic (1). Feldspathic porcelain first introduced in 1903 by Land, provided excellent esthetics and biocompatibility along with resistance to compressive forces. But it exhibited lower tensile strength leading to fracture (2). McLean and Hughes (3) in 1965, introduced a technique to strengthen conventional feldspathic porcelain with aluminous porcelain. By adding glass, the optical quality was improved, however the high alumina crystals content led to opacity. The first dental glass ceramic which achieved good esthetic value was a magnesium silicate glass ceramic introduced by Dicor (Dentsply, USA), in 1984 (4). A glass ceramic has a crystalline phase with a regular arrangement of atoms in a lattice and the amorphous phase lacks the long range arrangement of atoms in a regular manner. They too had modest survival rate in clinical situations and were discontinued (5, 6).

Different types of glass-ceramics and ceramics have been developed to answer esthetic and functional demands. Glass-ceramics are particularly suitable for fabricating inlays, crowns and small bridges, as these materials achieve good esthetic results (2).High-strength ceramics are preferred in situations where the material is exposed to high masticatory forces. A well designed and fabricated ceramic crown is often indistinguishable from the adjacent nature tooth. Although commonly used to replace decayed tooth structure, the esthetic ceramic material is also used to cover pathological conditions of the enamel and dentin such as unsightly stains, malformations of the teeth, or improper calcification. They are used to close spaces (diastema) existing between teeth and as enamel/dentin bonded partial or total coverage without macro-retention.

Leucite reinforced ceramics:

IPS Empress (Ivoclar Vivadent), introduced in 1991, used hot pressing and dispersion strengthening. It was a leucite reinforced glass ceramic with a flexural strength of 182 MPa. Leucite is potassium alumino silicate formed by heating Potassium feldspar to high temperatures with controlled crystallization (7). Initially it was used as a veneering material due to its improved strength and high coefficient of thermal expansions compared to glass ceramics (8). Hot pressing used in fabricating IPS Empress restorations reduced shrinkage and flaws resulting in higher flexural strength. But increased fracture rates in the posterior region have restricted its use to anterior FPDs (9).

Lithium disilicate glass ceramic – Empress 2 and e.max:

Empress 2 (Ivoclar Vivadent)a lithium disilicate-reinforced glass – ceramic was introduced in 1998 processed by hot pressing an ingot of the material into a mold. Empress 2 produced flexure strength of 350 MPa. Empress 2 consisted of an alumino-silicate glass containing lithium oxide in the form of needle-like crystals. The shape and volume of the crystals contribute to the increased flexural strength and fracture toughness compared to its predecessors (9). The low refractive index of the lithium-disilicate crystals made the material translucent and allowed its use for full-contour restorations. Initial clinical data for anterior restorations were excellent with this material (10).

In 2005, an improved pressed ceramic material called IPS e.max Press (Ivoclar-Vivadent) was introduced. The IPS e.max Press material consisted of a lithium disilicate (2 SiO-Li_2O) pressed glass ceramic,similar to Empress 2 but with improved mechanical properties. Empress 2 was produced by using a different firing process coupled with different a microstructure and concentration of lithium disilicate. Mechanical properties are the same, 400MPa flexural strength and Fracture toughness of 2.5 on both materials. IPS e. max Press frameworks were veneered with a new type of sintered fluoroapatite porcelain. In comparison with IPS Empress 2, IPS e. max Press exhibited substantially improved physical properties and greater translucency (9).

The zirconia core (900-1000 MPa flexural strength) is veneered with a ceramic material with a flexural strength of 80 to 110 MPa (11). The veneering material tends to chip or fracture and its survival depends on the ability to create a strong bond interface between the oxide-ceramic and silica-based glass ceramic, a bond that is not difficult to create (12). However, the quality of the bond interface can vary substantially because of cleanliness of the bond surface, furnace calibration, user experience, and other issues (12).

Monolithic glass-ceramic structures like lithium disilicate can provide exceptional esthetics without a veneering ceramic. This increases the structural integrity by eliminating the veneered ceramic and the required bond interface (13).The relative strength of the available glass-ceramic material has traditionally been the disadvantage of the veneering ceramics. Because of their moderate flexural strength, they are limited to single-tooth restorations and adhesive bonding techniques are needed for load sharing with the underlying tooth (13). This has been resolved through the development of highly esthetic lithium-disilicate glass ceramic materials.

IPS e.max press and CAD:

IPS e.max (Ivoclar Vivadent) lithium disilicate is composed of quartz, lithium dioxide, phosphor oxide, alumina, potassium oxide, and other components. Overall, this composition yields a highly thermal shock resistant glass ceramic due to the low thermal expansion. This type of resistant glass ceramic can be processed using either well-known lost-wax hot pressing techniques or CAD/CAM milling procedures.

The pressable lithium disilicate (IPS e.max Press [Ivoclar Vivadent]) is produced according to a unique bulk casting production process to create ingots. This involves a continuous manufacturing process based on glass technology (melting, cooling, simultaneous nucleation and growth of crystals) that is constantly optimized in order to prevent the formation of defects (eg, pores, pigments). The microstructure of the pressable lithium disilicate material consists of approximately 70% needle-like lithium disilicate crystals embedded in a glassy matrix. These crystals measure approximately 3 to 6 μm in length (fig:1).

(Fig 1 and 2 and tables 1 and 2 (Ivoclar Vivadent website)

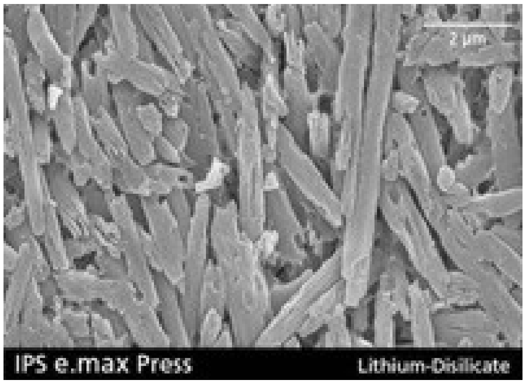


Fig.1. IPS e.max PRESS (Ivoclar Vivadent) lithium disilicate.

Table1. Properties of IPS e.max Press.

CTE (100-400°C [10^{-6}/K]	10.2
CTE (100-500°C) [10^{-6}/K]	10.5
Flexural strength (biaxial) [MPa]	400
Fracture toughness [MPa $m^{0.5}$]	2.75
Modulus of elasticity [GPa]	95
Vickers hardness [MPa]	5,800
Chemical resistance [$\mu g/cm^2$	40
Press temperature EP 600 [°C]	915 to 920

Polyvalent ions that are dissolved in the glass provide the desired color to the lithium disilicate material (14). These color-controlling ions are homogeneously distributed in the single-phase material, thereby eliminating color-pigment imperfections in the microstructure. Machineable lithium disilicate blocks are manufactured using a similar process, but an “intermediate” crystallization is achieved to ensure that the blocks can be milled efficiently in a blue, translucent state. The intermediate crystallization process forms lithium metasilicate crystals, which are responsible for the material’s processing properties, machineability and good edge stability. After milling the restorations are sintered to achieve their final crystallized state and high strength. The microstructure of intermediate crystallized IPS e.max CAD lithium disilicate consists of 40% platelet-shaped lithium metasilicate crystals embedded in a glassy phase (Figure 2). These crystals range in length from 0.2 to 1.0 µm. Post crystallization microstructure of IPS e.max CAD lithium disilicate material consists of 70% fine-grain lithium disilicate crystals embedded in a glassy matrix.

Similar to the pressable lithium disilicate, the millable IPS e.max CAD blocks are colored using coloring ions. However, the coloring elements are in a different oxidation state during the intermediate phase than in the fully crystallized state. As a result, the lithium disilicate exhibits a blue color. The material achieves its desired tooth color and opacity when lithium metasilicate is transformed into lithium disilicate during the post milling firing (15, 16, 17).

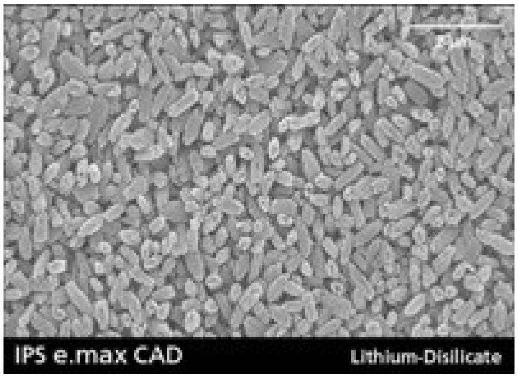


Fig 2. IPS e.max CAD (Ivoclar Vivadent) lithium disilicate.

Table 2. Properties of IPS e.max CAD.

