Effect of different silane coupling agents on the wettability and shear bond strength between glass ceramic and resin cement

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ผลของสารคู่ควบต่างชนิดต่อความเปียกผิวและค่าแรงยึดเฉือนระหว่างกลาสส์เซรามิกและเรซินซีเมนต์

นายธนพล ธาราธีรเศรษฐ์

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สารคู่ควบไซเลนเป็นสารประกอบสังเคราะห์ที่ช่วยเพิ่มการยึดติดระหว่างวัสดุสองชนิดที่ไม่เหมือนกันเข้าด้วยกัน ในปัจจุบันสารคู่ควบไซเลนหลากหลายยี่ห้อถูกวางจำหน่ายอย่างแพร่หลายตามท้องตลาด โดยแต่ละยี่ห้อจะมีสูตรการผสมสารคู่ควบไซเลนที่แตกต่างกันทำให้ทันตแพทย์มีตัวเลือกมากมายในการใช้งาน การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาผลของการปรับสภาพผิวของลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยสารคู่ควบไซเลนชนิดต่างๆเพื่อดูประสิทธิภาพในการเพิ่มการยึดติดหรือค่าความเปียกผิวของวัสดุ โดยการทดสอบจะแบ่งออกเป็นสองส่วนดังนี้

ส่วนแรก ทดสอบผลของการปรับสภาพพื้นผิวของลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยสารคู่ควบไซเลนต่อค่ากำลังค่าแรงยึดเฉือนระหว่างลิเทียมไดซิลิเกตกลาสส์เซรามิกและเรซินซีเมนต์ โดยการใช้สารคู่ควบไซเลนสามยี่ห้อที่สามารถหาซื้อได้ตามท้องตลาดและสารคู่ควบไซเลนที่ผสมเองในการทดสอบจะถูกใช้ในการเพิ่มการยึดติดระหว่างพื้นผิวของของลิเทียมไดซิลิเกตกลาสส์เซรามิกและเรซินซีเมนต์

ส่วนที่สอง ทดสอบผลของการปรับสภาพผิวของลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยสารคู่ควบไซเลนภายหลัง การปรับ/ไม่ปรับสภาพพื้นผิวลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยกรดไฮโดรฟลูออริกต่อค่าความเปียกผิวของวัสดุกับน้ำปราศจากไอออน โดยสารคู่ควบไซเลนที่ใช้เป็นสารเดียวกันกับในการทดสอบส่วนแรก

ผลการศึกษาพบว่า ชนิดของสารคู่ควบไซเลนที่ใช้มีผลต่อกำลังค่าแรงยึดเฉือนระหว่างลิเทียมไดซิลิเกตกลาสส์เซรามิกและเรซินซีเมนต์อย่างมีนัยสำคัญทางสถิติ การปรับสภาพผิวของลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยสารคู่ควบไซเลนทำให้ค่าความเปียกผิวของวัสดุต่อน้ำปราศจากไอออนลดลง และการปรับสภาพผิวของลิเทียมไดซิลิเกตกลาสส์เซรามิกด้วยกรดไฮโดรฟลูออริกก่อนการทาด้วยสารคู่ควบไซเลนทำให้ค่าความเปียกผิวเพิ่มขึ้นในทุกกลุ่มทดสอบยกเว้นกลุ่มที่ปรับสภาพผิวด้วยสารคู่ควบไซเลนที่มีเรซินโมโนเมอร์เป็นส่วนผสม

สาขาวิชา	ทันตกรรมประดิษฐ์	ลายมือชื่อนิสิต ....
ปีการศึกษา	2562	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
		ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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KEYWORD: Contact angle, Hydrofluoric acid, Lithium disilicate, Shear bond strength, Silane coupling agent, Surface treatment

Tanapon Tarateeraseth : Effect of different silane coupling agents on the wettability and shear bond strength between glass ceramic and resin cement. Advisor: Assoc. Prof. NIYOM THAMRONGANANSKUL, D.D.S., M.Sc., Ph.D. Co-advisor: Asst. Prof. Tool Sriamporn, D.D.S., M.Sc., Ph.D.

Silane coupling agents are synthetic hybrid inorganic-organic compounds that act as adhesion promoters which chemically unify dissimilar materials. Nowadays, many brands of silane coupling agent are commercially available in the market. Each brand formulate differently from one another providing the dentists various options to choose from. The aims of this study was to investigate the effect of treating the lithium disilicate glass ceramic surface with various types of silane coupling agents in term of bonding capability and wettability. The experiment was divided into two parts.

The first part of the research was to evaluate the effect of various type of silane coupling agent on the shear bond strength between lithium disilicate glass ceramic and resin cement. Three commercial dental silanes and one experimental silane were used, in vitro, to promote the bonding of resin cement to lithium disilicate glass ceramic surfaces.

The second part of the research was to investigate the effect of treating the hydrofluoric acid-etched/unetched lithium disilicate surface with various types of silane coupling agents on the contact angle measurement between lithium disilicate glass ceramic surface and deionized water. The silane coupling agents used were the same as those in the first part of the study.

The results of this study showed that the type of silane coupling agent used significantly influence the bond strength between lithium disilicate and resin cement and that application of silane coupling agents significantly reduced the wettability of deionized water on the silane-coated surface. The type of silane coupling agent selected significantly influenced the wettability of deionized water. Etching the surface with hydrofluoric acid prior to silane application significantly increased surface wettability in all treatment groups except for groups that were treated with resin-containing silane coupling agent.

Field of Study: Prosthodontics
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Student's Signature ....
Advisor's Signature ....
Co-advisor's Signature ....

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Tanapon Tarateeraseth

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CHAPTER I

INTRODUCTION

1.1 BACKGROUND AND RATIONALE

Metal ceramic restoration have been available for more than five decades because of its predictable performance and good esthetics outcome.(1) However, due to a great demand for improved esthetics and the concern about the usage of metal and its biocompatibility, all-ceramic restoration has gained popularity.(2) These restorations are able to mimick natural tooth appearance because of their optical behavior. All-ceramic restorations have been widely used in the field of prosthodontics dentistry for various applications such as inlays, onlays, veneers, crowns, bridges, implants, etc.

The trend in choosing material for all-ceramic restoration tend to be shifted from layered ceramic to monolithic ceramic to improve mechanical properties. Monolithic ceramic, mainly lithium disilicate and zirconia, offers superior chipping and flexural fracture resistance than its veneered counterparts. The veneering method also demonstrated several major drawbacks when compared to the monolithic ceramic(3) such as (i) fabrication requires multiple step processes (ii) lower toughness and susceptibility to chipping (iii) prone to surface delamination due to weak bonding between veneer and core (iv) residual tensile stresses acquired during the veneering process.

Apart from the properties of the restorative materials themselves, bonding between resin-ceramic restorations greatly influence the clinical outcome.(4) Restoration longevity depends upon several factors such as caries index, type of dentition, site of restoration, size of restoration, reasons for placement, oral cleanliness, etc.(5) Among these factors, the bond quality of tooth-restoration plays an important role. Reliable resin bond increases retention of the restoration,(6) improves marginal adaptability,(7, 8) reduces microleakage(7, 8) and enhances fracture resistance.(9)

Several methods had been proposed in order to achieve the optimal resin-ceramic bond including mechanical and chemical modification. The method must be carefully selected for different type of materials, since some methods may benefit a specific material but may have a negative effect on the others. A reliable bond between resin and silica-based ceramic can be achieved by hydrofluoric acid etching (mechanical bonding) along with silane priming (chemical bonding). Hydrofluoric acid etching roughens the surface of ceramic restoration which increases total surface area available for bonding(10) while silane coupling agent forms stable siloxane networks on the surface. Silane coupling agents were also believed to help in increasing the surface energy of the substrate and wettability of the luting agent to the coated ceramic surface.(11-13)

Nowadays, many types of silane coupling agents are commercially available in the market. Two-bottle system is known to provide a longer shelf life and increase initial reactivity compared to the one-bottle system.(14) To simplify the bonding procedure, manufacturers tend to produce prehydrolyzed single-bottle silanes and other universal adhesive primers which may include many other components such as bisphenol A glycidyl methacrylate (Bis-GMA), 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), etc.(4) However, studies regarding the resin-ceramic bond strength and the contact angle between deionized water and silanated surface is still limited.

The aim of this study was divided into two parts. The first part was to evaluate the effect of different types of composition of silane coupling agent on the shear bond strength of resin cement to lithium disilicate ceramic. The second part was to investigate the effect of treating the hydrofluoric-acid-etched/unetched lithium disilicate ceramic surface with various types of silane coupling agents on the contact angle measurement of deionized water. The null hypotheses were that the type of silane coupling agent used does not affect the shear bond strength between lithium disilicate glass ceramic - resin cement and the different types of silane coupling agents used would not affect the contact angle formed between the deionized water droplets and the etched/unetched lithium disilicate glass ceramic surfaces.

1.2 RESEARCH OBJECTIVES

1) To investigate the effect of different silane coupling agents on the shear bond strength between lithium disilicate glass ceramic and resin cement
2) To investigate the effect of treating the hydrofluoric-acid-etched/unetched lithium disilicate ceramic surface with various types of silane coupling agents on the contact angle measurement of deionized water

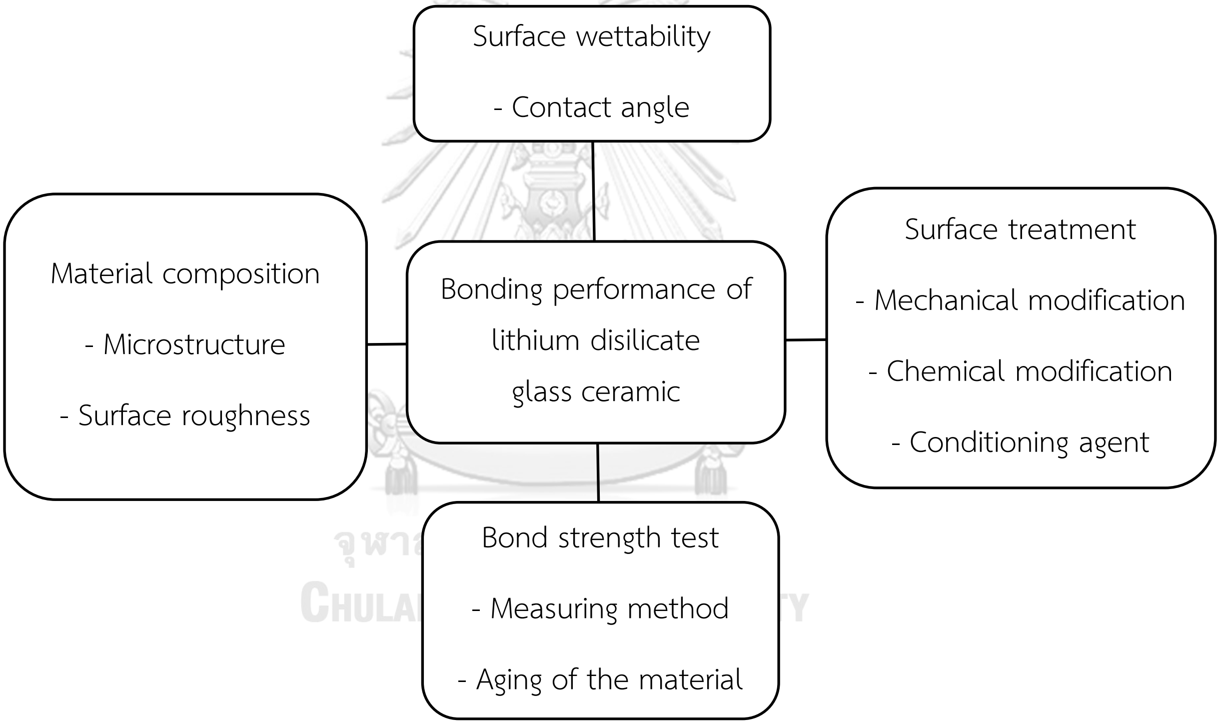
1.3 RESEARCH QUESTIONS

1) Does the different silane coupling agents yield similar shear bond strength value when applied to lithium disilicate surface prior to bonding with resin cement?
2) Does treating the hydrofluoric-acid-etched/unetched lithium disilicate ceramic surface with various types of silane coupling agent yield similar contact angle value when deionized water is used as the probing medium?

1.4 NULL HYPOTHESES

1) Types of silane coupling agent used does not affect the shear bond strength between lithium disilicate glass ceramic and resin cement.
2) Types of silane coupling agents used would not affect the contact angle formed between the deionized water droplets and the etched/unetched lithium disilicate glass ceramic surfaces.

1.5 CONCEPTUAL FRAMEWORK



1.6 KEYWORDS

Contact angle, Hydrofluoric acid, Lithium disilicate, Shear bond strength, Silane coupling agent, Surface treatment

1.7 RESEARCH DESIGN

Laboratory and experimental research

1.8 EXPECTED BENEFITS

1. To understand the effect of different silane coupling agents on the shear bond strength between lithium disilicate glass ceramic and resin cement
2. To understand the treating the hydrofluoric-acid-etched/unetched lithium disilicate ceramic surface with various types of silane coupling agents on the contact angle measurement of deionized water

CHAPTER II
REVIEW OF RELATED LITERATURE

2.1 Ceramic restoration

2.1.1 Overview

As previously stated, ceramic restorations are suitable to be used in a wide range of application, however, there are several contraindications to be kept in mind regarding the usage of the material. Because of their brittle nature and abrasive potential, all-ceramic restorations should be avoided where there are limited interocclusal distance or heavy occlusal forces such as patients with parafunctional habits (bruxer). Dry field must be maintained during impression taking and cementation to ensure positive outcome, therefore, in cases where good moisture control is hard to obtain such as in deep subgingival preparation cases, all-ceramic restorations are not recommended.

The advantages of all-ceramic restoration includes natural esthetics due to their ability to mimic the optical properties of natural enamel and dentin, chemical durability, precise contacts & contour, wear resistance and biocompatibility. Indirect restoration offers superior wear resistance, proper shape and location than directly placed restorations. Even though, toxicity of metal depends upon the type and composition of the metal alloy used in the fabrication of the prosthesis, the allergic reaction caused by certain type of metal, especially nickel, raised the concern of using a more biocompatible all-ceramic restoration. The placement of restorative margin for all-ceramic restoration is often acceptable at supra-gingival or at the gingival level. This reduces the chances of traumatic injuries during impression making procedure and emergence profiles are less likely to be overcontoured. Moreover, bacteria tend to colonize less on the ceramic surface. A study by Hahn et al.(15) found that dental porcelain significantly accumulated less plaque than the natural enamel surface and resin composite. Similar result was shown in a study by Kawai and Urano(16) who tested the adherence of plaque components on different restorative material including amalgam alloy, gold alloy, resin composite and three ceramics. It was demonstrated that the least amount of bacteria and glucan adhered to the ceramic surfaces compared with other materials.

Despite all the advantages listed above, there are several disadvantages in using all-ceramic restoration. They cost more time and money when compared to direct restorations. Since they are fabricated indirectly, at least two appointments are required before final placement of the restoration. Additional laboratory fee makes the restoration more expensive. They are brittle in nature, therefore providing an adequate thickness of ceramic is crucial to avoid restoration fracture. They have high abrasive potential which can cause problem to the opposing restoration and/or dentition. They have low repair potential and are difficult to polish intraorally.

2.1.2 Ceramic classification

Dental ceramic can be classified in a number of ways according to: indication, composition, processing method, firing temperature, microstructure, translucency, fracture resistance, and abrasiveness. Kelly(17) suggested two concepts to aid in understanding dental ceramic. One, it is easier to categorize ceramics by their main compositions including (i) predominantly glass, (ii) particle-filled glass, and (iii) polycrystalline. Second, understanding that ceramics are composite materials which means they are composed of two or more entities.

Table **1** *Substructure ceramics: basic composition, uses, and commercial examples. (Kelly, 2004)(17)*

Glass	Fillers	Uses	Commercial examples
Highly filled glassy ceramics			
Feldspathic glass	Leucite (~40-55 mass%)	Inlays, onlays, veneers, single-unit crowns	Empress (Ivoclar) OPC (Pentron) Finesse All-ceramic (Dentsply)
Feldspathic glass	Aluminum oxide (~55 mass%)	Single-unit crowns	Vitadur-N (Vita)
Lanthanum	Aluminum oxide (~70 vol%)	Single-unit crowns, anterior three-unit bridges	In-Ceram Alumina (Vita)
LABS	Aluminum oxide (~50 vol%) Zirconium oxide (~20 vol%)	Single-unit crowns, Three-unit bridges	In-Ceram Zirconia (Vita)
Modified Fledspathic glass	Lithium disilicate (~70 vol%)	Single-unit crown, anterior three-unit bridges	Empress 2 (Ivoclar) 3G (Pentron)
Polycrystalline ceramics			
Aluminum oxides	<0.5 mass%^{a}	Single-unit crowns	Procera (Nobel Biocare)
Zirconium oxide	Yttrium oxide (3-5 mass%)^a	Single unit crowns	Procera (Nobel Biocare)
Zirconium oxide	Yttrium oxide (3-5 mass%)^a	Single-unit crowns, Three-unit bridges Four-unit bridges (?)	Cercon (Dentsply) Lava (3M-ESPE) Y- (Vita)

Abbreviations: LABS, aluminoborosilicate

(i) *Predominantly glass ceramic*

Predominantly glass, belonged to aluminosilicate glass family, demonstrated the best ability to mimic optical properties of enamel and dentin, which make them highly esthetic. They derived from natural mineral feldspar, silica (silicon oxide), and alumina (aluminum oxide). Glasses are three-dimensional amorphous (non-crystalline, no regular pattern) networks of silica in which a silicon atom is bonded with four oxygen atoms in tetrahedron form which are linked by common oxygen atoms. The three-dimensional networks may be disrupted by modifying cations, the oxides of alkali metals, such as calcium, sodium and potassium. These alkali metal ions can modify the important properties of glass such as lowering the firing temperature, increasing the thermal expansion/contraction behavior, alter strength and chemical inertness of the material. For example, distruption of silicon-oxygen bonds with modifying cations result in the breakdown of three dimensional network. The non-bridging oxygen (more open network) lowers the firing temperature and offers a more fluid behavior during heating.

(ii) *Particle-filled glass ceramic*

Particle-filled glass, successfully developed in 1962, are composite materials that consisted of a glass-based material incorporated with filler particles to improve mechanical properties as well as controlling the optical effects such as opalescence, color and opacity. Weinstein, the inventor of metaloceramic, was the first person to mix the glass and glass-ceramic frits of different composition and coefficient of thermal expansion in the making of porcelain.(18) Such filler was leucite ($KAlSi_2O_6$), a potassium aluminium silicate mineral form by $(Si,Al)O_4$ tetrahedea.

