

**Assessment of the Bond Strength between Resin Cement and  
Lithium Disilicate Based  
Glass Ceramics with different Chemical Composition and  
Surface Treatments**

By

Muna Bebsh

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College of Dentistry, Department of Oral Biology, University of Manitoba  
Manitoba, Canada

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**Abstract:**

**Objective:** The purpose of this research project is to evaluate and compare the effect of different surface treatments on surface properties. Also the effect of different surface treatments with silane coupling agents on the bond strengths between resin cement and four CAD/CAM lithium disilicate-based glass ceramics (LDGC).

**Materials and methods:** This study had three levels of analyses. Part I: The physicochemical analyses of four CAD/CAM LDGC surfaces. The surface physicochemical compositions of the four LDGC products (e.max CAD, Vita Suprinity, Celtra Duo, n!ce) were analyzed using X-ray photoelectron spectroscopy (XPS). In addition, scanning electron microscopy (SEM) was used to analyze the microstructure of LDGC. Part II: The effect of different surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate- based glass ceramics. Atomic force microscopy (AFM) was used to measure the surface roughness and scanning electron microscopy (SEM) was used to analyze the changes in the surface micromorphology. Part III: The effect of an experimental silane coupling agent (TEOS) with different surface treatments on bond strength of four CAD /CAM lithium disilicate-based glass-ceramics. The shear bond strength between the ceramic surface and resin cement was tested using shear bond testing after a 30 day storage in distilled water.

**Results:** The chemical composition percentage on the nano surfaces of the LGGC changed after hydrofluoric acid treatment. Different surface treatments produced different values of roughness. The highest shear bond strength values were found with the use of hydrofluoric acid treatment and the combination of both hydrofluoric acid and sandblasting followed by manufacturer's recommendation of silane coupling application.

Conclusion: Surface treatments and silane coupling agents play a significant role to obtain reliable bond strengths between resin cement and LDGC restorations.

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## **Dedication**

I dedicate my thesis to my parents, brothers, and my sisters for their encouragement and support throughout all stages of my master's degree studies. Also I dedicate this educational achievement to my wonderful and supportive husband and my beautiful boys Abdossulam, Mouad, and Zubair.

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## Abbreviations

AFM .....	Atomic force microscopy
Al .....	Aluminium
Al <sub>2</sub> O <sub>3</sub> .....	Aluminum oxide
Ar .....	Argon
CAD/CAM .....	Computer-Aided Design and Computer-Aided Manufacturing Dental System
Ce .....	Cerium
CP .....	Clearfil® Ceramic Primer Plus
EDX.....	Energy Dispersive X-Ray Analysis
F .....	Fluorine
FTIR.....	Fourier-transform infrared spectroscopy
FWHM .....	Full Width at Half maximum
HF.....	Hydrofluoric acid
HR .....	High-resolution
K .....	Potassium
LDGC .....	Lithium disilicate-based glass ceramic
Li .....	Lithium

Li <sub>2</sub> SiO <sub>3</sub> .....	Lithium Metasilicate
Li <sub>3</sub> PO <sub>4</sub> .....	Lithium Phosphate
Mpa .....	Mega pascals
N .....	Nitrogen
Na .....	Sodium
NIST .....	National Institute of Standards and Technology
O .....	Oxygen
O1s .....	Oxygen XPS peak
P .....	Phosphorus
SB .....	Sandblasting
SBS .....	Shear bond strength
SEM .....	Scanning electron microscopy
Si .....	Silicone
Si 2p .....	Silicon XPS peak
Sr .....	Strontium
TEOS .....	Tetraethyl orthosilicate
XPS .....	X-ray photoelectron spectroscopy
XRD .....	X-Ray Diffraction Analysis

Y ..... Yttrium

Zn ..... Zinc

Zr ..... Zirconium

# **Chapter1: Introduction**

## **1.1 Introduction**

Ceramic is an important restorative material in the dental biomaterial field besides metals, polymers and composites. The word ceramic originally comes from the Greek word 'keramos' which refers to the substance that is produced by a firing or burning process (1). Ceramic was introduced to dentistry in 1789 (2). Currently, ceramic is widely used in clinical dentistry for mostly indirect fixed prostheses such as inlays, onlays, veneers, full coverage crowns, fixed partial dentures and implant-supported prosthesis. Its success is due to its good biocompatibility, high mechanical strength and excellent esthetic properties (3).

Dental ceramics are classified into three main categories: glass-matrix ceramics, polycrystalline ceramics and resin-matrix ceramics (4). Glass-ceramics are the most popular ceramic in dentistry and obtained from the melting of glass and a crystallisation process controlled by an appropriate heat treatment. This process is composed of two stages: nucleation and crystallization. The formation of fine grained ceramic begins through a crystallisation process and these grains are then grown to form crystals with desirable mechanical and esthetic properties (5-7). The chemical composition of the original glass, the heat method used for the melting process and the nucleation agents are responsible for the final crystal phase characteristics (8). In general, glass ceramic structures has two phases: crystalline and glass (amorphous). The crystalline phase is responsible for the mechanical and optical properties (translucency) and the glass phase contributes to the esthetic properties.

One subcategory of glass-matrix ceramics is synthetic ceramics which includes leucite-based, fluor-apatite-based, and lithium disilicate-based and its derivatives. Lithium disilicate-based glass ceramic (LDGC) was discovered by Stucky as a glass-ceramic with better mechanical properties compared to base glass and it had excellent esthetic properties (7). The main chemical compositions of LDGC are lithium oxide ( $\text{Li}_2\text{O}$ ) and silicon oxide ( $\text{SiO}_2$ ) which gives the ceramic mechanical strength characteristics. Also, they have other elements like cerium dioxide ( $\text{Ce}_2\text{O}_3$ ), calcium oxide ( $\text{CaO}$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) which are responsible for color, translucency and chemical solubility (3). The first generation of LDGC that was introduced to the dental market in 1998 was IPS Empress II (Ivoclar-Vivadent, Liechtenstein, Schaan). Later, Ivoclar-Vivadent produced two types of lithium disilicate-based glass ceramics, namely IPS e.max press and IPS e.max CAD that are processed with different fabrication mechanisms, The IPS e.max CAD ceramic is shown to be preferred by both the patient and dentist due to its excellent appearance and the reduction in fabrication time. More recently, zirconia reinforced with lithium silicate glass ceramic was introduced with two different brands (Vita Suprinity and Celtra Duo). Also, lithium alumina reinforced with lithium disilicate glass ceramic (n!ce) was introduced to the market too.

Dental cements (luting agents) are used to attach the ceramic restoration to the prepared tooth or implant abutment. The longevity and reliability of the bonding to dental ceramic restorations depend on cement characteristics and cement procedures. Resin cements are widely used for adhesive bonding of glass ceramic restorations (9). When glass ceramic restorations are bonded, both cement interfaces (tooth-cement and ceramic-cement) are considered in the bonding process. The ceramic-cement interface appears to be of greater concern. Several studies were done to assess the bond strengths between lithium disilicate-based glass ceramic and the resin



cement base of both mechanical and chemical bonding (10-12). However, the mechanical failure of glass ceramic restorations still concerns for the LDGC restoration. Ceramic surface treatments and silane coupling agent applications are critical steps to improve the adhesion between resin cement and the LDGC surface.

An understanding of the physicochemical composition and the microstructure of lithium disilicate-based glass ceramic are important to obtain optimal chemical bonding and long-term stability of ceramic restorations. There are various techniques available to assess the chemical composition and microstructure of ceramic surfaces. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) are powerful quantitative and qualitative techniques for nano surface analysis. In the case of CAD/CAM lithium disilicate-based glass ceramic is important to create surface roughness In order to obtain mechanical bonding. To measure the surface roughness, atomic force microscopy (AFM) is excellent method.

The research aims are to elucidate the physicochemical composition and the surface morphology of four types of CAD/CAM lithium disilicate based-glass ceramic. Also this research aims to evaluate and compare the effect of different surface treatments and silane coupling agents on the bond strength of four types of CAD/CAM lithium disilicate based-glass ceramic.

To address these goals, several in vitro experimental procedures were undertaken. The results are categorized and reported in three manuscripts titled:

1. Physicochemical surface analyses of four CAD/CAM lithium disilicate-based glass ceramics after HF etching: XPS study.

2. The effect of different surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate- based glass ceramics.
3. The effect of experimental silane coupling agent (TEOS) with different surface treatments on bond strength of four CAD /CAM lithium disilicate-based glass-ceramics.

## **Chapter 2: Objective and Hypothesis**

### **2.1 Overall Objective**

The overarching goal of this study was to investigate and compare the effect of different surface treatments on surface properties. As well as the effect of different surface treatment with silane coupling agents on the bond strength between resin cement and four CAD/CAM LDGC.

### **2.2 Overall Null Hypothesis**

Surface treatments will not have an effect on surface properties and the bond strength with silane coupling agent of four types of CAD/CAM lithium disilicate - glass ceramics.

There are three main objectives that are addressed in three separate manuscripts.

Manuscript I: Physicochemical surface analyses of four CAD/CAM lithium disilicate-based glass-ceramics.

Objective: The aim of this study to investigate the physicochemical composition of the nano surface of unetched and etched surfaces of four CAD/CAM LDGC.

Null Hypothesis: The acid etching protocol will not affect the nano-surface chemical composition of four LDGC.

Manuscript II: The effect of different surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate- based glass ceramics.

Objective: The aim of this study was to investigate and compare the effect of various surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate-based glass ceramics.

Null Hypothesis: Different surface treatments will not affect the surface roughness and micromorphology of four CAD/CAM lithium silicate glass ceramics.

Manuscript III: The effect of an experimental silane coupling agent (TEOS) with different surface treatments on the bond strengths of four CAD /CAM lithium disilicate-based glass-ceramics.

Objective: The purpose of this study was to evaluate and compare the effect of an experimental silane coupling agents (TEOS) with different surface treatments on the bond strength of four CAD/CAM LDGC against conventional silane.

Null hypothesis:

- 1) Different surface treatments would not affect the bond strength of CAD/CAM LDGC.
- 2) The bond strength performance of experimental silane coupling agents (TEOS) on LDGC would not differ from conventional silane.

## **Chapter 3: First Manuscript**

### **Physicochemical surface analyses of four CAD/CAM Lithium Disilicate-Based glass-ceramics after HF etching: A XPS study.**

Rodrigo França <sup>1,2</sup>, Muna Bebsh <sup>2</sup>, Asmaa Haimeur <sup>1</sup>, Ana Carla Fernandes<sup>2</sup> and Edward Sacher <sup>3</sup>

1. Dental Biomaterials Research Lab, Department of Restorative Dentistry.

University of Manitoba, Winnipeg, Manitoba, Canada.

2. Department of Oral Biology, University of Manitoba, Winnipeg, Manitoba,

3. Department of Physic Engineering, École Polytechnique de Montréal.

#### **3.1: Abstract:**

**Objective:** The surfaces of four lithium disilicate glass ceramics (LDGC) were assessed at the nanolevel. The goal was to detect the chemical alteration of the surface after etching with hydrofluoric acid (HF).

**Materials and Methods:** The four LDGC tested were: Celtra Duo, IPS e.max CAD, Straumann n!ce and Vita Suprinity. Four blocks of each LDGC were sectioned to ~1 mm thickness. The requirement for firing or not, were done according to the manufacturer's recommendations. The samples were then divided in two groups: a control and an etched group. For the etched group, the samples were etched with a solution of 5% HF for 20s, rinsed for 20s and dried for 10s. The atomic percentage of the first atomic layers was probed using X-ray photoelectron spectroscopy (XPS) using survey mode (n=12). The oxygen and silicone peaks (O1s and Si2p) were analyzed

in XPS high-resolution mode. The samples were also analyzed using scanning electronic microscopy with high magnification (100K x).

Results: XPS showed the amount of the major elements Si, O and Li were different with etching protocols. For all samples, trace elements such as P, Zn, Y, Na, Sr disappeared after the glass phase dissolution. Zr and Al percentages varied bases on the LDGC analyzed. XPS high resolution spectra of the O1s and Si2p peaks showed that the chemical environment were qualitative different in all samples. Following etching, SEM images for IPS e.max CAD and n!ce showed needle-like crystals and SEM images for Celtra Duo and Vita Suprinity showed rod-like crystals with nanometric sizes.

Conclusion: Acid etching using 5% HF for 20s, modifies not only the topographic structure, but also the chemical composition of the LDGC surface.

Keywords: lithium disilicate, acid etching, XPS, SEM.

### **3.2: Introduction**

Monolithic lithium disilicate-based glass-ceramics (LDGC) for computer-aided design and computer-aided manufacturing (CAD/CAM) have become popular in dentistry. Its popularity is due to its superior mechanical properties and satisfactory esthetic properties. Compared to feldspathic based glass-ceramics, LDGC has improved toughness strength by means of a controlled crystallization process resulting in high percentage of a crystalline phase and low amount of voids. LDGC presents an engineered microstructure composed of a glassy matrix and a crystalline phase (1-10). The matrix is mostly formed by a vitreous-silica glass and the crystals composed of a phyllosilicate as lithium disilicate ( $\text{Li}_2\text{Si}_2\text{O}_5$ ) (7, 10-13). Also, a small number of

other oxides are added to the structure to bring supplementary features such as color and fluorescence.

In dentistry, the popularity of LDGC restorations is also due to its good survival rates. A systematic review showed a 97.8% five-year cumulative survival rate for single crowns, and a 70.9% ten-year survival rate for multiple-unit prosthesis (14). In vitro studies revealed that when etching the surface with hydrofluoric acid (HF) and using a silane coupling agent, the bond strength at the resin cement/LDGC interface can be between 32 and 20 Mpa (15-19). These high values are related to the dissolution of the glassy matrix and the exposure of the residual crystalline phase. This surface treatment protocol produces superficial microporosities, increases the surface energy and allows a good interlocking with the resin cement. The application of a silane coat promotes a chemical reaction between the LDGC surface and the resin cement. Different chemical compositions of silane have been proposed, but few of them have obtained success (20). One of the challenges is that the reaction stoichiometry between HF and LDGC is not yet well understood. Thus, the development of an effective coupling agent becomes complicated when the chemical composition of the substrate is unknown.

Since its introduction in the 90's, LDGC is a material in continuous development. Different chemical compositions are available in the dental market. The first product available, IPS e.max® CAD (see Table 1), was followed by products with high concentrations of either zircon: Vita Suprinity® and Celtra Duo®, or aluminum: Straumann n!ce®. Also, conventional LDGC blocks are provided in an intermediary stage of crystallization containing lithium metasilicate ( $\text{Li}_2\text{SiO}_3$ ); these “soft” stage ingots can be easily milled by a CAD/CAM machine. The final fully

crystallized restoration is obtained after heat treatment ( $> 800^{\circ}\text{C}$ ), where the  $\text{Li}_2\text{SiO}_3$  phase becomes  $\text{Li}_2\text{Si}_2\text{O}_5$  crystals (7, 11). More recently, some manufacturers released LDGC blocks that are fully crystallized advertising a gain in completion time and improved mechanical strength. However, all these modifications and improvements brought more variables that could affect the reactions between HF/substrate and silane/substrate.

It becomes clear that the chemical composition of the first atomic layers of the LDGC is fundamental to understand the process of adhesion with the resin cement. Manufacturers only provide the bulk composition of their products, and the details are normally vague (Table 1). As a result of its thermodynamic instability, ceramic surfaces rarely present the same composition of the bulk (21). Previous investigations provided good qualitative or semi-quantitative chemical analyses (12, 15, 22). Unfortunately, techniques like FTIR, Raman, EDX or XRD have no sensitivity to probe the nano-surface. To date, no information is available about the chemical composition of the outermost atomic layers of dental LDGC products.

This study was designed to study the physicochemical composition of the nano surfaces of four LDGC products available on the dental market. The effect of HF etching also will be evaluated. The samples will be characterized using X-ray Photoelectron Spectroscopy (XPS). This powerful technique can provide qualitative and quantitative (%) analyses of the first atom layers. To assess the effect of HF on the samples, the null hypothesis is that the acid etching protocol will not cause any difference in the nano-surface chemical composition of the four LDGC.



### **3.3: Materials and Methods**

#### *Samples tested*

Table 3.1 shows the LDGC samples used in this study with their chemical composition provided by the manufactures. Each LDGC product was sectioned into four blocks (~7 x 7 by 1 mm of thickness) using a low-speed sectioning saw Isomet (Isomet1000, Buehler Ltd, Lake Bluff, IL, USA). IPS e.max CAD and Vita Suprinity (that are provided in a partially crystallized stage) were then fully crystallized in a furnace (Programat P310, Ivoclar Vivadent, Schaan, Liechtenstein) following the manufacturer's recommendations. Celtra Duo and n!ce ceramic blocks are provided as fully crystallized and no additional heat-treatments were not required. All samples were cleaned with alcohol and sonicated for 15 minutes, and then kept in distilled water at room temperature. Specimens of each type of LDGC (n=12) were randomly divided into two groups: a control and an etched group. Each sample of the etched group had one of the surfaces etched with a solution of HF at 5% for 20s, rinsed for 20s and dried for 10s, following the manufacturer's recommendations.

#### *Sample Characterization*

*SEM:* Topographic analyses of the samples (before and after the acid etching using 5% HF) were performed using a FEI Nova NanoSEM 450 high-resolution scanning electron microscope (ThermoFisher, Oregon, USA). Using an SEI detector, the accelerating voltage for all materials was 20 kV, and magnifications were on the 20-micron scale and 500 nm scale. The beam current used was 100 nA.