CTE (100-400°C [10^{-6}/K]	10.2
CTE (100-500°C) [10^{-6}/K]	10.5
Flexible strength (biaxial) [MPa]	360
Fracture toughness [MPa $m^{0.5}$	2.25
Modulus of elasticity [GPa]	95
Vickers hardness [MPa]	5,800
Chemical solubility [µg/cm^2]	40
Crystallization temperature [°C]	840 to 850

Ceramic veneers:

Among all laminate veneer options, ceramic veneers have the longest history, with the first veneer applied in 1937 in the film industry for cosmetic reasons (18). When it became possible to etch enamel with phosphoric acid (19) and condition the intaglio surfaces of the ceramics with hydrofluoric acid followed by silanization (20, 21) bonding ceramic laminates to teeth became a clinical reality.

Ceramics have higher fracture toughness and color stability and are often chosen as veneering materials due to these properties (22, 23).

In spite of the success of ceramic veneers, clinical studies report failures such as debonding, fracture, chipping, marginal defects or marginal leakage (24, 25, 26, 27).

Due to the progress in adhesive technologies, conservative veneers can be bonded to enamel and dentin with minimal or no tooth preparation. This enables clinicians to preserve the enamel that protects the dentin and the pulp (27).

Hydrofluoric acid etching:

The intagilo surface of the ceramic restoration must be prepared to optimize the micromechanical bond between the ceramic and the resin. Porcelain laminate veneers and dentin bonded crowns rely on the bond created between the porcelain and resin cement to survive the rigors of the oral environment (36).Pre-cementation ceramic surface modification increases the surface area available for bonding by creating undercuts to increase the bond to the resin luting cement.

In 1983 Horn suggested using hydrofluoric acid (HF) to etch porcelain laminate veneers (37) and subsequent examination of the etched porcelain surfaces demonstrated that different porcelain phases dissolve preferentially depending on the porcelain composition thereby creating a retentive surface more conducive to bonding (38). HF acid etching can increase the strength of glasses by removing or stabilizing surface defects (39). This statement makes no sense to me the greater the porosity the weaker the material (ceramic).

The reaction kinetics between HF acid and the ceramic are controlled by HF acid etching time and concentration, temperature and the physical structure of the porcelain substrate (40).

Bottino et al (41) reported changes in ceramic surface topography after different surface conditioning methods such as HF acid etching and alumina abrasion. SEM images revealed that the ceramic surfaces of a high alumina ceramic (In-Ceram Alumina, Vita-Zahnfabrik) and a glass-based ceramic (Vitadur Alpha, Vita-Zahnfabrik) following air-abrasion with aluminum oxide presented sharp edges.

Ayad et al.(42) compared the effect of HF acid etching, orthophosphoric acid etching and aluminum oxide particle -abrasion on the surface roughness and bond strength of a leucite-containing ceramic (IPS Empress, Ivoclar-Vivadent). Etching with HF acid generated irregularities and porosities that produced the highest bond strength, while the airborne particle abrasion with alumina did not create a retentive ceramic profile, although it was substantially rougher.

Similarly, Torres et al (43) stated the highest micro-shear bond strength of a lithium disilicate ceramic (IPS Empress 2, Ivoclar-Vivadent) was obtained when 9.5% HF acid treatment was followed by 50μ airborne particle abrasion treatment. The SEM micrographs revealed that the HF acid etching affected the surface of IPS Empress 2 (Ivoclar-Vivadent) by generating elongated crystals with shallow irregularities.

A recent study by Naves et al (44) evaluated the effect of 10% HF acid with etching times of 10,20,40,60 and 120 seconds on the surface morphology and bond strength of a leucite-containing ceramic (Empress Esthetic, Ivoclar-Vivadent) with or without unfilled resin application. All the ceramic surfaces were treated with silane following etching with HF acid. The results showed that the resin bond strength to ceramic decreased with increased HF time of 60 and 120 seconds when only silane was used but gave similar results for all etching times when unfilled resin was applied. More importantly, the ceramic specimens treated with silane and unfilled resin provided higher bond strength than specimens treated with silane alone.

Silanization:

The bond between composite and ceramic relies on the mechanical retention of ceramic surfaces due to lack of chemical interaction (45-47). Silane is a coupling agent that provides a bridge between dental composites and dental ceramics (48-51). Newburg and Pameijer (1978) pioneered the use of silane in dentistry to repair broken or fractured porcelain (52). Since then, numerous studies have reported that silane significantly reduced microleakage while increasing bond strength (53-55).

Silane acts as an adhesion-promoting interphase between organic and inorganic materials. Along with surface area, available undercuts and surface energy of the substrate, silane increases the bond of composite to ceramic (56-60) created by micromechanical retention formed by HF etching.

Silane used in ceramic repair consists of an organofunctional group (Y) that can polymerize with methacrylate-based dental composite. It can also polymerize with hydrolysable groups (X) in compound **Y-R-Si-X3**, where R is a chain of hydrocarbons and Si is silicon (61).

The silane most commonly applied in dental laboratories and chairside procedures is a monofunctional–methacryloxypropyltrimethoxysilane (3-trimethoxysilylpropyl methacrylate [MPS]). A prehydrolyzed MPS, usually less than 2% in weight of a water-ethanol solution, is adjusted to a pH of 4 to 5 with acetic acid (48).

For the chemical interaction to begin, the X functional group, such as methoxy [-Si-(OCH3)3] is hydrolyzed by the presence of moisture, producing methanol and reactive silanol groups [-Si-(OH)3][16]. The silanol groups produced above condense with the silanol groups of the ceramic surface to form a cross-linked siloxane bond (Si-O-Si)(61). The organofunctional groups copolymerize with the adhesive resin to produce chemical bonds.

$$\mathbf{R'{-}Si(OR)3 + 3H2O \rightarrow R'{-}Si(OH)3 + 3R{-}OH}$$

If excess silane is applied to the ceramic surface, the compound can separate into 3 layers of distinct physical and chemical differences (49). The innermost layer is cross-linked and provides a strong siloxane bond, whereas the outermost and intermediate layers are only physically adsorbed and could readily be washed away by organic solvents or water. In order to prevent layer separation and loss of chemical adhesion the amount of silane applied should be controlled based (49).

Roulet et al (1995) reported that separated layers of silane could be consolidated through heat treatment at 100^0C without an intermediate layer and increase the bond of composite to ceramic (62). This heat treatment also evaporated solvent and volatile reaction products formed during condensation of the silanol groups. It was hypothesized that evaporation of alcohol or acetic acid may increase the density of bond sites available for silane solution to react with ceramic.
But the high-temperature heat treatment of silane is not feasible for chairside ceramic repair.

Chen el at (2004) stated a stream of warm air assisted evaporation of solvents in the silane and its reaction products resulting in increased bond strengths to ceramic (63).

Matinlinna et al (2006) noted differences in pH of solvent systems and application of silane based on time and pH. They concluded that dental silane provide different bond strengths when applied between a luting cement and silica coated titanium surfaces (64). This layer of silica is similar to that found on glass and may indicate the differences in silane activity.

A recent review by Lung and Matinlinna (2012) also showed there were wide variations in composition of commercially available silanes (65).

Table 3 : Examples of commercial silanes used in dentistry. - Lung and Matinlinna (2012)						
Name	Manufacturer	Effective silane (%)	pH	Solution and concentration (%)	Indication	Date of information
Bisco Porcelain Primer	Bisco, Schaumburg, IL, USA	‘A silane’, >1	5.9	‘Alcohol > 45, Acetone > 45’	Porcelain, composite	April-10
Bisco Bis Silane	Bisco, Schaumburg, IL, USA	‘A silane’, 1–10	4	‘Alcohol 30–95’	Porcelain, composite	Noveber-07
Cimara Silane Coupling agent	VOCO, Cuxhaven, Germany	‘Silane’, N/A	5.5	2-Propanol 50–100	Repair of ceramics, metals	January-11
Clearfil Ceramic Primer	Kuraray, Osaka, Japan	MPS, <5, MDP N/A	3	Ethanol > 80	Porcelain, ceramics, resin-based materials	October-08
Clearfil Porcelain Bond Activator	Kuraray, Osaka, Japan	MPS 40–60	2.3	Hydrophobic aromatic dimethacrylate	Porcelain	October-08
ESPE Sil	ESPE Dental, Seefeld, Germany	‘MPS’, <3	4.5	Ethanol, > 97 Methyl ethyl ketone < 2	Metals, ceramics, composites	September-10
ESPE RelyX Ceramic Primer	3M ESPE, St. Paul, MN, USA	‘MPS’, <2	4.6	Ethanol, 70–80 Water, 20–30	Ceramics, Porcelain, metals	February-10
Monobond-S	Ivoclar Vivadent, Schaan, Liechtenstein	MPS, <2.5	4	Ethanol, 50–100	Porcelain, composite	January-11
Pulpdent Silane Bond Enhancer	Pulpdent, Watertown, MN, USA	A silane, N/A	6.3	Ethanol, 92 Acetone, 7	Porcelain, composites	January-08
Silicoup A and B (a two bottle system)	Heraeus Kulzer, Hanau, Germany	N/A, MPS (Silicoup B)	N/A	Ethanol, 25–50 Ethylacetate, 25–50 Acetic acid, 5–10	N/A	August 2010
Ultradent Silane Ultradent Products,	South Jordan, UT, USA	MPS, 5–15	5.3	2-Propanol, 92	Porcelain, resin coupling agent	Jan-06
Vectris Wetting Agent Ivoclar Vivadent,	Schaan, Liechtenstein	MPS, 1	N/A	Ethanol, <52	Crowns, bridges	Jul-06
VITA Zahnfabrik VITA SIL, Bad	Säckingen, Germany	MPS, <2.5	N/A	Ethanol, 25–50	Ceramic and resin composite	Apr-08