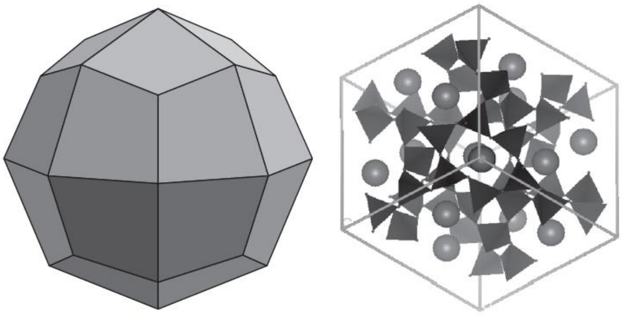


Figure 1 The single leucite crystal (left) and the crystal structure of tetragonal leucite (right); spheres - K^+ ions, tetrahedra - $[SiO_4]^{4-}$, $[AlO_4]^{5-}$.
(Mrázová M KA, 2009) (18)

Leucite is a two polymorphic structure that exists as cubic form at high temperature which has a relatively low coefficient of thermal expansion (10-12 x 10^{-6}/°C). At low temperature, leucite exists in tetragonal form in which has a high coefficient of thermal expansion (22-30 × 10^{-6}/°C).(19) The mismatch of coefficient of thermal expansion between dental alloy (12-14 x 10^{-6}/°C) and feldspartic glasses (~8 x 10^{-6}/°C) posed a problem in term of bonding. While leucite has a high coefficient of thermal expansion (~20x10^{-6}/°C), it is added to feldspartic glasses about 17-25 mass% to compensate the need to increase the thermal expansion coefficient which in turn created a thermally compatible porcelain, making it possible to successfully fire the porcelain onto metal substructure.(17) There are multiple major benefits when using leucite as a filler choice. Leucite has a reflective index approximately similar to that of feldspartic glass. Therefore, incorporating leucite into the glassy matrix of feldspartic glass will not alter its translucency but will also enhance the strength of the ceramic by inhibiting microcrack propagation when the particles are disperse homogeneously throughout the glass.(19) This technique was termed “dispersion strengthening”.(17) Particles of aluminum oxide were the first filler to succeed in strengthening the substructure ceramic when they were incorporated into feldspathic glass (~55 mass%). Leucite was also used to strengthen the ceramic with the concentration much higher than those needed for metal-porcelain bonding (~40-50 mass%). Another reason is that leucite can be etched much faster than its surrounding glassy matrix. This property offers sufficient surfaces to allow resin cement to adequately bond to the substrate, obtaining reliable micromechanical retention.

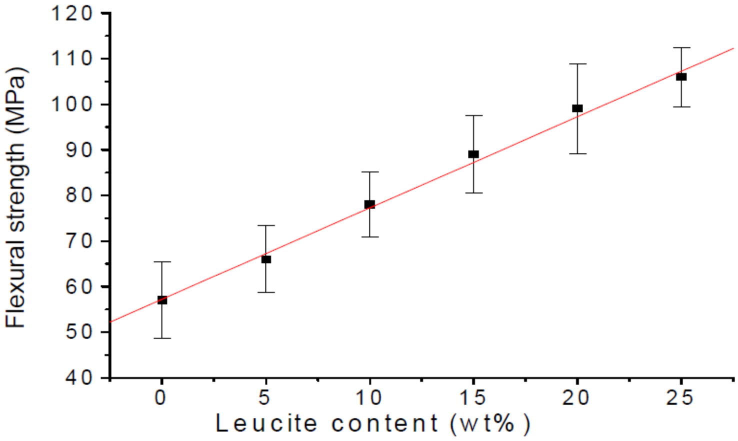


Figure 2 Relationship between the content of leucite and flexural strength. (Yang et al., 2007) (19)

Glass-ceramics, another type of particle-filled glasses, are formed by incorporating crystalline filler particles into the glass. The simplest method would be mixing crystalline and glass powder prior to firing. With a controlled crystallization process by heat treatment, the crystalline phases are allowed to nucleate and grown uniformly within the glass.(20) Dicor (Dentsply), used crystalline mica (~50 vol%) as filler particle, was claimed to be the first commercial glass-ceramic available for fixed prosthesis. Later, Empress 2 (Ivoclar-Vivadent), glass-ceramic that used 70 vol% of crystalline lithium disilicate was introduced to the market.(17)

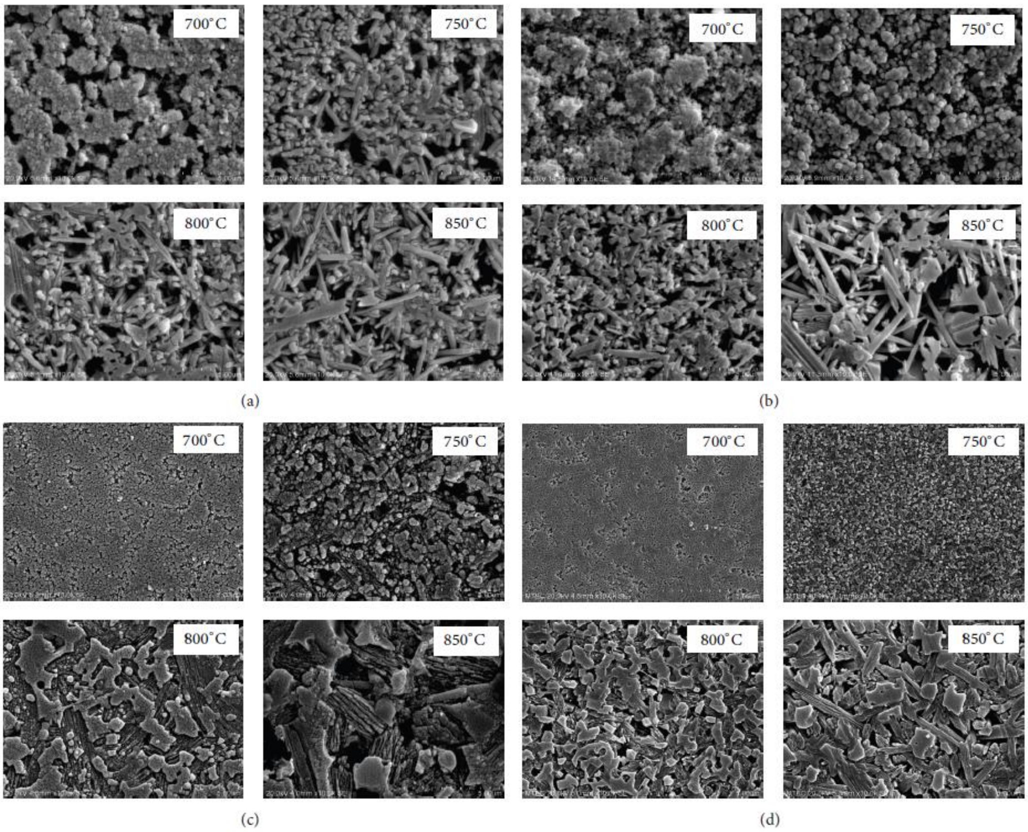


Figure 3 SEM micrographs of lithium disilicate samples after heat treatment at different temperature for 2 hrs. (a) LD1, (b) LD2, (c) LD3, (d) LD4 (Monmaturapoj et al., 2013) [20]

***Composition of the lithium disilicate samples*

Oxides	LD1	LD2	LD3	LD4
SiO_2	60.0	59.0	63.0	62.0
Li_2O	32.0	31.0	29.0	28.0
K_2O	1.0	1.0	1.0	1.0
Al_2O_3	2.0	2.0	2.0	2.0
P_2O_3	2.0	2.0	2.0	2.0
CaF_2	3.0	3.0	3.0	3.0
MgO	-	2.0	-	2.0
Total	100.0	100.0	100.0	100.0
SiO_2:Li_2O	1.88	1.90	2.17	2.21

(iii) *Polycrystalline ceramic*

Polycrystalline ceramics, including alumina and zirconia, are solid-sintered monophase ceramics that contains no glass and no intervening matrix as they are formed by directly sintering the crystals together. The first fully dense polycrystalline material available in this family was Procera AllCeram system by Nobel Biocare. They are known for superior mechanical properties and chemical stability. The atoms in polycrystalline ceramics are densely and uniformly packed which make them much tougher and stronger than glass ceramics where the atoms are less dense and irregularly arranged. However, these features become problematic when it comes to processing and bonding. Sufficient surface modification is difficult to obtain and adhesion to different substrates is a great challenge. Processing polycrystalline ceramics into complex shapes was not practical until highly controlled starting powders and computer-aided manufacturing was available.(17)

2.2 Lithium disilicate glass-ceramic

Lithium disilicate glass-ceramic ($Li_2Si_2O_5$), discovered by Stookey,(21) was the first material that was classified as glass-ceramic. The term glass-ceramic was first used by Corning Glass Works Inc. on May 23, 1957. The material have been used mainly for anterior and posterior single restorations, three-unit fixed dental prostheses and other applications. Studies have shown that the material offers promising outcome and is a suitable option for all-ceramic restoration. Fasbinder et al.(22) evaluated the performance of chairside computer-aided design/computer-aided manufacturing system of monolithic lithium disilicate crown and reported no clinically identified cases of restoration fracture or surface chipping after two-year follow-up. Valenti and Valenti(23) conducted a retrospective study regarding the survival rate of lithium disilicate crowns. The author concluded that lithium disilicate restorations had a low clinical failure rate after up to 120 months. As previously mentioned, according to Kelly,(17) lithium disilicate falls into the particle-filled glass category. Since the mechanical properties of this material is stronger than base glass, the binary Li_2O-SiO_2 system gained popularity among researchers. However, due to the lack of chemical durability, it was not a popular material of choice to be used as a restorative material until improvements have been made. Various components have been added to its composition, known as multi-component glass-ceramics system, to improve its properties such as Al_2O_3, K_2O, ZnO, ZrO_2, CaO and P_2O_5, Al_2O_3 and K_2O have been known to improve the chemical durability of lithium disilicate ceramic whereas P_2O_5 plays an important role as nucleating agent which is crucial in phase formation and crystallization process.

The material performance of all-ceramic restoration is determined by many factors, for example, crystallinity, crystal size and geometry, modulus of elasticity, phase transformation, or thermal expansion mismatch all contributed to the how the material's mechanical response. The microstructure of lithium disilicate is made of approximately 70% of needle-like lithium disilicate crystals embedded in a glassy matrix. The lithium disilicate crystal size is approximately 5 µm in length and 0.8 µm in diameter.(24)

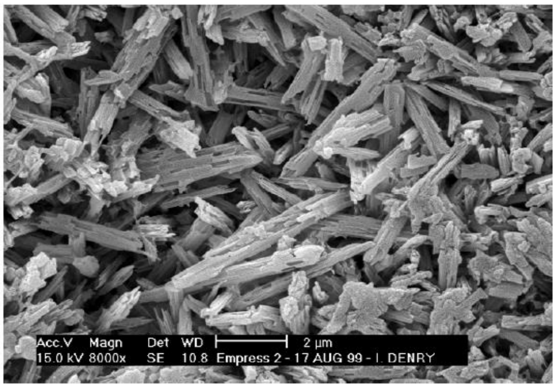


Figure 4 Microstructure heat-pressed lithium disilicate glass-ceramic. (Denry et al., 2010) $^{(24)}$

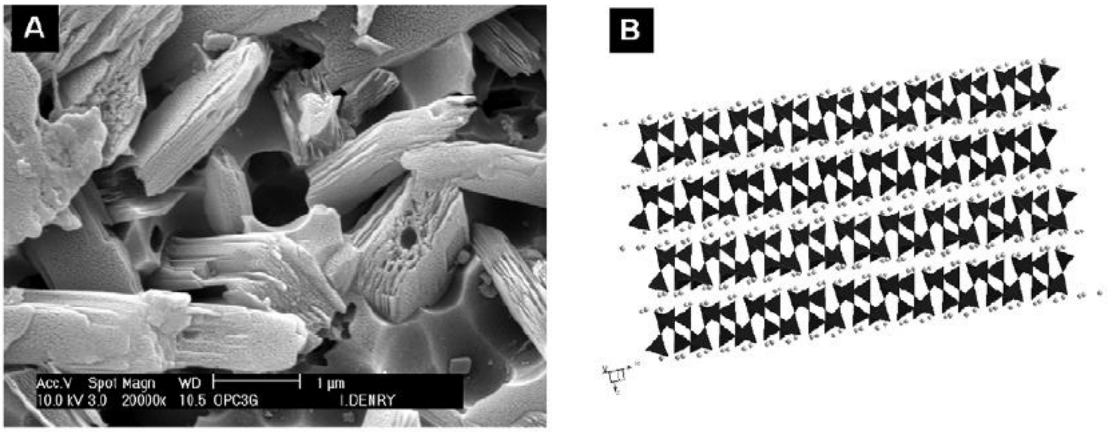


Figure 5 (a) Interlocked crystals in lithium disilicate glass-ceramic;
(b) Crystallographic structure of $Li_2Si_2O_5$, layers are composed of SiO_4 tetrahedra sharing corners, Li atoms in gray. (Denry et al., 2010) (24)

The crystal size depends upon the annealing temperature, increasing the temperature increases the crystal size. Medium-sized lithium disilicate crystals offer the highest flexural strength since larger-sized crystals tend to counteract the "interlocking effect" of crystals.(24, 25) The presence of P_2O_5 in LiO_2-SiO_2 system, as mentioned, aids in initiating of heterogeneous nucleation within the ceramic by acting as a nucleating site for lithium phosphate (Li_3PO_4) and fluorapatite ($Ca_5(PO_4)_3F$), which in turn produces fine-grained, randomly-oriented interlocking microstructure within the glassy matrix that offer high mechanical strength (360-400 MPa).(20) This random orientation of lithium disilicate crystal is capable of ceasing crack propagation since crack propagates much easier along the cleavage plane, the random array of these crystal tend to deflect cracks by making it harder for them to travel across the plane, which in turn increases the flexural strength.(24, 26) Moreover, the mismatch in coefficient of thermal expansion between the lithium disilicate crystals and the glassy matrix result in tangential compression stress around the crystals which also contribute to crack deflection and enhances strength.(24)

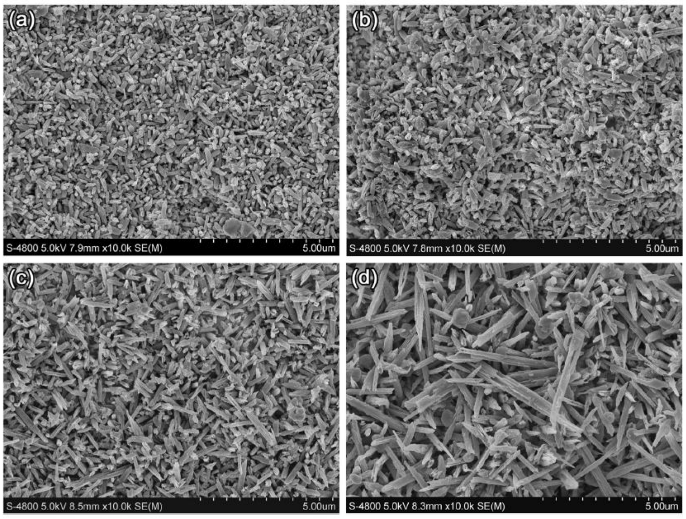


Figure 6 SEM images of the glass-ceramic specimens:

(a) G1, (b) G2, (c) G3 and (d) G4. (Li et al., 2016) (25)

**Crystallization annealing profiles for the glass-ceramic specimens

Group No.	Annealing profiles
(a) G1	610 ℃/1 h + 755 ℃/8 h
(b) G2	610 ℃/1 h + 799 ℃/8 h
(c) G3	610 ℃/1 h + 843 ℃/8 h
(d) G4	610 ℃/1 h + 900 ℃/8 h

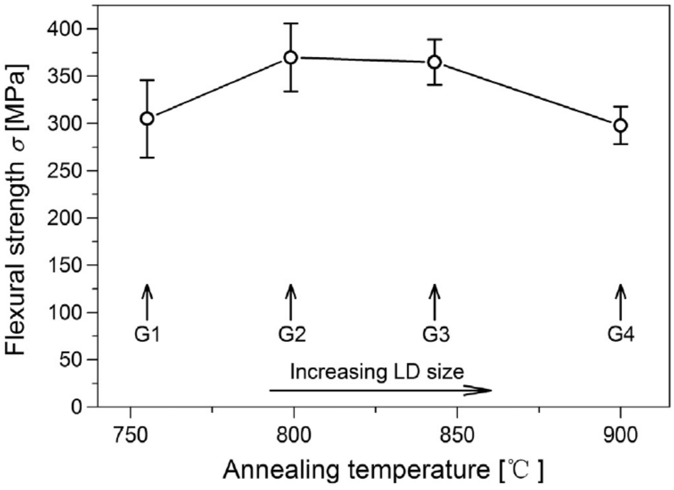


Figure 7 Dependence of the flexural strength (σ) of the glass-ceramic on the annealing temperature. (Li et al., 2016) (25)

Popular processing method of lithium disilicate are heat-pressing and computer-aided design/computer-aided manufacturing (CAD/CAM milling). The compositions of the components used in fabrication of ceramic block/ingot are different for each brand. Ivoclar-Vivadent offers its products from both of the methods mentioned above. The composition of IPS e.max lithium disilicate includes quartz, lithium oxide, and other components. The process of manufacturing the ceramic ingots include powdering the components and combine them together prior to melting and pouring into a separable steel mold. The ceramic is left cooled inside the mold until no future deformation occurs. The method is claimed to produce minimal amount of pores and internal defects. The ceramic blocks or ingots can now be used for lost-wax pressing techniques (IPS e.max Press) or CAD/CAM milling (IPS e.max CAD).

2.3 Surface treatment of dental ceramics

Surface modification is an important procedure to improve the bond strength of the dental material to the desired substrate. Hydrofluoric etching along with the use of silane coupling agent is a common method to treat the surface of silica-based ceramic such as porcelain and lithium disilicate. Several surface treatment methods have been used to enhance the bond strength of ceramic restoration to different substrate. The type of surface treatments can be classified into two main groups: mechanical and chemical modification.

2.3.1 Mechanical modifications

Mechanical bonding techniques uses either mechanical, chemical, or lasers treatments to create roughen surfaces that increase surface area and surface energy to allow better micromechanical interlocking. The penetration and in situ polymerization of resin luting agent is the key to produce a reliable bond between the luting agent and restorative material. The most common methods used to treat ceramic surfaces are acid-etching, mechanical grinding, airborne-particle abrasion and the combination of these methods.