*XPS*: Physicochemical analyses were performed using a XPS machine manufactured by Kratos Axis, (Manchester, UK). An Al K $\alpha$  monochromatic radiation source ( $h\nu = 1486.6$  eV) was used with a current of 15 mA and voltage of 15 kV. The charge neutralizer was turned on because the samples were not electrically conductive. Samples were placed into loading tray slots and introduced into the analyzing chamber at a base pressure of  $< 1 \times 10^{-9}$  Torr. Before the analysis, an etching was performed using an Argon (Ar) laser gun for 75s to eliminate the adventitious carbon layer. Survey and high-resolution (HR) photoelectron spectra were collected with a take off angle of  $15^\circ$ , with a probing depth of approximately 10 nm. All four slices of each LDGC were randomly analyzed in 3 different regions with a spot size of  $\sim 2$  mm<sup>2</sup> (n=12). The presence of residual Ar in the samples was negligible ( $< 0.1\%$ ). After Shirley background removal, the element identification, the atomic percentages, and the peak deconvolutions were processed using CasaXPS software version 2.3.1 (Casa Software Ltd, UK). After the peaks were properly fitted, the calibration of the spectra was made using the assigned highest intensity Si2p peak, at 102.5 eV, referring to Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, (23) due to the low intensity of C1s. The full width at half-maximum (FWHM) for peak deconvolution was kept constant in 1.8 eV for O1s and 1.6 eV for Si2p. The peak attributions were established using the XPS database of the National Institute of Standards and Technology (NIST) (24). The average and standard deviation for each chemical element were calculated using survey and high-resolution mode results.

Table 3.1: Chemical composition of four LDGC products provided from the manufacturer.

Materials	Abbreviation	Manufacturer	Chemical composition
IPS e. max® CAD	e.max CAD	Ivoclar-Vivadent, Schaan, Liechtenstein,	57-80% SiO <sub>2</sub> ; 11-19% Li <sub>2</sub> O; 0-13% K <sub>2</sub> O; 0-11% P <sub>2</sub> O <sub>5</sub> 0-8% ZrO <sub>2</sub> -ZnO, 0-5% Al <sub>2</sub> O <sub>3</sub> ; 0-5% MgO - colouring oxides
Vita Suprinity®	Suprinity	Vita Zahnfabrik, Bad Sackingen, Germany	56-64% SiO <sub>2</sub> ; 5-21% Li <sub>2</sub> O; 1-4% K <sub>2</sub> O; 3-8% P <sub>2</sub> O <sub>5</sub> ; 8-12% ZrO <sub>2</sub> ; 0-4% CeO <sub>2</sub> 0-6% pigments
Celtra Duo®	Celtra	Dentsply Sirona, Hanau-Wolfgang, Germany	58% SiO <sub>2</sub> ; 18.5% Li <sub>2</sub> O; 5% P <sub>2</sub> O <sub>5</sub> ; 10.1% ZrO; 1.9% Al <sub>2</sub> O <sub>3</sub> ; 2% CeO <sub>2</sub> ; 1% Tb <sub>4</sub> O <sub>7</sub>
Straumann n!ce®	n!ce	Straumann Basel Switzerland	64-70% SiO <sub>2</sub> ; 10.5 - 12.5% Li <sub>2</sub> O; 0 – 3% K <sub>2</sub> O; 0-0.5% P <sub>2</sub> O <sub>5</sub> ; 10.1% ZrO; 10.5-11.5% Al <sub>2</sub> O <sub>3</sub> ; 0-0.5% CaO ; 0-9% pigments

### 3.4. Results

Figures 3.1 to 3.4 are SEM images that show the surface morphology of the LDGC after being etched with 5% HF. The samples from e.max CAD and n!ce presented needle-like crystals after the glassy matrix dissolution by the etchant. The size of the crystals varies from being a few nanometers wide and a few micrometers in length. Also, Celtra and Suprinity showed to be composed of rod-like crystals with nanometric size. The presence of the glassy matrix is noticeable in e.max CAD and n!ce.

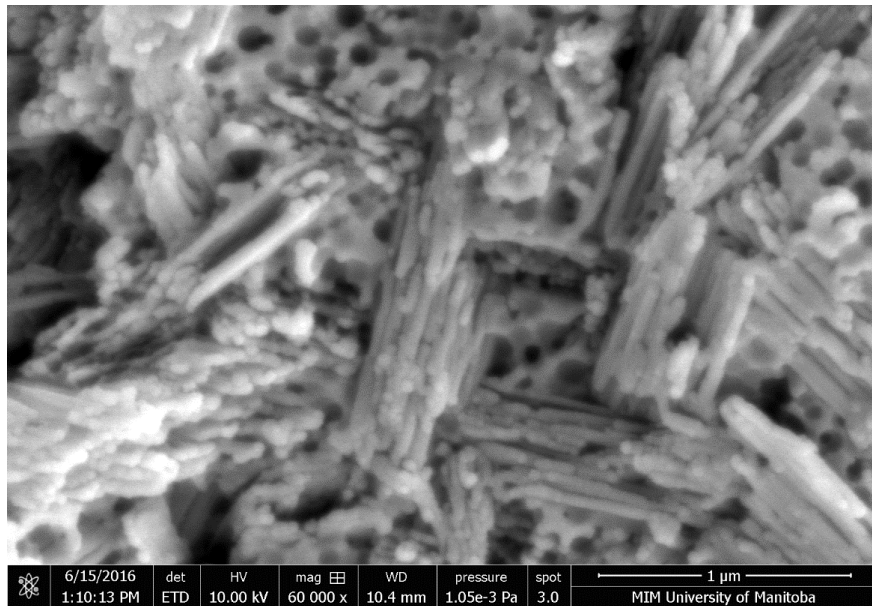


Figure 3.1: SEM image shows the surface microstructure of e.max CAD after etching with 5% HF.

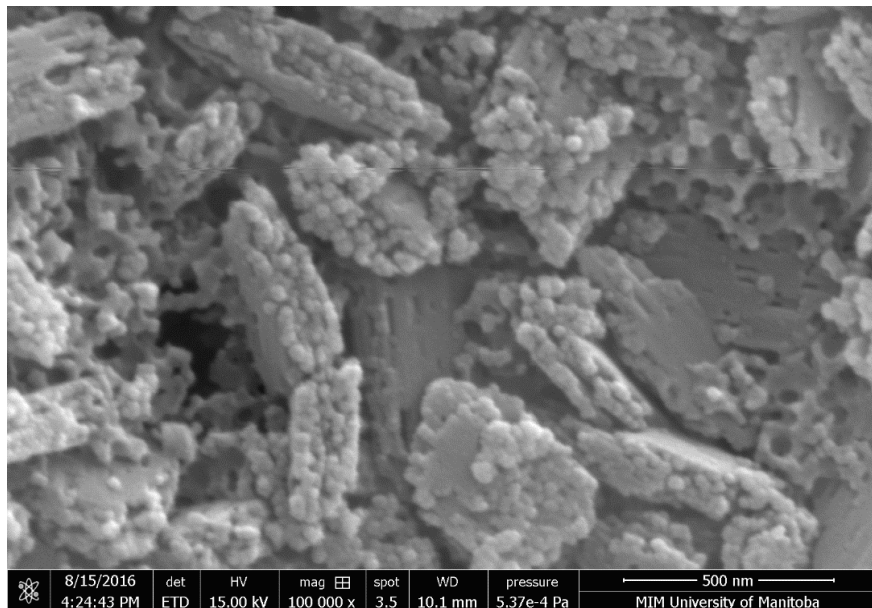


Figure 3.2: SEM image the surface microstructure of Vita Suprinity after etching with 5% HF.

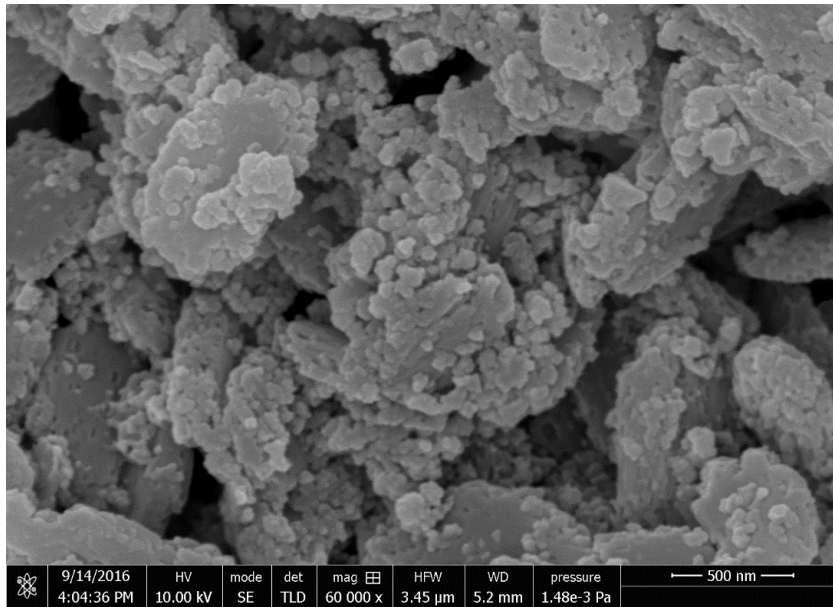


Figure 3.3: SEM image the surface microstructure of Celtra after etching with 5% HF.

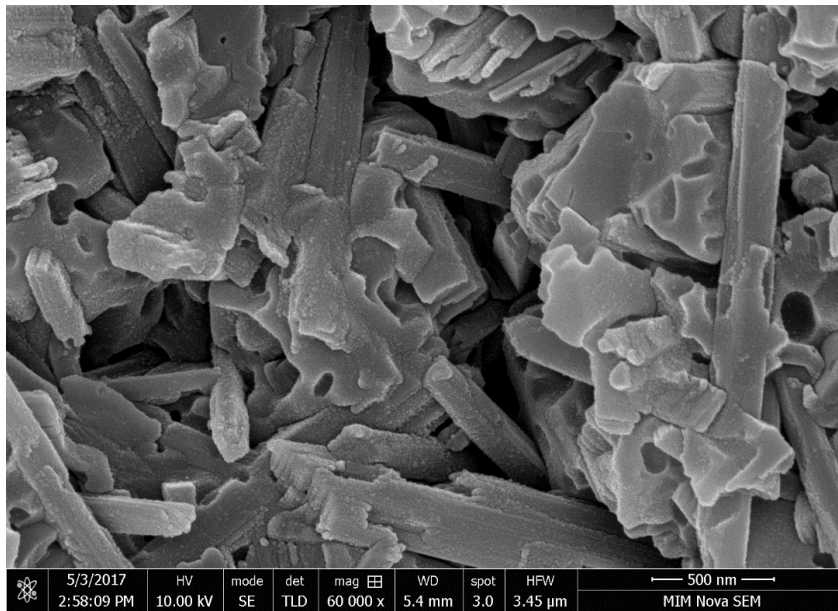


Figure 3.4: SEM image the surface microstructure of n/lce after etching with 5% HF.

Table 3.2: XPS survey analyses of four LDGC, with control and 5% HF etched groups showing the change of chemical elements percentage on the surface (1s, 2p, 3p,3d: energy level and orbital positions) . n = 12

Elements %	Celtra		e.max CAD		n!ce		Suprinity	
	Control	Etched	Control	Etched	Control	Etched	Control	Etched
<b>O 1s</b>	49.2	45.5	50	46.6	44.7	45.6	45.1	43.1
<b>Si 2p</b>	22.9	21.4	26.9	25.6	25.2	22.1	24.8	22.2
<b>Li 1s</b>	19.7	21.2	11.8	12.1	8.4	14.2	16.9	19.6
<b>C 1s</b>	2.1	6.6	5.5	9.5	12.8	11.5	2.1	9.4
<b>Al 2p</b>	1.5	1.5	1.0	1.1	5.9	4.9	1.5	1.8
<b>P 2p</b>	0.8		2.1				1.1	
<b>K 2p</b>	0.5	0.5	1.1	2.2			0.4	0.5
<b>Zn 2p</b>			0.2	0.2				
<b>Y 3p</b>	0.2		0.3		0.3	0.2	0.6	
<b>Zr 3p</b>	2.4	2.9	0.2	0.2	1		4.7	2.2
<b>Sr 3p</b>	0.2		0.3	0.3				
<b>Ce 3d</b>	0.1	0.3	0.3	0.3	0.1	0.3	0.2	
<b>N 1s</b>	0.2		0.3		1.4	0.7	0.1	
<b>Na 1s</b>	0.2						0.6	
<b>F 1s</b>					0.2	0.5		

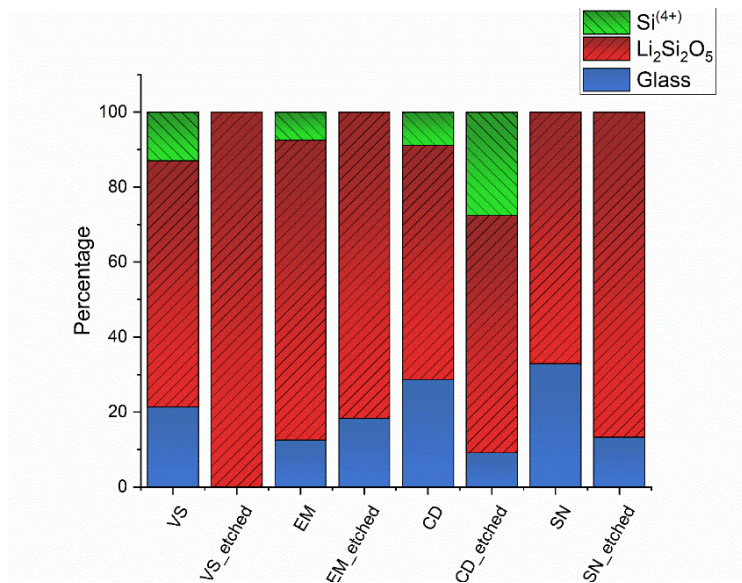


Figure 3.5: Percentage for the O1s phase HR XPS peaks

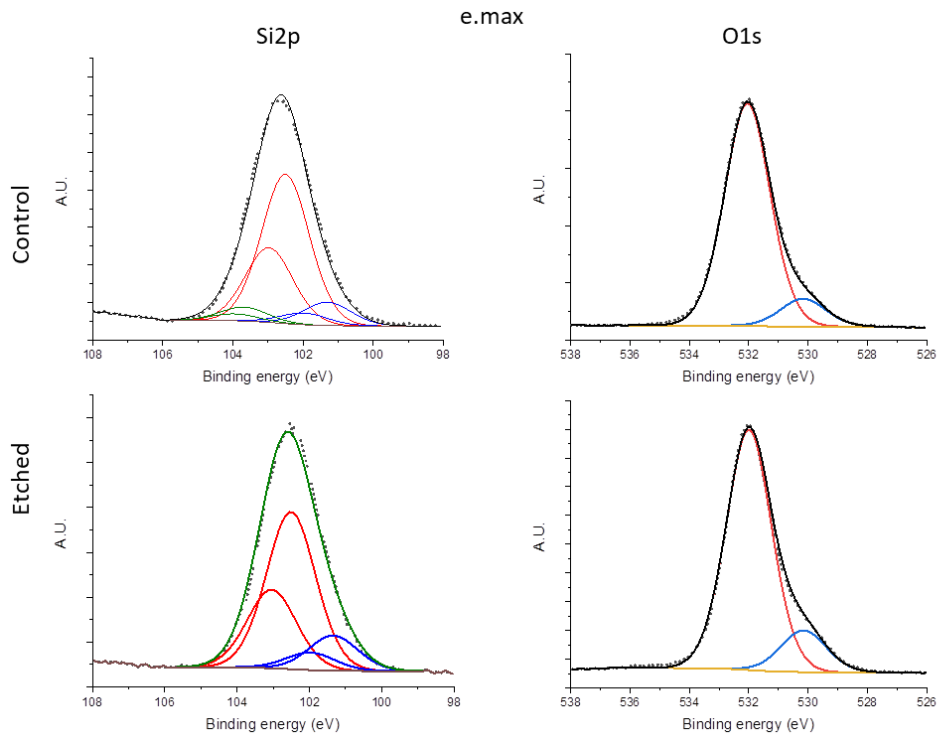


Figure 3.6: Si and O peaks for e.max CAD, for control and 5%HF etched groups.

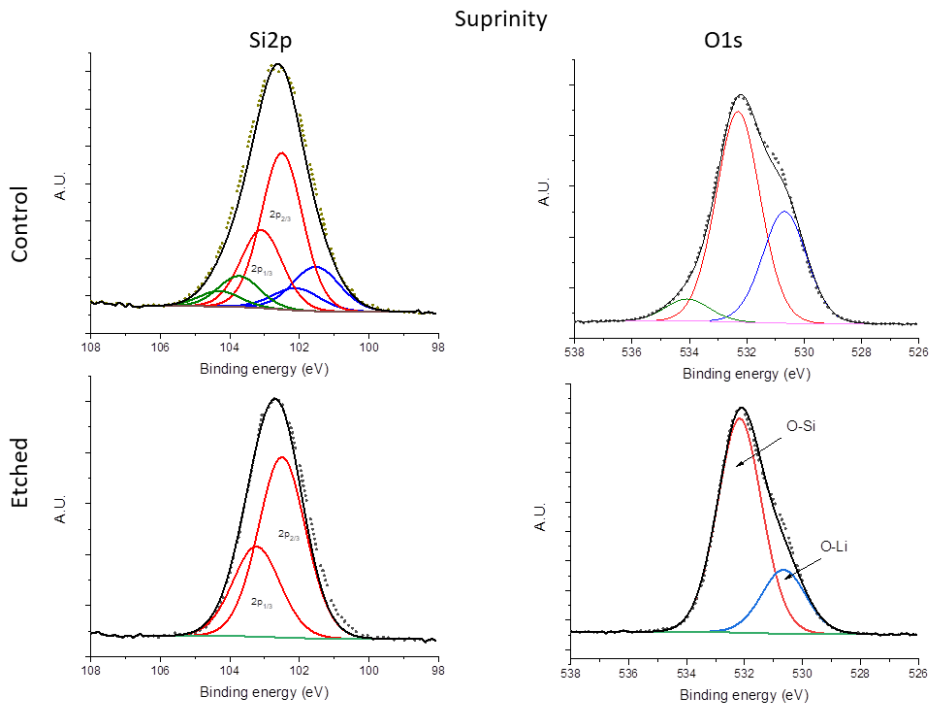


Figure 3.7: Si and O peaks for Vita Suprinity, for control and 5% HF etched groups.