Contamination of intaglio surfaces:

Schalkwyk et al (2003) said that resin–ceramic bonds obtained in strictly controlled laboratory conditions might be compromised in clinical situations due to contamination from saliva and blood, leading to a significantly reduced bond. During the try-in procedure of any restoration in the oral situation, the contamination of the inner surface by saliva and blood is very difficult to avoid (66). Saliva contamination is frequently a reason for decreased resin bond strength of porcelain veneers intraorally (66, 67).

Cleaning a contaminated ceramic surface before adhesive cementation is crucial and the use of 37% phophoric acid and alcohol as cleaner agents were effective according to a study by Klosa et al (2009).

It is crucial to follow instructions for use of modern adhesive composite resins which recommend phosphoric acid gel treatment to remove contaminants from the inner surface of restorations (Kuraray Medical, Inc., Osaka, Japan).

Universal adhesive system:

Adhesion to tooth and metals, metal oxides (alumina and zirconia), glass ceramics (feldspathic, leucite-reinforced porcelains, lithium disilicate) and gold alloys has been the ‘holy grail’ of adhesive systems. Until recently, clinicians had to use a variety of materials to achieve universal bonding to multiple substrates. Scotchbond Universal contains a variety of components to enhance bonding to multiple substrates.

Table 4: Active components in Scotchbond™ Universal Adhesive
MDP Phosphate Monomer
Dimethacrylate resins
HEMA
Vitrebond™ Copolymer
Filler
Ethanol
Water
Initiators
Silane

Silane added to SBU, could behave as a chemical coupler forming covalent bonds with acid etchable glass silicas (feldspathic, leucite-reinforced, or lithium disilicates), resin nanoceramics, and to resin cements. Another component of the adhesive is Methacryloyloxydecyl dihydrogen phosphate (MDP), an acidic self-etching monomer with a phosphate ester group, which forms a chemical bond to metals, alloys and metal oxide ceramics such as zirconia and alumina.

When composite is bonded to lithium disilicate using Scotchbond Universal, no significant difference in the Shear bond strength will be produced by HF etching, adjuvant silane application (coats and heat), thermocycling and salivary contamination with and without cleaning.

MATERIALS AND METHODS

Table 5: Materials

Material	Manufacturer	Lot No	Expiration
IPS e.max CAD	Ivoclar Vivadent	-	-
Scotchbond Universal	3M ESPE	472585	2014-03
IPS Ceramic Etching gel (5 % Hydrofluoric acid)	Ivoclar Vivadent	R05638	2015-07
Porcelain Etchant (9.5% Hydrofluoric acid)	Bisco	1200006564	2015-04
RelyX Ceramic Primer(silane)	3M ESPE	N371615	2015-02
Monobond Plus(silane)	Ivoclar Vivadent	R26662	2014-02
Elipar S10 (1200 mW/cm^2)	3M ESPE		-
Z-100 (A2)	3M ESPE	N352896	2014-11

Table 6: Manufacturers recommendations	
Material	Application
Scotchbond Universal	1. Material dispensed into mixing well 2. Apply adhesive to the prepared surface with a microbrush and rub in for 20 seconds 3. Gentle air drying of adhesive for 5 seconds to evaporate solvent. 4. Light cure for 10 seconds
RelyX Ceramic Primer (Silane)	1. Material dispensed into mixing well 2. Silane applied with a microbrush over the prepared surface for 20 seconds with agitation 3. Gentle air drying of the surface done till evaporation is complete
Monobond Plus (Silane)	1. Material dispensed into mixing well 2. Silane applied with a microbrush over the prepared surface for 60 seconds with agitation 3. Gentle air drying of the surface till evaporation is complete
IPS Ceramic Etching gel (5 % Hydrofluoric Acid)	1. Material dispensed into mixing well 2. Application of Etching gel onto prepared surface and agitation for 20 seconds 3. Wash thoroughly for 10 seconds to remove all etchant.
Adper Scotchbond Etchant (35% Phosphoric acid gel)	1. Material dispensed into mixing well 2. Application of Etching gel onto prepared surface and agitation for 15 seconds 3. Wash thoroughly for 10 seconds to remove all etchant.
Bisco Porcelain Etchant (9.5 % Hydrofluoric Acid)	1. Material dispensed into mixing well 2. Application of Etching gel onto prepared surface and agitation for 60 seconds 3. Wash thoroughly for 10 seconds to remove all etchant.

Effect of Surface treatment – Study 1

Specimen Preparation:

Lithium Disilicate blocks were sectioned into 5 mm thick rectangular coupons using a low-speed cutting device (Isomet, Buehler Ltd, IL, USA) and sintered (Programat CS, 3MESPE). The sections were polished with 180 and 320- grit SiC disks, 4 minutes per grit (3MESPE) on a rotational polishing device (Buehler Ltd, IL, USA). Sections were rotated 90º every 1 minute to produce a uniformly smooth surface. The specimens were finished with 0.5μ Al_2O_3 slurry rotating the specimens 90° every 30 seconds for a total of 2 minutes. All specimens were subjected to ultrasonic cleaning in distilled water for 15 seconds. The polishing and finishing protocol was repeated for specimens with visually observable surface imperfections.

Fig 3: Lithium meta and disilicate

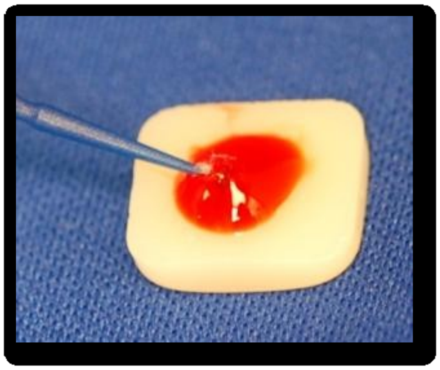
Surface Pretreatment and Bonding agent Application:

The specimens were divided into groups (n=20) based on surface pretreatments (Table.1), such as different concentrations of HF etching gels and varying chemistries of silane or no pretreatment at all. Following various pretreatments, ceramic surfaces of all groups were treated with Scotchbond Universal (SBU/20sec) and cured (10 sec) (Elipar S10/ 3M ESPE/ 1200 mW/cm^2).

Hydrofluoric acid etching:

For the etching procedure using 5% HF, a drop of etchant was evenly spread for 20 seconds over the bonding surface of the ceramic using a microbrush. The surfaces were cleaned with water from the 3 way syringe for 10 seconds. The 9.5% HF was applied for 60 seconds and cleaned with water from the 3 way syringe for 10 seconds.

Fig 4: Hydrofluoric acid



Silane Application:

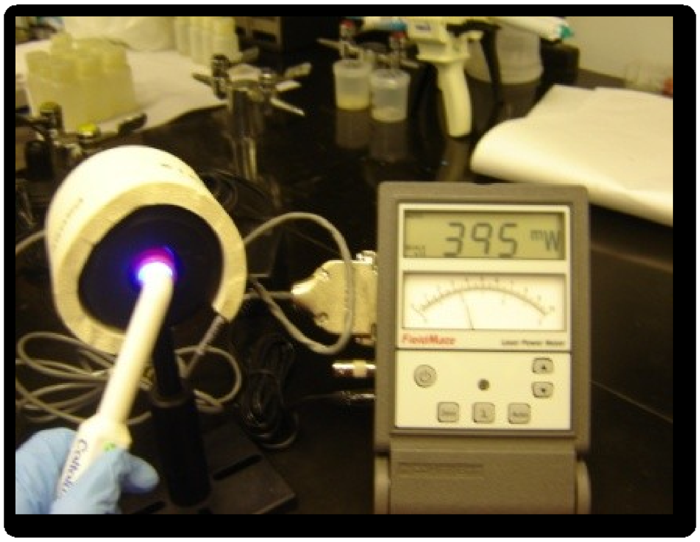
RelyX Ceramic Primer was applied for 20 seconds using a microbrush and air dried for 10 seconds using an air syringe. The Monobond Plus had an application time of 60 seconds followed by air drying for 10 seconds.