(i) Acid-etching

Acid-etching have been extensively studied. The use of hydrofluoric acid along with silane application is proved to be a successful method in treating silica-based ceramic. The clinical recommendation for bonding with lithium disilicate ceramic is to apply a 5% hydrofluoric acid etch for 20 seconds. Among the methods of surface treatment to obtain optimal micromechanical retention, etching with hydrofluoric acid is proven to be the most successful in enhancing the bond strength of lithium disilicate glass-ceramic.(27-29)

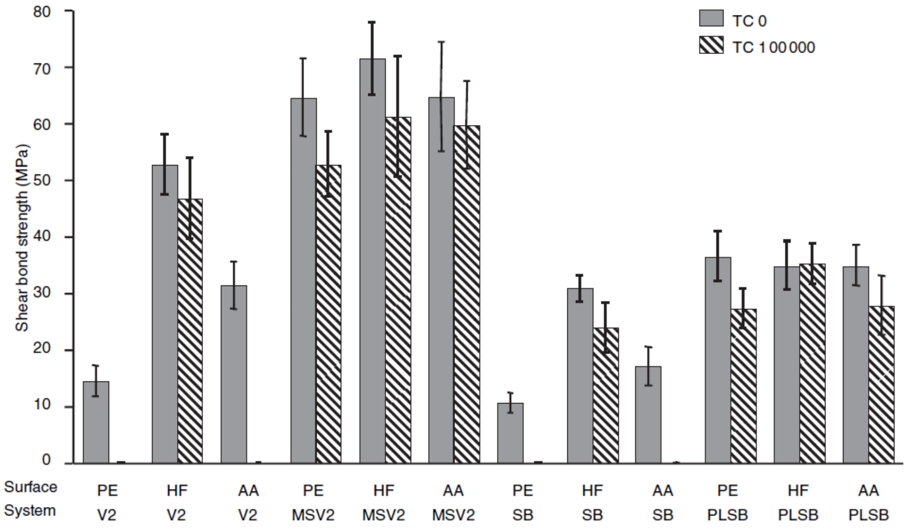


Figure 8 Shear testing results. TC, Thermocycling; PE, phosphoric acid etching; HF, hydrofluoric acid etching; AA, air-abrasion with alumina; V2, Variolink II; MS, Monobond-S; SB, Super-Bond C&B; PL, Porcelain Liner M. (Nagai et al., 2005) (27)

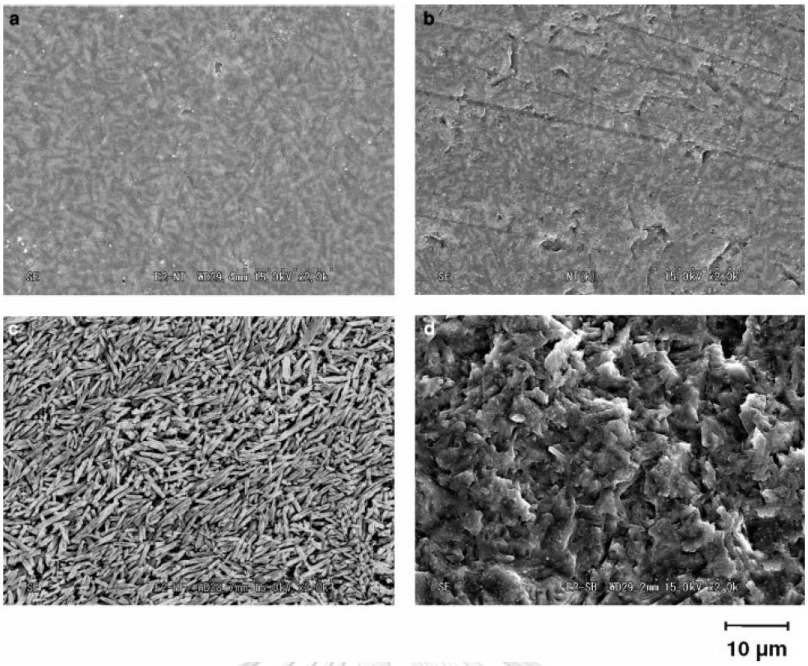


Figure 9 Scanning electron micrographs of the Empress 2 ceramic material: a, ground; b, etched with phosphoric acid; c, etched with hydrofluoric acid and d, air-abraded with alumina. Ground surface (a) was not used for shear testing but presented for the reference to the prepared surfaces. (Nagai et al., 2005) (27)

In feldspathic ceramic, the hydrofluoric acid reacts with the silica phase forming water soluble silicic derivatives (hexafluorosilicates) that can be rinsed away, leaving a honeycomb-like micropitting on the surface of the ceramic.(30, 31) In the case of lithium disilicate, the etching procedure produces elongated crystals in the ceramic surface, allowing the ideal condition for bonding with the resin luting agents.(32) According to Menees et al.(32) the application of hydrofluoric acid may, but not significantly, reduces the flexural strength of lithium disilicate ceramic at various concentration (5, 9.5%) and exposure time (20,120s). The procedure might produce a shallow uniform etch pattern on the lithium disilicate surface without creating sufficient stress to significantly affects the flexural strength, in contrast to airborne-particle abrasion. Contrarily, Zogheib et al.(33) reported that increasing the HF etching time significantly affected the surface roughness and flexural strength of lithium disilicate-based glass ceramic, mainly due to the excessive loss of the amount of glass phase. Della Bona et al.(34) suggested that the etching mechanisms differ according to the composition of ceramic, type and time of the etchant used, which will be very difficult to compare the result of studies that used different ceramic and etching protocol. Ammonium bifluoride (ABF), 9.6% hydrofluoric acid (HF), and 4% acidulated phosphate fluoride (APF) were used in his study, which HF produced the most prominent etching pattern of all dental ceramics examined. A recent study by Maruo et al.(35) suggested that phosphoric acid might be a good alternative to hydrofluoric acid since the acid is less hazardous that also offers good bond strength when used together with silane. Etching lithium disilicate glass-ceramic with hydrofluoric acid might yield a more reliable and constant bond but may also produces insoluble silica-fluoride salts by-products that could remain on the prepared surface and interfere the complete penetration of resin cement or silane coupling agent. On the other hand, when phosphoric acid is used, no deposition of phosphorus-containing by-product was presented on the surface or the by-product produced might not have a complex structure and can be rinse off easily by water.

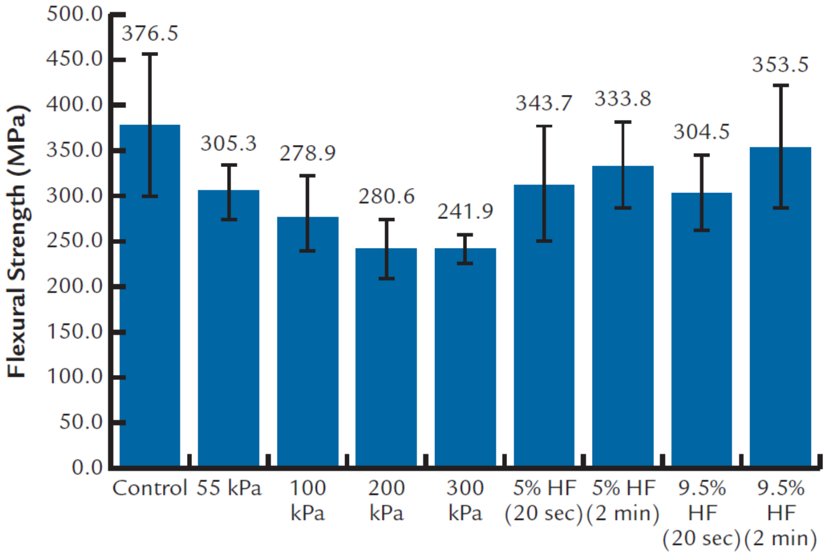


Figure 10 Flexural strength comparison of lithium disilicate after hydrofluoric acid etching or particle abrasion. (Menees et al., 2014) (32)

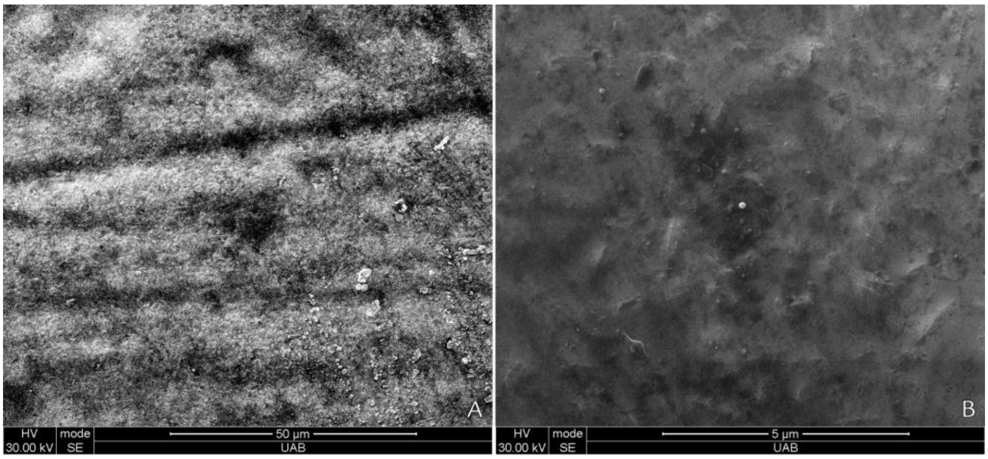


Figure 11 Scanning electron micrographs of control surface: A (3000 magnification) and B (30 000 magnification). (Menees et al., 2014) (32)

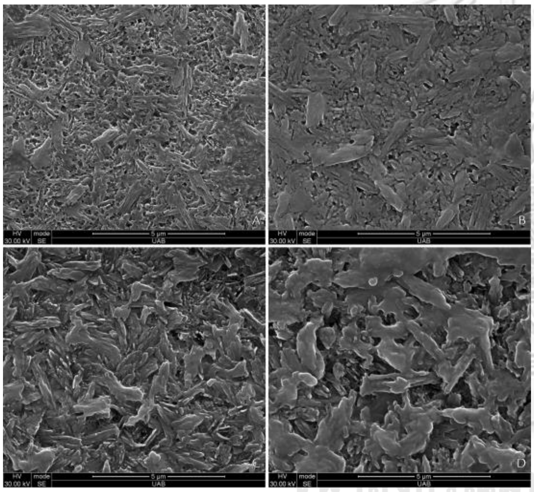


Figure 12 Scanning electron micrographs of hydrofluoric acid etched surfaces.
A, 20 seconds with 5% hydrofluoric acid.
B, 120 seconds with 5% hydrofluoric acid.
C, 20 seconds with 9.5% hydrofluoric acid.
D, 120 seconds with 9.5% hydrofluoric acid.
(30 000 magnification) (Menees et al., 2014) (32)

Table 2 Mean values and standard deviations for surface roughness and flexural strength in all experimental groups. (Zogheib et al., 2011) (33)

Surface treatment (HF etching time)	Surface roughness (*Ra*: µm)	Flexural strength (MPa)
Untreated (A)	0.06 ± 0.01 a	417 ± 55 a
20 s (B)	0.09 ± 0.05 b	367 ± 68 ab
60 s (C)	0.12 ± 0.05 bc	363 ± 84 ab
90 s (D)	0.14 ± 0.06 cd	329 ± 70 b
180 s (E)	0.16 ± 0.10 d	314 ± 62 b

Different letters indicate statistically significant difference (Tukey's test; $P<0.05$).

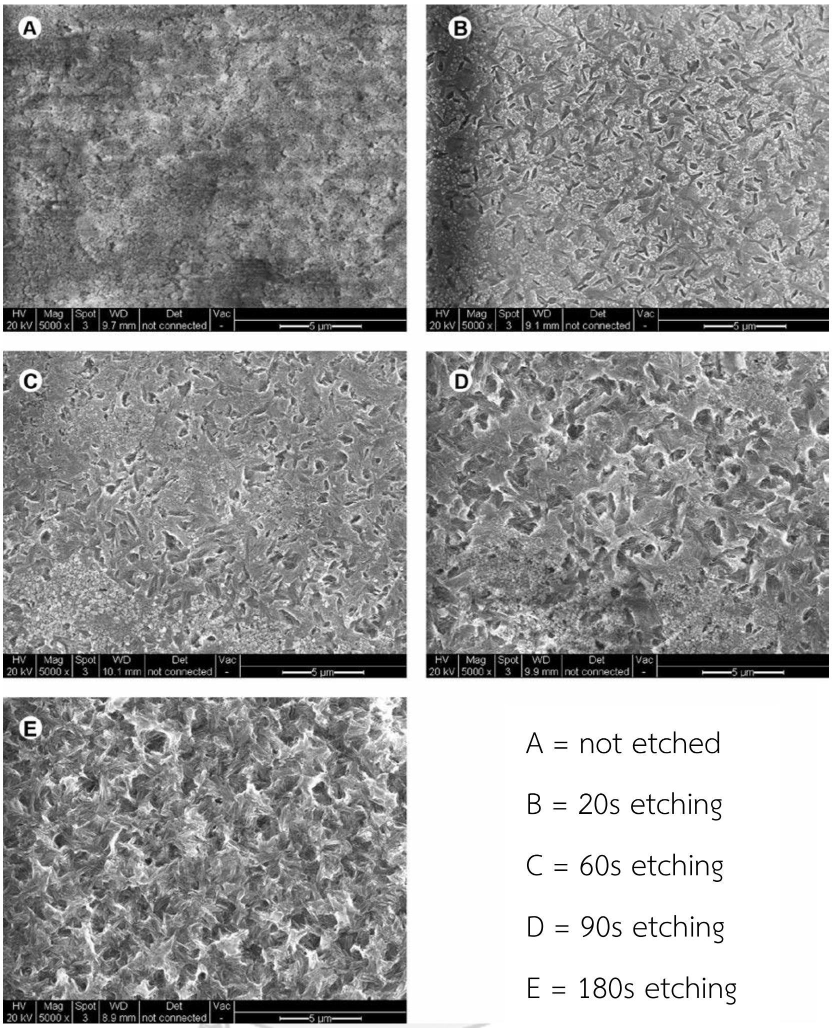


Figure 13 Panel of representative SEM micrographs of the surface of HF-etched lithium disilicate-based glass ceramic after application of the different etching times evaluated in the study. Original magnification ×5,000. (Zogheib et al., 2011) (33)

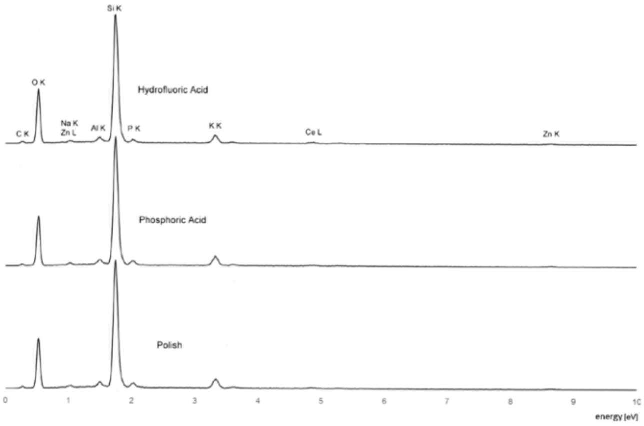


Figure 14 Energy-dispersive X-ray spectroscopy (EDXS) analysis of pretreated lithium dislocate glass ceramic surface.(Maruo et al., 2017) (35)

After treated with hydrofluoric acid, silane application is recommended. Silane helps to increase surface energy and wettability by promoting adhesion between the inorganic phase of the ceramic and the organic phase of the resin cement by siloxane network (-Si-O-Si-O). Non-silica based ceramics are highly crystallized and are chemically stable. They cannot be etched with hydrofluoric acid in a normal condition. For hydrofluoric etching to be effective on non-silica based ceramic such as zirconia, longer application time, a higher concentration and temperature of the solution is required. Since hydrofluoric etching on zirconia surface is harder to perform, the technique may not be a practical method for clinical use.

(ii) Mechanical grinding

Mechanical grinding is performed with coarse diamond rotary instruments. It is a simple chairside technique used to increase mechanical retention. This method produces rougher surface when compared with other technique but it is also an aggressive method that may result in microcracks and surface chipping. Medium-grain diamond bur with the grain size of 30 μm (red halo) is commonly used in many studies. Erdemir et al.(29) reported that although diamond bur can clearly produce irregular and rough surfaces on AFM and SEM, the bond strength did not improve. This concluded that medium-grain diamond bur can create macrosurface irregularities without adequate undercuts for reliable micromechanical retention. Similar findings was reported from Neis et al,(36) grinding the surface of lithium disilicate glass-ceramic did not improve the bond strength but etching with hydrofluoric acid resulted in highest tensile bond strength values. However, in the case of leucite-reinforced glass-ceramic that has a higher vitreous proportion when compared to lithium disilicate glass-ceramic, mechanical grinding with diamond burs can efficiently create surface irregularities. The author concluded that to successfully enhance the bond strength, the type of surface treatment method must be carefully selected to suit the type of ceramic used.

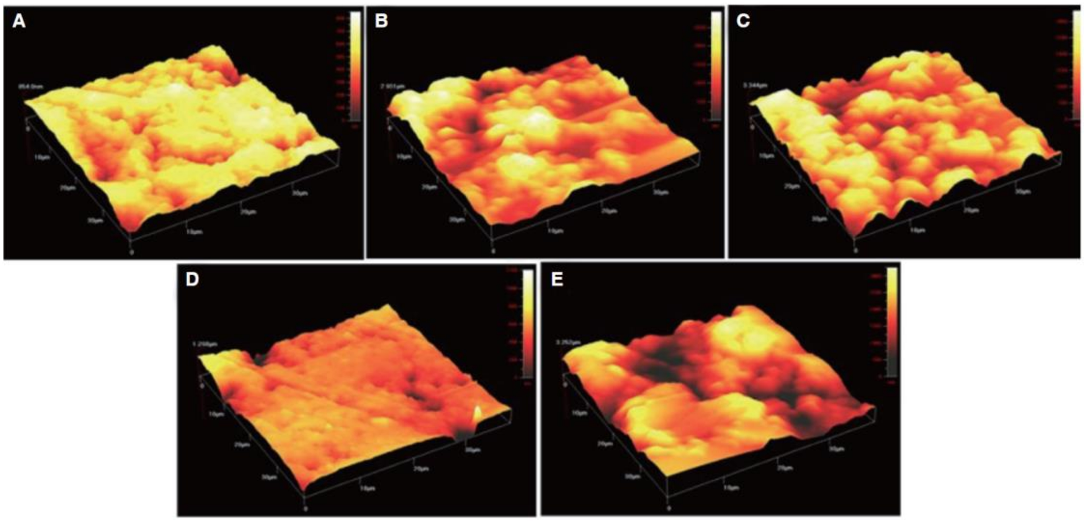


Figure 15 The representative Atomic Force Microscopy (AFM) images for the control and pretreated ceramic groups. (A) Er:YAG laser irradiation, (B) Tribochemical silica coating (Cojet-Sand), (C) 9.6% Hydrofluoric acid etching, (D) Untreated-control, (E) High-speed diamond bur. (Erdemir et al., 2014) (29)

Table 3 Mean surface roughness values (Sq in nm) and standard deviations (SD) of each pretreatment group on lithium disilicate reinforced CAD/CAM ceramic. (Erdemir et al., 2014) (29)

Pre-treatment group	N	Surface roughness	Significance
Group L	10	11.80 (6.70)	A
Group SC	10	472.10 (15.08)	B
Group HF	10	607.30 (6.05)	C
Group C	10	113.20 (8.88)	A
Group DB	10	602.10 (11.41)	C

Different letters in the significance column indicate statistically significant difference ($P<0.05$, Tukey HSD test).