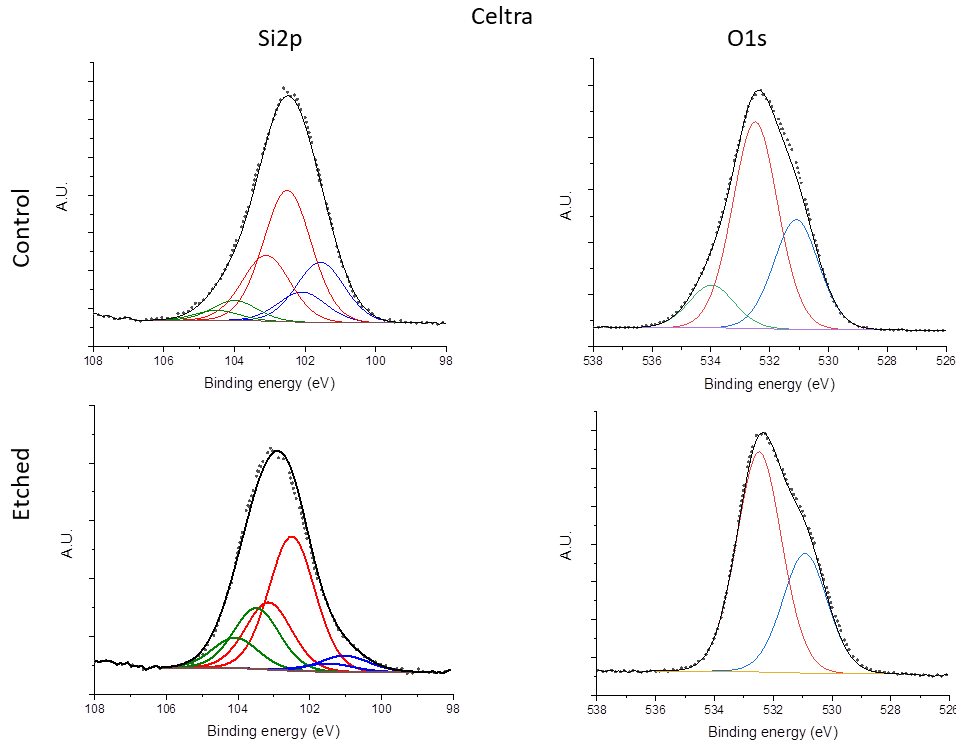


Figure 3.8: Si and O peaks for Celtra, for control and 5% HF etched groups.

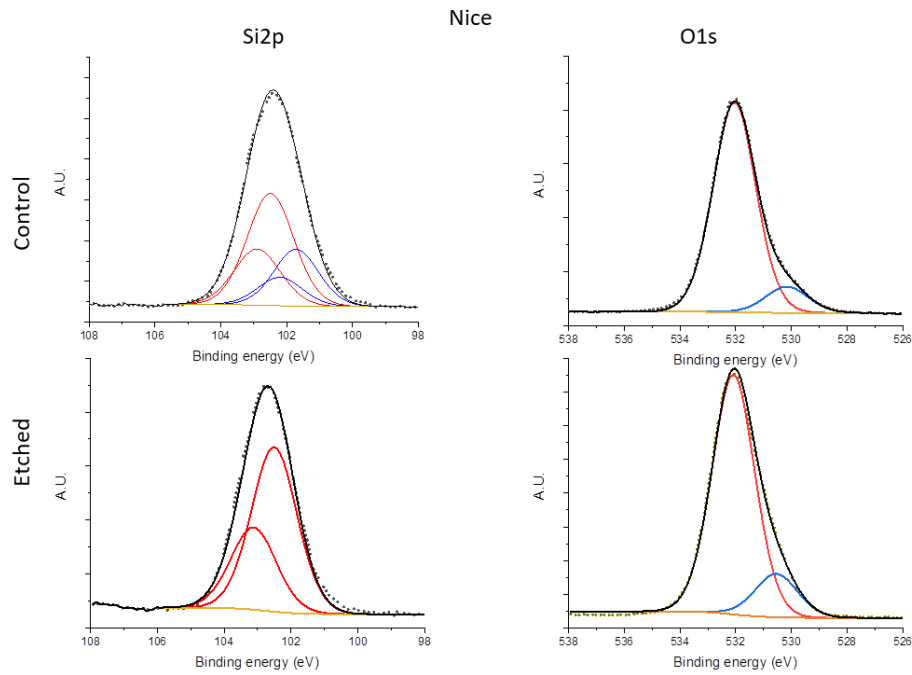


Figure 3.9: Si and O peaks for nice, for control and 5% HF etched groups.



Table 3.3: The peak positions for silicone and oxygen of four LDCG, for control and 5% HF etched groups.

Chemical Element	Peak deconvolution	Peak position (eV)	FWHM (eV)	Attribution	Celtra (%)		e.max (%)		n!ce (%)		Suprinity (%)	
					Control	Etched	Control	Etched	Control	Etched	Control	Etched
Silicon	Si2p A	~ 101.8	1.6	SiO <sub>2</sub> Glass	28.7 <sup>(-.3)</sup>	9.1 <sup>(-.7)</sup>	12.5 <sup>(-.5)</sup>	18.3 <sup>(+.2)</sup>	32.9 <sup>(-.1)</sup>	0	21.3 <sup>(-.3)</sup>	0
	Si2p B	~ 102.5	1.6	Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	62.5	63.4	80	81.7	67.1	100	65.7	100
	Si2p C	~ 104	1.6	SiO <sub>2</sub> Crystal	8.8	28.4 <sup>(-.5)</sup>	7.5 <sup>(-.3)</sup>	0	0	0	13 <sup>(-.3)</sup>	0
Oxygen	O1s A	~ 531	1.8	O-Li	30.5 <sup>(-.3)</sup>	35.2 <sup>(-.1)</sup>	11.1 <sup>(-.8)</sup>	14.8 <sup>(+.1)</sup>	13.5 <sup>(+.5)</sup>	15.4 <sup>(+.5)</sup>	32.5 <sup>(-.3)</sup>	22.9 <sup>(-.3)</sup>
	O1s B	~ 532	1.8	O-Si	57.5	64.8 <sup>(+.4)</sup>	88.9 <sup>(-.1)</sup>	85.2	85.4 <sup>(+.1)</sup>	84.6 <sup>(+.1)</sup>	61.1 <sup>(+.3)</sup>	77.1 <sup>(+.2)</sup>
	O1s C	~ 534	1.8	O-P	11.9 <sup>(-.4)</sup>	0	0	0	0	0	6.4 <sup>(+.1)</sup>	0

Table 3.2 displays the survey XPS results from the samples before and after being etched with 5% hydrofluoric acid. Oxygen, silicon, and lithium are the major constituents of all LDGC. The amount of adventitious carbon present was greatly reduced in all samples, due to the argon pre-etch treatment. However, n!ce has more than 10% of carbon in its composition. Zircon was detected in all samples. In the control group, Celtra and Suprinity have 2.4% and 4.7% zircon respectively; these amounts changed to 2.9% and 2.2% after etching. n!ce samples displayed zircon only without etching (1%), and e.max CAD showed very small amounts in both experimental conditions. Control and etched samples from n!ce had approximately 5.9% and 4.9% of aluminum respectively; while the other LDGC presented with less than 1.8% of aluminum. Trace elements (< 1%) such as phosphorus, yttrium, strontium, nitrogen, and sodium were detected only in the control samples. Cerium, also a trace element, was found in both the control and etched conditions for all LDGC, except for etched Suprinity samples. Less than 1% of fluorine was detected in n!ce in control and etched samples.

Table 3.3 shows the results of peak deconvolutions obtained in HR XPS analyses displayed in Figures 3.6 to 3.9. The control groups for Celtra, e.max CAD and Suprinity showed three contributions for Si2p peak: A) ~ 101.8 eV attributed to an amorphous silicate phase ( $\text{Si}^{2+}$ ) like Si-Si<sub>2</sub>O<sub>2</sub> and Li<sub>4</sub>SiO<sub>4</sub>; (25, 26) B) ~ 102.5 eV attributed to the main crystalline phase Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (LS<sub>2</sub>) and small input from other silicates such as Al<sub>2</sub>SiO<sub>5</sub> (102.7 eV) (27) and ZrSiO<sub>4</sub> (102.8 eV); (28) C) ~ 104 eV attributed to a crystalline form of Si<sup>(4+)</sup> (29, 30). The control group from n!ce presented only the Si2p contributions A and B. The O1s spectrum for both e.max and n!ce contained two contributions: A) ~ 531 eV, attributed to oxygen in lithium compounds such as LiOH, Li<sub>3</sub>PO<sub>4</sub>, LiPO<sub>3</sub>; B) ~ 532 eV attributed to oxygen linked to silicon, as in silicates and Li<sub>2</sub>-

Si-O<sub>2</sub>. The Celtra and Suprinity spectra contained a third contribution: C) ~ 534 eV, attributed to oxygen present in oxidized carbon.

The HR peak fitting showed that the intensity of the compounds varies after etching. In other words, the degradation of the matrix phase, after applying 5% of HF for 20s, produces a completely different surface chemical composition for all LDGC. Figures 3.1 to 3.4 illustrates that after etching, not only did the intensity of the peaks changed, but the position of the assigned peaks also changed. The amount of the shifting of each peak from the expected position is in superscript between brackets on Table 3.3. This shift indicates a chemical alteration on the electronegativity inside the assigned peak, due to the chemical composition changes.

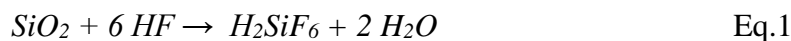
### **3.5: Discussion**

The results from this study showed that the concentration of the major elements, O, Si and Li vary significantly after using an acid etching protocol for all LDGC. The null hypothesis was therefore rejected.

The atomic percentages from our finding differs from that reported in the literature (15, 22, 32-36). The manufacturers' reports show a different percentage of components, and some investigations did not show any difference in the chemical composition of the surface before and after acid etching. One of the reasons for this discrepancy could be the fact that these investigations performed chemical analyses using energy dispersive x-ray spectroscopy (EDS or EDX) (15, 22, 32). EDX is a limited experimental technique to characterize the surface composition (37). The EDX probing beam can penetrate 1- 2 microns deep, and it assesses the bulk composition, not the surface. EDX cannot detect lithium, and this could affect the accuracy of the LDGC data. However, XPS can detect quantitatively even small concentrations (0.01%) of

all elements, except for H and He. In addition, XPS can provide only the composition of a limited number of atomic layers in depth (~ 4 nm). This limitation makes XPS a perfect tool for surface analyses.

The reaction between the glass and HF is described in equation 1. Among dental researchers, there is a predominant opinion that only the glassy matrix is dissolved by HF (17, 22, 38). However,  $LS_2$  crystals seem to be more resistant to dissolution than  $SiO_2$ . As shown in the equation 2, to dissolve one molecule of  $LS_2$  more than double the HF concentration is needed than in Equation. 1. Furthermore, the literature shows that the higher the degree of crystallization is, the lower the solubility of the LDGC (39). Our XPS results seem to point in the same direction, showing a reduction or elimination of the peaks assigned to the glass phase after etching. Curiously, no fluorine was detected either by survey mode or by HR mode in the etched samples. In fact, if Si-F compounds like hexafluorosilicate were present, there would be an expected to appear as a peak with high binding energy (~ 104.5 eV) (26). No sample showed this kind of contribution. A direct clinical implication of this finding could be to validate that the rinsing for 20s is enough to wash off all by-products.



Analyzing the Si2p and O1s peaks from HR XPS results, it is possible to have a better understanding of what happened in the outer most atomic layer of LDGC before and after etching. As mentioned before, in the control groups for Celtra, Suprinity and e.max CAD there are three chemical environments of Si: a glass phase, the main phase ( $LS_2$ ) and the third phase at ~ 104 eV (Table 3.3). This unexpected third contribution is related to a crystalline form of  $SiO_2$

like quartz (29, 30). Tashiro and Wada reported that in a systems using  $ZrO_2$ , as nucleate agents, this can result in partial crystallization of the base glass in  $\alpha$ -quartz solid-solution precursor (40). Huang and coworkers also describe the formation of quartz, cristobalite and tridymite during the crystallization of  $LS_2$ , even in systems with low Zr concentration (41). The same authors observed that the quartz normally disappears at 980 °C (42). Certainly, the presence of this residual quartz (or another form of crystalline  $SiO_2$ ) would be beneficial to increase the mechanical properties. The amount of this phase in the analyzed samples were: 8.8% in Celtra, 13% in Suprinity and 7.5% in e.max. Even though n!ce has 1% of Zr in its composition, this phase was not detected. Further investigations will be needed to better understand the nature of this residual “quartz” .

Observing Figure 3.7, it is possible to predict that, after etching, the surface of Suprinity is mainly composed of  $LS_2$  crystals, because the  $Si2p$  peak has only one contribution. Also,  $O1s$  peak reveals that the Li:Si ratio of this compound is 1:2.41, which is very close to the expected ratio of 1:2.39 of the system  $[Li_2O]_2[SiO_2]$  proposed by Holand et al (7, 43). However, for Celtra (called “zirconia-reinforced lithium silicate glass ceramic”, like Suprinity) the atomic composition of the surface is quite different (Fig. 3.8). After etching, Celtra presented the same three chemical environments as before etching. The amount of glass phase reduced from 28.7% to 9.1%, the  $LS_2$  phase remained the same, while the “quartz” phase increased from 8.8% to 27.5%. A possible explanation for this is that as the glass phase dissolves, the crystals of “quartz” became more noticeable. The peak  $O1s$  presents a Li:Si ratio equal to 1:1.84. It indicates that Celtra’s surface has a higher content of lithium than Suprinity. It would be possible if the 9.1% of the residual glassy matrix is rich in  $Li_2SiO_3$  and/ or  $Li_3PO_4$ .

For all four LDGC products that were assessed, e.max CAD appears to be the least affected by the acid etching protocol. The small change was due to the dissolution of the phase at  $\sim 103.7$  eV. Without etching, e.max CAD had the highest percentage of  $LS_2$  phase (Figure 3.6). This feature contributes positively to its mechanical performance. The peak O1s shows a ratio Li:Si of 1:5.75 that indicates a very low amount of lithium in the reminiscent glassy matrix. This finding can also be confirmed by the XPS survey result, which shows that, after etching, e.max CAD had the highest amount of Si and lowest de? Li (Table 3.2).

In the control group, the n!ce surface showed distinctive features. First, it is the only LDGC which does not show a third contribution for the Si2p peak. An explanation for this is that n!ce is provided as a fully-crystallized glass ceramic, and compared to celtra, the manufacturer does not recommend additional firing. As discussed before, should the e.max CAD ingot reaches more the  $900^\circ\text{C}$  during the fabrication phase, no crystalline form (like quartz) will remain in the glass phase. Secondly, the amount of aluminum is about four times more compared to the other LDGC. Even though the manufacturer describes n!ce as a lithium aluminosilicate ceramic reinforced with lithium disilicate, this study was able to detect Al only in the matrix phase. The assigned peak of the glass at  $\sim 102.7$  eV indicates the presence of  $Al_2SiO_5$ . This finding was also confirmed by the convolution of the Al2p peak (not presented here), and by the literature (44). No presence of Al-Li compound was found, for that, a peak should appear at  $\sim 75.8$  eV (45). Finally, the elevated amount of carbon on n!ce samples could indicate a high roughness of the samples which could allow to trap more adventitious carbon. After etching, n!ce present a ration Li:Si equal 1:3.56.

The clinical significance of this study is because a 5% HF acid etching surface treatment has become the “good standard” clinical protocol, it is important to obtain satisfactory bond strength for LDGC restorations. However, the mechanical interlocking is only part of the bonding process, a chemical adhesion is also achieved by using a silane coupling agent. For the first time, the physicochemical composition of the first atomic layers and the effect of the HF etching on dental LDGC are shown. This information will help to understand the challenges of adhesive processes and to share light on targeted coupling agents for specific surface chemical composition. By these methodologies, future studies will be able to assess the ideal ratio concentration /time for HF application.

### **3.6. Conclusion**

Within the limitations of this investigation, it is possible to conclude that the surfaces of all LDGC have a distinctly different chemical composition after acid etching.