Scotchbond Universal Application:

The Scotchbond Universal adhesive was applied onto the bonding/pretreated ceramic surface for 20 seconds using a microbrush followed by air thinning for 10 seconds using an air syringe. The adhesive was cured for 10 seconds with the curing light (Elipar S10/ 3M ESPE/ 1200 mW/cm^2) less than 3 mm from the ceramic surface.

Curing light output was tested before the start and after finishing every 10 specimens to check for uniformity of light output using a irradiance measuring device know as a radiometer. (Power Max, Molectron Detector, Inc., Portland, OR).

Fig 5: Radiometer



Composite Bonding:

A 5 mm long, transparent, hollow plastic tube with an internal diameter of 1.5 mm was filled with Z100 composite (A2). Following pretreatment and SBU application, the composite filled tube was placed on the ceramic surface and light cured (Elipar S10/ 3M ESPE/ 1200 mW/cm^2) on four sides for 20 seconds each.

An excess of composite was extruded out of the tube before placement to ensure a uniform, void-free contact of the composite cylinder to ceramic surface.

Fig 6: Bonded specimen

Specimen Storage and Artificial Accelerated Aging

After storage in deionized water for 24 hours at 37°C, the bonded sections were divided into two groups. The first group was tested after the 24 hours storage while the second group was tested after thermocycled for 10,000 cycles (6 days between 5-50°C/ 15 sec dwell time).

Bond strength Testing

For shear bond strength testing the specimens were mounted onto a steel fixture and subjected to shear loading until failure using a universal testing machine

Fig 7: Shear bond test

Fig 8: Instron 5565

(Instron 5565, MA, USA) at a crosshead speed of 1 mm/min. The peak failure load was used to calculate the shear bond strength (MPa).

SEM Imaging

Photomicrographs of randomly selected specimens from each tested group were sputter coated and imaged under a SEM for a mixed failure fracture pattern characteristic of shear testing. The surfaces of etched e.max using 5%HF for 20 sec and 9.5% HF for 60 sec were sputter coated and viewed.

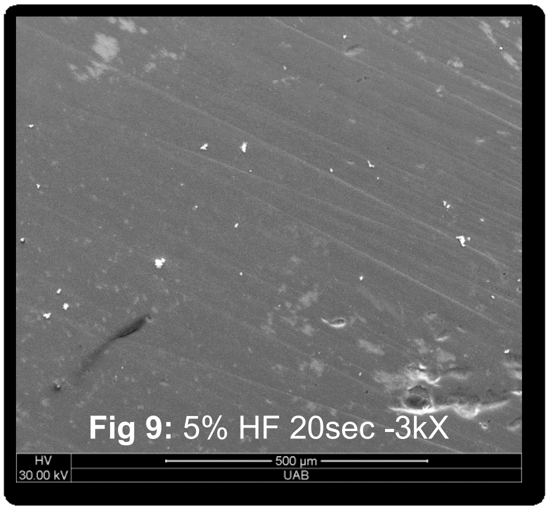


Fig 9: 5% HF 20sec -3kX

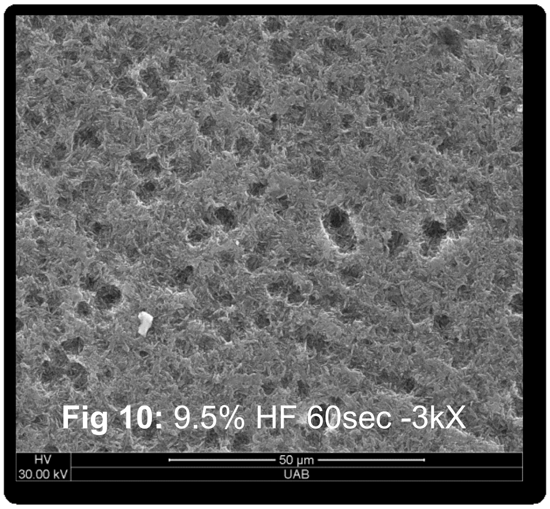


Fig 10: 9.5% HF 60sec -3kX

,

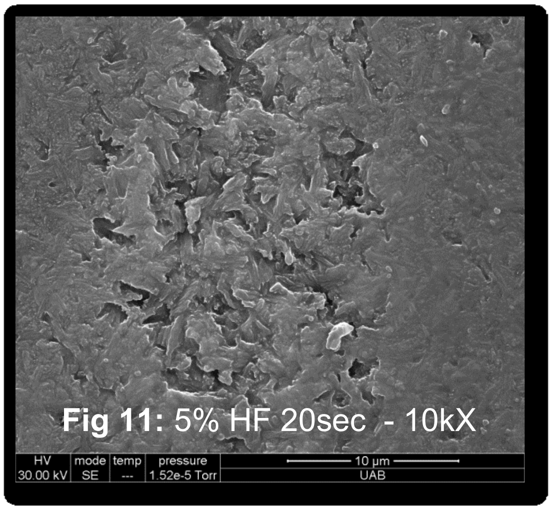


Fig 11: 5% HF 20sec - 10kX

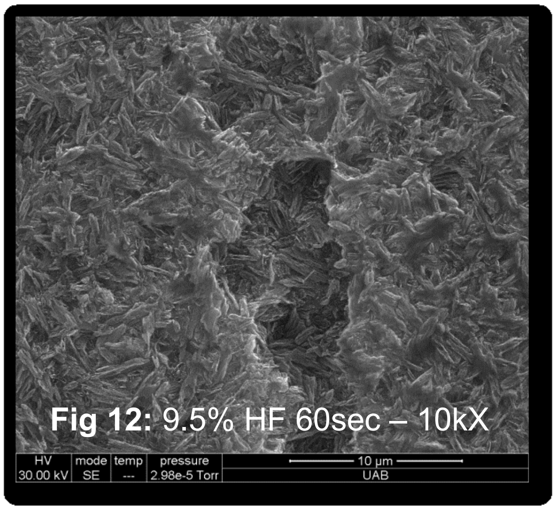


Fig 12: 9.5% HF 60sec – 10kX

Statistics:

A 3-way ANOVA and Tukey-Kramer t-test was used to analyze the differences between the bond strength values of the groups tested.

Salivary contamination and Cleaning – Study 2

Specimen Preparation:

Lithium Disilicate blocks were sectioned into 5 mm thick squares using a low-speed cutting device (Isomet, Buehler Ltd, IL, USA) and sintered (Programat CS, 3M ESPE). The sections were polished with 180 and 320- grit SiC disks, 4 minutes per grit (3MESPE) on a rotational polishing device (Buehler Ltd, IL, USA). Sections were rotated 90º every 1 minute so that uniformly smooth surface was obtained. The specimens were finished with 0.5µ Al_2O_3 slurry rotating the specimens 90° every 30 seconds for a total of 2 minutes. All specimens were subjected to ultrasonic cleaning in distilled water for 15 seconds. The polishing and finishing protocol was repeated for specimens with visually observable surface imperfections.

Fig 13: Lithium Mono and Di silicate

Surface Pretreatment:

The specimens were divided into 5 groups of 20 (Table 7). The surface was pretreated with a 5% HF etching gel (IPS Ceramic Etching gel) followed by silane (RelyX Ceramic Primer) application, according to manufacturer recommendations (table.2).

Table 7: Groups and treatments in study 1

Pretreatment			Cleaning		Bonding Agent	Groups
5% HF	Silane	-	-	-	SBU	Group-1 (Control)
5% HF	-	Saliva	-	-	SBU	Group-2
5% HF	Silane	Saliva	-	-	SBU	Group-3
5% HF	Silane	Saliva	35% Phosphoric acid	Silane	SBU	Group-4
5% HF	Silane	Saliva	Alcohol	Silane	SBU	Group-5

Hydrofluoric acid etching:

For the etching procedure using 5% HF, a drop of etchant was evenly spread for 20 seconds over the bonding surface of the ceramic using a microbrush. The surfaces were cleaned with water from the 3 way syringe for 10 seconds.

Silane Application:

RelyX ceramic Primer was applied for 20 seconds with a micro-brush and air dried for 10 seconds with an air syringe.

Salivary contamination:

Unstimulated saliva was obtained from a single participant 2 hours after eating and stored in a sterile container till use. The saliva was pipetted (0.4 ml) at room temperature and spread onto the e.max ceramic surfaces using a microbrush. After 3 minutes of contact, an air syringe was used to dry (1 min) the saliva.

Scotchbond Universal Application:

The Scotchbond Universal adhesive was applied onto the bonding/pretreated ceramic surface for 20 seconds using a microbrush followed by air thinning for 10 seconds using an air syringe. The adhesive was cured for 10 seconds with the curing light (Elipar S10/ 3M ESPE/ 1200 mW/cm^2) using a device that positioned the curing light less than 3 mm from the ceramic surface.