Table 4 Mean shear bond strength values (MPa), standard deviations (SD), statistical difference and the number of the pre-test failures of the tested specimens. (Erdemir et al., 2014) (29)

Group	Mean	SD	N	No. of pre-failed specimens (%)	Significance
Group L	0.91	1.48	16	4 (25%)	A
Group SC	5.36	2.58	16	0 (0%)	B
Group HF	6.82	4.4	16	0 (0%)	B
Group C	1.36	1.86	16	4 (25%)	A
Group DB	0.82	0.48	16	0 (0%)	A

Different letters in the significance colum indicate statistically significant difference ($P<0.05$)

(iii) Airborne-particle abrasion

Airborne-particle abrasion (APA), also known as sandblasting, increases surface energy, increases wettability of the restoration and reduces inorganic contaminants. This is the most popular method used in clinical situation as well as in most research protocols to treat high-strength ceramic material such as alumina or zirconia. However, this method is not recommended for silica-based ceramics such as lithium disilicate. Airborne-particle abrasion at the pressures higher than 100kPa caused a significant reduction in the flexural strength of lithium disilicate material due to the creation of concentrated areas of mechanical stress and microfractures at the material surface.(32) Kern and Thompson(37) studied the effect of sandblasting of glass-infiltrated alumina ceramic in term of volume loss, morphology and changes in the surface composition. In-Ceram ceramic and IPS Empress were used in this study. The author suggested that excessive airborne particle abrasion may result in volume loss of the ceramic which may affect the fitting of restoration. Empress ceramic lost its volume 36 times greater than In-Ceram ceramic. In the Empress ceramic, a mere one second of sandblast removed almost 1 mm^3 of ceramic material.

Table 5 Volume loss of ceramics after sandblasting (in mm^3)
(Kern and Thompson, 1994) (37)

Treatment	**In-Ceram*** (n = 10)	**Empress*** (n = 6)	**Empress †** (n = 6)
Rocatec-Pre	0.348 ± 0.029	11.981 ± 0.428	6.271 ± 0.159
Rocatec-Plus after Rocatec-Pre	0.388 ± 0.050	-	-
Rocatec-Plus	0.363 ± 0.038	-	-

Values are means ± standard deviations; sandblasting at 2.5 bars, distance 10 mm.

One-way ANOVA for treatment with In-Ceram Ceramic p>0.05

Wilcoxon rank-sum test between different ceramics and blasting times for Rocatec-Pre treatment p≤0.0001.

*Blasting time 14 seconds

†Blasting time 7 seconds.

Kato et al.(31) compared the effect of acid-etching with various etchants (ammonium hydrogen bifluoride, acidulated phosphate fluoride, hydrofluoric acid, phosphoric acid, sulfuric acid-hydrofluoric acid) and sandblasting on the bond strength of feldspathic porcelain and unfilled resin. The author concluded that alumina blasting may roughened the porcelain surface but post-thermocycling bond strength shown that air abrasion was not retentive due to insufficient production of undercuts (unless used in combination with silane). Similar result was obtained by Filho et al.(38) reported that sandblasting alone did not provide adequate bond strength. Etchant that contains hydrofluoric acid can effectively etch the porcelain and provided a significant increase in bond strength even after thermocycling. On the other hand, Panah et al.(39) claimed that treating the lithium disilicate substrate with airborne-particle abrasion along with hydrofluoric acid and silane coupling agent yield the best result in providing the highest and most durable bond.

Table 6 Porcelain surface conditioning assessed. (Kato et al., 2000) (31)

Group	Surface	Abbreviation	Material	Trade name	Lot no.	Period
1	Ground	GRD	No. 1000 SiC abrasive paper			5 s
2	Alumina blasted	AAA	50 µm grain sized alumina	Hi-Alumina		60 s
3	Etched	AHB	10% ammonium hydrogen bifluride gel	Dicor Etching Gel	082388	60 s
4	Etched	APF	Acidulated phosphate fluoride (0-9% F)	Fluorident Gel	16366	60 s
5	Etched	HFA	5% hydrofluoric acid gel	G-C HF Gel		60 s
6	Etched	PHA	40% phosphoric acid gel	K-etchant	113	60 s
7	Etched	SHF	Sulfuric acid-hydrofluoric acid (6-25% HF)	Stripit	506	60 s
8	Etched	APF	Acidulated phosphate fluoride (0-9% F)	Fluorident Gel	16366	10 min

Table 7 Shear testing results in MPa and Tukey-Kramer groupings. (Kato et al., 2000) (31)

Group	Abbreviation	Bond strength (thermocycle 0)	s.d.	Grouping*	Bond strength (5000 cycles)	s.d.	Grouping*
1	GRD	9.1	1.6	c	0	0	f
2	AAA	11.7	2.9	c	0	0	f
3	AHB	18.4	1.0	b	6.2	1.6	e
4	APF	8.1	1.5	c	0	0	f
5	HFA	21.3	2.2	a,b	15.5	4.1	d
6	PHA	9.5	1.7	c	0	0	f
7	SHF	23.7	4.9	a	15.2	3.2	d

*Identical letters indicate that the values are not statistically different (P>0.05).

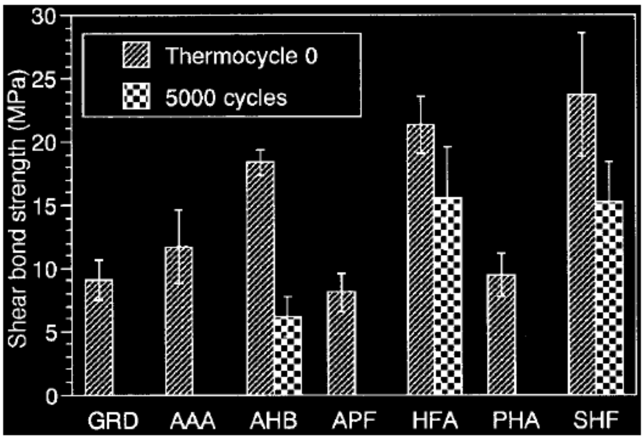


Figure 16 Shear bond strength of MMA-TBB resin joined to the VMK 68 porcelain. (Kato et al., 2000) (31)

2.3.2 Chemical modifications

Chemical modification is the process of unifying two dissimilar materials by the use of a chemically active coupling agent which processes the bonding affinity of both materials. Mechanical modification of the ceramic surface alone is insufficient to provide a durable bond between ceramic and resin cement. A reliably strong resin-ceramic bond extends the lifetime of the restoration. Combined mechanical-chemical adhesive strategies which involve the use of various primer and resin cement along with creating micromechanical retention has been developed. Chemical modification alters the surface chemistry. For this reason, many manufacturers try to invent suitable agents that can be used to promote chemical bonding. Chemical bonding techniques is crucial for the formation of a durable bond to increase the bond strength value. These techniques focus on creating chemical interaction that helps to improve the strength of resin-ceramic bond such as usage of coupling agents.

(i) Silane coupling agent

Silane coupling agents, widely used in the field of dentistry, are known for their excellent performance and biocompatibility. The silane monomers are initially hydrophobic in nature and are required to be dissolved in alcohol-water solvent. When use, the addition of acid activates the hydrolysis process and convert hydrophobic nature of the silane monomer into hydrophilic. The silane molecules later condense and set into hydrophobic siloxane film which are chemically active with various substrate depending on the composition of silane. Silane coupling agent can be generally classified into two types: functional and non-functional.(14)

Functional silane(14). Organofunctional silanes, act as adhesion promoters, are bifunctional silane molecules. Each molecule contains two different reactive functional group which can react and adheres various inorganic and organic materials together. For example, the hydrolysable functional group on one end reacts with the hydroxyl group on the surface of inorganic substrates. The organic functional group, on the other end, reacts and copolymerize with functional group of resins thus adheres the two dissimilar surfaces together. However, the organic functional group of silane should match the type of desired substrate.

Non-functional silane(14). Non-functional silanes have reactive alkoxy (-OR) functional groups. After hydrolysis, the functional groups change to silanol groups that can react with hydroxyl groups on the surface of inorganic substrates. Bis-functional silane, also known as dipodal silane, works as a cross-linker that contains two silicon atoms each have three hydrolysable alkoxy groups. Cross-linking silanes are water-soluble and are non-toxic. They are used in various application, not only in the field of dentistry. Adding cross-linker silane with functional silane improves bonding efficacy and hydrolytic stability by connecting the silane molecule to form rigid siloxane networks that also interconnect with functional silane. As the degree of cross-linking siloxane network increases, the hydrolytic cleavage of the siloxane bond becomes more difficult resulting in lesser penetration of water molecules.

Activation mechanism(40). The chemical formula for a functional silane coupling agent is composed of three main components: organofunctional group, linker group, and alkoxy group. The formular can be written as R-$(CH_2)_n$-Si-$(OR)_3$. R is a reactive organofunctional group, a non-hydrolysable group, which can bind to the organic polymer. -$(CH_2)_n$- is a linker group. Si is a silicon atom. -$(OR)_3$ is a hydrolysable alkoxy group. Activation of a functional silane coupling agent requires the hydrolysis of the alkoxy group in which a reactive silanol group is formed. The reactive silanol group can condense with other silanol groups to form siloxane linkages or form stable condensation products with other substrates such as aluminium, zirconium, tin, titanium, and nickel. Other oxides such as boron, iron, and carbon can form a less stable bond.

The hydrolysis of the alkoxy group is a fast and reversible protonation process which occurs at the pH level of 4(40). Then a bimolecular nucleophilic substitution (S_N2) reaction takes place at the central silicon atom. The water molecule H-O-H, a nucleophile, attacks the backside silicon atom forming a short-term penta-coordinate trigonal bipyramidal transition state. During the process, a new bond is formed between water (nucleophile) and silicon atom, meanwhile another bond on the leaving group (alcohol) is cleaved, resulting with a hydrolyzed product with an inversion of configuration. The hydrolysis process continued until all the remaining alkoxy groups are substituted.

Other factors that affect the silane hydrolysis process. Other factors that affect the rate of silane hydrolysis includes the molecular structure of silane molecule, concentration, pH, temperature, humidity and solvent system(14).

The size of the molecular structure of silane directly affects the steric effect of the alkoxy group. The larger the size of the alkoxy group, the stronger the steric repulsion effect, making it harder for the water molecule to reach the silicon atom.

Therefore, this means that the hydrolysis rate decreases when the size of the alkoxy group is large.

pH level significantly influence the silane hydrolysis. The hydrolysis process of alkoxysilane is faster in acidic and alkaline environment. However, the process is slowest at the neutral pH.

Temperature. The rate of hydrolysis process may change according to the change in temperature following Arrhenius law.

The nature of co-solvent in the solvent mixture has a direct impact on the rate of hydrolysis. Hydrophilic property of the solvent attract free water molecule to participate in the hydrolysis reaction. As hydrophilicity increases from propan-1-ol, ethanol, and methanol, the rate of hydrolysis increases. This means that the rate of hydrolysis will be highest if methanol is used. However, manufacturers substituted ethanol for methanol due to its toxicity in human.

(ii) Silane application in Dentistry(14)

a. Luting ceramic restoration and repairs

Many types of ceramic restoration have been used in the field of dentistry due to their superior esthetic appearance and metal-free substructure. Silane coupling agent help to improve the bond strength and durability of resin and ceramic but the bond may not be stable over time and is susceptible to moisture(41). However, the problem of ceramic fracture persists since ceramic materials are brittle in nature. They have high compressive strength but low tensile strength.

There are several other factors that contribute to the fracture such as the micro defect in the material, impact and fatigue load, imperfect design, mastication, parafunction and intraoral occlusal force that gives repetitive dynamic load.

When fracture occurs and the repair is feasible, it is more cost-effective and time-saving to repair the fractured part than to fabricate and replace the whole restoration.

b. Glass fiber-reinforced composites

Glass fibers are used in various application in the field of dentistry such as glass fiber-reinforced resin composite post, removable prosthodontics, periodontal splints, fixed partial dentures, and retention splints. Cooperating glass fiber with resin matrices helps to improve mechanical strength of the material and also reduces the polymerization shrinkage during processing, therefore, less dimensional change. Treating the surface of glass fiber with silane coupling agent is a crucial step to obtain a reliable bond between resin matrices and glass fibers. This step improves the physical and mechanical integrity of fiber-reinforced composites. By increasing the chain length of the spacer group also increase hydrolytic stability.

c. Resin composites

Dental composite is composed of five main components including resin matrix, free-radical initiator and inhibitor (also known as stabilizer), colourant (pigment), fillers, and silane coupling agent. Various fillers can be used such as silica, lithium aluminum silicates, hydroxyapatite, boron silicates, etc. The fillers are added to enhance mechanical properties of the composite and also reduce polymerization shrinkage after curing. However, the dental resin composite are not simply mixed but silane coupling agent is added to unify the filler particles and resin matrix. The methoxy group of the silane reacts with alkoxy groups on the surface of fillers to produce siloxane bond(42). The process of light curing activates the organofunctional group of silane coupling agent which reacts with the functional group of resin monomers. Silanized fillers improve mechanical strength and hydrolytic stability of resin composite.

d. Titanium, base metal and noble metal alloys

The siloxane to metal bond greatly depends on the type of metal alloy and its surface chemistry. Generally, the metal surface is required to be pre-treated prior to the application of silane coupling agent. Grit blasting is a crucial step to obtain a durable bonding. Tribochemical silica coating is the process that uses air-abrasion along with the beneficial properties of silane coupling agent. The surface of the restoration such as metal or zirconia is air-blasted with silica-modified aluminum oxide. This method produces rough surface and incorporate silica on to the metal surface which promotes chemical bonding, enhancing the bonding capacity when used together with silane application [2,4,28]. When a thin layer of silica is formed on the metal surface, the chemical –O–Si–O–M– linkage is formed. The application of silane result in the formation of siloxane and metal linkage that can be written as –(Si–O–Si)–O–M–. Alternatively, other types of primers such as metal or alloy primer can be used to bond resin composite to metal or metal alloy. Some studies reported that these primers give superior result when compared to silane coupling agent. Generally, they are composed of two reactive primer components. For base metal alloys, phosphate esters, carboxylic acids, and acid anhydrides are often used. For noble metal alloys, thione or thiol groups are often used.

Trialkoxysilanes, such as 3-methacryloyloxypropyltrimethoxysilane (MPS), is one of the commonly used silane coupling agent in the field of dentistry(41). As mentioned previously, silane helps to increase surface energy and wettability of silica-based ceramic. In the case of lithium disilicate ceramic, silane application is one of the most crucial steps in obtaining optimal bond. Filho el al.(38) conducted an experiment on examining the effect of different surface treatment on lithium disilicate on microtensile bond strength. The author stated that silanization of ceramic surface is the most significant factor in enhancing the bond strength. Acid etching followed by silanization yield the best result in promoting maximum bond strength.

Table 8 Mean Microtensile Strength (μ-tbs) in MPa, Standard Deviation (SD), Number of Specimens Per Group (N), and Coefficient of Variation (CV).
Group 1: Treat with hydrofluoric acid and silane coupling agent;
Group 2: Treat with silane coupling agent;
Group 3: Treat with hydrofluoric acid alone. (Filho et al., 2004) (38)

Group	**Group 1 (HF+S)**	**Group 2 (S)**	**Group 3 (HF)**
Means	56.8^a	44.8^b	35.1^c
SD	10.4	11.6	7.7
N	18	21	22
CV	18.3	25.8	21.8

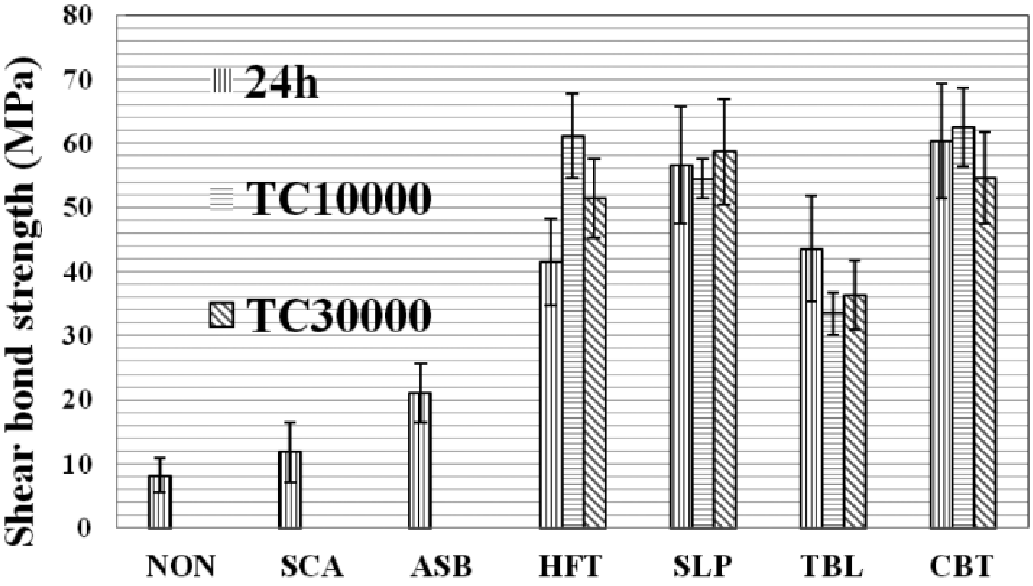
Means with different letter are significantly different at p≤0.05.

In contrast, Sato et al.(43) reported that application of silane coupling agent alone on the surface of lithium disilicate was not useful due to the debonding of specimens after themocycling. The author suggested alternative method apart from using hydrofluoric acid and encouraged the use of additional treatment along with silanization such as special gas emission method and tribochemical treatment with phosphoric acid ester monomer to enhance the activation effect of silane coupling agent.

Table 9 Surface modification methods examined. (Sato et al., 2015) (43)

Code	**Surface treatment**	**Surface modifications**	**Silane coupling agent**	**Primer**
NON	None	None	None	None
SCA	None	None	Espesil	None
ASB	Rocatec Pre	None	Espesil	None
HFT	None	Hydrofluoric acid solution	Espesil	None
SLP	Rocatec Pre	Silano pen	Espesil	None
TBL	Rocatec Pre	Rocatec Plus	Espesil	None
CBT	Rocatec Pre	Rocatec Plus	Espesil	Epricord

Table 10 Shear bond strengths of the non-modified and modified LDC specimens. In the table supplied, across a particular row, samples denoted by the same superscript letters are not significantly different (P > 0.05). Across a particular column, samples denoted by the same subscripted letters are not significantly different (P > 0.05). (Sato et al., 2015) $^{(43)}$



	NON	SCA	ASB	HFT	SLP	TBL	CBT
24h	8.2 (2.7)^{a}	11.8 (4.7)^{a}	21.1 (4.6)^{b}	41.5 (6.8)$^{c}_{A}$	56.5 (9.1)$^{d}_{A}$	43.6 (8.3)$^{c}_{A}$	60.3 (9.0)$^{d}_{A}$
TC10000	Debonding	Debonding	Debonding	61.2 (6.6)$^{e}_{B}$	54.5 (3.1)$^{e}_{A}$	33.5 (3.2)$^{f}_{A}$	62.6 (6.2)$^{e}_{A}$
TC30000	Debonding	Debonding	Debonding	51.4 (6.1)$^{g}_{AB}$	58.7 (8.3)$^{g}_{A}$	36.4 (5.4)$^{h}_{A}$	54.6 (7.1)$^{g}_{A}$

(iii) Contact angle measurement in relation to silane coupling agent

The adhesion between dental ceramic and resin cement depends upon both physical and chemical interaction. Wetting is the ability of a liquid to interact and forms interface with solid surfaces.(44) The degree of wettability of the substrate can physically contributes to the adhesion process.(45) Contact angle values indicate the wettability of a surface and can be used to calculate the surface energy.(46) Contact angle is defined as the angle where the liquid/vapor interface meets a liquid interface/solid surface. The degree of wettability depends upon the surface energy (surface tension) of the interfaces involved such that the total energy is minimized. If a solid surface attracts a probing liquid, for example, water on a hydrophilic surface, the droplet of the probing liquid would spread out on the solid surface and the contact angle measurement will be close to zero degrees. Less hydrophilic surface will produce a contact angle up to 90°. When the angle is larger than 90°, it indicates that the surface is hydrophobic and if the angle is over 150°, the surface is superhydrophobic.