### 3.7 References:

1. Beall GH. Structure, properties and nucleation of glass-ceramics. In: Hench LL, Freiman SW, editors. *Advances in Nucleation and crystallization in Glasses*. Columbus OH: American Ceramic Society; 1971. p. 251–61.
2. Beall GH. Design and properties of glass-ceramics. *Annual Reviews of Materials Science*. 1992; 22:91-119.
3. Iqbal Y, Lee WE, Holland D, James PF. Crystal nucleation in P2O5-doped lithium disilicate glasses. *Journal of Material Science*. 1999; 34:4399–411.
4. Schweiger M, Frank M, Rheinberger V, Hoeland W, inventors Sinterable lithium disilicate glass ceramic. United States 1999.
5. Höland W, Schweiger M, Frank M, Rheinberger V. A comparison of the microstructure and properties of the IPS Empress®2 and the IPS Empress® glass-ceramics. *Journal of Biomedical Materials Research*. 2000; 53(4):297-303.
6. Apel E, van't Hoen C, Rheinberger V, Höland W. Influence of ZrO2 on the crystallization and properties of lithium disilicate glass-ceramics derived from a multi-component system. *Journal of the European Ceramic Society*. 2007;27(2-3):1571-7.
7. Höland W, Apel E, van 't Hoen C, Rheinberger V. Studies of crystal phase formations in high-strength lithium disilicate glass–ceramics. *Journal of Non-Crystalline Solids*. 2006;352(38-39):4041-50.
8. Holand W, Rheinberger V, Apel E, Van 't Hoen C, Holand M, Dommann A, et al. Clinical applications of glass-ceramics in dentistry. *Journal of Materials Science: Materials in Medicine*. 2006; 17(11):1037-42.



9. Goharian P, Nemati A, Shabani M, Afshar A. Properties, crystallization mechanism and microstructure of lithium disilicate glass-ceramic. *Journal of Non-Crystalline Solids*. 2010;356(4-5):208-14.
10. Zanotto ED. A bright future for glass-ceramics. *American Ceramic Society Bulletin*, 2010; 89(8):19-27.
11. Holand W, Beall GH. *Glass Ceramic Technology*. 2nd ed: Wiley; 2012. 440 p.
12. Belli R, Wendler M, de Ligny D, Cicconi MR, Petschelt A, Peterlik H, et al. Chairside CAD/CAM materials. Part 1: Measurement of elastic constants and microstructural characterization. *Dental Materials*. 2017;33(1):84-98.
13. Wen G, Zheng X, Song L. Effects of P<sub>2</sub>O<sub>5</sub> and sintering temperature on microstructure and mechanical properties of lithium disilicate glass-ceramics. *Acta Materialia*. 2007;55(10):3583-91.
14. Pieger S, Salman A, Bidra AS. Clinical outcomes of lithium disilicate single crowns and partial fixed dental prostheses: a systematic review. *Journal of Prosthetic Dentistry*. 2014;112(1):22-30.
15. El-Damanhoury HM, Gaintantzopoulou MD. Self-etching ceramic primer versus hydrofluoric acid etching: Etching efficacy and bonding performance. *Journal of Prosthodontic Research*. 2018; 62(1):75-83.
16. Aboushelib MN, Sleem D. Microtensile bond strength of lithium disilicate ceramics to resin adhesives. *Journal of Adhesive Dentistry*. 2014;16(6):547-52.
17. Al-Thagafi R, Al-Zordk W, Saker S. Influence of Surface Conditioning Protocols on Reparability of CAD/CAM Zirconia-reinforced Lithium Silicate Ceramic. *Journal of Adhesive Dentistry*. 2016; 18(2):135-41.

18. Puppini-Rontani J, Sundfeld D, Costa AR, Correr AB, Puppini-Rontani RM, Borges GA, et al. Effect of Hydrofluoric Acid Concentration and Etching Time on Bond Strength to Lithium Disilicate Glass Ceramic. *Operative Dentistry*. 2017;42(6):606-615
19. Prochnow C, Venturini AB, Grasel R, Bottino MC, Valandro LF. Effect of etching with distinct hydrofluoric acid concentrations on the flexural strength of a lithium disilicate-based glass ceramic. *Journal of Biomedical Materials Research B Applied Biomaterials*. 2016.
20. Lanza MDS, Rodrigues Lanza FJS, Manso AP, Matinlinna JP, Carvalho RM. Innovative surface treatments for improved ceramic bonding: Lithium disilicate glass ceramic. *International Journal of Adhesion and Adhesives*. 2018;82:60-6.
21. Castner DG, Ratner BD. Biomedical surface science: Foundations to frontiers. *Surface Science* 2002;500:28-60.
22. Murillo-Gomez F, Palma-Dibb RG, De Goes MF. Effect of acid etching on tridimensional microstructure of etchable CAD/CAM materials. *Dental Materials*. 2018.
23. Radvanyi E, De Vito E, Porcher W, Jouanneau Si Larbi S. An XPS/AES comparative study of the surface behaviour of nano-silicon anodes for Li-ion batteries. *Journal of Analytical Atomic Spectrometry*. 2014;29(6):1120.
24. NIST X-Ray Photoelectron Spectroscopy (XPS) Database. . In: Dept. of Commerce NIST, editor. NIST Standard Reference Database Gaithersburg, MD:U.S. 20899.
25. Nguyen TP, Lefrant S. XPS study of SiO thin films and SiO-metal interfaces. *Journal of Physics: Condensed Matter*. 1989;1(31):5197-204.
26. Philippe B, Dedryvere R, Gorgoi M, Rensmo H, Gonbeau D, Edstrom K. Improved performances of nanosilicon electrodes using the salt LiFSI: a photoelectron spectroscopy study. *Journal of the American Chemical Society*. 2013;135(26):9829-42.

27. Hughes AEH, MM, Sexton, B. A. Reactions at the Al/SiO<sub>2</sub>/SiC layered interface. *Journal of Materials Science*. 1990; 25(11):4856-65.
28. Dementjev AP, Ivanova OP, Vasilyev LA, Naumkin AV, Nemirovsky DM, Shalaev DY. Altered layer as sensitive initial chemical state indicator\*. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 1994;12(2):423-7.
29. Taylor JA, Lancaster GM, Ignatiev A, Rabalais JW. Interactions of ion beams with surfaces. Reactions of nitrogen with silicon and its oxides. *The Journal of Chemical Physics*. 1978; 68:1776-84.
30. Kerkhof FPJMM, J.A. ;Heeres, A. The XPS spectra of the metathesis catalyst tungsten oxide on silica gel. *Journal of Electron Spectroscopy and Related Phenomena*. 1978;14(6):453-66.
31. Chowdari B.V.R., Tan K.L., Chia W.T., R. G. X-ray photoelectron spectroscopic studies of molybdenum phosphate glassy system. *Journal of Non-crystalline Solids*. 1990;119:95-102.
32. Traini T, Sinjari B, Pascetta R, Serafini N, Perfetti G, Trisi P, et al. The zirconia-reinforced lithium silicate ceramic: lights and shadows of a new material. *Dental Materials Journal*. 2016;35(5):748-55.
33. Kohal RJ, Att W, Bachle M, Butz F. Ceramic abutments and ceramic oral implants. An update. *Periodontology 2000*. 2008;47:224-43.
34. Poulin S, França R, Moreau-Bélanger L, Sacher E. Confirmation of X-ray Photoelectron Spectroscopy Peak Attributions of Nanoparticulate Iron Oxides, Using Symmetric Peak Component Line Shapes. *The Journal of Physical Chemistry C*. 2010;114(24):10711-8.
35. Dentsply Sirona Prosthetics. Celtra Duo safety data sheet. version 1.6 GB. Issue data 21.03.2013. Revision date 14.03.2017..

36. Esquivel-Upshaw JF, Chai J, Sansano S, Shonberg D. Resistance to staining, flexural strength, and chemical solubility of core porcelains for all-ceramic crowns. *International Journal of Prosthodontics*. 2001;14(3):284-8.
37. Buddy D. Ratner, Allan S. Hoffman, Frederick J. Schoen, Lemons JE. *Biomaterials Science - An Introduction to Material in Medicine*. 3rd ed.2004
38. Ramakrishnaiah R, Alkheraif AA, Divakar DD, Matinlinna JP, Vallittu PK. The Effect of Hydrofluoric Acid Etching Duration on the Surface Micromorphology, Roughness, and Wettability of Dental Ceramics. *International Journal of Molecular Sciences*. 2016;17(6).
39. Khalkhali Z, Eftekhari yekta B, Marghussian VK. Mechanical and Chemical Properties of Zr and P-Doped Lithium Disilicate Glass Ceramics in Dental Restorations. *International Journal of Applied Ceramic Technology*. 2012;9(3):497-506.
40. Tashiro T, Wada M. *Glass-ceramics crystallized with zirconia*. New York: Plenum Press; 1963. quoted in Holand W, Beall GH. *Glass-ceramics*. In: Kaneno M, S. Sm, editors. *Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties*. Academic Press, Available from: eBook Collection (EBSCOhost). ed2013. p. 371-412.
41. Huang S, Cao P, Li Y, Huang Z, Gao W. Nucleation and Crystallization Kinetics of a Multicomponent Lithium Disilicate Glass by in Situ and Real-Time Synchrotron X-ray Diffraction. *Crystal Growth & Design*. 2013;13(9):4031-8.
42. Huang S, Huang Z, Gao W, Cao P. Structural Response of Lithium Disilicate in Glass Crystallization. *Crystal Growth & Design*. 2014;14(10):5144-51.
43. Holand W, Rheinberger V, Schweiger M. Control of nucleation in glass ceramics. *Phil Trans R Soc Lond A*. 2003;361:575-89.

44. Gonzalez-Elipe AR, Espinos JP, Munuera G, Sanz J, Serratosa JM. Bonding-state characterization of constituent elements in phyllosilicate minerals by XPS and NMR. *The Journal of Physical Chemistry*. 1988;92(12):3471-6.
45. McGuire GE, Schweitzer GK, Carlson TA. Core electron binding energies in some Group IIIA, VB, and VIB compounds. *Inorganic Chemistry*. 1973;12(10):2450-3.

## Chapter 4: Second Manuscript

### **The effect of different surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate- based glass ceramics.**

Muna Bebsh,<sup>1,2</sup> Asmaa Haimeur,<sup>1</sup>, Rodrigo França,<sup>1</sup>.

1. Dental Biomaterials Research Laboratory, Department of Restorative Dentistry. University of Manitoba, Winnipeg, Manitoba, Canada.

2. Department of Oral Biology, University of Manitoba, Winnipeg, Manitoba,

#### **4.1: Abstract**

Objective: The aim of this study was to investigate and compare the effect of various surface treatments on the micromorphology and the roughness of four CAD/CAM lithium disilicate-based glass ceramics.

Method: Eighty specimens of four lithium disilicate-based glass ceramic materials (IPS e. max® CAD (Ivoclar-Vivadent, Liechtenstein, Schaan), Vita Suprinity® (Vita Zahnfabrik, Bad Säckingen, Germany), Celtra Duo® (Dentsply, Hanau-Wolfgang, Germany) and n!ce (Straumann, Basel, Switzerland) were used for this study (n = 5). All specimens were highly polished with 400, 600, 1200 grit silicon carbide paper and then polished with 3 µm and 1 µm polycrystalline diamond suspension liquid with grinding devices. Each group of ceramic was assigned to one of the following three surface treatments (1) sandblasting (SB) with 50 µm Al<sub>2</sub>O<sub>3</sub> at 70 psi for 10s, (2) hydrofluoric acid etching (HF) with 5% hydrofluoric acid for 20s, or 30s according to the manufacturer instructions, (3) and a combination of sandblasting and hydrofluoric acid (SB+HF). All specimens were cleaned with ethanol for 2 minutes and placed in

an ultrasonic unit with distilled water for 15 minutes. The microstructure was analyzed by scanning electron microscopy (SEM). The surface roughness and topography was evaluated with atomic force microscopy in tapping mode (AFM). Statistical analysis was done using two-way ANOVA and Tukey tests ( $\alpha = 5\%$ ). Results: All surface treatments had a significant effect on LDGC surface roughness compared to the untreated surface ( $P < .05$ ). The sandblasting treatment had a significantly higher mean surface roughness value for Vita Suprinity and Celtra Duo compared to other surface treatments ( $P < .05$ ). However, there was no significant difference for surface roughness between sandblasting and sandblasting + etching for e.max CAD and n!ce. The hydrofluoric acid produced less surface roughness compared to other surface treatments but was able to change the surface structure.

Conclusions: The sandblasting + etching treatment could be a sufficient method to produce surface roughness for all ceramic types.

Keywords: Lithium disilicate-based glass ceramic, surface treatments, atomic force microscopy.

## **4.2: Introduction**

Glass-ceramics, polycrystalline ceramics and resin-matrix ceramics are the most frequently used materials for prosthodontic restorations (1). In fact, glass-ceramics are widely used in dentistry as restorative materials for different applications such as crowns, inlays, onlays, and veneers. The success of glass-ceramic dental restorations is in part due to their excellent mechanical and biocompatibility properties (2-4). One of the subcategories of glass-ceramics is synthetic ceramics which include lithium disilicate and its derivatives. The first generation of LDGC introduced to the dental market was IPS Empress II (Ivoclar-Vivadent, Liechtenstein, Schaan) in 1998. Development of computer-aided design and computer-aided manufacturing (CAD/CAM)

technology lead to the introduction of another generation of CAD-CAM LDGC called IPS e.max CAD in 2006. IPS e.max CAD is popular for use in both single and multiple unit indirect restorations due to its high mechanical strength (~360 MPa), excellent esthetic properties and good clinical success (5). In addition, CAD/CAM technology allows the dentist to prepare and deliver an indirect restoration in one appointment (6). Recently, two new CAD/CAM glass-ceramic materials were introduced to the dental market: 1) zirconia reinforced lithium silicate glass ceramics: Vita Suprinity®, and Celtra Duo® (from Vita Zahnfabrick, Bad Säckingen, Germany and Dentsply DeTrey Hanau-Wolfgang, Germany respectively); and 2) lithium alumina silicate reinforced with lithium disilicate: n!ce (from Strauman). Both Vita Suprinity and Celtra Duo ceramics are enriched with zirconia (≈10% by weight). They claim to be the first zirconia reinforced lithium silicate ceramic (3). Like e.max CAD, Vita Suprinity is supplied in a pre-crystalline stage suitable for milling procedures and is crystallized following the milling procedure. Celtra Duo and n!ce are provided as fully sintered blocks. Celtra Duo may be heat treated to improve its mechanical properties (7, 8). According to the manufacturers, both celtra Duo and n!ce can be immediately seated and cemented after fabrication with a CAD/CAM system.

The quality of the ceramic-resin bonding is a key factor for clinical success. The ceramic-resin interface are subjected to the moist oral environment and functional forces present in the oral cavity. The adhesion at the ceramic-resin interface is the result of a physico-chemical interaction across the interface involving the adhesive and the ceramic surface (9, 10). A durable bond between the resin cement and glass ceramic restoration is obtained by two mechanisms: micro mechanical retention provided by different surface treatments, such as acid etching or



sandblasting with  $\text{Al}_2\text{O}_3$  or a combination of any two of these methods (9, 11). The second mechanism is the chemical bonding provided by a silane coupling agent (12).

The lithium disilicate-based glass-ceramic microstructure has two phases, a glassy matrix phase (silica) and a crystals phase (lithium disilicate oxide,  $\text{Li}_2\text{Si}_2\text{O}_5$ ). The glassy matrix phase contributes to micromechanical bonding as certain surface treatments can affect the glassy matrix. Specifically, hydrofluoric acid etching and aluminum-oxide particle sandblasting of the ceramic surface produces microporosities that contributes to micromechanical bonding (11). These microporosities increases the surface area, and expose and generate hydroxyl groups on the ceramic surface that are responsible for chemical bonding via silane coupling agents (13). The crystals phase (lithium disilicate oxide,  $\text{Li}_2\text{Si}_2\text{O}_5$ ) is responsible for its mechanical properties and ceramic strength (14). ]

Scanning electron microscopy (SEM) is a valuable tool to investigate the morphology and microstructural changes of glass ceramic surfaces (15). Atomic force microscopy (AFM) are used in biomaterial science to provide a quantitative measurement of surface roughness and it describes the topography of the biomaterial surface with less effort of sample preparation (16, 17). Although surface treatments of lithium disilicate-based glass-ceramic of the pressed technique have been studied previously, the CAD/CAM lithium disilicate-based ceramics such as IPS e.max CAD, Vita Suprinity®, Celtra Duo®, and n!ce have not been fully investigated. The optimal glass ceramic surface treatment has not been confirmed as yet. The aim of this study is to evaluate the effect of sandblasting with aluminum-oxide ( $\text{Al}_2\text{O}_3$ ), etching with 5% hydrofluoric acid and the use of a combination of sandblasting and hydrofluoric acid treatment on the surface roughness of IPS e. max® CAD, Vita Suprinity®, Celtra Duo® and n!ce. The null hypothesis is

that different surface treatments would not have effect on the surface roughness and micromorphology of four CAD/CAM lithium silicate glass ceramics.

### 4.3: Materials and methods

#### *Sample preparation*

Eighty specimens of four different types of lithium disilicate-based glass ceramics (see Table 1) were selected for this study, 20 specimens of each of the four materials (n=5).

Table 4.1: The chemical composition of four LDGC products provided from the manufacturer, manufacturer information and clinical information of the four LDGC used in this study.