Composite Bonding:

A 5 mm long, transparent, hollow plastic tube with an internal diameter of 1.5 mm was filled with Z100 composite (A2). Following pretreatment and SBU application, the composite filled tube was placed on the ceramic surface and light cured (Elipar S10/ 3M ESPE/ 1200 mW/cm^2) on four sides for 20 seconds each.

An excess of composite was extruded out of the tube before placement to ensure a uniform, void-free contact of the composite cylinder to ceramic surface.

Specimen Storage and Artificial Accelerated Aging:

For debonding, the specimens were mounted onto a steel fixture and subjected to shear loading until failure using a universal testing machine (Instron 5565, MA,USA) at a crosshead speed of 1 mm/min. The Shear bond strength was calculated from the peak failure load.

Fig 14: Shear bond test

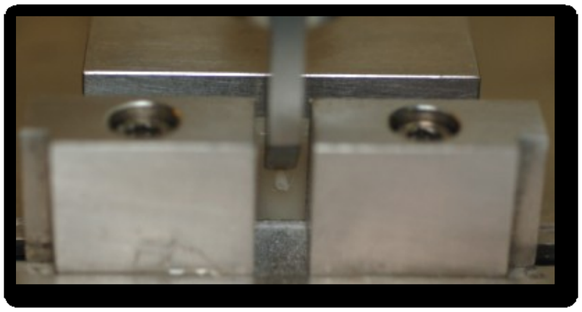


Fig 15: Instron 5565

Artificial accelerated aging through thermocycling was done by using a moving arm transporting the specimens between water baths thermostatically maintained at 5 and 50°C each. The specimens were alternated between the compartments after a dwell time of 15 seconds. Each cycle was completed after subjecting the specimens to both the compartments and specimens were subjected to a total of 10,000 thermocycles.

Contact Angle Measurements:

Contact angle measurement using dynamic sessile drop method with a goniometer was used to analyze the treated surfaces of specimens. The specimen to be tested was placed on a metal platform and the device leveled carefully (Fig 12). The camera was set at 40X (fine resolution) with a white background placed opposite the camera on the leveled stand. The resolution of the camera was adjusted to fine picture quality. After leveling the equipment, a micro pipette was filled with distilled water (3μl) and placed 3mm above the surface of the specimen using precise gridlines from the Keyence software. After the camera started recording followed by drop placement, the angle made by the distilled water with the specimen surface was measured at a 20 sec interval from the beginning of drop placement).

Data was analyzed with repeated measures ANOVA and Tukey/Kramer post hoc tests (p=.05)

Fig 16: Goniometer setup

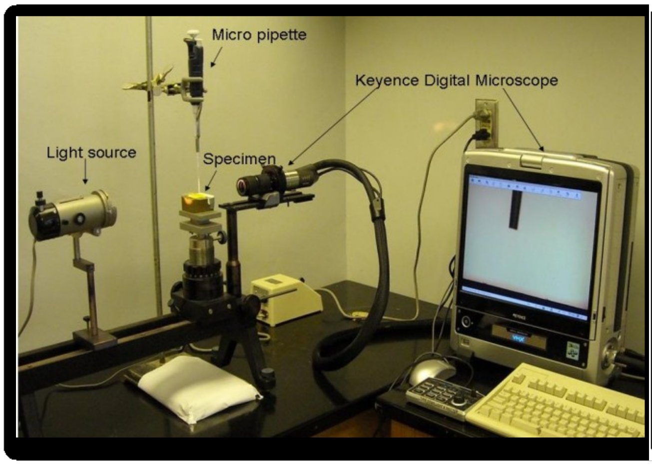
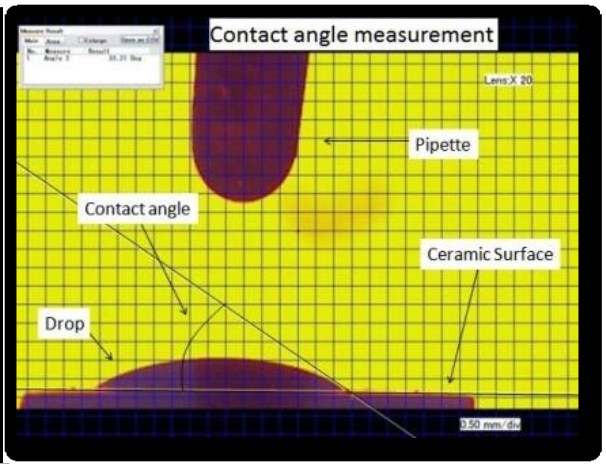


Fig 17: Contact angle measurement



Changes in the contact angle of the bonding agent after silane application and etching was conducted.

Surface Roughness Measurements:

The surface roughness (R_a) of the samples was analyzed using the Proscan 2000 (Scantron Industrial Products Ltd, Taunton, England) and tabulated.

Surface Dimensions Analyzed: 400 Steps X

: 40 steps Y

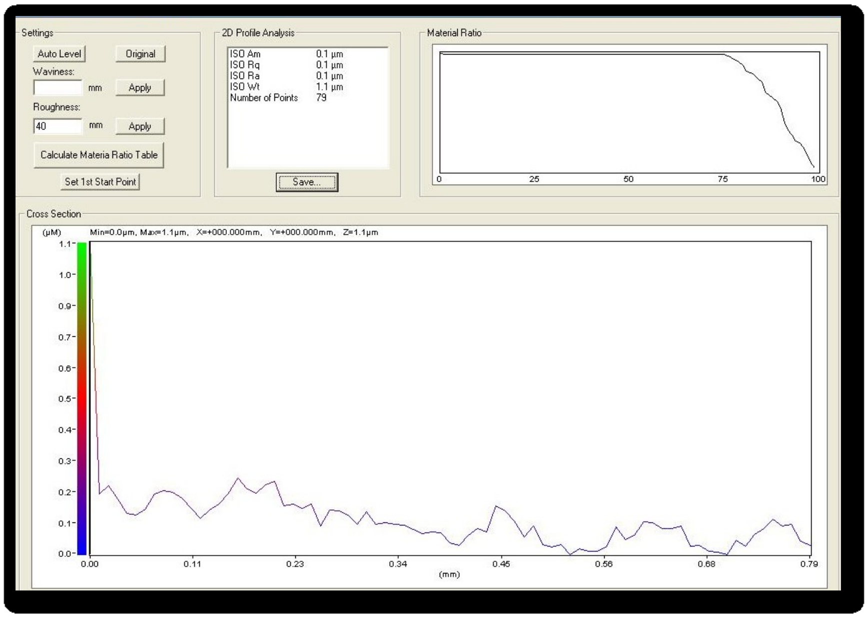
Roughness Filter Value: (Cut-off filter in mm / 2) / step size in mm = 40

Step Size: 0.01

Cut off filter: 0.8 mm

Table 8: R_a measurement	
Specimen	**Ra(μ)**
1	0.1
2	0.1
3	0.1
4	0.1
5	0.1
6	0.1
7	0.1
8	0.1
9	0.1
10	0.1

Fig 18: R_a measurement on Proscan



Waviness: mm

Roughness: 40 mm

2D Profile Analysis

```
ISO Am            0.1 µm
ISO Rq            0.1 µm
ISO Ra            0.1 µm
ISO Wt            1.1 µm
Number of Points  79
```

Min=0.0µm, Max=1.1µm, X=+000.000mm, Y=+000.000mm, Z=1.1µm

RESULTS

The analysis was divided into 2 sections as study -1 and study-2.

Study-1

The study design for study-1 was a three way by three way design and the analysis was done using 3-factorial ANOVA. A significant 3-way interaction was found. Those samples that had failed before testing were noted as zero values and were not included in the analysis.