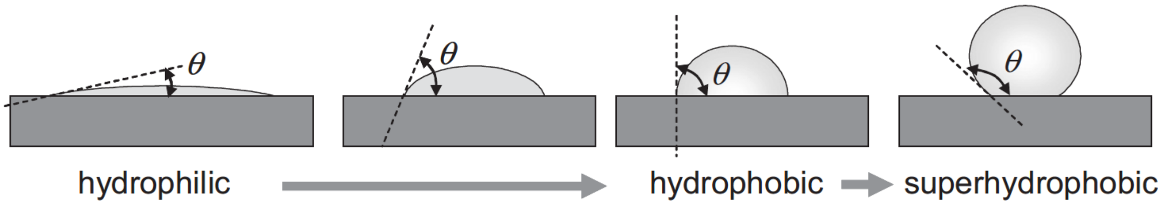


Figure 17 Schematic of different levels of wettability of surfaces.
(Surface Design: Applications in Bioscience and Nanotechnology, 2009) (57)

It is believed that the bond strength between ceramic and resin is improved with higher ceramic surface energy. The wettability of a solid surface by liquid is represented in Young's equation (46):

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\ \mathrm{Cosq} \qquad (1)$$

γ_{SL} is the interfacial energy. γ_{SV} is the free energy per unit area of the solid surface in equilibrium with vapor. γ_{LV} is the surface tension of liquid balanced with its vapor tension and q is the contact angle.

The work of adhesion (W_A) of the liquid drop on a substrate is represented in Dupré's equation:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (2)$$

Combining equation (1) and (2) results in Young-Dupré equation:

$$W_A = \gamma_{LV}\ (1 + \mathrm{Cosq}) \qquad (3)$$

As described by equation (3), the work of adhesion depends upon the surface tension of the liquid and its contact angle on the substrate.(46)

Many researches were conducted regarding the surface treatment of ceramic surfaces in relation to contact angle measurements. Banthitkhunanon P. (47) studied the flow of distilled water on the silane treated ceramic surface. Three different types of silane were used including MPS (3-methacryloxypropyl Trimethoxysilane), APS (3-aminopropyl Triethoxysilane), and AAPS (N-2(aminoethyl)3-aminopropyltriethoxysilane). The author concluded that any types of silane treatment on ceramic surface could significantly lower the contact angle between distilled water and the substrate compared to the control group (no silane treatment). The group that produced the smallest contact angle was the MPS group (57.2°), followed by APS (62.8°), AAPS (78.1°) and the control (84.7°). Lower contact angle and better wettability would promote the bond strength of between the substrate and resin. The author suggested that the MPS molecules may alter the surface polarity of the substrate which resulted in better wetting of the distilled water. Also, the MPS molecules were smaller than those of APS and AAPS which allowed them to react on the substrates' surfaces faster than the other groups, producing durable siloxane bond.

Table 11 Average contact angles (standard deviations) in degree (°) of various silanized groups. (Banthitkhunanon P., 2017) (47)

Silane coupling agents (n=10)	Contact angles (standard deviations)
Control	84.7 (1.3)^{D}
MPS	57.2 (2.5)^{A}
APS	62.8 (2.7)^{B}
AAPS	78.1 (2.8)^{C}

*Values with the different letters are statistically significant different ($p<0.05$)

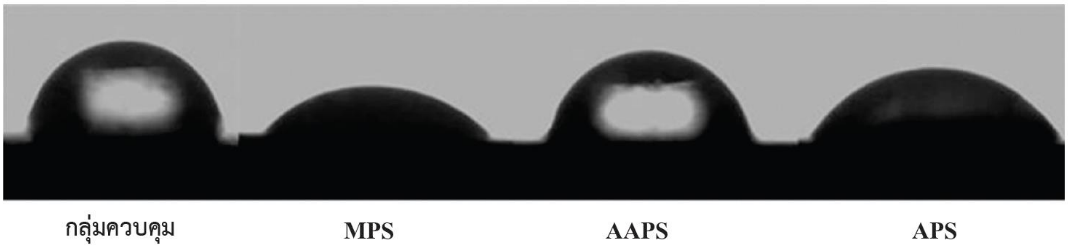


Figure 18 Contact angles of all groups. (Banthitkhunanon P., 2017) (47)

Della Bona et al.(48) conducted an experiment using lithium disilicate-based ceramic treated with different protocols including application of silane coupling agent and/or etching with hydrofluoric acid/acidulated phosphate floride (APF) gel before measuring the contact angle. The author explained that treating the ceramic surface with silane makes the surface hydrophobic. The hydrophobic property may reduce hydrolytic degradation of the bond and would also promote the wetting of adhesive (due to organophilic surface). In the study, 8% Methacryloxy propyl trimethoxy silane (MPTMS) was used to treat the ceramic surface. High-performance liquid chromatography grade water (HPLC water) and liquid resin of known surface tension were used as the probing liquid (72.6 mN/m and 39.7 mN/m, respectively). However, when the silane coupling agent was applied and the liquid resin was dropped, ‘beads up’ of the liquid resin was observed on the silanated ceramic surface. The author explained that for an adhesive to completely wet the substrate surface, it must be of low viscosity and the surface tension of the adhesive must be lower than the critical surface energy of the substrate.

Table 12 Work of adhesion (mJ/m^2), and mean values for the apparent advancing (ϑ_a) and receding contact angles (ϑ_r) for experimental groups.
(Della Bona et al., 2004) (48)

Group	Surface treatment	Silane coating	Probing medium	Work of adhesion (mJ/m^2)	Apparent **θa** *mean (SD)	Apparent **θr** *mean (SD)
1	As-polished	No	HPLC water	134.7	31.2(4.6)^{B}	16.1(6.3)^{B}
2	HF	No	HPLC water	143.0	14.0(8.3)^{C}	18.3(7.1)^{B}
3	As-polished	No	Resin	73.3	32.1(3.0)^{B}	0^{C}
4	HF	No	Resin	77.4	18.5(2.0)^{C}	0^{C}
5	APF	No	Resin	76.6	21.5(3.5)^{C}	0^{C}
6	As-polished	Yes	Resin	61.9	55.9(2.0)^{A}	44.4(1.2)^{A}
7	HF	Yes	Resin	63.4	53.3(6.6)^{A}	42.1(8.6)^{A}
8	APF	Yes	Resin	61.8	56.2(2.5)^{A}	43.7(2.3)^{A}

*The values in each column with same superscript letters do not differ significantly by Duncan’s multiple range test (α = 0.05).

Farge et al.(49), conducted a research on the wetting of dentin, also demonstrated the relationship of surface energy/tension to its wetting property. The author used different adhesive systems that differed in the composition of the solvent. It was reported that the liquid (solvent) with lower surface tension had better wettability than ones with higher surface tension; for example, ethanol (22.4 mN/m) shown superior wetting property than ethanol-water.

Chen et al.(50) studied the effect of incorporating BisGMA resin on the bonding properties of silane and zirconia primers. The application of Monobond Plus (silane containing 10-MDP and sulphide monomer) on zirconia significantly increased the contact angle of deionized water when compared to the unconditioned surface (15.1° to 74.1°). However, the author believed that incorporating BisGMA resins to silane coupling agents may reduce the contact angle formed between deionized water and the silanated lithium disilicate surface. The author explained that the extra resins might inhibit the condensation reaction, thus, lowering both the contact angle and bond strength.

Table 13 Shear bond strength (in MPa) on primed ceramic surface. (Chen et al., 2013) (50)

Silane Primer	**Lithium Disilicate**	**Zirconia Primer**	**Zirconia**
Control (no primer)	18.0 (4.2) $^{c;3}$	Control (no primer)	4.2 (2.9) $^{C;3}$
Porcelain Primer	34.3 (7.6) $^{a;1}$	Monobond Plus	18.2 (5.0) $^{B;2}$
BisGMA-Modified Porcelain Primer	27.8 (6.1) $^{b;1,2}$	BisGMA-Modified Monobond Plus	22.0 (6.0) $^{B;2}$
Kerr Silane	23.1 (5.6) $^{b;2}$	ZPrime Plus	29.0 (6.3) $^{A;1}$

Data are presented as mean (standard deviation). Means followed by a different letter in same column are statistically different ($P<0.5$). Logarithm-transformed shear bond strength data were also subjected to statistical analysis. Means of logarithm-transformed data followed by different number in the same column are statistically different ($P<0.05$).

Table 14 Contact angle (degrees) on primed ceramic surface. (Chen et al., 2013) (50)

Silane Primer	**Lithium Disilicate**	**Zirconia Primer**	**Zirconia**
Control (no primer)	20.9 (6.8) ^{c}	Control (no primer)	15.1 (4.0) ^{B}
Porcelain Primer	88.3 (9.5) ^{a}	Monobond Plus	74.1 (6.7) ^{A}
BisGMA-Modified Porcelain Primer	32.9 (8.1) ^{b}	BisGMA-Modified Monobond Plus	71.7 (3.8) ^{A}
Kerr Silane	22.5 (7.4) ^{c}	ZPrime Plus	75.0 (6.1) ^{A}

Data are presented as mean (standard deviation). Means followed by different letter in same column are statistically different ($P<0.05$).

Tani et al.(51) studied the contact angle of dentin bonding agent on the dentin surface. The author used a dual-cured dentin bonding agent (Clearfil Photo Bond, Kuraray, Osaka, Japan) as the probing liquid. The study had a total of six experimental groups including; a group without any further surface treatment after surface grounding (control), a group that had been clean with EDTA, and four other groups that had been clean with EDTA along with different primers. It was concluded that the primed dentin surface have superior wettability and surface energy to dentin bonding agent and that the contact angle was immeasurable. Interestingly, the control group also exhibited superior wetting property. The author explained that the phenomenon was cause by the microcapillary reaction of the smear layer. Therefore, even though the control group may exhibit higher surface energy, the bond strength may not improve since the smear layer will disturb the bonding between dentin and the resin materials.

Table 15 Contact angles of tested solutions on the dentin surface. (Tani et al., 1996) (51)

	Distilled water	**1-Bromonaphtalene**	**Diiodomethane**	**Clearfil Photo Bond**
Smear layer	22.0±4.9	13.6±1.7	51.6±6.4	Unmeasureable*
EDTA	52.0±5.3	40.4±2.3	76.2±3.2	13.2±1.3
EDTA & GM	10.2±3.2	35.0±4.0	58.0±3.2	Unmeasureable*
EDTA &HEMA	16.0±5.1	32.8±1.3	50.0±2.6	Unmeasureable*
EDTA & Ethylene glycol	29.8±6.1	49.2±6.1	68.4±9.0	Unmeasureable*
EDTA & Hexanediol	7.6±4.4	36.6±8.7	66.4±9.7	Unmeasureable*

*The commercial dentin bonding agent did not form a hemispherical shape because it rapidly spread on the surface

Table 16 Surface free energy. (Tani et al., 1996) (51)

Smear layer	74.2 mN/m
EDTA	56.9 mN/m
EDTA & GM	76.2 mN/m
EDTA &HEMA	72.9 mN/m
EDTA & Ethylene glycol	65.1 mN/m
EDTA & Hexanediol	76.8 mN/m

After EDTA cleaning, priming with the four aquous solutions increased the surface free energy.

Ramakrishnaiah et al.(52) studied the effect of hydrofluoric acid etching duration on the surface micromorphology, roughness, and wettability of dental ceramics. Five different brands of silica-based glass ceramic were used, including; IPS e-max, Dentsply Celtra, Vita Suprinity, Vita mark II and Vita Suprinity FC. The samples were divided into five groups depending on the etching duration, using hydrofluoric acid from 0, 20, 40, 80 and 160 seconds, respectively. Deionized water was used as probing agent and contact angle measurements for each group were recorded. The results showed that increasing the etching duration significantly reduced contact angle value on every groups. The author concluded that there was a positive correlation between the surface roughness and wettability and etching duration affects the number and width of pores that are formed on the substrate surfaces. Porous surface promotes superior wetting and thus allows easy spreading and reaction of silane and resin composites which improves bondability.

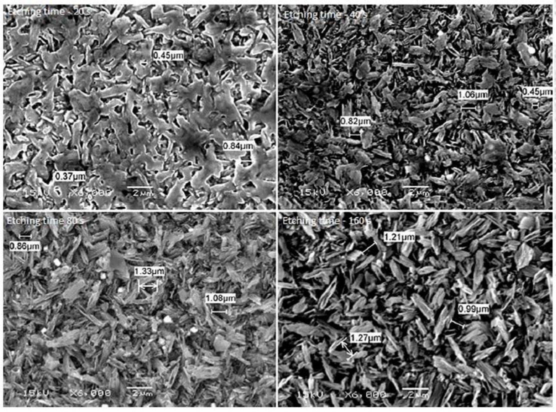


Figure 19 SEM photomicrographs showing microstructure of ceramics etched for different etching times (from the left, upper line: 20, 40, 80 and 160 s). Original magnification 6000x ; bar = 2 µm. (Ramakrishnaiah et al., 2016) (52)

Table 17 Comparison of mean surface roughness (S_a) among different experimental groups. (Ramakrishnaiah et al., 2016) (52)

Materials	**Mean Surface Roughness (Mean ± SD)**					**p-Value**
	Control	**20 s**	**40 s**	**80 s**	**160 s**	
Celtra	0.08 ± 0.008^{a}	0.14 ± 0.006^{b}	0.22 ± 0.02^{c}	0.28 ± 0.03^{d}	0.33 ± 0.020^{e}	0.001*
e-max	0.16 ± 0.030^{a}	0.21 ± 0.030^{b}	0.30 ± 0.02^{c}	0.56 ± 0.05^{d}	0.65 ± 0.016^{e}	0.001*
Mark II	0.14 ± 0.016^{a}	0.36 ± 0.020^{b}	0.41 ± 0.01^{c}	0.59 ± 0.01^{d}	0.60 ± 0.010^{d}	0.001*
Suprinity	0.09 ± 0.010^{a}	0.46 ± 0.020^{b}	0.55 ± 0.06^{c}	0.56 ± 0.03^{d}	0.64 ± 0.010^{d}	0.001*
Supri FC	0.08 ± 0.009^{a}	0.26 ± 0.010^{b}	0.29 ± 0.03^{c}	0.35 ± 0.03^{d}	0.53 ± 0.030^{e}	0.001*

Key: SD = standard deviation; test applied: one-way ANOVA with the post hoc Tukey test. The one-way ANOVA: *indicates statistically significant at $p<0.05$. The post hoc Tukey test: values with different letters superscripted vary significantly

Mayara Prado et al.(53) studied the ceramic surface treatment with a single-component primer. In this study, lithium disilicate glass ceramic (IPS e.max CAD) and feldspathic ceramic (VITA Mark II) were used. The samples were divided into two group based upon the surface treatment (hydrofluoric acid along with silane application [Monobond Plus] or single-component ceramic conditioner alone [Monobond Etch & Prime]) and storage condition (baseline or aged with 70 water storage along with 12,000 thermal cycles). The results showed that hydrofluoric acid etching increased surface energy and allowed better wetting before silane application. The increase in surface energy of the substrate can improve bonding potential. Conventional ceramic surface treatment (hydrofluoric acid along with silane coupling agent) provided higher bond strength than the single-component ceramic conditioner group. However, after aging procedure, the mean microshear bond strength significantly dropped when compared to the baseline. The mean microshear bond strength was not affected in the single-component ceramic conditioner group. The author suggested that this might be due to the reaction mechanism of Monobond Etch & Prime which produced stable adhesion.

Table 18 Microshear bond strength (mean ± standard deviation) in MPa and failure analysis (Prado et al., 2018) (53)

Surface treatment	Baseline condition							Aging condition						
	μSBS (Mpa)	Produced, lost, and tested samples			Failure analysis, n(%)			μSBS (Mpa)	Produced, lost, and tested samples			Failure analysis, n(%)		
		TOT	PTF	TES	AD	MIX	CO		TOT	PTF	TES	AD	MIX	CO
Lithium disiliscate MEP	10.4 ± 2.4^{Ba}	40	16	24	18(75)	5(20)	1(5)	9 ± 3.4^{Ba}	40	12	28	23(83)	4(15)	1(2)
Lithium disiliscate HF+S	21.2 ± 2.1^{Aa}	40	5	35	28(80)	7(2)	-	14.6 ± 2.3^{Ab}	40	13	27	24(90)	3(10)	-
Feldspathic MEP	13.5 ± 5.4^{Ba}	39	13	26	23(90)	3(10)	-	11.0 ± 3.2^{Ba}	40	16	24	21(88)	3(12)	-
Feldspathic HF+S	19.5 ± 4.2^{Aa}	36	6	30	19(64)	9(30)	2(6)	14.7 ± 3.3^{Ab}	39	7	32	28(87)	4(13)	-

Different superscript capital letters indicate statistically significant difference in the same column for the same ceramic type, comparing surface treatments. Different superscript lowercase letters indicate statistically significant difference in the same line, comparing aging conditions. ADHE: adhesive failure between cement and ceramic; MIX: mixed adhesive failure between cement and ceramic/cohesive failure of the cement; CO: cohesive failure of the cement.
TOT: Total number of resin cement cylinders; PTF: number of pre-test failures; TES: total number of tested cylinders

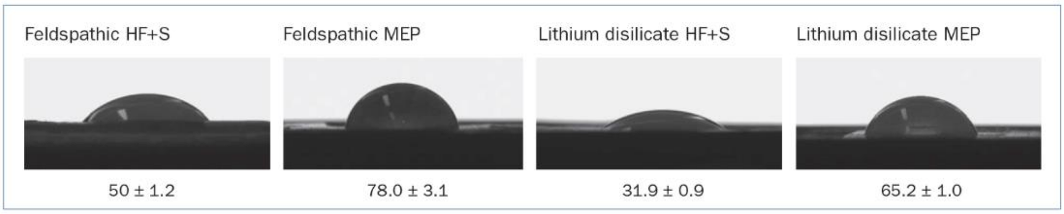


Figure 20 Contact angle images (means standard ± deviation in degrees) of ceramic surface subjected to each treatment types. (Prado et al., 2018) (53)

Prochnow et al.(10) studied the adhesion to lithium disilicate glass ceramic (IPS e.Max CAD) etched with hydrofluoric acid at distinct concentrations. The samples were divided into eight groups depending on the acid concentration (1, 3, 5 and 10% hydrofluoric acid) and type of storage (baseline or aged with water storage for 150 days along with 12,000 thermal cycles). The result showed that hydrofluoric acid concentration significantly influenced the contact angle value and the bond strength. Surface roughness greatly depends upon the hydrofluoric acid concentration. However, 1% and 3% hydrofluoric acid could not significantly increase the roughness of the substrate surface when compared to the control group. The increase in surface wettability (low contact angle) after acid-etching allowed superior bonding potential. The bond strengths for each group were reduced after aging process.