	<b>Chemical composition</b>	<b>Manufacturer</b>	<b>Description</b>	<b>Clinical indication</b>
<b>IPS e.max® CAD</b>	57-80%SiO <sub>2</sub> 11-19%Li <sub>2</sub> O 0-13%K <sub>2</sub> O 0-11%P <sub>2</sub> O <sub>5</sub> 0-8%ZrO <sub>2</sub> -ZnO 0-5%Al <sub>2</sub> O <sub>3</sub> 0-5%Mgo-colouring oxides	(Ivoclar-Vivadent, Liechtenstein, Schaan	Lithium disilicate LS <sub>2</sub> glass ceramic	Veneers; inlays; onlays; anterior and posterior crowns; anterior and posterior implant abutment; three-unit bridges up to bicuspid; overlay veneers for multi-unit frameworks

<b>Vita Suprinity®</b>	56-64%SiO <sub>2</sub> 5-21%Li <sub>2</sub> O 1-4%K <sub>2</sub> O 3-8%P <sub>2</sub> O <sub>5</sub> 8-12%ZrO <sub>2</sub> 0-4%CeO <sub>2</sub> 0-6%pigments	(Vita Zahnfabrik, Bad Säckingen, Germany)	Pre-sintered Lithium silicate/phosphate (LSP) glass-ceramic  Zirconia-reinforced (10% by weight ) Lithium silicate ceramic	Veneers; inlays; onlays; anterior and posterior crowns
<b>Celtra Duo®</b>	58% SiO <sub>2</sub> ; 18.5% Li <sub>2</sub> O; 5% P <sub>2</sub> O <sub>5</sub> ; 10.1% ZrO; 1.9% Al <sub>2</sub> O <sub>3</sub> ; 2% CeO <sub>2</sub> ; 1% Tb <sub>4</sub> O <sub>7</sub>	(Dentsply DeTrey Hanau-Wolfgang, Germany)	Fully- sintered Lithium silicate/ phosphate (LSP) glass- ceramic  Zirconia-reinforced (10% by weight ) Lithium silicate ceramic	Veneers; inlays; onlays; anterior and posterior crowns
<b>n!ce.</b>	. 64-70% SiO <sub>2</sub> ; 10.5 - 12.5% Li <sub>2</sub> O; 0 – 3% K <sub>2</sub> O; 0-0.5% P <sub>2</sub> O <sub>5</sub> ; 10.1% ZrO; 10.5-11.5% Al <sub>2</sub> O <sub>3</sub> ; 0-0.5% CaO ; 0-9% pigments	Straumann  Basel Switzerland	Fully-sintered	Veneers; inlays; onlays; anterior and posterior crowns

CAD/CAM ceramic blocks were sectioned into rectangular slices with a 2 mm height, using a low-speed saw diamond (Isomet1000, Buehler Ltd, Lake Bluff, IL, USA). IPS - e.max CAD and Vita Suprinity specimens were cleaned with ethanol for 2 minutes and then ultrasonically cleaned in distilled water for 15 minutes. Thereafter it was sintered in a furnace according to the firing program recommended by the manufacturer. Celtra Duo and n!ce specimens are fabricated

from fully crystallized lithium disilicate-based glass ceramic blocks and they do not need additional sinterization. To obtain a smooth flat surface, all specimens were polished on wet 400, 600 and 1200 grit size silicon carbide paper (Buehler Ltd, Lake Bluff, IL, USA) and then polished with a 3  $\mu\text{m}$  and 1  $\mu\text{m}$  polycrystalline diamond suspension liquid (Buehler Ltd, Lake Bluff, IL, USA) on a grinding device. The samples were then cleaned with ethanol for 2 minutes and placed in an ultrasonic machine (Branson cleaning equipment company, Shelton, CT, USA) for 15 minutes. The ceramic specimens were labeled on the treated surfaces and then randomly assigned to four treatment groups.

**Group C-** no treatment applied to the ceramic surfaces (n=20). This group served as a control.

**Group SB-** sandblasted (n=20): labeled surfaces of ceramic specimens were sandblasted ( $\text{Al}_2\text{O}_3$ ; Perlblast® Micro; Bego, Bremen, Germany) with 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  at 70 psi for 10s. Specimens were held at a distance of 20 mm between the surface of the specimen and the blasting tip to ensure an equal distance for each specimen. Following sandblasting, the specimens were rinsed under running water for the 20s and then dried for 20s with oil-free compressed air.

**Group HF-** hydrofluoric acid etched (n=20): labeled surfaces of ceramic specimens etched with 5% hydrofluoric acid for 20s (e.max CAD, Vita Suprinity, and n!ce) and for 30s (Celtra Duo) based on manufacturer recommendations for each type. The etching gel was removed under running water for 20s then dried for 20s with oil-free compressed air.

**Group S+E-** sandblasted and hydrofluoric acid etched (n=20): in this group, the specimens were first sandblasted with 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  at 70 psi for 10s. After cleaning, the specimens were etched with 5% hydrofluoric acid for 20s and then cleaned under running water for 20s following by drying.

All specimens were then cleaned with ethanol and subjected to ultrasonic treatment in distilled water to remove any surface residues and then dried with free oil compressed.

#### *Topographic Analyses*

*Scanning electron microscopy:* All ceramic specimens were coated with gold and loaded in a SEM unit (ThermoFisher, Oregon, USA). All SEM images were captured at 10.000 × magnification.

*Atomic force microscopy:* All ceramic specimens were evaluated under AFM Multimode nanoscope IIIa, Digital Instruments (Veeco metrology group, Santa Barbara, CA, USA). Images were taken in tapping mode at 50 um × 50 um scan size with a slow scan rate (0.1 Hz). The average surface roughness (Ra) of the ceramic after different surface treatments was recorded as a numeric value (in nanometer) using appropriate software (Nanoscope v613R1).

*Statistical Analysis:* Data were analyzed using a two way ANOVA with  $\alpha=0.05$ . The means were analyzed for contrasting using Tukey's *post Hoc Test*.

#### **4.4: Results**

Means and standard deviations for the roughness Ra (nm) of four CAD/CAM LDGC were extrapolated from the AFM digital images and are displayed in Table 4.2. Sandblasting created significantly higher mean roughness values ( $p<0.05$ ) compared to other surface treatments for Vita Suprinity and Celtra Duo (figure 4.3), However, sandblasting and S+E had no significant difference for e.max CAD and n!ce. Although hydrofluoric acid demonstrated less roughness than other surface treatments, it changed the micromorphology and produces microporosities on the surface of all four ceramic types. SEM images for HF specimens had a honeycomb shape for

n!ce and Celta, and a needle shape for e.max CAD and Vita Suprinity (figure 4.1). Our results showed that hydrofluoric acid reduced the surface roughness for more than 50% when applied after sandblasting. This was true for both Vita Suprinity and Celtra Duo. However, there was a slight increase in the roughness after sandblasting for e.max CAD and n!ce.

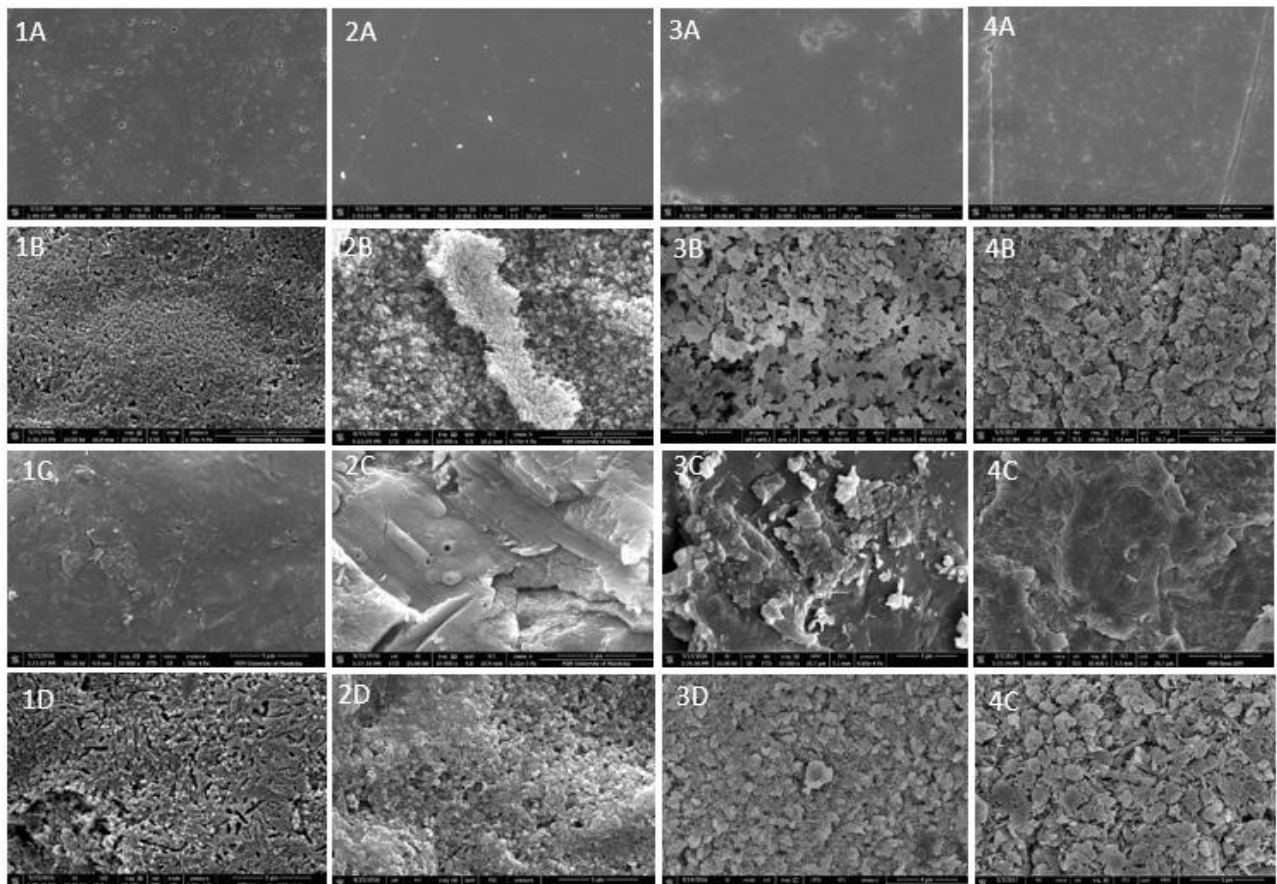


Figure 4.1: SEM images show the surface microstructure after different surface treatments of four LDGC, IPS e. max® CAD (1) Vita Suprinity® (2), Celtra Duo® (3), n!ce (4). (a) Control, (b) HF, (c) SB, (d) SB+HF.

Table 4.2: Mean (Ra) nm and (standard deviation) of lithium silicate-based glass ceramic roughness with different surface treatments (n=5)

Surface treatments	IPS e. max® CAD	Vita Suprinity®	Celtra Duo®	n!ce®
Untreated Control	1.9 (±0.3)	3 (±6.6)	1.21 (±0.17)	1.59 (±0.1)
Hydrofluoric acid	32.9 (±2.6)	34.1 (±3.4)	46.3 (±7.7)	43.5 (±8.1)
Sandblasting	228.8 (±79.7)	867.8 (±139.8)	609.6 (±93.3)	227 (±63.9)
Sandblasting+etching	237.8 (±91.4)	373 (±39.9)	216.8 (±21.5)	235.2 (±59.2)

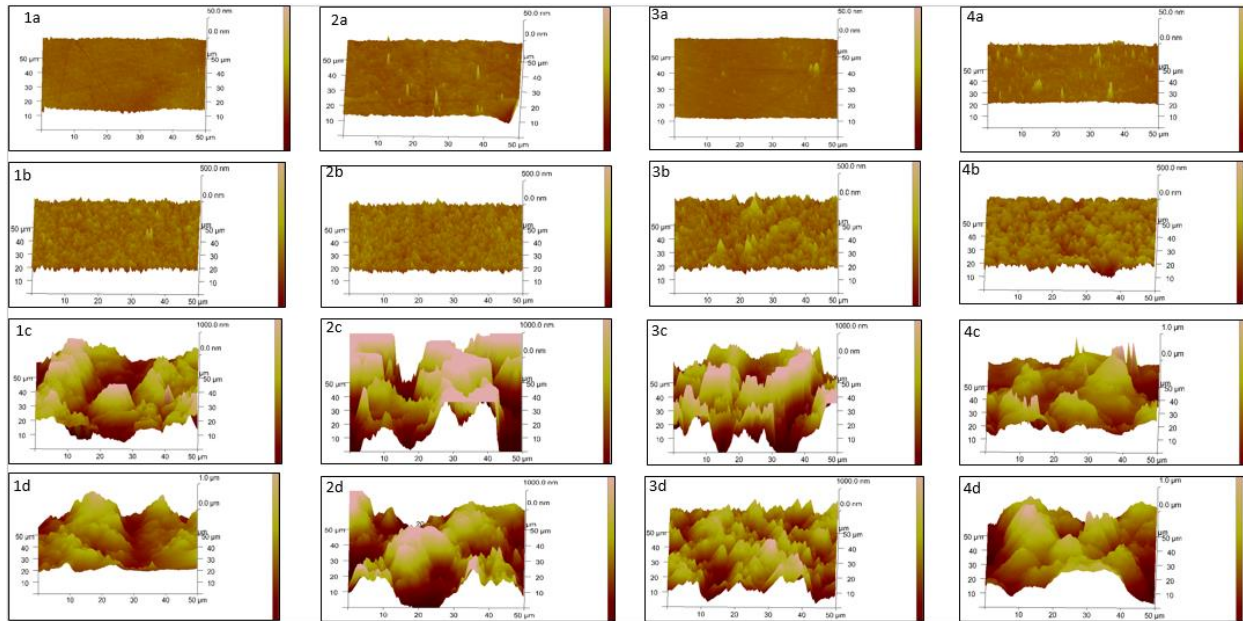


Figure 4.2: Atomic force microscopy images (AFM). ). IPS e. max® CAD (1) Vita Suprinity® (2), Celtra Duo®(3), n!ce (4). (a) Control, (b) HF, (c) SB, (d) SB+HF.

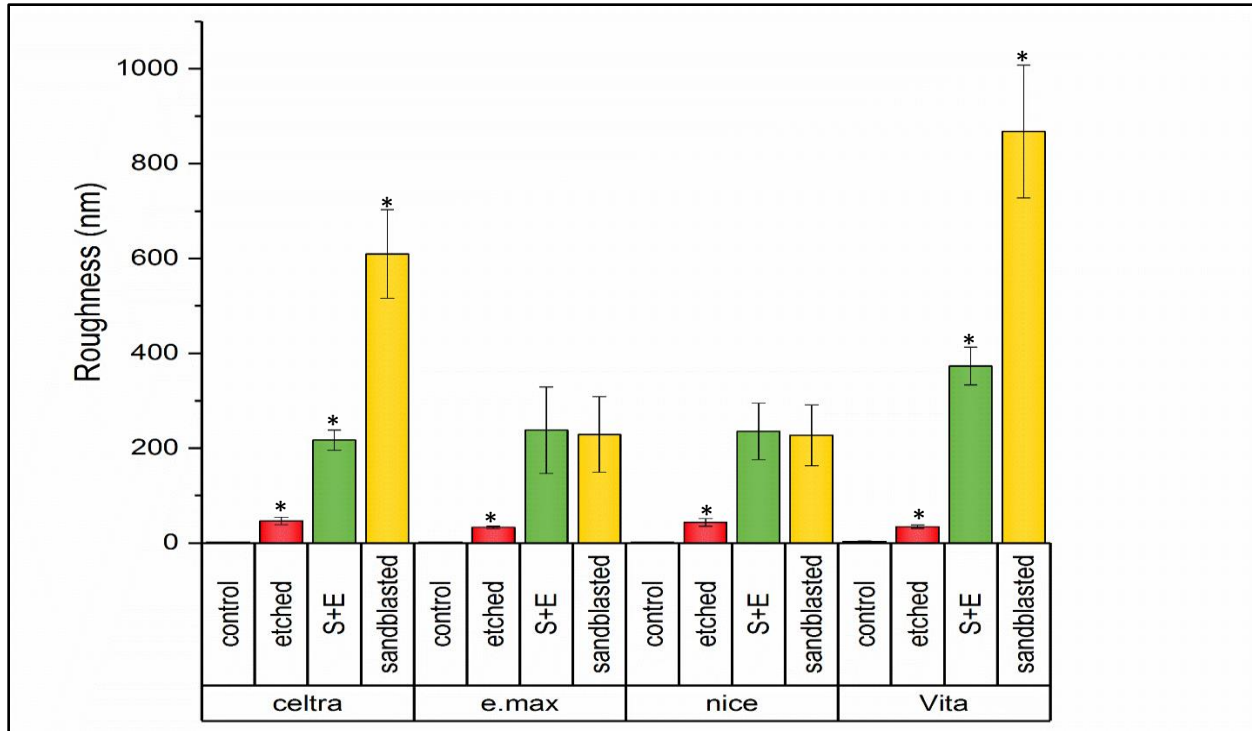


Figure 4.3: The mean and standard deviation of different surface roughness on lithium silicate-based glass ceramic. The asterisks on the top of the columns means that the average is statistic different from other surface treatments ( $p < 0.05$ ) inside the group. Data were analyzed using a two way ANOVA with  $\alpha = 0.05$ . The means were analyzed for contrasting using Tukey's *post Hoc Test*.

#### 4.5: Discussion

A reliable bond between resin cement and glass ceramic restorations contributes to the longevity of glass ceramic restorations and its overall clinical success (18). Several studies focused on cement selection and the use of silane coupling agents to improve the bonding between resin cement and glass ceramic (19-22). However, there are a number of lithium disilicate glass ceramics used for the fabrication of indirect dental restorations and still lacking supportive evidence for its functionality. Vita Suprinity and Celtra Duo are two such products. The ideal clinical protocol for predictable bonding between resin cement and lithium disilicate-based glass



ceramic restoration remain undetermined. The surface treatment of glass ceramic restorations before cementation is an essential step to improve the clinical performance of lithium disilicate-based glass ceramic restorations. Increasing the surface roughness of the intaglio surface of restorations increases the bonding area and improves the mechanical retention. It also decreases the surface tension to create the desired interlocking retention with resin cement. This laboratory study investigated the effect of different surface treatments on the micromorphology and roughness of four CAM/CAM lithium disilicate-based glass ceramics. The null hypothesis of the present study was rejected, since, difference surface treatments, significantly increased the roughness and changed the micromorphology.