The effects were designated as follows,

Group 1: No additional silane application
Group 2: Ceramic Primer application
Group 3: Monobond Plus application

Time 1: Testing done after 24 Hrs
Time 2: Testing done after 24 Hrs+ 10,000 thermocycles (6 days)

HF 0: No HF treatment
HF 5: 5% HF treatment at 20 seconds
HF 9.5: 9.5% HF treatment at 90 second

Descriptive statistics by group, time and HF:

Table 9: Descriptive statistics by group, time and HF

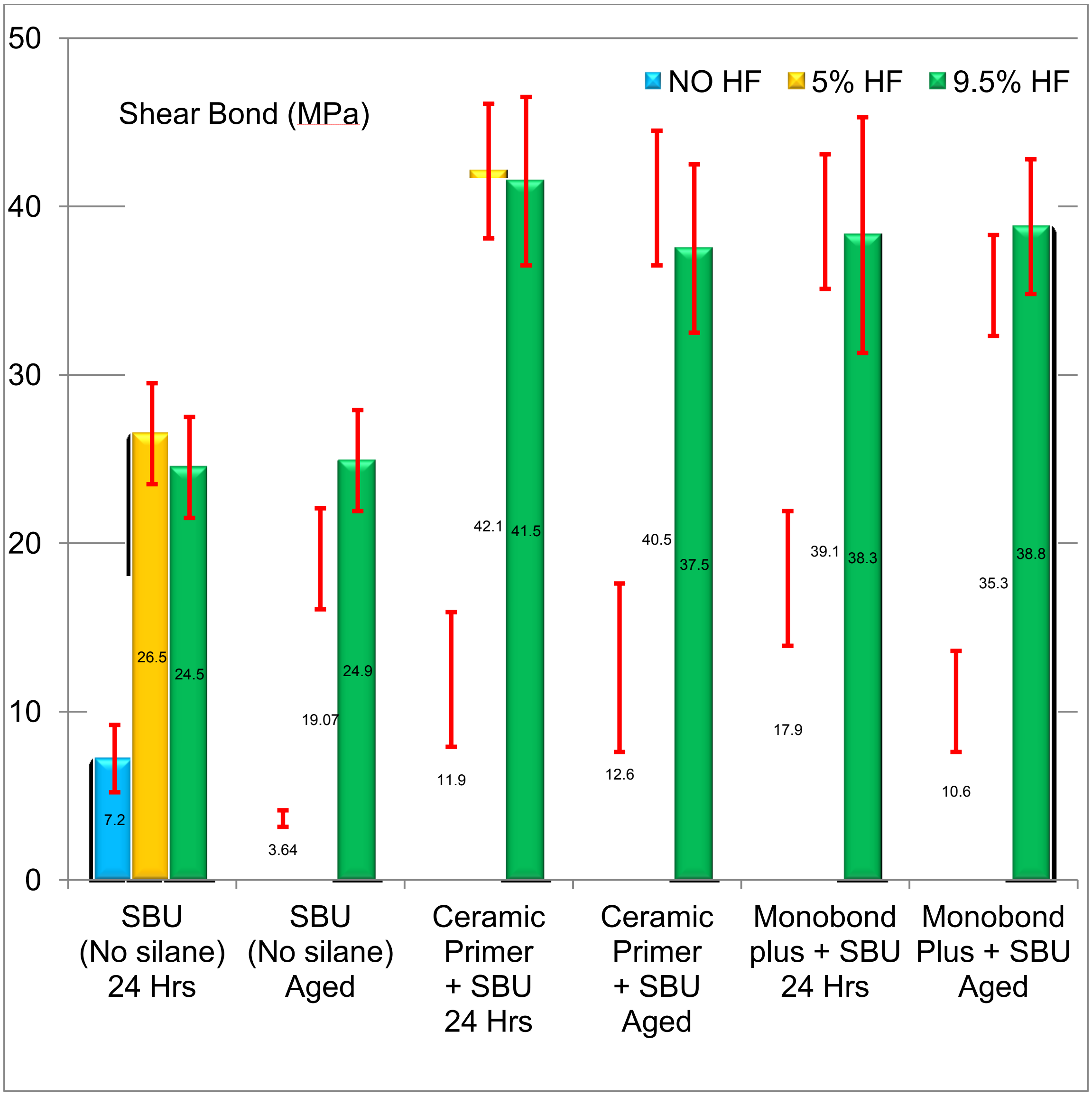
Silane	HF	TIme	Analysis Variable : Shear				
			N	Mean	Std Dev	Minimum	Maximum
1	1	1	10	7.1848800	2.0026396	4.3738000	11.1135000
1	5	1	10	26.4760200	2.8444001	22.8347000	32.6379000
1	9.5	1	10	24.3909200	3.2293621	19.7525000	29.6097000
1	0	2	5	3.6466160	0.4945231	2.8948000	4.1713100
1	5	2	10	19.0751500	3.0213905	12.7447000	23.4192000
1	9.5	2	10	24.9361670	2.6302517	21.7562000	30.0784200
2	0	1	10	11.9040200	3.8728373	7.6200000	21.3415000
2	5	1	9	42.1140444	4.0443537	38.3855000	51.7416000
2	9.5	1	10	41.5015200	4.7140528	34.9240000	47.7409000
2	0	2	10	12.5544400	4.9785311	7.4733000	23.0781000
2	5	2	10	40.4737820	4.1658962	31.8322700	46.9366100
2	9.5	2	10	37.4987200	5.1227922	29.9592000	46.3122000
3	0	1	8	17.8896975	3.7357737	11.9229700	23.3651900
3	5	1	8	39.0792750	3.7507417	33.7926000	45.5674000
3	9.5	1	10	38.3319300	6.5827420	28.2580000	51.6248000
3	0	2	10	10.5671230	3.3983589	5.6635500	15.6082500
3	5	2	10	35.2637740	3.4006056	29.2963800	39.6609600
3	9.5	2	10	38.8771800	4.9659396	30.3150000	45.5866000

Least square means adjustment for Multiple Comparisions/Tukey-Kramer:

Class Level Information		
Class	**Levels**	**Values**
group	3	1 2 3
time	2	1 2
HF	3	0 5 9.5

Number of Observations Read	171
Number of Observations Used	170

Fig 19: Graph representing shear values of groups



Least Squares Means for effect group*time*HF
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: Shear

i/j	1	2	3	4	5	6	7	8	9	10	11	12
1		<.0001	<.0001	0.9783	<.0001	<.0001	0.4381	<.0001	<.0001	0.2170	<.0001	<.0001
2	<.0001		0.9995	<.0001	0.0073	1.0000	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
3	<.0001	0.9995		<.0001	0.2318	1.0000	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
4	0.9783	<.0001	<.0001		<.0001	<.0001	0.0260	<.0001	<.0001	0.0095	<.0001	<.0001
5	<.0001	0.0073	0.2318	<.0001		0.1112	0.0116	<.0001	<.0001	0.0385	<.0001	<.0001
6	<.0001	1.0000	1.0000	<.0001	0.1112		<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
7	0.4381	<.0001	<.0001	0.0260	0.0116	<.0001		<.0001	<.0001	1.0000	<.0001	<.0001
8	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001		1.0000	<.0001	1.0000	0.5310
9	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	1.0000		<.0001	1.0000	0.7296
10	0.2170	<.0001	<.0001	0.0095	0.0385	<.0001	1.0000	<.0001	<.0001		<.0001	<.0001
11	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	1.0000	1.0000	<.0001		0.9713
12	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.5310	0.7296	<.0001	0.9713	
13	<.0001	0.0017	0.0738	<.0001	1.0000	0.0311	0.1515	<.0001	<.0001	0.3218	<.0001	<.0001
14	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.9845	0.9984	<.0001	1.0000	1.0000
15	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.8383	0.9490	<.0001	0.9993	1.0000
16	0.9128	<.0001	<.0001	0.1500	0.0007	<.0001	1.0000	<.0001	<.0001	0.9997	<.0001	<.0001

Least Squares Means for effect group*time*HF
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: Shear

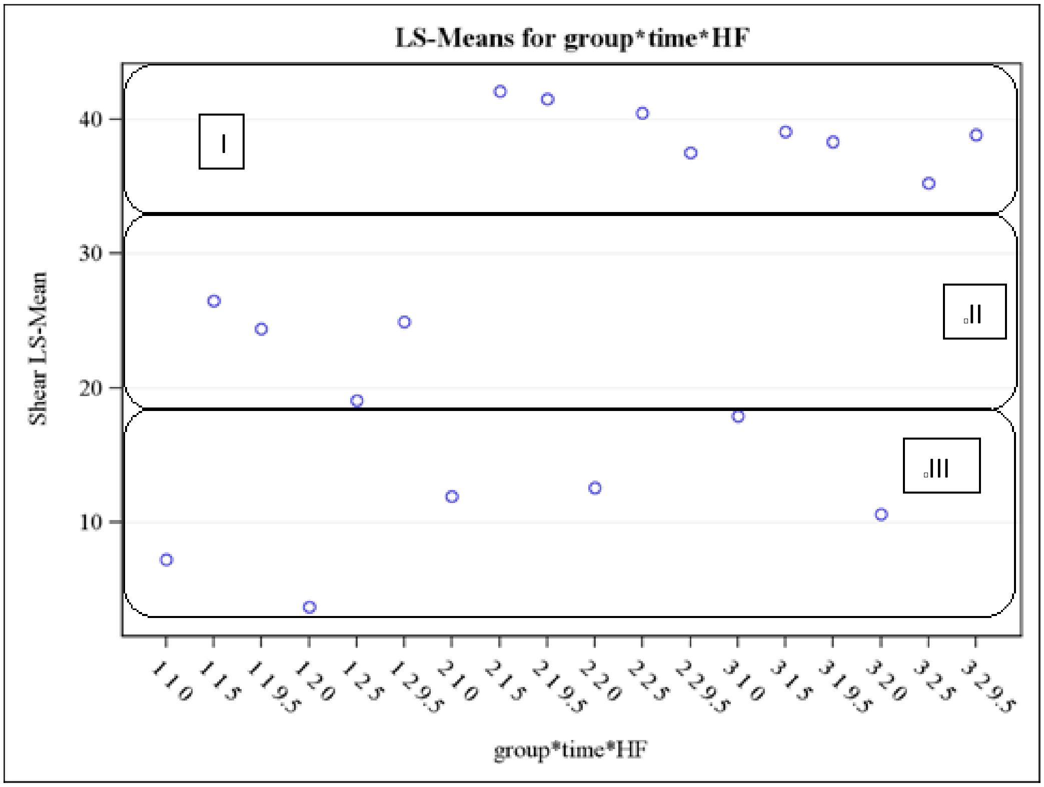
i/j	1	2	3	4	5	6	7	8	9	10	11	12
17	<.0001	0.0003	<.0001	<.0001	<.0001	<.0001	<.0001	0.0297	0.0620	<.0001	0.2630	0.9987
18	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	0.9516	0.9919	<.0001	1.0000	1.0000