Table 19 Means and standard deviation of bond strength data (MPa) as a function of storage condition, total number of tested samples in conditions without and with aging, total number of pre-tested failures (PTF) during thermocycling (TC), contact angle, and roughness (Sa and Sz parameters in nm) (Prochnow et al., 2018) (10)

	Mean bond strength		Total tested samples without aging	Total tested samples with aging*	Total number (%) of PTF during TC	Contact angle	Roughness	
	Without aging	With aging*					Sa (nm)	Sz (nm)
Ctrl	-	-	-	-	-	28.4 ± 1.5^{A}	9.2 ± 3.2^{C}	134.5 ± 25.1^{B}
HF1	11.2 ± 4.5^{Ba}	1.8 ± 2.9^{Bb}	40**	4	36 (90%)	15.9 ± 2.5^{B}	24.9 ± 3.1^{BC}	205.3 ± 29.6^{B}
HF3	13.9 ± 3.9^{Aba}	7.8 ± 6.1^{Ab}	38**	25	15 (37.5%)	7.8 ± 0.4^{C}	30.4 ± 2.4^{B}	275.0 ± 43.3^{B}
HF5	15.9 ± 2.9^{Aa}	11.0 ± 7.5^{Ab}	39**	33	7 (17.5%)	8.3 ± 2.9^{C}	56.6 ± 18.2^{A}	563.8 ± 185.5^{A}
HF10	14.5 ± 5.2^{Aba}	9.8 ± 7.5^{Ab}	37**	27	13 (32.5%)	10.4 ± 2.1^{C}	52.5 ± 2.4^{A}	469.8 ± 25.4^{A}

*Storage (37℃ for 150 days) and thermocycling (12,000 cycles; 5℃ and 55℃). Means in the same column with the same capital letter are statistically similar. Different lowercase letters mean statistical difference between storage conditions. **Forty (40) resin cement cylinders were produced for each condition; for baseline groups, specimen with bubbles and defects in the interface were not tested; for aged groups, all the specimens were checked before the storage period, being the non-tested samples all pre-test failure (during thermocycling).

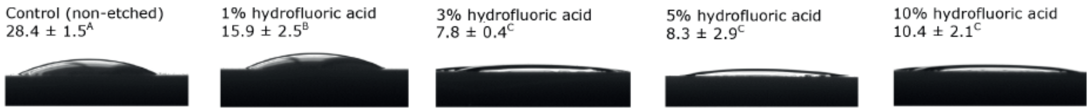


Figure 21 Images and means ± SD (in degrees) of contact angle measurements of surfaces subjected to the following conditions: non-etched (CTRL); etched for 20 s with 1%, 3%, 5%, and 10% hydrofluoric acid. The same superscript letters indicate no significant differences (Tukey's test; α= 5%). (Prochnow et al., 2018) (10)

2.4 Testing Methods

2.4.1 Shear bond strength test

Shear bond strength test (SBS) is a popular method due its simplicity, no additional procedure is require after the bonding procedure is completed. However, the technique is criticized for the nonhomogeneous stress distribution in the adhesive interface which may result in overestimation or misinterpretation of the results. The micro-shear bond test does not require trimming of the specimen, therefore, the bonding surface is left intact. Moreover, the defined bonding area is very small which result in the uniform stress distribution.(39) Larger bonded area may have more defect compared to the smaller ones.(54) The loading direction barely has an impact on the result, preparation is much easier than the tensile measurement.(55) Tensile test might be a more reliable method that is used to evaluate the true adhesion. However, tough material will not fail cohesively under shear loading thus real bond strength value can be accurately obtained.(54, 56) Therefore, in the case of lithium disilicate, shear bond strength test seems to be a suitable choice.

2.4.2 Contact angle measurement

Several methods can be used to measure contact angle of surfaces and there are different ways to classify these methods. For example, in Table 20, (44) the methods are classified into two main groups; direct (sessile-drop goniometry, tilting plate) and indirect (Wilhelmy plate).

Table 20 Different wetting characterization methods. (Huhtamäki et al., 2018) (44)

Method	Description	Advantages	Disadvantages
Direct methods			
Sessile-drop goniometry	The volume of a drop deposited on the measured surface is increased, and the value of the ACA is obtained from the advancing contact line. For the RCA, the volume of the drop is reduced, and the value of the RCA is obtained from the receding contact line	Simple	Susceptible to operator error if a strict protocol is not used
		Small amounts of water are required	Collecting information from a large area requires measurements at multiple locations, and is thus time consuming
		It is possible to measure samples with small surface areas	Small amounts of impurities in the water may cause experimental error
		Provides information about the uniformity of the sample	
Tilting plate	Contact angles are measured from the leading edge and the trailing edge of a distorted drop on an inclined plane when the drops starts sliding. The tilt angle at which the drops starts sliding is called 'sliding angle', and is a measure of droplet mobility.	Simple	The measured contact angles do not necessarily correspond to the ACA and the RCA. The sliding angle does not necessarily correspond to the contact angle hysteresis.
		It is quick to perform	The recorded values also depend on the size of the drop used in the measurements- the obtained value are not necessarily a property of the measured surface alone
Indirect methods			
Wilhelmy plate	The sample surface in the form of a thin plate is dipped vertically into water, and the contact angle is determined from the measured force. The change in the force is a combination of buoyancy and the force of wetting	No operator error	Does not provide information about the uniformity of the surface
		Ease of automation	There is no visual feedback to help detect how wetting occurs
	The ACA and the RCA can be measured by dipping the sample into water or withdrawing the sample from the water	Information from large areas of the sample is gathered quickly	The sample should have the same composition and morphology on all surfaces: front, back and sides
			The relationship between the measured force and the obtained contact angle depends on the length of the contact line, which may be hard to determine for rough surfaces

Sessile-drop method can be further performed in either static or dynamic procedure. Static sessile drop is the most convenient method to measure contact angle between the liquid/solid interface and liquid/vapor interface. The procedure requires a microscope optical system or a high-resolution camera and a software to record and analyze the contact angle.(57)

Dynamic sessile drop is similar to static sessile drop but with the modification of the drop during measuring. During the measurement, the volume of the drop can be increased or reduced to obtain the largest and smallest possible angle without increasing the solid/liquid interfacial area. When the volume is added, yielding the maximum angle of the drop, the advancing angle (ACA) is obtained. Similarly, when the volume is reduced yielding the smallest possible angle, the receding angle (RCA) is obtained. The differences between these angles is the contact angle hysteresis. Another way to measure dynamic contact angle can be done by measuring a drop travelling down a sloped flat surface, known as the tilting plate method.(57)

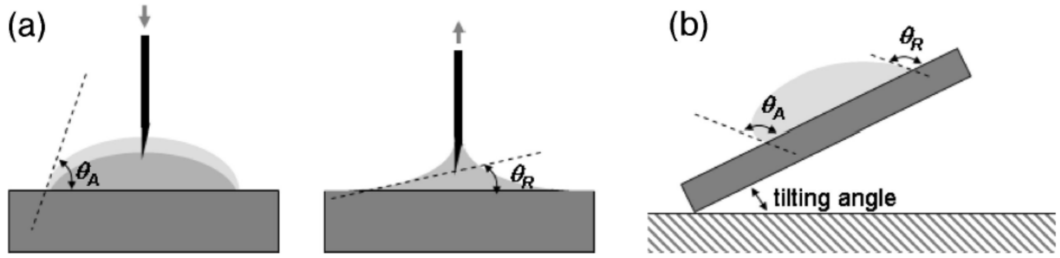


Figure 22 Different methods to measure the advancing and receding contact angle at solid surfaces (a) dynamic sessile drop and (b) advancing drop method. (Surface Design: Applications in Bioscience and Nanotechnology, 2009) (57)

Dynamic Wilhelmy plate method uses a solid of uniform geometry to calculate the average of both advancing and receding contact angles upon dipping the solid into a liquid with known surface tension. The requirement of this method is that both sides of the solid must have the same properties.(57)

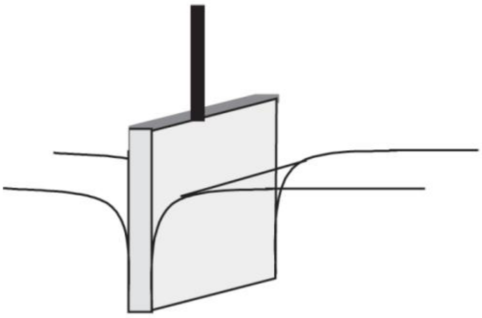


Figure 23 Schematic of the dynamic Wilhelmy method.(Surface Design: Applications in Bioscience and Nanotechnology, 2009) (57)

Selecting a probing medium is an important aspect when measuring the contact angle. Liquid of known surface tension such as 1-bromo-naphthalene (44.4 mJ/m^2), diiodomethane (50.8mJ/m^2) and water (72.8mJ/m^2) are commonly used.(58) However, selecting an appropriate probing liquid depends on the objective of the study.(46) To examine the wettability of a specific liquid on a substrate, it is best to use the liquid or other liquid with similar properties as the probing medium. If the purpose was to examine the wettability of silane coupling agent on a ceramic plate, the respective silane coupling agent should be used as the probing liquid.

In the current study, static sessile drop was used due to its convenient operation and popularity.(44) Deionized water was used as a probing liquid to investigate

CHAPTER III

RESEARCH METHODOLOGY

In this study, the experiment was divided into two parts.

Part I: Shear bond strength test

The first part was to evaluate the effect of different type of silane coupling agent on the shear bond strength between lithium disilicate glass ceramic and resin cement. Shear bond strength test was used evaluate the bond strength and stereo microscope was used to identify the mode of failure. Three commercial dental silanes (Kerr silane primer, Monobond N, Rely X ceramic primer) and one experimental silane were evaluated in vitro as adhesion promoters bonding a resin cement to lithium disilicate glass ceramic surfaces.

Part II: Contact angle analysis

The second part of the study was to investigate the effect of treating the hydrofluoric-acid-etched/unetched lithium disilicate surface with various types of silane coupling agents on the contact angle measurement. The samples were randomly divided into two groups: hydrofluoric etched and unetched lithium disilicate surfaces before silane application. Each group was further divided into five subgroups, according to type of silane coupling agent used to treat the prepared surfaces. The contact angles between deionized water and the prepared surface were measured using a contact angle tester via sessile drop method.

Table 21 List of material used

Brand name	**Type**	**Composition**	**Manufacturer/ Supplier**
IPS e.max Press (Lot Y10318)	Lithium disilicate glass ceramic	SiO_2, Li_2O, K_2O, P_2O_5, ZrO_2, ZnO, other oxides and ceramic pigments	Ivoclar-Vivadent, Schaan, Liechtenstein
Filtek Z350 Universal (Lot N989726)	Composite resin	Silane treated ceramic, silane treated silica, diurethane dimethacrylate (UDMA), bisphenol A polyethylene glycol diether dimethacrylate, bisphenol A diglycidyl ether dimethacrylate (BIS-GMA), silane treated zirconia, polyethylene glycol dimethacrylate, triethylene glycol dimethacrylate	3M ESPE, St. Paul, MN, USA
RelyX U200 (Lot 4683905)	Self-adhesive resin cement	Base: Methacrylate monomers containing phosphoric acid groups, Methacrylate monomers, Silanated fillers, Initiator components, Stabilizers, Rheological additives Catalyst: Methacrylate monomers, Alkaline(basic) fillers, Silanated fillers, Initiator components, Stabilizers, Pigments, Rheological additives	3M Deutschland GmbH, Neuss, Germany
Rely X ceramic primer (Lot N988623)	Silane	Ethanol, water, methacryloxypropyltrimethoxysilane	3M ESPE, St. Paul, MN, USA
Monobond N (Lot X41367)	Silane	Ethanol, methacrylated phosphoric acid ester, sulphide methacrylate, 3-trimethoxysilylpropyl methacrylate	Ivoclar-Vivadent, Schaan, Liechtenstein

Kerr Silane primer (Lot 7072259)	Silane	Ethanol, (1-methylethylidene)bis[4,1-phenyleneoxy(2- hydroxy-3,1-propanediyl)] bismethacrylate Poly(oxy-1,2-ethanediyl), α,α'-[(1-methylethylidene)di-4,1-phenylene]bis[ω-[(2- methyl-1-oxo-2-propen-1-yl)oxy]- 2,2'-ethylenedioxydiethyl dimethacrylate 3-trimethoxysilylpropyl methacrylate	Kerr corporation, West Collins Avenue Orange, CA, USA
Experimental silane (Lot SHBJ3136)	Silane	Methacryloxypropyltrimethoxysilane, Inhibitors (hindered phenol and/or hydroquinone derivatives), Methanol	Sigma-Aldrich, MO, USA
IPS ceramic etching gel (Lot Y06707)	Hydrofluoric acid	4.5% Hydrofluoric acid	Ivoclar-Vivadent, Schaan, Liechtenstein

3.1 Part I: Evaluating the effect of different type of silane coupling agent on the shear bond strength between lithium disilicate glass ceramic and resin cement

Before getting into the shear bond strength test, the lithium disilicate samples and the resin composite rods were prepared.

Lithium disilicate rod preparation

Fifty lithium disilicate rods (IPS e.max Press, Ivoclar-Vivadent, Schaan, Leichtenstein) were prepared by waxing up rod-shaped samples with diameters of 5 millimeters and heights of 5 millimeters (Figure 24). The lost wax technique and heat-pressed processes were performed according to the manufacturer's instructions.

Figure 24 (left) lithium disilicate samples for part I and II, (right) lithium disilicate sample for part I

Lithium disilicate rod mounting

Fifty lithium disilicate rods were embedded into a PVC pipe (12.7 mm in diameter, 25 mm in height) with dental gypsum (stone type IV). The ceramic specimens were placed to a depth where their margins were approximately 1 mm higher than the edge of the tube.After the gypsum reached its final setting time, the mounted samples were polished using a polishing machine (Nano 2000 grinder-polisher with FEMTO 1000 polishing head, Pace Technologies, AZ, USA) with 300 and 600-grit silicon carbide abrasive paper, respectively. The polishing process was done under running water with the pressure of 2kg/cm^2, spinning in clockwise motion 200 rounds/minute for 5 minutes. The used abrasive papers were replaced with a new one for each samples. The samples were ultrasonically cleaned in distilled water for 10 minutes before proceeding to the bonding procedure.

Composite resin rod preparation

Composite resin rods were prepared using a silicone template (3 mm diameter, 3 mm thick). A composite resin (Filtek Z350 XT (A3), 3M ESPE, Dental products, St. Paul, MN, USA) was filled and compacted into the silicone mold and then light-irradiated by a light-curing unit (Elipar Freelight 2 LED curing light, 3M ESPE, St. Paul, MN, USA) at 1000 mW/cm^2 for 40 seconds.. The silicone mold were removed from the prepared resin rods and the rods were light-irradiated for another 20 seconds. Every time the silicone mold is reuse, the mold was wiped clean with ethyl alcohol gauze and air-dried for 30 seconds.

Experimental silane preparation

The experimental silane was (3-(Trimethoxysilyl)propyl methacrylate, Sigma-Aldrich, MO, USA) prepared by mixing a solution of 95% ethanol / 5% distilled water in a beaker. The pH of the solution was adjusted to 4.5-5.5 with acetic acid using a digital pH meter shown in Figure 25 (Orion 420A pH meter, Thermo Electron Corp., Beverly, MA, USA). The solution was transferred to a plastic bottle and silane coupling agent was added with stirring to yield a 2% final concentration. The solution was left untouched for five minutes allowing the hydrolysis and silanol formation. A magnetic stirrer and bar (Hotplate stirrer UC152, Stuart Scientific, Staffordshire, UK) was used to gently mix the solution for 1-2 minutes.

Figure 25 pH adjustment of the solution using pH meter (Orion 420A)

Setting up the experimental groups

The samples were divided into five groups depending on the type of silane coupling agent applied.

Group 1. No silane (NS), control group (baseline for all other groups)

Group 2. Kerr silane primer (KP)

Group 3. Monobond N (MN)

Group 4. RelyX ceramic primer (RX)

Group 5. Experimental silane (ES)

After the samples were treated according to the protocol mentioned above. The composite resin rods were bonded to the samples.

Composite resin rod cementation

To standardize the bonding area of each samples, a one-sided tape was prepared. 80-micron thick one-sided sticky tape (Scotch blue Painter's tape, 3M ESPE, St. Paul, MN, USA) were cut into a square shape with the size of 10x10 mm. A 2 mm diameter hole was made in the middle of the sticky tape using a hole-puncher. This area represents the bonding site for composite resin. The tape was placed onto the surface of the lithium disilicate glass-ceramic disks after the surface treatment. A prepared composite rod was attached to the bonding site with a thin uniform layer of a resin cement (RelyX U200, 3M Deutschland GmbH, Neuss, Germany). The weight of one kilogram was applied on the composite rod during the bonding procedure by using a modified durometer (Figure 26). The excess cement was tack-cured for two seconds on each surfaces and was removed with an explorer. Glycerine gel was applied to the margin of the bonded interface and light-irradiated for 40 seconds to prevent oxygen-inhibited layer. The samples were immerged into distilled water at 37℃ for 24 hours before proceeding to the shear bond strength test.

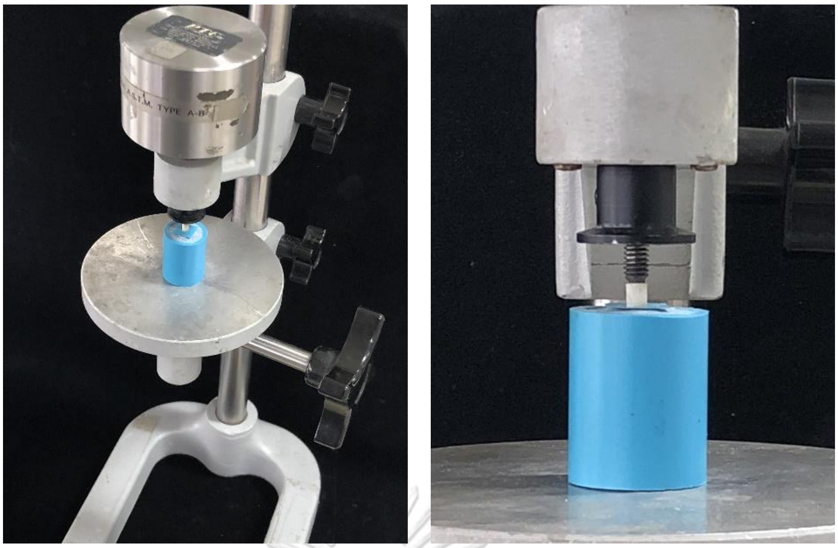


Figure 26 Cementation step using a modified durometer

Shear bond strength test

The samples were mounted on the jig of the shear stress testing machine (Universal testing machine; EZ-S 500N, Shimadzu Corporation, Kyoto, Japan). The test was conducted with the shearing blade placed on the resin composite at 1 mm away and parallel to the bonding site. The crosshead speed of 0.5 mm/min. was used. The amount of stress used until the failure occurred for each samples were recorded in mega Pascal (MPa) with a corresponding software (Shimadzu Trapezium X).