The application of hydrofluoric acid resulted in an increase of roughness and changed the micromorphology of all four types of lithium disilicate-based glass ceramics. This occurred due to the chemical interaction between hydrofluoric acid and silica which represents the glass phase in lithium disilicate-based glass-ceramic materials formed of the hexafluorosilicates (23). Following HF etching, these silicates are removed under running water and results in small porosities creating an irregular roughness on the surface (13, 24). SEM images of etched surfaces of Celtra Duo and n/ce appear like a honeycomb surface. However, e.max CAD and Vita Suprinity were different and showed needle-like shapes. This could be related to the amount of glass phase, crystal size and shape exposed in the surface of each material. Hydrofluoric acid in this study increased the roughness of all four types of lithium disilicate-based glass ceramics. These results are in agreement with Kara *et al* and Ramakrishnaiah *et al* who reported that hydrofluoric acid increases the roughness and changes the surface structure as well as the wettability (17, 25). In addition, hydrofluoric acid produced less roughness compared to other

surface treatments. Even though both celtra Duo and Vita Suprinity are zirconia reinforced with lithium silicate glass ceramic, hydrofluoric acid produced greater roughness on celtra Duo than Vita Suprinity (table 4.2). This could be attributed to its glass phase content. According to other authors, surface treatment with hydrofluoric acid provides the best bond strength between resin cement and lithium disilicate based-glass ceramic (18, 26, 27). However, another study reported that HF is not the best surface treatment choice to provide reliable bond strength (28).

Some studies suggest that sandblasting is a not a recommended method to treat the internal surface of CAD/CAM glass ceramic restorations because it produces a weak bond strength (18, 29). In this study sandblasting produced higher surface roughness compared to other surface treatments for Vita Suprinity and Celtra Duo. These observations are in agreement with some previous studies (17). Most of the studies for lithium disilicate-based glass ceramic reports that sandblasting is an insufficient method to improve the bond strength with resin cement (18, 28). However, Al-Thagafi *et al.* reported that zirconia-reinforced lithium silicate ceramic (Vita Suprinity ) and lithium disilicate glass ceramic (IPS e-max CAD) had higher repair bond strength value when treated by sandblasting with Co Jet sand than treated with hydrofluoric acid (30). Also, another study on the effect of different surface treatment on bond strength of lithium disilicate glass ceramic (IPS e.max press) in vitro found that sandblasting with Co-Jet-silica-coated  $Al_2O_3$  powder provide the best shear bond strength compared to HF and SB with aluminum oxide (28). In this study sandblasting with aluminum oxide does not change the micromorphology of the surface, but it created small cracks around the crystal phase which can cause propagation and restoration failure in future.

The combination of SB and HF showed that the surface roughness created first by sandblasting could be decreased to more than a half with subsequent treatment with hydrofluoric acid for Vita Suprinity and Celtra Duo. In contrast, the surface roughness was minimally increased for e.max CAD and n!ce.

A sandblasting + hydrofluoric surface treatment method could be an option to control the roughness value on ceramic and avoid the hazard of increasing the HF concentration or application time to provide reliable bond strengths. However, further investigations are needed to evaluate the effect of different surface treatments on bond strengths for predictable bonding with these four types of CAD/CAM lithium disilicate-based glass ceramics.

#### **4.6. Conclusion**

Within the limitations of this in vitro study, the following conclusions are drawn:

- All surface treatments produced higher surface roughness compared to untreated surface of all ceramic products in this study.
- Sandblasting produced a higher surface roughness for Vita Suprinity and Celtra Duo. However, there is no significant difference between sandblasting and sandblasting + etching treatments for surface roughness for e.max CAD and n!ce.
- Hydrofluoric acid produced less surface roughness compared to other surface treatments.

## 4.7 References

1. Gracis S, Thompson VP, Ferencz JL, Silva NR, Bonfante EA. A new classification system for all-ceramic and ceramic-like restorative materials. *The International Journal of Prosthodontics*. 2015;28(3):227-35.
2. El-Meliegy E and Noort R. *Glasses and Glass Ceramics for Medical Applications*. Springer, New York, NY, USA, 2012..
3. Elsaka SE, Elnaghy AM. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. *Dental Materials* 2016;32(7):908-14.
4. Serbena FC, Mathias I, Foerster CE, Zanotto ED. Crystallization toughening of a model glass-ceramic. *Acta Materialia*. 2015;86:216-28.
5. Fasbinder DJ, Dennison JB, Heys D, Neiva G. A clinical evaluation of chairside lithium disilicate CAD/CAM crowns A two-year report. *Journal of the American Dental Association*. 2010;141:10s-4s.
6. Miyazaki T, Hotta Y. CAD/CAM systems available for the fabrication of crown and bridge restorations. *Australian Dental Journal*. 2011;56(s1):97-106.
7. Kalavacharla VK, Lawson NC, Ramp LC, Burgess JO. Influence of Etching Protocol and Silane Treatment with a Universal Adhesive on Lithium Disilicate Bond Strength. *Operative Dentistry*. 2015;40(4):372-8.
8. D'Arcangelo C, Vanini L, Rondoni GD, De Angelis F. Wear properties of dental ceramics and porcelains compared with human enamel. *Journal of Prosthetic Dentistry*. 2016;115(3):350-5.
9. Della Bona A, Shen CY, Anusavice KJ. Work of adhesion of resin on treated lithia disilicate-based ceramic. *Dental Materials*. 2004;20(4):338-44.

10. Özcan M, Vallittu PK. Effect of surface conditioning methods on the bond strength of luting cement to ceramics. *Dental Materials*. 2003;19(8):725-31.
11. Borges GA, Sophr AM, de Goes MF, Sobrinho LC, Chan DCN. Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. *Journal of Prosthetic Dentistry*. 2003;89(5):479-88.
12. Lacy AM, LaLuz J, Watanabe LG, Dellinges M. Effect of porcelain surface treatment on the bond to composite. *Journal of Prosthetic Dentistry*. 1988;60(3):288-91.
13. Lung CY, Matinlinna JP. Aspects of silane coupling agents and surface conditioning in dentistry: an overview. *Dental Materials*. 2012;28(5):467-77.
14. Chen JH, Matsumura H, Atsuta M. Effect of different etching periods on the bond strength of a composite resin to a machinable porcelain. *Journal of Dentistry*. 1998;26(1):53-8.
15. Della Bona A, Van Noort R. Ceramic surface preparations for resin bonding. *American Journal of Dentistry*. 1998;11(6):276-80.
16. Dilber E, Yavuz T, Kara HB, Ozturk AN. Comparison of the Effects of Surface Treatments on Roughness of Two Ceramic Systems. *Photomedicine and Laser Surgery*. 2012;30(6):308-14.
17. Kara HB, Kara O, Sayin G, Cakan U, Ozturk AN. Atomic force microscopy investigation of lithium disilicate glass ceramic after various surface treatments. *Advances in Applied Ceramics*. 2014;113(5):301-6.
18. Frankenberger R, Hartmann E, Krech M, Kramer N, Reich S, Braun A, et al. Adhesive luting of new CAD/CAM materials. *International Journal of Computerized Dentistry*. 2015;18(1):9-20.

19. Gre CP, de Re Silveira RC, Shibata S, Lago CT, Vieira LC. Effect of Silanization on Microtensile Bond Strength of Different Resin Cements to a Lithium Disilicate Glass Ceramic. *Journal of Contemporary Dental Practice* 2016;17(2):149-53.
20. Nagai T, Kawamoto Y, Kakehashi Y, Matsumura H. Adhesive bonding of a lithium disilicate ceramic material with resin-based luting agents. *Journal of Oral Rehabilitation*. 2005;32(8):598-605.
21. Maruo Y, Nishigawa G, Yoshihara K, Minagi S, Matsumoto T, Irie M. Does 8-methacryloxyoctyl trimethoxy silane (8-MOTS) improve initial bond strength on lithium disilicate glass ceramic? *Dental Materials* . 2017;33(3):e95-e100.
22. Lambade DP, Gundawar SM, Radke UM. Evaluation of adhesive bonding of lithium disilicate ceramic material with dual cured resin luting agents. *Journal of Clinical and Diagnostic Research*. 2015;9(2):ZC01-5.
23. Matinlinna J, Vallittu P. Bonding of resin composites to etchable ceramic surfaces—an insight review of the chemical aspects on surface conditioning. *Journal of Oral Rehabilitation*. 2007;34(8):622-30.
24. Thurmond JW, Barkmeier WW, Wilwerding TM. Effect of Porcelain Surface Treatments on Bond Strengths of Composite Resin-Bonded to Porcelain. *Journal of Prosthetic Dentistry*. 1994;72(4):355-9.
25. Ramakrishnaiah R, Alkheraif AA, Divakar DD, Matinlinna JP, Vallittu PK. The Effect of Hydrofluoric Acid Etching Duration on the Surface Micromorphology, Roughness, and Wettability of Dental Ceramics. *International Journal of Molecular Science*. 2016;17(6):E822
26. Mokhtarpour F, Alaghehmand H, Khafri S. Effect of hydrofluoric acid surface treatments on micro-shear bond strength of CAD/CAM ceramics. *Electronic physician*. 2017;9(10):5487.

27. Maruo Y, Nishigawa G, Irie M, Yoshihara K, Matsumoto T, Minagi S. Does acid etching morphologically and chemically affect lithium disilicate glass ceramic surfaces? *Journal of Applied Biomaterials and Fundamental Materials*. 2017;15(1):e93-e100.
28. Özdemir H, Aladag LI. Effect of different surface treatments on bond strength of different resin cements to lithium disilicate glass ceramic: an in vitro study. *Biotechnology and Biotechnological Equipment*. 2017;31(4):815-20.
29. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. *Journal of Prosthetic Dentistry*. 2003;89(3):268-74.
30. Al-Thagafi R, Al-Zordk W, Saker S. Influence of Surface Conditioning Protocols on Reparability of CAD/CAM Zirconia-reinforced Lithium Silicate Ceramic. *The Journal of Adhesive Dentistry*. 2016;18(2):135-41.

## Chapter 5: Third Manuscript

### The Effect of Experimental Silane Coupling Agent (TEOS) with Different Surface

### Treatments on Bond Strength of Four CAD /CAM Lithium Silicate- Based Glass Ceramic.

M. Bebsh, <sup>1,2</sup> R. França. <sup>1</sup>.

Dental Biomaterials Research Lab, Department of Restorative Dentistry. University of Manitoba, Winnipeg, Manitoba, Canada. 2. Department of Oral biology, University of Manitoba, Winnipeg, Manitoba,

#### 5.1: Abstract

Purpose: the purpose of this study was evaluate and compare the effect of an experimental silane coupling agent (Tetraethyl Orthosilicate, Sigma-Aldrich, USA) (TEOS) with different surface treatments on the bond strengths of four CAD/CAM lithium disilicate-base glass ceramics.

Materials and method: Two hundred and twenty specimens of lithium disilicate -based glass ceramics (LDGC) namely IPS e. max® CAD (Ivoclar-Vivadent, Liechtenstein, Schaan), Vita Suprinity® (Vita Zahnfabrik, Bad Säckingen, Germany), Celtra Duo® (Dentsply, Hanau-Wolfgang, Germany) and n!ce ( Straumann, Basel, Switzerland ) were selected for this study. All specimens were highly polished with 400, 600, 1200 grit silicon carbide papers and then polished with 3 µm and 1 µm polycrystalline diamond suspension liquid with a grinding device. All specimens were divided into 3 main groups for each ceramic material: (1) surface treatment + manufacturer recommended silane, Clearfil® Ceramic Primer Plus (CP). (2) Surface treatment + TEOS silane +cold dry (24 °c) + universal adhesive, (3) surface treatment +TEOS silane + hot dry (45±50 ° c) + universal adhesive. Four subgroups were assigned to one of the following surface treatments: (1) Control (C) no treatment. (2) Sandblasting (SB) with 50 µm Al<sub>2</sub>O<sub>3</sub> at 70 psi for 10s, (3) hydrofluoric acid etched (HF) with 5% hydrofluoric acid for 20s or 30s according



to the manufacturer, (4) sandblasting +hydrofluoric acid (S+E) with 50  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  at 70 psi for 10s followed by etching with 5% hydrofluoric acid. All specimens were cleaned with ethanol for 2 minutes and cleaned in ultrasonic for 15 minutes. Resin cement (Panavia V5) was applied and light cured for 5s. Silicone molds were used to prepare resin cement cylinders on the ceramic surface. The specimens were submerged in distilled water at 37 ° C for 30 days and then subjected to a shear test (SBS). Optical microscopy was used to evaluate the type of failure, namely mixed, adhesive or cohesive.

For Statistical analysis, a three-way ANOVA and Tukey tests were used in this study.

**Results:** All surface treatments with manufacturer's recommended silane (CP), produced higher bond strength values compared to untreated surfaces of e.max CAD, Vita Suprinity and Celtra Duo ( $p < 0.05$ ). Significant differences were found between surface treatments and silanes for Vita Suprinity and n!ce. However, there was no significant different between surface treatments of e.max CAD and Celtra Duo.

Hydrofluoric acid and S+E produced the highest bond strengths with CP silane for all ceramics. However, TEOS silane did not enhance the bond strength compared to CP silane for all ceramics except e.max CAD treated with hydrofluoric acid.

**Conclusion:** The combination of sandblasting and hydrofluoric acid with manufacturer's recommended silane could be an acceptable choice to increase the bond strength of all CAD/CAM LDGC materials.

Keywords: lithium disilicate-based glass ceramic, TEOS, bond strength, surface treatments.

## 5.2: Introduction

Lithium disilicate-based glass ceramics (LDGC) are widely used in dentistry since its introduction to the dental market as a high strength esthetic ceramic material (1-3). LDGC provided a solution to the non-esthetic polycrystalline ceramic like zirconia and low strength feldspathic porcelains. Zirconia is an excellent alternative treatment for posterior indirect restoration because of its high strength mechanical properties. However, it is fairly opaque in appearance and is resistant to acid etching as a surface treatment (4). Feldspathic has excellent esthetic properties and strong mechanical bonding with resin cements due to its acid sensitivity. However, it lacks the mechanical strength often needed in posterior restorations that are subjected to higher functional loads (5). Unlike porcelain and zirconia, LDGC has mechanical strength around 400 MPa and high acid sensitivity because of its glass phase and has excellent esthetic appearance.

In 1998, IPS Empress II, first generation of LDGC was introduced to the dental market from Ivoclar-Vivadent manufacture (6). Later, Ivoclar-Vivadent produced two types of LDGC with different fabrication mechanisms: IPS e.max press and IPS e.max CAD. IPS e.max CAD is particularly popular because of its high esthetics and ease of fabrication methods (7, 8). IPS e.max CAD is marketed as a pre-crystallized block (blue state) of meta-silicate ( $\text{Li}_2\text{SiO}_3$ ). After the complete restoration is designed using CAD technology, the pre-crystallized block e.max CAD block is then milled in a milling machine. The milled restoration is then exposed to  $850^\circ\text{C}$  to transform the meta-silicate to lithium disilicate with higher mechanical properties and superior

esthetic properties (9). Recently, new CAD/CAM zirconia which is reinforced by lithium silicate glass ceramic have been introduced from two different companies, namely Vita Suprinity® (Vita Zahnfabrick, Bad Säckingen, Germany) and Celtra Duo® (Dentsply DeTrey Hanau-Wolfgang, Germany) (10). More recently, Straumann, Basel, Switzerland introduced a CAD/CAM lithium alumina silicate reinforced with lithium disilicate called n!ce. An interesting aspect of Celtra Duo and n!ce is the fact that they can be immediately seated after fabrication via CAD/CAM system according to the manufacturer.

LDGC restorations bond to the dentin or enamel surface by means of a resin cement. An understanding of the LDGC and tooth substrate interface is important to optimize adhesive bonding in a chemically and functionally dynamic oral environment. Adhesion between LDGC restoration and the natural tooth surface includes two interfaces; adhesion between tooth substrate and resin cement and the adhesion between LDGC restoration and the resin cement. Many studies have suggested different resin cements and different protocols to obtain reliable bonding of LDGC restorations(11). However, the ideal bonding protocol between LDGC restorations and resin cement has not been established. Adhesion between LDGC and resin cement can be obtained by means of mechanical and chemical bonding. Micromechanical retention is a prerequisite to obtain predictable bonding between resin cement and LDGC restorations. Micromechanical retention can be produced with the application of different surface treatments such as hydrofluoric acid etching, and / or sandblasting with aluminum-oxide particles ( $\text{Al}_2\text{O}_3$ ) (5, 11, 13). Surface treatments create an irregular surface to increase the surface area for bonding and promote micromechanical retention.

Chemical bonding is provided by means of silane coupling agents (14). In dentistry, several silane coupling agents are used to enhance the chemical bonding between the ceramic surface and the resin cement (15-18). Silane coupling agents work as mediators between inorganic and organic matrices to promote adhesion of resin cement to ceramic restorations. In general, silane coupling agents have two molecular groups, (1) an organo-functional terminal (R) group and (2) a hydrolyzable group (R')(19). The carbon chain that connects the two functional groups is called spacer. Organo-functional terminal (R) groups creates chemical bonding with the methacrylate groups of the resin cement. Hydrolyzable groups (R') create chemical bonding with the ceramic surface after hydrolyzed by acid or water to form (Si OH) which reacts with silica on ceramic surface to form oxane bond (Si-O-Si). The spacer has hydrophobic properties and can be affected by the oral environment (20). It is expected that the silane coupling agent with short or non-hydrocarbons could promote the adhesion between resin cement and ceramic and decrease the possibility of hydrolysis of the hydrocarbon chain.