Scheffe’s adjustment:

Because the comparisons were suggested by the data, rather than a priori, Scheffe’s adjustment was used.

All 3 of the cluster means are significantly different, p < 0.0001 for each pairwise comparison. The clusters were I, II and III

Fig 20: Clusters suggested by Data

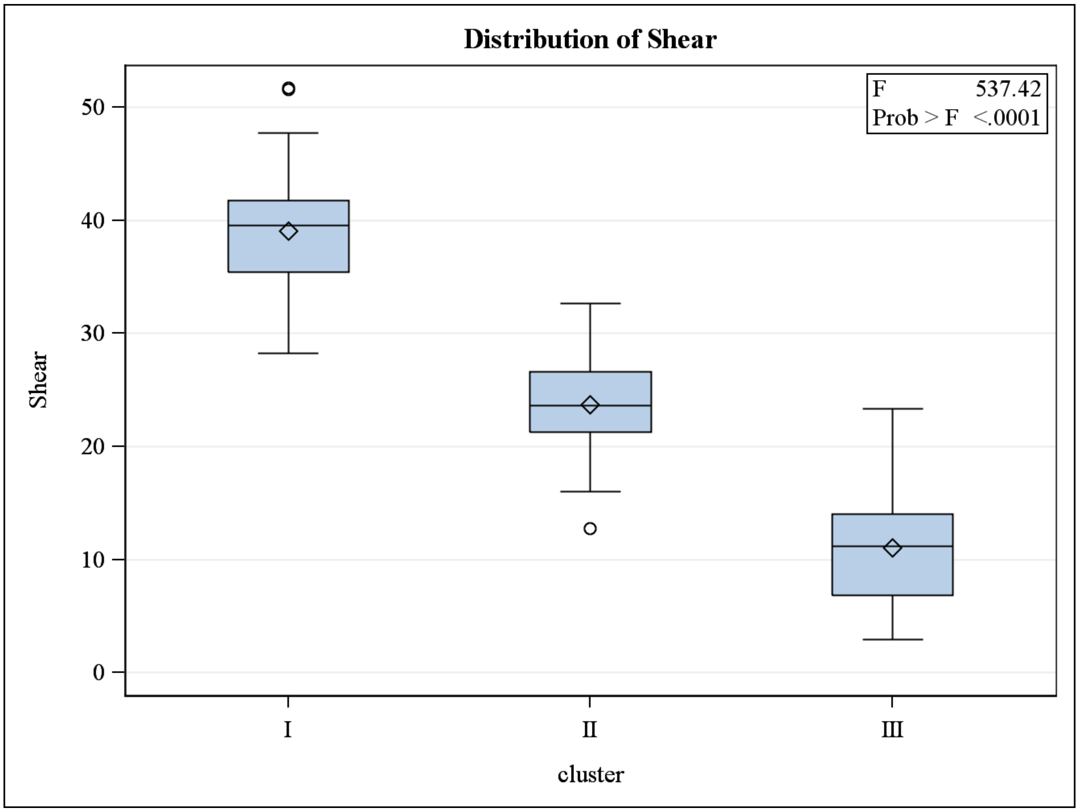


Class Level Information		
Class	**Levels**	**Values**
cluster	3	I II III

Number of Observations Read	171
Number of Observations Used	170

The mean values along with the standard deviations of the least mean squares for each cluster group is shown below.

Fig 21: Distribution of Cluster groups



Study 2:

The study was analyzed as a two-way factorial design, with group and time as the factors.

Zero values of shear were deleted, as they cannot be included in ANOVA.

The data was rank-transformed for the analysis, due to a markedly smaller variance for one group and time combination (group 2, time 2). The p-values from the ranked analysis are the ones to use.

A 2-factor analysis was also conducted using the untransformed data.

Specimens that failed before testing were given the value of zero and were not included in the analysis.

The groups have been assigned as follows,

Table 10: Groups and treatments in study-2

Pretreatment			Cleaning		Bonding Agent	Groups
5% HF	Silane	-	-	-	SBU	Group-1 (Control)
5% HF	-	Saliva	-	-	SBU	Group-2
5% HF	Silane	Saliva	-	-	SBU	Group-3
5% HF	Silane	Saliva	35% Phosphoric acid	Silane	SBU	Group-4
5% HF	Silane	Saliva	Alcohol	Silane	SBU	Group-5

The times of the testing were assigned as follows,

time 1: Testing done after 24 Hrs

time 2: Testing done after 24 Hrs+ 10,000 thermocycles (6 days)

Table 11: Least square means for study-2		
group	**time**	**Shear LSMEAN**
1	1	39.4876670
1	2	32.5536389
2	1	17.4873540
2	2	3.2304800
3	1	40.5099010
3	2	35.5227510
4	1	41.4780270
4	2	40.2964160
5	1	42.7922220
5	2	38.7693840

Least Squares Means for effect group
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: Shear

i/j	1	2	3	4	5
1		0.0001	0.2541	0.0023	0.0070
2	0.0001		<.0001	<.0001	<.0001
3	0.2541	<.0001		0.3815	0.5961
4	0.0023	<.0001	0.3815		0.9969
5	0.0070	<.0001	0.5961	0.9969	