Figure 27 Universal testing machine

Failure mode analysis

After the shear strength tests were performed, the failed samples were retrieved for stereomicroscope analysis (Olympus Stereo Microscopes, SZ61, Tokyo, Japan) to observe the mode of failure. The bonded interfaces were magnified 40x. The mode of failure can be classified into four groups;

1. Adhesive failure, the failure that occurs at the interface between lithium disilicate disk and the composite resin
2. Cohesive failure within the body of resin cement
3. Cohesive failure within the body of the ceramic
4. Mixed failure (involves both adhesive and cohesive failure)

3.2 Part II: Investigating the effect of treating the etched/unetched lithium disilicate surface with various types of silane coupling agents on the contact angle measurement

Lithium disilicate disk preparation

One hundred lithium disilicate disks (IPS e.max Press, Ivoclar-Vivadent, Schaan, Leichtenstein) were prepared and polished in similar fashion with the lithium disilicate rods prepared in part 1, however, the diameters of the disks were adjusted to 10 millimeters and heights of 3 millimeters and the samples were polished with 1000-grit silicon carbide abrasive paper instead (Figure 28).

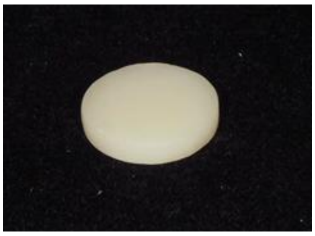


Figure 28 Lithium disilicate sample for part II

Setting up the experimental groups

The samples were randomly assigned into ten groups (n=10) based on the type of silane coupling agent used to treat the surface of lithium disilicate and whether the sample was acid-etched;

Group 1. No silane (NS), serves as a control group

Group 2. Kerr silane primer (KP)

Group 3. Monobond N (MN)

Group 4. RelyX ceramic primer (RX)

Group 5. Experimental silane (ES)

Group 6-10 were identical to Groups 1-5 in terms of the silane coupling agent used; however, these groups were etched with 4.5% hydrofluoric acid gel (IPS ceramic etching gel, Ivoclar-Vivadent, Schaan, Liechtenstein) for 20 seconds, rinsed with deionized water spray for 60 seconds and gently air dried(59) prior to application of respective silane coupling agents.

A drop of the respective silane coupling agent was applied to each sample using a micropipette (10 microliters) and smeared into thin coat using a microbrush (Citisen Micro Applicator, Huanghua Promisee Dental, Hebei, China). After silane application, the treated samples were left untouched, allowing the silane to react with the disk surfaces according to the manufacturers' instruction. New applicator tips were used to remove any remaining excess around the borders of the samples. Then, the sample were air-dried for ten seconds using a triple syringe from a mobile dental unit (10 millimeters from the sample, pressure 40-50 pound per square inch). Before proceeding to the next step, the samples were checked to make sure that the surface was completely dried (no movement of solution).

Sessile drop test, contact angle measurement

The degree of wettability was determined by contact angle measurement. Using a needle, ten microliters of deionized water was placed on the center of the treated/untreated substrate surface to examine the contact angle formed between the deionized water droplet and the prepared substrate. The contact angles were measured digitally with a goniometer shown in Figure 29 (DSA10 MK2, Krüss, Hamburg, Germany) after five seconds. For each drop, the angles obtained from both ends of the captured image were averaged and the mean values of each tested group recorded.

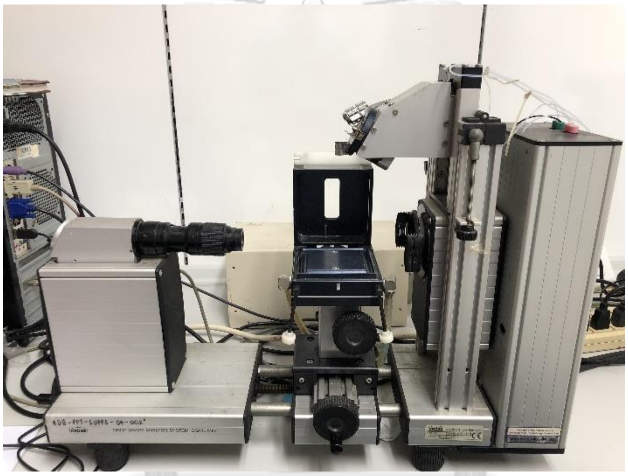


Figure 29 Goniometer

3.3 Data analysis for Part I and Part II

The shear bond strength values and contact angle between deionized water and the substrate surface are presented as mean ± SD. The statistical analysis of the data for all groups were performed using SPSS 20.0 software for Windows (SPSS Inc, Chicago, IL, USA). The data were normally distributed. One-way analysis of variance was applied to the data in Part 1 and Two-way analysis of variance was applied in Part 2. Tukey’s multiple comparison tests were conducted to determine the significant differences between all treatment groups (α=0.05).

CHAPTER IV
RESULTS

4.1 Results of Part I: Evaluating the effect of different type of silane coupling agent on the shear bond strength between lithium disilicate glass ceramic and resin cement

Mean shear bond strength values and the distribution of failures are shown in Table 22. According to the statistical analysis result using ANOVA, the bond strength was significantly influenced by the type of silane coupling agent used.

RelyX ceramic primer (RX) exhibited significantly higher shear bond strengths compared to all other groups. Experimental silane group demonstrated significantly higher bond strength than Monobond N, Kerr silane primer, and negative control group (No silane, NS). Monobond N (MN) demonstrated significantly higher bond strengths than both the negative control group (NS) and Kerr silane primer group (KP). There were no significant differences in the mean shear bond strength of negative control group (NS) and Kerr silane primer group (KP).

Table 22 Average shear bond strength value of respective silane group in MPa and mode of failure

Silane coupling agent (n=10)	Min (MPa)	Max (MPa)	Mean shear bond strength (Mean±SD)	Failure (Ad/Co-resin/ Co-ceramic/Mixed)
No silane (NS)	5.13	7.62	6.07 (0.76)^{a}	10/0/0/0
Kerr silane primer (KS)	4.84	8.94	7.17 (1.48)^{a}	10/0/0/0
Monobond N (MN)	12.96	17.78	15.03 (1.65)^{b}	3/0/0/7
RelyX ceramic primer (RX)	15.67	23.13	19.47 (2.72)^{c}	2/0/0/8
Experimental silane (ES)	18.02	27.52	23.20 (3.24)^{d}	3/0/0/7

Note: SD = Standard deviation

Values with different letters superscripted vary significantly.

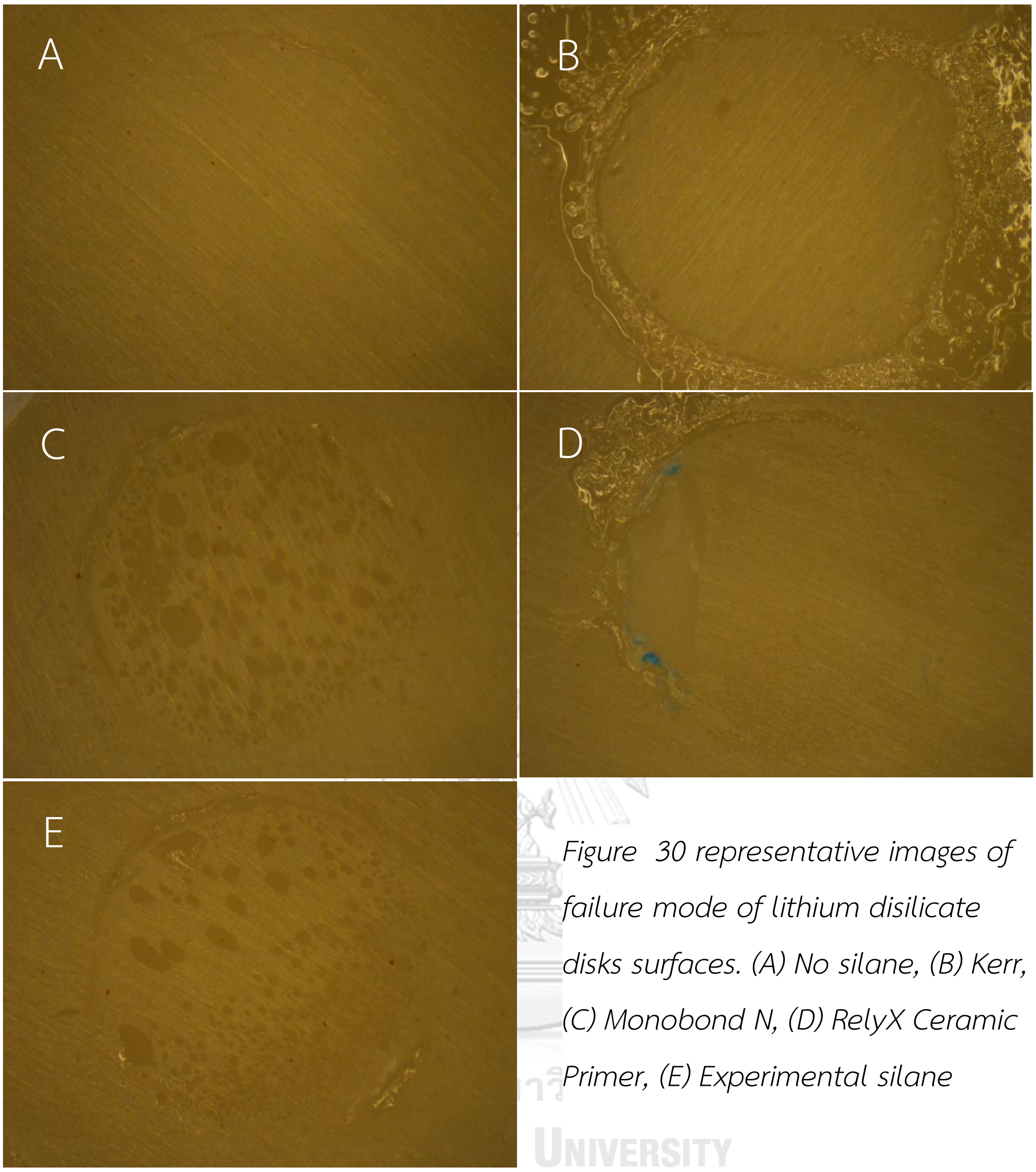


Figure 30 representative images of failure mode of lithium disilicate disks surfaces. (A) No silane, (B) Kerr, (C) Monobond N, (D) RelyX Ceramic Primer, (E) Experimental silane

Figure 30 shows stereomicroscopic images of the fracture surfaces of lithium disilicate disks and resin cement. Mode of failure indicates the bonding quality. The failed samples were retrieved and observed under stereoscope at the magnification of 40x. The samples with low bond strength tend to result in adhesive failure while the samples with high bond strength tend to result in cohesive failure. According to the result in Table 22, all samples in both the negative control (no silane, NS) and the Kerr silane (KP) group failed adhesively. Mixed failures were observed in Monobond N (MN), RelyX ceramic primer (RX) and experimental silane group. No cohesive failure was observed in this study.

4.2 Results of Part II: Investigating the effect of treating the etched/unetched lithium disilicate surface with various types of silane coupling agents on the contact angle measurement

Figure 31 shows contact angle images for all experimental groups. The average contact angles obtained from each respective silane groups are shown in Table 23. According to the data, the non-etched samples (G1-5) generally yielded larger contact angles than the etched samples (G6-10). In unetched groups, the control group exhibited smallest contact angle (G1, 16.94°), while that of the Monobond N group shown the largest contact angle (G3, 46.85°). Samples applied with Kerr silane primer exhibited larger contact angle (G2, 38.91°) than both RelyX ceramic primer (G4) and experimental silane groups (G5), which were relatively similar (32.47° and 32.42°, respectively). There was a significant different in all tested group except RelyX ceramic primer and experimental silane groups.

In hydrofluoric acid-etched groups, the control group also exhibited smallest contact angle (G6, 8.70°), while the group applied with Kerr silane primer demonstrated largest degree of contact angles (G7, 38.81°). The Monobond N group shown significantly larger contact angles (G8, 20.88°) than both RelyX ceramic primer (G9) and experimental silane groups (G10), which were relatively similar (13.36° and 13.65°, respectively). The photos of contact angle of all experimental group is showed in Figure 31.

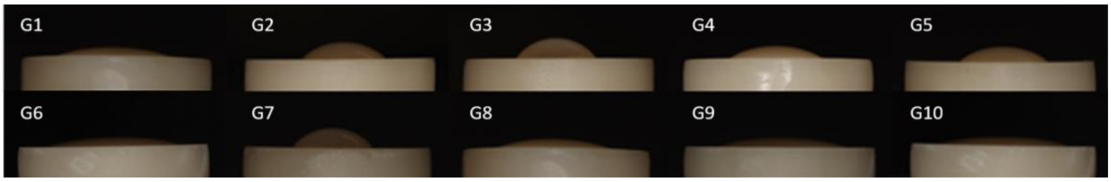


Figure 31 Contact angle measurement of deionized water on etched and unetched lithium disilicate disks treated with different types of silane coupling agent. Group without hydrofluoric etching: (G1) Control, (G2) Kerr silane primer, (G3) Monobond N, (G4) RelyX ceramic primer, (G5) Experimental silane primer. Group with hydrofluoric etching prior to silane application: (G6) HF-no silane, (G7) HF-Kerr silane primer, (G8) HF-Monobond N, (G9) HF-RelyX ceramic primer, (G10) HF-Experimental silane

Table 23 Average contact angle of respective silane group in degree (°) on hydrofluoric-acid-etched and unetched lithium disilicate glass ceramic disks

Silane coupling agents (n=10)	**Mean contact angle Mean (SD)**	
	Unetched disks	**Etched disks**
Control	17.22 (2.12)^{a}	8.60 (1.07)^{e}
Kerr silane primer	39.07 (3.94)^{b}	38.51 (3.63)^{b}
Monobond N	47.47 (4.15)^{c}	20.72 (1.95)^{f}
RelyX ceramic primer	32.48 (3.88)^{d}	13.43 (1.41)^{g}
Experimental silane	32.40 (3.76)^{d}	13.41 (1.52)^{g}

Note: SD = Standard deviation

Values with different letters superscripted vary significantly.

CHAPTER V
DISCUSSION

5.1 Discussion: Part I

In the first part of the study, the effect of different types of silane coupling agent on the shear bond strength between lithium disilicate glass ceramic and resin cement was evaluated. Based on the result of the study, there were significant different of shear bond strength between each group tested except the negative control group and Kerr silane primer group. Therefore, the null hypothesis that the type of silane coupling agent used does not affect the shear bond strength between lithium disilicate glass ceramic - resin cement was rejected.

Nowaday, many silane coupling agent brands are not composed of pure MPS but of a mixture of MPS and other adhesive substances. Recent studies have suggested that the simplified systems, using combinations of different functional groups along with other components, may reduce the bond strength of glass ceramic and resin cement when compared to the conventional two-bottle system.(4, 60)

The lithium disilicate disks were polished differently in the first and second part of this study. The first part used 300 and 600-grit silicon carbide abrasive paper to mimic internal surface of a monolithic lithium disilicate glass ceramic crown whereas the second part used 1000-grit silicon carbide abrasive paper to standardize the roughness of the disks' surfaces since alteration of surface topography (e.g. grinding, acid-etching, air-borne particle abrasion) can physically contribute to the adhesion process by altering the surface area and wetting behavior of ceramic which in turn affects the surface energy and adhesive potential to resin.(48, 61)

Surface modification is an important procedure to improve the bond strength of the dental material to the desired substrate.(62, 63) Several surface treatment methods have been used to enhance the bond strength of ceramic restoration to different substrate. Mechanical and chemical surface treatment are used to promote adhesion (physical, mechanical, or chemical) when bonding dental ceramics.(61)

Hydrofluoric etching along with the use of silane coupling agent is a common method to treat the surface of silica-based ceramic such as porcelain and lithium disilicate. The clinical recommendation for bonding with lithium disilicate ceramic is to apply a 5% hydrofluoric acid etch for 20 seconds.(4, 27, 64-66) Among the methods of surface treatment to obtain optimal micromechanical retention, etching with hydrofluoric acid is proven to be the most successful in enhancing the bond strength of lithium disilicate glass-ceramic.(27-29) However, in Part 1 of the study hydrofluoric acid was not used prior to the application of silane coupling agent since the aim was to focus on the effect of silane coupling agent on the bond strength of lithium disilicate and resin cement alone. Accord to the results from previous studies(4, 65, 67-70), application of silane alone without hydrofluoric acid etching can significantly increases the bond strength of lithium disilicate ceramic.

In this study, the negative control group demonstrated lowest bonding ability since no silane was used, thus, no strong siloxane linkages were formed between the silane and substrate.(14) All other groups, except Kerr silane primer group, demonstrated significantly higher shear bond strength value than the control and the bonding ability varies greatly among the type of silane used. This might be due to multiple factors that may influence the bond strength of material such as the variations in chemical composition, wetting ability, viscosity, or the properties of the resin cements.(68) Factors those influence the rate of hydrolysis of silane may also contribute to the outcome of the bond strength such as silane molecular structure, concentration of silane, pH, temperature, humidity, and solvent system.(14) When silane is applied onto the surface of lithium disilicate ceramic, the surface become more hydrophobic which is beneficial since it increases the wettability of composite/resin material.(71, 72) RelyX ceramic primer (RX) and experimental silane group demonstrated significantly higher bond strength than other groups. Both RelyX ceramic primer and experimental silane groups are composed of mainly solvent (ethanol and water) and γ-MPS alone with the pH value of 4.6(14) and 4.7, respectively.

Monobond N (MN) offered significantly higher bond strength than Kerr silane and the negative control groups. Monobond N has a pH value of 1.63.(73) The solution is a universal primer that contains multiple components other than γ-MPS. According to the manufacturer's IFU, this primer is composed of silane methacrylate, phosphorus-containing monomer and other sulfur-containing monomer which make it capable of bonding to glass ceramic, oxide ceramic, metal, composite, and fiber-reinforced composites. However, the 10-MDP may cause a change pH which might affects the rate of hydrolysis of silane monomer and may impair the stability of functional silane.(74) The co-existance of the different types of hydrophobic/hydrophilic monomers may act as a barrier, preventing the silane monomer from establishing intimate contact with the ceramic surface.(75)

Kerr silane primer (KP), silane containing resin-monomer, offered the least strength compared to other groups of silane coupling agent. The bond strength achieved when Kerr silane primer was applied was not significantly differ than that of the negative control group (NS) even though the wettability of the resin was improved.(50) Kerr silane has the pH value of 7.3. The resin monomers were added presumably to eliminate further application of unfilled resin to the silanated surface prior to the application of resin cement. According to Chen et al.,(50) incorporating Bis-GMA resin into silane solution significantly reduced the contact angle and bond strength. The additional resin may inhibited the chemical reaction between silane primer and lithium disilicate ceramic. Kerr silane demonstrated similar contact angle to that of the unprimed lithium disilicate surface which means the chemical bonding that the silane offered is limited or nonexistent. The low contact angle suggested that the extra resin may interfere with the condensation process of forming the siloxane bond by inhibiting the liberation of water molecules resulted from the process. Moreover, the rate of silane hydrolysis is strongly influenced by pH. Silane can hydrolyze faster in acidic and alkaline environment. However, the hydrolysis process is slowest at neutral pH for alkoxysilanes.(14)

5.2 **Discussion: Part II**

In the second part of the study where the effect of treating the hydrofluoric-acid-etched/unetched lithium disilicate ceramic surface with various types of silane coupling agents on the contact angle measurement of deionized water was investigated, there were significant differences in the contact angle formed between the deionized water and the etched/unetched lithium disilicate glass ceramic surface treated with various types of silane coupling agent. Therefore, the null hypothesis that the different types of silane coupling agents used would not affect the contact angle formed between the deionized water droplets and the etched/unetched lithium disilicate glass ceramic surfaces was also rejected.