Tetraethyl Orthosilicate (TEOS) is a new and experimental silane coupling agent. TEOS is the ethyl ester of orthosilicate acid, and has a non hydrocarbon chain. It has been used before as a silane coupling agent for different applications and in dentistry to improve the bond strengths between resin cement and zirconia (21). In this study we evaluated and compared the effect of an experimental silane coupling agent (TEOS) with different surface treatments and a manufacturer's recommended silane coupling agent used in dental practice.

The null hypotheses tested in this study were:

- Different surface treatments would not affect the bond strengths of LDGC.
- The bond strength performance of an experimental silane coupling agent (TEOS) on lithium disilicate based- glass ceramics would not differ from manufacturer's recommended silane coupling agent

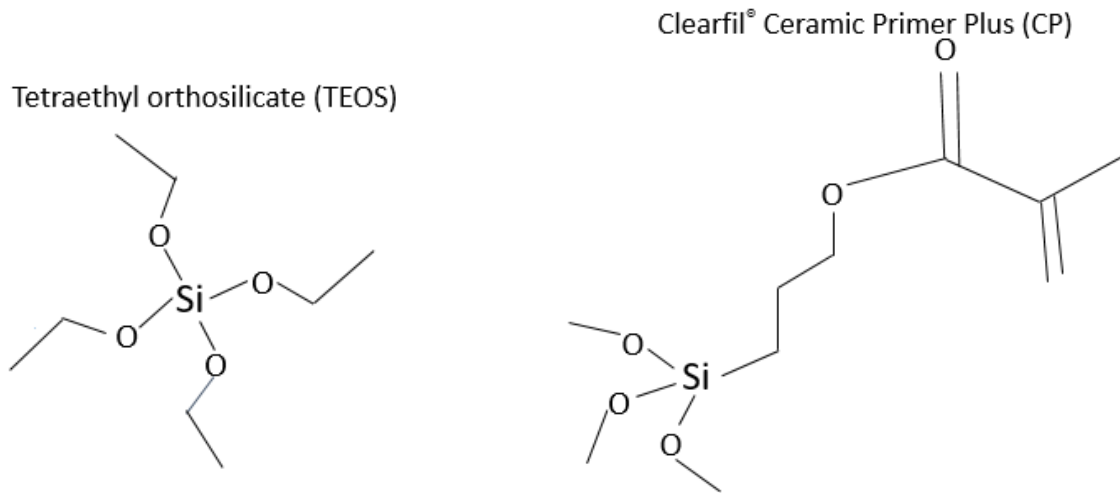


Figure 5.1: Structural formulas of silane coupling agents used in this study, products provided from the manufacturer.

### 5.3: Material and Methods

#### *Samples preparation*

Two hundred and forty specimens of LDGC have been selected for this study. The LDGC products used in this study are described in Table 1.

Table 5.1: The chemical composition of four types of LDGC products provided from the manufacturer, manufacturer description and clinical information.

Materials	Chemical composition	Manufacturer	Description	Clinical indication
IPS e. max® CAD	57-80%SiO <sub>2</sub> 11-19%Li <sub>2</sub> O 0-13%K <sub>2</sub> O 0-11%P <sub>2</sub> O <sub>5</sub> 0-8%ZrO <sub>2</sub> -ZnO 0-5%Al <sub>2</sub> O <sub>3</sub> 0-5%MgO- colouring oxides	(Ivoclar- Vivadent, Liechtenstein, Schaan	Lithium disilicate LS <sub>2</sub> glass ceramic	Veneers; inlays; onlays; anterior and posterior crowns; anterior and posterior implant abutment; three- unit bridges up to premolars; overlay veneers for multi-unit frameworks
Vita Suprinity®	56-64%SiO <sub>2</sub> 5-21%Li <sub>2</sub> O 1-4%K <sub>2</sub> O 3-8%P <sub>2</sub> O <sub>5</sub> 8-12%ZrO <sub>2</sub> 0-4%CeO <sub>2</sub> 0-6%pigments	(Vita Zahnfabrik, Bad Säckingen, Germany)	Pre-sintered Lithium silicate/phosphate (LSP) glass- ceramic Zirconia- reinforced (10% by weight ) Lithium silicate ceramic	Veneers; inlays; onlays; anterior and posterior crowns
Celtra Duo®	56-64%SiO <sub>2</sub> 5-21%Li <sub>2</sub> O 1-4%K <sub>2</sub> O 3-8%P <sub>2</sub> O <sub>5</sub> 8-12%ZrO <sub>2</sub> 0-4%CeO <sub>2</sub> 0-6%pigments	(Dentsply DeTrey Hanau- Wolfgang, Germany	Fully- sintered Lithium silicate/ phosphate (LSP) glass- ceramic  Zirconia- reinforced (10% by weight ) Lithium silicate ceramic	Veneers; inlays; onlays; anterior and posterior crowns

n!ce	. 58% SiO <sub>2</sub> ; 18.5% Li <sub>2</sub> O; 5% P <sub>2</sub> O <sub>5</sub> ; 10.1% ZrO; 1.9% Al <sub>2</sub> O <sub>3</sub> ; 2% CeO <sub>2</sub> ; 1% Tb <sub>4</sub> O <sub>7</sub>	Straumann, Basel, Switzerland	Fully-sintered	
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E.max CAD and Vita Suprinity specimens were initially fabricated from pre-crystallized ceramic blocks. The ceramic blocks were sectioned into rectangular slices with ~2 mm in thickness using a low-speed saw diamond (Isomet1000, Buehler Ltd, Lake Bluff, IL, USA). The slices were cleaned with ethanol for 2 minutes and ultrasonically cleaned (Branson cleaning equipment company, Shelton, CT, USA) in distilled water for 15 minutes. The crystallization of specimens were completed in the furnace according to the firing program recommended by the manufacturer each material. The Celtra Duo® and n!ce specimens were fabricated from LDGC fully crystallized blocks. They were sectioned into 2mm thick slices. All specimens were supported with acrylic bases (Instant Tray Mix, Lang Dental Mfg Co Inc.) to secure the treated specimens during shear bond testing.

All specimens were ground on wet 400, 600 and 1200 grit size silicon carbide papers (Buehler Ltd, Lake Bluff, IL, USA) and then polished with 3 μm and 1 μm polycrystalline diamond suspension liquid (Buehler Ltd, Lake Bluff, IL, USA) to remove external irregular scratches and defects to obtain a smooth flat surface. Double-sided adhesive tape was placed on the surface for each specimen. On each double-sided square tape five round perforations of the same diameter (2.50 mm) were made. The holes were positioned at each corner and center of the square tape on the ceramic specimen. The five exposed perforated surfaces on each LDGC specimen served as the bonding surface, therefore representing five bonding surfaces per specimen. All specimens

were randomly assigned to three main groups (n=3), according to the silane coupling agents that were applied and the dry temperatures that were used.

Group (1) surface treatment + silane (CP) for 20s and dry.

Group (2) surface treatment + TEOS silane for 20s and dried with cold air 24° C for 20s +universal adhesive applied for 20s.

Group (3) surface treatment + TEOS silane for 20s and dried with hot air (45±50° C) for 20s + universal adhesive applied for 20s. The ceramic specimens were labeled and then randomly assigned to four subgroups according to surface treatment.

*Surface treatments:*

Group C: Untreated (control) (n=60): no treatment was applied to the ceramic surface.

Group SB: Sandblasted (n=60): surface of ceramic were sandblasted with 50 µm Al<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub>; Perlblast® Micro; Bego, Bremen, Germany) at 70 psi for 10s. A distance of 2cm was maintained between the surface of the specimens and the blasting tip for consistency. Following sandblasting, the specimens were rinsed under running water for the 20s and then dried for 20s with oil free compressed air.

Group HFA: Hydrofluoric acid etched (n=60): the ceramic specimens were etched with 5% hydrofluoric acid for 20s (e.max CAD, Vita Suprinity and n!ce) and for 30s (Celtra Duo) based on the manufacturer's recommendations for each type. The gel was removed under running water for 20s, then air dried for 20s with oil free compressed air.



Group S+E: Sandblasted and hydrofluoric acid etched (n=60): The specimens were sandblasted with 50 um Al<sub>2</sub>O<sub>3</sub> at 70 psi for 10 s, within a 2 cm distance. The specimens were cleaned and then etched with 5% hydrofluoric acid for 20s. The etch gel was removed under running water for 20s followed by air drying. All specimens were then cleaned with ethanol and distilled water.

Table 5.2: Treatment materials, resin cement and silane coupling agent with methodology descriptions have been used in this study

<b>Treatments</b>	<b>Description</b>	<b>Time</b>	<b>Manufacture</b>
Hydrofluoric acid	5% HF	20s HF+ 20s clean under water + 20s dry	Ivoclar-Vivadent
Sandblasted	50 um Al <sub>2</sub> O <sub>3</sub> at 70 psi	10s SB +20s clean under water +20s dry	Perlablast® Micro; Bego, Bremen, Germany
sandblasted and hydrofluoric acid	50 um Al <sub>2</sub> O <sub>3</sub> at 70 psi +5% HF	10s SB +20s clean under water +20s dry 20s HF +20s clean under water +20s Dry	Perlablast® Micro; Bego, Bremen, Germany Ivoclar-Vivadent
Panavia V5(PV5)			Kuraray Dental
silane coupling agent CP	Clearfil® Ceramic Primer Plus	20s+dry for 20s+ resin cement +5s light cure	Kuraray Dental
silane coupling agent TEOS	Tetraethyl orthosilicate (TEOS)	20s+ cold air dry for 20s+universal adhesive+ risen cement +20 light cure	Sigma-Aldrich
		20s+ hot air (45-50) for 20s+universal adhesive+resin cement +light cure 20s	
Scotchbond™ Universal Adhesive		20s	Ivoclar-Vivadent

### *Resin cement:*

The samples of resin cement were prepared using a catheter tubing by MED-RX (size 10 FR X 16''- inner diameter =2.3mm) as a template. The tubes were cut with a scalpel into 5 mm heights. These tubes were used as housings or molds for the resin cement and were bonded to the exposed LDGC surface of the specimens. The tubes were placed over the tape under the microscope to ensure the tube lumen and the exposed surfaces coincided with the perforation on the adhesive tape. Resin cement (Panavia V5) was inserted into the tubing ensuring that the dispensing tip was immersed in the cement to prevent formation of bubbles. This process was done for each exposed LDGC surface for each specimen. The resin cement (Panavia V5) was then light cured according to manufacturer's recommendations. All the specimens were stored for 30 days at 38° C to simulate the oral environment before performing bond strength tests.

### *Shear Bond Testing*

Following a 30-day storage process, all samples were removed from the distilled water to perform the shear bond test. The catheter tubes were gently removed (from around the cured resin cement) by making a vertical incision alongside the tubes. The sectioned tubes were removed under microscopic magnification to expose the resin cement cylinder that was shaped through this process. Excess resin cement beyond the cylindrical resin cement samples was removed with a scalpel under a microscope. An external shear force was transmitted by a flat, blunt, 1-mm-broad shearing edge at a crosshead speed of 0.5 mm/min, and at a 90-degree angle to the direction of the load and at the back of the loading plate. Stress at failure was automatically calculated and recorded as the shear bond strength via the accessory software.

Shear bond strength is calculated as  $= F/\pi r^2$ , where F is the load force at fracture in Newton, and r is the radius of the resin composite cylinder in meters. Following the shear bond strength testing, the fractured surfaces of ceramic specimens were examined under a light microscope. The failure caused by shear fracture was classified into three types: (i) an adhesive failure between resin cement and ceramic (ii) a cohesive failure within resin cement or (iii) a mixed-mode failure.

the data from each sample was tabulated and submitted to statistical analysis using 3 way ANOVA and Tukey *post-hoc* test ( $\alpha=0.05$ ), and the analysis was performed using OriginLab software version 2017 (Northampton, MA, USA). The three factors studied were: kind of LFGC, surface treatments, kind of silane.

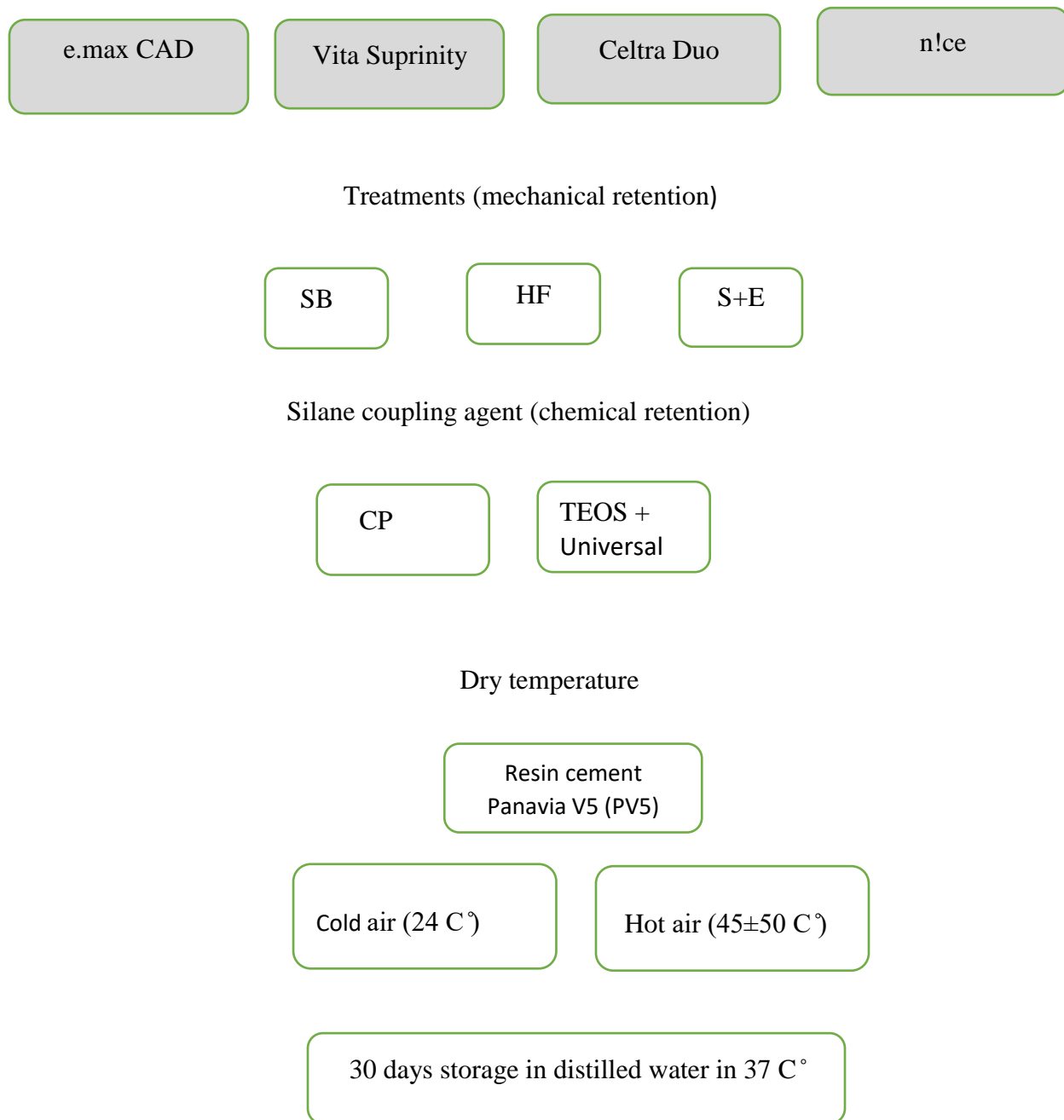


Figure 5.2: Schematic diagram shows the specimen preparations and cementation process.



Figure 5.3: LDGC Blocks, partially crystallized to the left (e.max CAD and Vita Suprinity), and fully crystallized block to the right (Celtra Duo and n!ce).



Figure 5.4: cementation process of four spicemans LDGC ,e.max CAD (E). Vita Suprinity (V). Celtra Duo (C). n!ce (N).

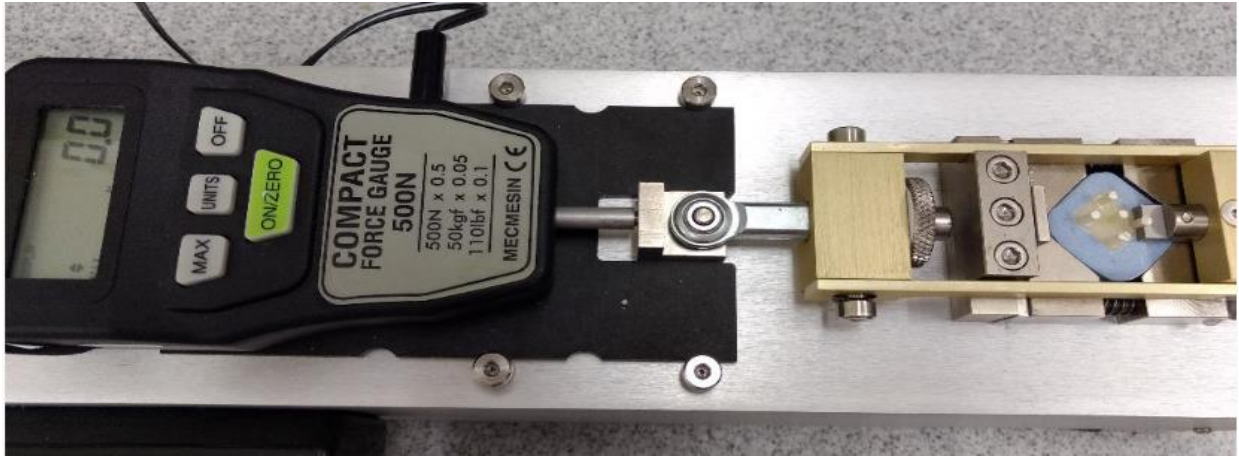


Figure 5.5: Shear bond testing machine

#### 5.4. Results

The mean and standard deviations of bond strength values (MPa) are presented in Table 5.3. The most surface treatments with manufacturer recommended silane (CP) produced higher bond strength compare to control ( $p < 0.05$ ). There were significant differences between the bond strengths for surface treatments for e.max CAD and Celtra Duo inside CP (control\_s) group and TEOS D group. No significant difference was found between the surface treatments for vita Suprinity and n!ce inside the groups as show in figure 5.6. Hydrofluoric acid and S+E with CP silane showed the highest bond strength value for all ceramic types in figure 5.6. However, the bond strengths obtained from hydrofluoric acid and S+E with CP silane (11.5 MPa), (12.5 MPa) for e.max CAD are quite similar of that obtained from hydrofluoric acid followed by TEOS silane in cold dry (11.9 MPa). TEOS silane produced low values of bond strengths, less than 7 MPa for all ceramic types, except e.max CAD compare with CP silane. Also, no significant difference was found in the bond strength of the TEOS silane group using different dry temperatures in all four ceramic types (figure 5.6). In general, silane coupling agent recommended from manufacturer produced better bond strengths with hydrofluoric acid and S+E

for Vita Suprinity, Celtra Duo and n!ce compared to TEOS silane ( $P < .05$ ). Adhesive failure was found in all TEOS silane groups and untreated surfaces of CP groups. However, CP silane with different surface treatments classified as mixed-mode failure.