Fig 22: Graph representing shear values of groups

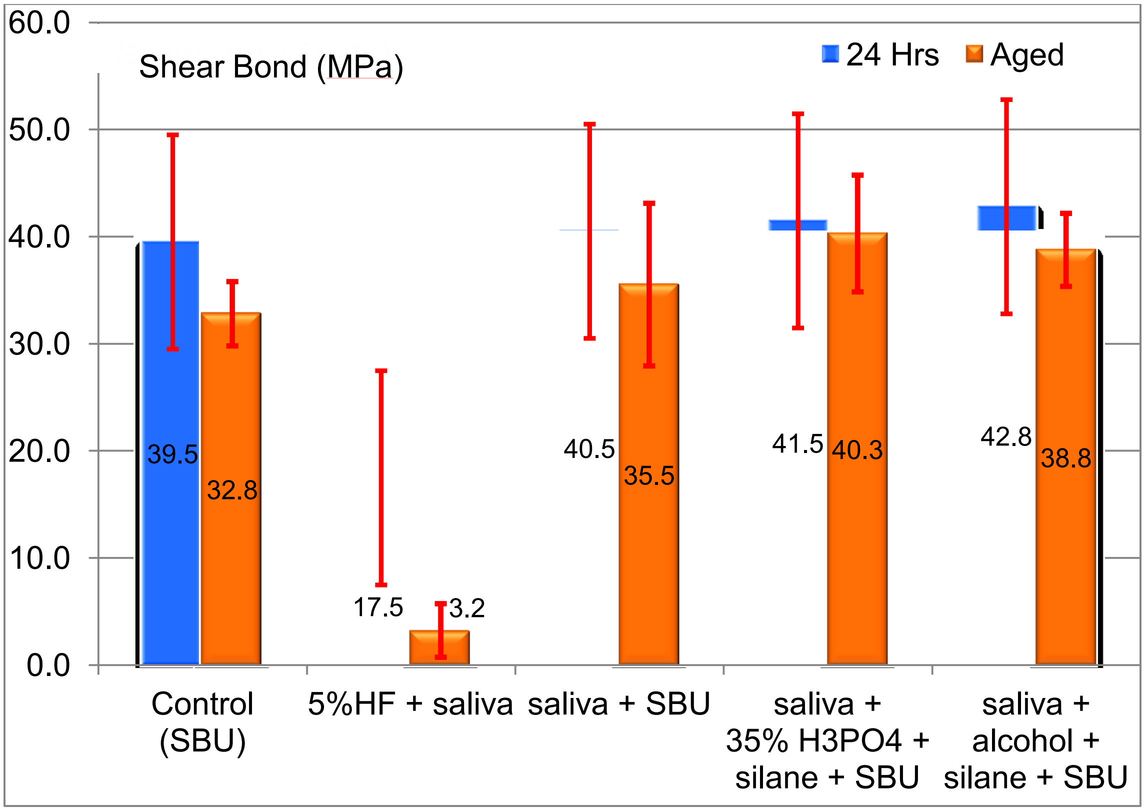


Fig 23: Graph representing least square means of groups

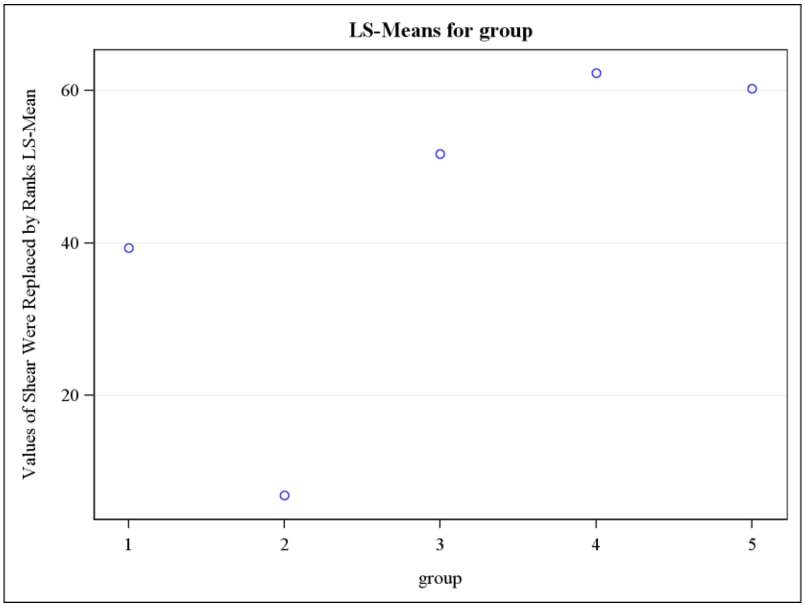
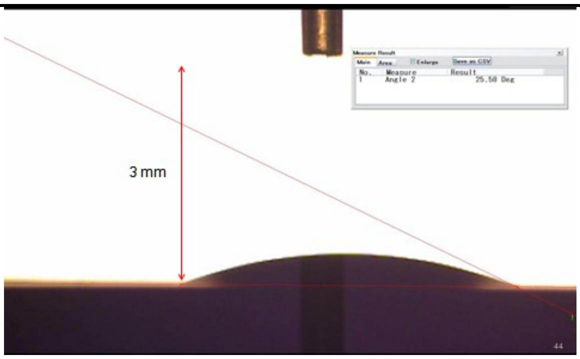
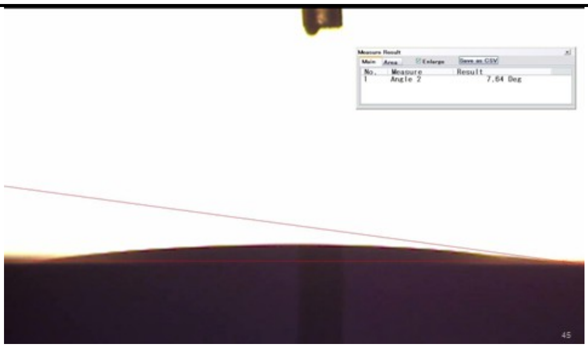
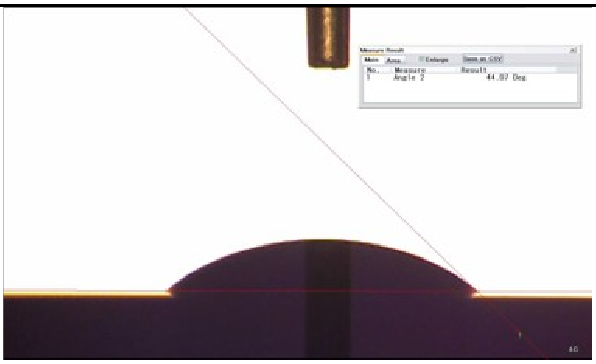


Table 12: Contact angle measurements

Surfaces	**Contact angle °**	**Contact angle ° pictures**
Control (e.max polished)	**25 ± 1**	
5% HF (20 sec)	**8 ± 2**	
silane	**45 ± 2**	

DISCUSSION

The 7th generation universal adhesive Scotchbond universal was designed to prime and bond to most substrates including glass containing ceramics without an additional surface treatment. Within the limitations of this study, the findings indicate that the bond of composite to lithium disilicate using SBU without surface treatments was significantly lower than when an additional coat of silane is applied at 24 hours or after 10,000 thermocyles. Etching the e.max surface with 5 or 9.5% HF produced a significantly greater bond than no surface treatment or applying silane only. The strongest bond of composite to lithium disilicate was produced when treating the surface with 5% or 9.5% HF followed by additional silane application. There was no significant difference in shear bond strength when the lithium disilicate was etched with either 5 or 9.5% HF.

To date there has been only minimal data about the universal adhesives and no published data regarding the bonding to lithium disilicate using SBU, which is the only 7th generation universal adhesive in the market containing silane to bond to glass ceramics. Some preliminary data has been available in the form of abstracts but remains unverified by peer review. If you say this then add references to abstracts. Might mention that further research may be indicated in this area by increasing the amount of silane contained in SBU to see if that will increase the SBS.

Piwowarczyk et al (68) compared shear bond strengths of various cements to lithium disilicate ceramics. It can be concluded that there were significant differences in the bond strengths between composite resin cements and lithium disilicate substrate. There was a trend that application of HF acid etching provided better bond strength values although differences in chemical composition of cements were present.

Kato et al (69) compared cementation systems that required HF etching versus those not requiring an additional etching step to ceramic substrate and concluded that HF etching provided the highest and most durable bond strengths which was similar to the findings of our study.

Another study by Spohr et al investigated the short-term bond strength of a luting cement to lithium disilicate ceramic (7 days, 5000 thermal cycles), where combined application of 10% hydrofluoric acid and silane enhanced the bond strength between the ceramic framework and the resin luting agent.

The use of the varying concentrations of HF along with different etching times produced different etching patterns even though the manufacturer's directions for etch times was followed for each HF concentration. Initially the etched appearance led us to think that there was increased micro-mechanical retention between the surfaces etched with 5% HF for 20 seconds and the 9.5% HF for 60 seconds. It was speculated that this would translate into increased bond strength when composite was bonded onto the 9.5% etched lithium disilicate surface.

However no statistical difference that in the bond strengths obtained when etching the surface with the varying concentrations and application times of HF was produced. It is speculated that the increased size and depth of the porosities produced by the 9.5% HF in the lithium disilicate may reduce its strength after fatigue. Load cycling would certainly be produced during the chewing cycle and may be in part responsible for bulk fracture of the material. Therefore at this time, the lower concentration of 5% HF at the shorter etch time is recommended.

Within the limitations of the second part of the study, salivary contamination was detrimental to bond strength when a silane was not applied prior to salivary contamination. The control group and the groups contaminated with saliva after additional silane treatment produced bond strengths that were statistically significantly different than the non silane treated group ($p=0.05$).

The surface contact angle was influenced by the surface treatments of HF and silane (ceramic primer). The use of HF decreased in the contact angle to 8° with distilled water. This was in indicative of a more hydrophilic surface compared to the 25°contact angle produced by distilled water with untreated lithium disilicate surface. The application of silane increased the contact angle of distilled water to the lithium disilicate surface to 45°. This may have been the result of the increased hydrophobicity of the lithium disilicate surface and may have contributed to decreased adhesion of the saliva. Clinically this is an important discovery especially with clinicians using the CAD/CAM systems and chairside milling of e.max. Initially etching with 5% HF for 20 seconds followed by an application of silane should be completed prior to try in. Then after removal the intaglio surface is rinsed with air-water spray and bonded to place.

CONCLUSIONS

Within the limitations of this study we conclude that,

1. Surface treatments with HF etching and additional silane application were required to produce the highest bond strengths with Scotchbond Universal.
2. Application of silane produced a more hydrophobic surface than the HF etched or polished e.max surfaces.
3. There was no difference in shear bond strength produced by 5 or 9.5% HF etching of lithium disilicate.

FUTURE RESEARCH

- Effect of salivary contamination on the bonding agent efficacy

- Effect of HF concentration and etching time on ceramic flexural strength

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