The non-etched lithium disilicate group, all silanated surfaces (G2-5) exhibited significantly larger contact angles than the control group (G1). This result suggests that application of silane coupling agents may lower the surface energy of the substrate which is in agreement with a study by Della Bona et al.(48) The contact angle shown in the pure silane groups, RelyX ceramic primer (G4) and experimental silane (G5), were not significantly different from one another but were significantly smaller than groups with additives, Kerr silane primer and Monobond N. Additional components other than MPS may result in an increase or decrease in the contact angle. In the current study, silane with additives produced larger contact angles than ones without additives. The additives such as extra resins in Kerr silane primer, which was meant to eliminate the bonding steps following the priming procedure or the 10-MDP and sulphide methacrylate monomers in Monobond N and were believed to promote chemical adhesion with various substances, may alter the polarity of substrate surfaces and/or the surface energy leading to an increase in contact angle. The result of contact angle in this study partially agree to another study, mentioned previously, by Chen et al. (50) In his study, the application of Monobond Plus (silane containing 10-MDP and sulphide monomer) on zirconia significantly increased the contact angle of deionized water when compared to the unconditioned surface (15.1° to 74.1°). However, Kerr silane primer in the current study exhibited large contact angle value even after the surfaces of lithium disilicate disks were etched with hydrofluoric acid.

In the hydrofluoric acid-etched lithium disilicate groups (G6-10), all treatment groups exhibited lower contact angles than the unetched group, except for Kerr silane primer group (G7). Generally, the results can be explained by the effect of acid-etching. Acid-etching altered the surface topography of the samples.(48) The total surface area and surface energy were increased in the roughened surfaces allowing them to draw more medium onto their surface, increasing the wettability of the substrate. However, when Kerr silane primer was applied on the etched-surfaces, a thin layer of resin was formed on the substrate’s surface. This layer of resin may have filled the pits created from the etching process which may have masked the roughening effect of hydrofluoric acid.

Correlation analysis was performed to determine whether the shear bond strength and contact angle values obtained in this study were related. The correlation coefficient showed that the strength of the relationship between shear bond strength and contact angle values were very weak. It could be concluded that the shear bond strength and contact angle values were not related.

The degree of surface wettability and surface energy may contribute to the improvement of bond quality; however, its physical contribution is not the only factor. Adhesion of dental ceramics to resin based material is the result of physico-chemical interactions between the substrate and adhesive.(46) A clean and dry surface of the restoration is a prerequisite to create a proper bond with the adherend,(41, 51) as surface contamination or surface impurity can reduce the surface energy of the substrate,(61) and thus have a negative effect on the quality of bond. In a study by Tani et al.,(51) it was proven that a surface with superior wettability and surface energy might not be able to provide optimal bond. Therefore, chemical adhesion also plays an important role in obtaining good bond quality. As long as the bonding site is clean and has a sufficient amount of Si-OH site on the ceramic surface, a reliable bond is achievable.(61)

Although treating the lithium disilicate surfaces with silane coupling agent may seem to reduce the wettability of the substrate surface to deionized water, hydrofluoric acid etching along with silane application are proven to be the gold standard treatment protocols that are crucial to obtain optimal bond.(27, 76)

5.3 Conclusion

Within the limitations of this in vitro study, the following can be concluded:

1. The type of silane coupling agent used significantly influence the bond strength between lithium disilicate and resin cement.
2. Application of any type of silane coupling agent significantly increased the bond strength when compared to untreated group, however, the bond strengths varies in accordance with the type of silane used.
3. Silane coupling agents significantly reduced the wettability of deionized water on treated lithium silicate surfaces. The types of silane coupling agent used significantly influence the degree of wettability.
4. Hydrofluoric acid etching generally significantly increased the wettability, except in the group that used resin-containing silane coupling agent.

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APPENDIX

Statistical analysis of shear bond strength data using universal testing machine

Descriptives

	Group			Statistic	Std. Error
SBS	Control	Mean		6.0690	.23909
		95% Confidence Interval for Mean	Lower Bound	5.5281	
			Upper Bound	6.6099	
		5% Trimmed Mean		6.0350	
		Median		5.9000	
		Variance		.572	
		Std. Deviation		.75608	
		Minimum		5.13	
		Maximum		7.62	
		Range		2.49	
		Interquartile Range		1.21	
		Skewness		.895	.687
		Kurtosis		.477	1.334
	Kerr	Mean		7.1720	.46875
		95% Confidence Interval for Mean	Lower Bound	6.1116	
			Upper Bound	8.2324	
		5% Trimmed Mean		7.2033	
		Median		7.7450	
		Variance		2.197	
		Std. Deviation		1.48232	
		Minimum		4.84	
		Maximum		8.94	
		Range		4.10	
		Interquartile Range		2.57	
		Skewness		-.560	.687
		Kurtosis		-1.220	1.334
	Monobond	Mean		15.0310	.52284
		95% Confidence Interval for Mean	Lower Bound	13.8483	
			Upper Bound	16.2137	
		5% Trimmed Mean		14.9933	
		Median		14.7050	
		Variance		2.734	
		Std. Deviation		1.65335	

	Minimum		12.96	
	Maximum		17.78	
	Range		4.82	
	Interquartile Range		3.12	
	Skewness		.463	.687
	Kurtosis		-1.162	1.334
RelyX	Mean		19.4750	.85966
	95% Confidence Interval for Mean	Lower Bound	17.5303	
		Upper Bound	21.4197	
	5% Trimmed Mean		19.4833	
	Median		19.3350	
	Variance		7.390	
	Std. Deviation		2.71849	
	Minimum		15.67	
	Maximum		23.13	
	Range		7.46	
	Interquartile Range		4.68	
	Skewness		.068	.687
	Kurtosis		-1.703	1.334
Experimental	Mean		23.2040	1.02374
	95% Confidence Interval for Mean	Lower Bound	20.8881	
		Upper Bound	25.5199	
	5% Trimmed Mean		23.2522	
	Median		23.0500	
	Variance		10.480	
	Std. Deviation		3.23734	
	Minimum		18.02	
	Maximum		27.52	
	Range		9.50	
	Interquartile Range		5.74	
	Skewness		-.164	.687
	Kurtosis		-1.296	1.334

Tests of Normality

	Group	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
SBS	Control	.163	10	.200*	.936	10	.513
	Kerr	.203	10	.200*	.902	10	.229
	Monobond	.186	10	.200*	.934	10	.486
	RelyX	.234	10	.130	.904	10	.245
	Experimental	.181	10	.200*	.950	10	.665

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

ANOVA

Shear bond strength

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2250.937	4	562.734	120.381	.000
Within Groups	210.357	45	4.675		
Total	2461.294	49			

Multiple Comparisons

Dependent Variable: SBS

Tukey HSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Control	Kerr	-1.10300	.96691	.784	-3.8504	1.6444
	Monobond	-8.96200*	.96691	.000	-11.7094	-6.2146
	RelyX	-13.40600*	.96691	.000	-16.1534	-10.6586
	Experimental	-17.13500*	.96691	.000	-19.8824	-14.3876
Kerr	Control	1.10300	.96691	.784	-1.6444	3.8504
	Monobond	-7.85900*	.96691	.000	-10.6064	-5.1116
	RelyX	-12.30300*	.96691	.000	-15.0504	-9.5556
	Experimental	-16.03200*	.96691	.000	-18.7794	-13.2846
Monobond	Control	8.96200*	.96691	.000	6.2146	11.7094
	Kerr	7.85900*	.96691	.000	5.1116	10.6064
	RelyX	-4.44400*	.96691	.000	-7.1914	-1.6966
	Experimental	-8.17300*	.96691	.000	-10.9204	-5.4256
RelyX	Control	13.40600*	.96691	.000	10.6586	16.1534
	Kerr	12.30300*	.96691	.000	9.5556	15.0504

	Monobond	4.44400*	.96691	.000	1.6966	7.1914
	Experimental	-3.72900*	.96691	.003	-6.4764	-.9816
Experimental	Control	17.13500*	.96691	.000	14.3876	19.8824
	Kerr	16.03200*	.96691	.000	13.2846	18.7794
	Monobond	8.17300*	.96691	.000	5.4256	10.9204
	RelyX	3.72900*	.96691	.003	.9816	6.4764

*. The mean difference is significant at the 0.05 level.

SHEAR BOND STRENGTH

Tukey HSD[a]

Group	N	Subset for alpha = 0.05			
		1	2	3	4
Control	10	6.0690			
Kerr	10	7.1720			
Monobond	10		15.0310		
RelyX	10			19.4750	
Experimental	10				23.2040
Sig.		.784	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 10.000.

Statistical analysis of contact angle data using contact angle tester

Group without hydrofluoric acid etching etching

Descriptives

	Group			Statistic	Std. Error
ContactA	Control	Mean		17.2200	.66949
		95% Confidence Interval for Mean	Lower Bound	15.7055	
			Upper Bound	18.7345	
		5% Trimmed Mean		17.2033	
		Median		17.3800	
		Variance		4.482	
		Std. Deviation		2.11713	
		Minimum		14.11	
		Maximum		20.63	
		Range		6.52	
		Interquartile Range		3.71	
		Skewness		.061	.687
		Kurtosis		-.976	1.334
	Kerr	Mean		39.0700	1.24461
		95% Confidence Interval for Mean	Lower Bound	36.2545	
			Upper Bound	41.8855	
		5% Trimmed Mean		39.0533	
		Median		39.4000	
		Variance		15.490	
		Std. Deviation		3.93579	
		Minimum		34.18	
		Maximum		44.26	
		Range		10.08	
		Interquartile Range		7.63	
		Skewness		-.050	.687
		Kurtosis		-1.945	1.334
	Monobond	Mean		47.4720	1.31156
		95% Confidence Interval for Mean	Lower Bound	44.5051	
			Upper Bound	50.4389	
		5% Trimmed Mean		47.4489	
		Median		48.0700	
		Variance		17.202	

	Std. Deviation		4.14751	
	Minimum		41.92	
	Maximum		53.44	
	Range		11.52	
	Interquartile Range		7.64	
	Skewness		-.021	.687
	Kurtosis		-1.165	1.334
RelyX	Mean		32.4790	1.22719
	95% Confidence Interval for Mean	Lower Bound	29.7029	
		Upper Bound	35.2551	
	5% Trimmed Mean		32.4428	
	Median		32.0100	
	Variance		15.060	
	Std. Deviation		3.88073	
	Minimum		27.41	
	Maximum		38.20	
	Range		10.79	
	Interquartile Range		8.22	
	Skewness		.274	.687
	Kurtosis		-1.298	1.334
Experimental	Mean		32.4020	1.18763
	95% Confidence Interval for Mean	Lower Bound	29.7154	
		Upper Bound	35.0886	
	5% Trimmed Mean		32.4289	
	Median		32.8150	
	Variance		14.105	
	Std. Deviation		3.75563	
	Minimum		26.88	
	Maximum		37.44	
	Range		10.56	
	Interquartile Range		7.22	
	Skewness		-.202	.687
	Kurtosis		-1.154	1.334

Tests of Normality

	Group	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
ContactA	Control	.142	10	.200*	.968	10	.876
	Kerr	.191	10	.200*	.885	10	.149
	Monobond	.158	10	.200*	.927	10	.420
	RelyX	.172	10	.200*	.923	10	.383
	Experimental	.170	10	.200*	.924	10	.394

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

ANOVA

ContactA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4932.668	4	1233.167	92.944	.000
Within Groups	597.053	45	13.268		
Total	5529.722	49			

Multiple Comparisons

Dependent Variable: ContactA

Tukey HSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Control	Kerr	-21.85000*	1.62898	.000	-26.4787	-17.2213
	Monobond	-30.25200*	1.62898	.000	-34.8807	-25.6233
	RelyX	-15.25900*	1.62898	.000	-19.8877	-10.6303
	Experimental	-15.18200*	1.62898	.000	-19.8107	-10.5533
Kerr	Control	21.85000*	1.62898	.000	17.2213	26.4787
	Monobond	-8.40200*	1.62898	.000	-13.0307	-3.7733
	RelyX	6.59100*	1.62898	.002	1.9623	11.2197
	Experimental	6.66800*	1.62898	.002	2.0393	11.2967
Monobond	Control	30.25200*	1.62898	.000	25.6233	34.8807
	Kerr	8.40200*	1.62898	.000	3.7733	13.0307
	RelyX	14.99300*	1.62898	.000	10.3643	19.6217
	Experimental	15.07000*	1.62898	.000	10.4413	19.6987
RelyX	Control	15.25900*	1.62898	.000	10.6303	19.8877

	Kerr	-6.59100*	1.62898	.002	-11.2197	-1.9623
	Monobond	-14.99300*	1.62898	.000	-19.6217	-10.3643
	Experimental	.07700	1.62898	1.000	-4.5517	4.7057
Experimental	Control	15.18200*	1.62898	.000	10.5533	19.8107
	Kerr	-6.66800*	1.62898	.002	-11.2967	-2.0393
	Monobond	-15.07000*	1.62898	.000	-19.6987	-10.4413
	RelyX	-.07700	1.62898	1.000	-4.7057	4.5517

*. The mean difference is significant at the 0.05 level.

ContactA

Tukey HSD[a]

Group	N	Subset for alpha = 0.05			
		1	2	3	4
Control	10	17.2200			
Experimental	10		32.4020		
RelyX	10		32.4790		
Kerr	10			39.0700	
Monobond	10				47.4720
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 10.000.

Group without hydrofluoric acid etching etching

Descriptives

	Group			Statistic	Std. Error
ContactA	Control	Mean		8.5990	.33937
		95% Confidence Interval for Mean	Lower Bound	7.8313	
			Upper Bound	9.3667	
		5% Trimmed Mean		8.6361	
		Median		8.7250	
		Variance		1.152	
		Std. Deviation		1.07317	
		Minimum		6.67	
		Maximum		9.86	
		Range		3.19	
		Interquartile Range		1.39	
		Skewness		-.952	.687
		Kurtosis		-.005	1.334
	Kerr	Mean		38.5090	1.14894
		95% Confidence Interval for Mean	Lower Bound	35.9099	
			Upper Bound	41.1081	
		5% Trimmed Mean		38.5572	
		Median		38.7800	
		Variance		13.201	
		Std. Deviation		3.63326	
		Minimum		32.75	
		Maximum		43.40	
		Range		10.65	
		Interquartile Range		6.69	
		Skewness		-.143	.687
		Kurtosis		-.919	1.334
	Monobond	Mean		20.7210	.61748
		95% Confidence Interval for Mean	Lower Bound	19.3242	
			Upper Bound	22.1178	
		5% Trimmed Mean		20.6917	
		Median		20.2400	
		Variance		3.813	
		Std. Deviation		1.95265	

		Minimum		17.82	
		Maximum		24.15	
		Range		6.33	
		Interquartile Range		3.12	
		Skewness		.421	.687
		Kurtosis		-.494	1.334
	RelyX	Mean		13.4320	.44739
		95% Confidence Interval for Mean	Lower Bound	12.4199	
			Upper Bound	14.4441	
		5% Trimmed Mean		13.4506	
		Median		13.4150	
		Variance		2.002	
		Std. Deviation		1.41479	
		Minimum		10.63	
		Maximum		15.90	
		Range		5.27	
		Interquartile Range		1.70	
		Skewness		-.245	.687
		Kurtosis		1.298	1.334
	Experimental	Mean		13.4100	.48139
		95% Confidence Interval for Mean	Lower Bound	12.3210	
			Upper Bound	14.4990	
		5% Trimmed Mean		13.4467	
		Median		13.7100	
		Variance		2.317	
		Std. Deviation		1.52229	
		Minimum		10.55	
		Maximum		15.61	
		Range		5.06	
		Interquartile Range		2.27	
		Skewness		-.545	.687
		Kurtosis		-.008	1.334

Tests of Normality

	Group	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
ContactA	Control	.245	10	.091	.881	10	.134
	Kerr	.144	10	.200*	.946	10	.620
	Monobond	.179	10	.200*	.968	10	.869
	RelyX	.160	10	.200*	.966	10	.850
	Experimental	.160	10	.200*	.974	10	.925

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

ANOVA

ContactA

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5539.728	4	1384.932	307.980	.000
Within Groups	202.357	45	4.497		
Total	5742.085	49			

Multiple Comparisons

Dependent Variable: ContactA

Tukey HSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Control	Kerr	-29.91000*	.94835	.000	-32.6047	-27.2153
	Monobond	-12.12200*	.94835	.000	-14.8167	-9.4273
	RelyX	-4.83300*	.94835	.000	-7.5277	-2.1383
	Experimental	-4.81100*	.94835	.000	-7.5057	-2.1163
Kerr	Control	29.91000*	.94835	.000	27.2153	32.6047
	Monobond	17.78800*	.94835	.000	15.0933	20.4827
	RelyX	25.07700*	.94835	.000	22.3823	27.7717
	Experimental	25.09900*	.94835	.000	22.4043	27.7937
Monobond	Control	12.12200*	.94835	.000	9.4273	14.8167
	Kerr	-17.78800*	.94835	.000	-20.4827	-15.0933
	RelyX	7.28900*	.94835	.000	4.5943	9.9837

	Experimental	7.31100*	.94835	.000	4.6163	10.0057
RelyX	Control	4.83300*	.94835	.000	2.1383	7.5277
	Kerr	-25.07700*	.94835	.000	-27.7717	-22.3823
	Monobond	-7.28900*	.94835	.000	-9.9837	-4.5943
	Experimental	.02200	.94835	1.000	-2.6727	2.7167
Experimental	Control	4.81100*	.94835	.000	2.1163	7.5057
	Kerr	-25.09900*	.94835	.000	-27.7937	-22.4043
	Monobond	-7.31100*	.94835	.000	-10.0057	-4.6163
	RelyX	-.02200	.94835	1.000	-2.7167	2.6727

*. The mean difference is significant at the 0.05 level.

ContactA

Tukey HSD[a]

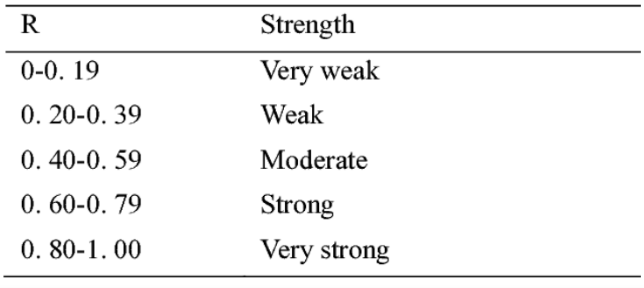
Group	N	Subset for alpha = 0.05			
		1	2	3	4
Control	10	8.5990			
Experimental	10		13.4100		
RelyX	10		13.4320		
Monobond	10			20.7210	
Kerr	10				38.5090
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 10.000.

Correlation analysis of shear bond strength and contact angle

	Correlation (r)	P-Value	Interpretation
Control	-0.337	0.341	Weak
Kerr	0.263	0.463	Weak
Monobond	0.012	0.973	Very Weak
Rely X	0.110	0.763	Very Weak
ES	-0.122	0.737	Very Weak
Total	-0.104	0.774	Very Weak



R	Strength
0-0. 19	Very weak
0. 20-0. 39	Weak
0. 40-0. 59	Moderate
0. 60-0. 79	Strong
0. 80-1. 00	Very strong

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