Table 5.3: The mean and standard deviations of bond strength (Mpa) after 30 days of storage in distilled water at 37 °C for four LDGC with different surface treatments and silane coupling agents and dry temperatures (CP clearfil ceramic primer plus), (TEOS D Tetraethyl orthosilicate dry with cold air), (TEOS H Tetraethyl orthosilicate dry with hot air). (n=5) The asterisks on the top of the values means that the average is statistic different from other surface treatments (p<0.05) inside the group. The analysis was performed using 3 way ANOVA and Tukey *post-hoc* test ( $\alpha=0.05$ ).

Materials	Control			Hydrofluoric acid			Sandblasted			Sandblasted + hydrofluoric acid		
	CP	TEOS D	TEOS H	CP	TEOS D	TEOS H	CP	TEOS D	TEOS H	CP	TEOS D	TEOS H
<b>IPS e. max®CAD</b>	0	0	0	11.5 (±7.1)	* 11.9 (±5.1)	2.3 (±0.2)	* 1.6 (±0.5)	1.6 (±0.5)	0	12.5 (±6.0)	2.7 (±1.0)	5.1 (±3.0)
<b>Vita Suprinity®</b>	0	1 (±0.5)	0	10.7 (±8.3)	4.5 (±1.2)	3.9 (±2.4)	5.2 (±1.2)	0.7 (0)	0.2 (±0.2)	16.7 (±5.1)	2.2 (±1.9)	0.6 (±0.2)
<b>Celtra Duo®</b>	1.6 (±0.2)	0	0	12.0 (±3.0)	1.6 (±0.6)	2.7 (±1.0)	5.9 (±4.7)	0	0.6 (±0.2)	* 23.6 (±6.4)	* 6.5 (±1.9)	4.8 (±2.7)
<b>n!ce</b>	3.4 (±0.9)	0	0	16.9 (±6.6)	4.3 (±1.2)	2.1 (±2.6)	1.6 (0.5)	1.4 (±0.3)	0	12.4 (±3.8)	2.3 (±1.3)	1.1 (±0.3)



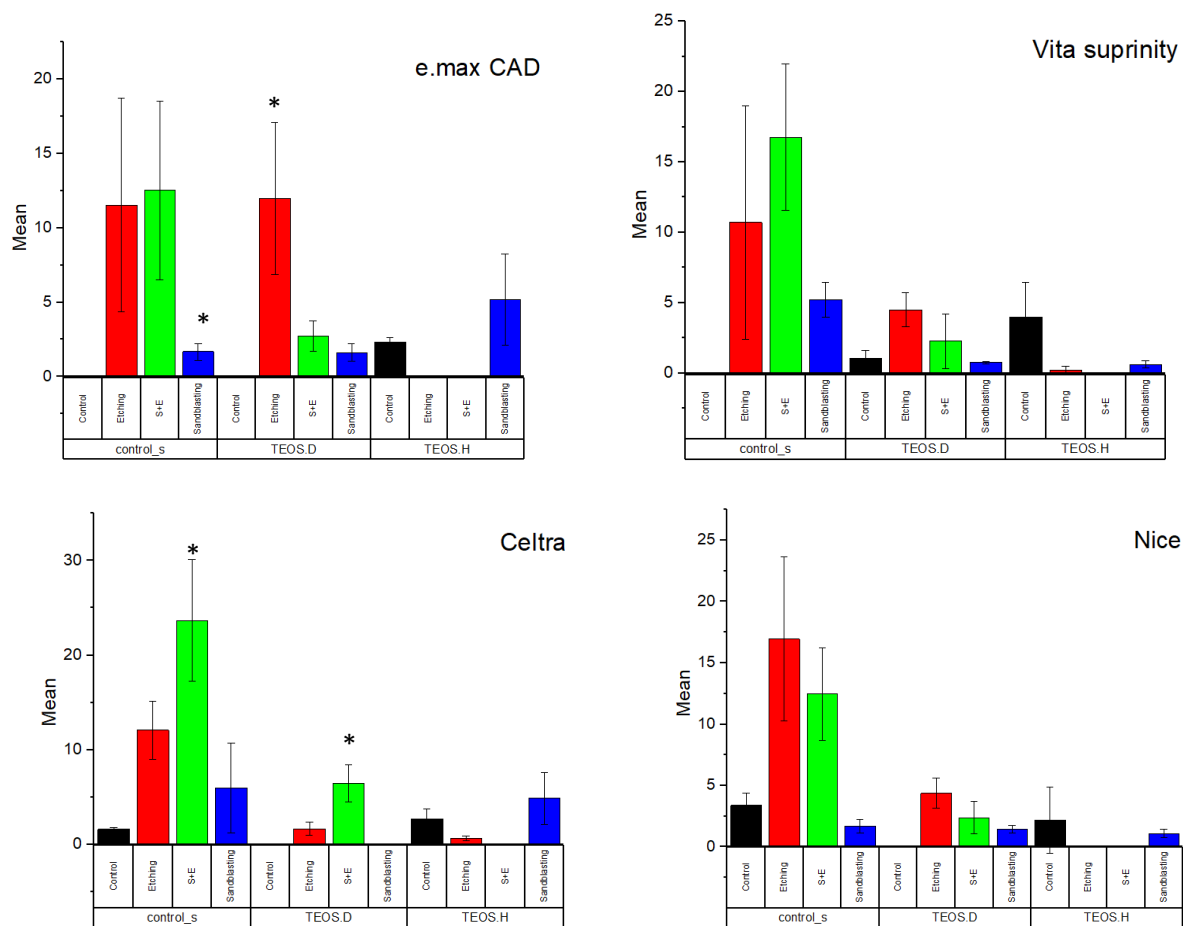


Figure 5.6: Bond strength results of four LDGC with different surface treatments and silane coupling agent. n = 5. The asterisks on the top of the columns means that the average is statistic different from other surface treatments (p<0.05) inside the group. The analysis was performed using 3 way ANOVA and Tukey *post-hoc* test ( $\alpha=0.05$ ).

## 5.5: Discussion

The aim of this study was to evaluate and compare the different surface treatments and silane coupling agents in order to identify the best surface treatment and silane coupling product for resin cement bonding to LDGC. Both null hypothesis were rejected in this study. This study demonstrated that the bond strengths between resin cements and LDGC is influenced by surface

treatments and silane coupling agents. However, when ceramics are compared (without consider silane factor): a) e.max CAD there was no significant difference found between surface treatments. The difference between surface treatments were significant for Vita Suprinity, Celtra and n!ce.

Predictable bonding between resin cements and the intaglio surface of LDGC restorations is a significant factor for clinical success of indirect restorations (22). Apart from resin cement character, cementation procedure and restoration framework plays a key role to the overall bonding success. The dentist must be informed about the some critical factors in the cementation process of the LDGC restorations. These include the fact that surface treatments and silane agent play an important role to improve the bond strengths (18, 23, 24).

The application of CP silane on untreated surfaces (control group) did not show any value for bond strength of e.max CAD and Vita Suprinity. This finding suggests that the chemical reaction between CP silane and surface LDGC is very small. It could not act without a mechanical interlocking. On the other hand, TEOS silane show low bond strength values to an untreated surfaces. This information could help to improve chemical bonding between LDGC and resin cement.

Both hydrofluoric acid and S+E with CP silane produced high values for bond strengths for all LDGC type. Except for Celtra Duo, there is no significant difference of bond strength between hydrofluoric acid and S+E followed by CP for all LDGC. The highest bond strength means was obtained by S+E with CP silane for e.max CAD, Vita Suprinity and Celtra Duo. In n!ce, the hydrofluoric acid surface treatment followed by CP application showed the highest bond

strength means when compared with other surface treatments. Multiple authors reported that the high bond strength between LDGC and resin cements can be obtained by hydrofluoric surface treatment followed by silane coupling application using a different mechanical test such as micro tensile, tensile, shear, and micro shear testing (25-28). Recently, Sato et al reported that the hydrofluoric acid is an effective surface treatment method to improve the bond strengths between resin cement and zirconia-reinforced lithium silicate ceramic (5). This is due the presence of a glass phase of LDGC which can be affected by acid to produce nano / microporosities on the surface. This supports mechanical retention to resin cements and expose silicon on the ceramic surface to chemically react with resin cement (24).

Many studies reported that sandblasting is not a recommended method to obtain desired mechanical retention for decreasing bond strengths between resin cement and LDGC restorations (18, 25, 29, 30). The results of this study confirms and affirms previous reports. Sandblasting with aluminum oxide showed low bond strength values for all LDGC groups regardless of silane coupling agent used. However, sandblasting with alumina oxide is a recommended method to treat polycrystalline ceramic surface with a crystalline phase only like zirconia (31). LDGC has a combination of crystalline and matrix phases, so sandblasting could be an effective method for the crystalline phase. However, sandblasting has high pressure on glass phase when treat LSGC which creates split around crystalline phase which could propagate and leads to ceramic restoration failure in future.

A combination of sandblasting and hydrofluoric acid provided an interesting result of bond strength values for all LDGC types. S+E showed the highest bond strength mean for e.max

CAD, Vita Suprinity and Celtra Duo. According to AFM results in second manuscript of this thesis, treating the ceramic surface with sandblasting followed by hydrofluoric acid decreases the roughness for Vita Suprinity and Celtra Duo as show in table 4.2. It also creates a more uniform surface roughness compared to sandblasting alone. Sandblasting + etching method could be a good choice to prevent the risk of increase hydrofluoric concentration or application time to obtain a reliable bond strength for CAD\CAM LDGC restorations.

TEOS silane showed low bond strength values with all surface treatments except for e.max CAD treated with hydrofluoric acid. This could be due to contamination on the cemented area during surface treatment. Contamination creates a layer to prevent (Si OH) in resin cements to react with the Si on the ceramic surface. There is no change of the bond strength when the hot dry air is used with TEOS silane. However, the use of TEOS silane with hydrofluoric acid to treat e.max CAD surface is a serious concern. According to our XPS results for analysis of surface physicochemical compositions in first manuscript, we can say that the high Si percentages on the surface of e.max CAD before and after hydrofluoric acid could be reason to had high value of shear bond strength as show in table 3.2. Long-time clinical evaluation of these material and methodology are recommended.

## **5.6: Conclusions**

Within the limitations of this study, we can conclude that surface treatments produced different bond strengths for LDGC. Sandblasting +hydrofluoric acid with manufacturer's recommended silane coupling agent could be one of the better surface treatment options to obtain strong mechanical retention and chemical bonding between LDGC and resin cement.

## 5.7: References

1. Fasbinder DJ, Dennison JB, Heys D, Neiva G. A clinical evaluation of chairside lithium disilicate CAD/CAM crowns A two-year report. *Journal of the American Dental Association*. 2010;141:10s-4s.
2. Wolfart S, Eschbach S, Scherrer S, Kern M. Clinical outcome of three-unit lithium-disilicate glass–ceramic fixed dental prostheses: up to 8 years results. *Dental Materials*. 2009;25(9):e63-e71.
3. van den Breemer CR, Vinkenborg C, van Pelt H, Edelhoff D, Cune MS, van den Breemer CR. The Clinical Performance of Monolithic Lithium Disilicate Posterior Restorations After 5, 10, and 15 Years: A Retrospective Case Series. *International Journal of Prosthodontics*. 2017;30(1).
4. El-Shrkawy ZR, El-Hosary MM, Saleh O, Mandour MH. Effect of different surface treatments on bond strength, surface and microscopic structure of zirconia ceramic. *Future Dental Journal*. 2016;2(1):41-53.
5. Sato T, Anami L, Melo R, Valandro L, Bottino M. Effects of surface treatments on the bond strength between resin cement and a new zirconia-reinforced lithium silicate ceramic. *Operative Dentistry*. 2016;41(3):284-92.
6. Sundfeld D, Correr-Sobrinho L, Pini Ninocência P, Costa AR, Sundfeld RH, Pfeifer CS, et al. Heat treatment-improved bond strength of resin cement to lithium disilicate dental glass-ceramic. *Ceramic International* . 2016;42(8):10071-8.
7. Miyazaki T, Hotta Y. CAD/CAM systems available for the fabrication of crown and bridge restorations. *Australian Dental Journal*. 2011;56(s1):97-106.

8. Willard A, Gabriel Chu TM. The science and application of IPS e.Max dental ceramic. *Kaohsiung Journal of Medical Sciences*. 2018;34(4):238-42.
9. Li RW, Chow TW, Matinlinna JP. Ceramic dental biomaterials and CAD/CAM technology: state of the art. *Journal of Prosthodontic Research*. 2014;58(4):208-16.
10. Elsaka SE, Elnaghy AM. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. *Dental Materials : official publication of the Academy of Dental Materials*. 2016;32(7):908-14.
11. Ozdemir H, Aladag LI. Effect of different surface treatments on bond strength of different resin cements to lithium disilicate glass ceramic: an in vitro study. *Biotechnology& Biotechnological Equipment*. 2017;31(4):815-20.
12. Borges GA, Sophr AM, de Goes MF, Sobrinho LC, Chan DCN. Effect of etching and airborne particle abrasion on the microstructure of different dental ceramics. *Journal of Prosthetic Dentistry*. 2003;89(5):479-88.
13. Puppin-Rontani J, Sundfeld D, Costa AR, Correr AB, Puppin-Rontani RM, Borges GA, et al. Effect of Hydrofluoric Acid Concentration and Etching Time on Bond Strength to Lithium Disilicate Glass Ceramic. *Operative Dentistry*. 2017.
14. Lacy AM, LaLuz J, Watanabe LG, Dellinges M. Effect of porcelain surface treatment on the bond to composite. *Journal of Prosthetic Dentistry*. 1988;60(3):288-91.
15. Matsumura H, Kato H, Atsuta M. Shear bond strength to feldspathic porcelain of two luting cements in combination with three surface treatments. *Journal of Prosthetic Dentistry*. 1997;78(5):511-7.

16. Nogami T, Tanoue N, Atsuta M, Matsumura H. Effectiveness of two-liquid silane primers on bonding sintered feldspathic porcelain with a dual-cured composite luting agent. *Journal of Oral Rehabilitation*. 2004;31(8):770-4.
17. Kalavacharla VK, Lawson NC, Ramp LC, Burgess JO. Influence of Etching Protocol and Silane Treatment with a Universal Adhesive on Lithium Disilicate Bond Strength. *Operative Dentistry*. 2015;40(4):372-8.
18. Spohr AM, Sobrinho LC, Consani S, Sinhoreti MAC, Knowles JC. Influence of surface conditions and silane agent on the bond of resin to IPS Empress 2 ceramic. *International Journal of Prosthodontics*. 2003;16(3):277-82.
19. Matinlinna J, Vallittu P. Bonding of resin composites to etchable ceramic surfaces—an insight review of the chemical aspects on surface conditioning. *Journal of Oral Rehabilitation*. 2007;34(8):622-30.
20. Maruo Y, Nishigawa G, Yoshihara K, Minagi S, Matsumoto T, Irie M. Does 8-methacryloxyoctyl trimethoxy silane (8-MOTS) improve initial bond strength on lithium disilicate glass ceramic? *Dental Materials : official publication of the Academy of Dental Materials*. 2017;33(3):e95-e100.
21. Oliveira-Ogliari A, Collares FM, Feitosa VP, Sauro S, Ogliari FA, Moraes RR. Methacrylate bonding to zirconia by in situ silica nanoparticle surface deposition. *Dental Materials*. 2015;31(1):68-76.
22. Diaz-Arnold AM, Vargas MA, Haselton DR. Current status of luting agents for fixed prosthodontics. *Journal of Prosthetic Dentistry*. 1999;81(2):135-41.

23. Baratto SS, Spina DR, Gonzaga CC, Cunha LF, Furuse AY, Baratto Filho F, et al. Silanated Surface Treatment: Effects on the Bond Strength to Lithium Disilicate Glass-Ceramic. *Brazilian Dental Journal*. 2015;26(5):474-7.
24. Tian T, Tsoi JKH, Matinlinna JP, Burrow MF. Aspects of bonding between resin luting cements and glass ceramic materials. *Dental Materials*. 2014;30(7):E147-E62.
25. Frankenberger R, Hartmann E, Krech M, Kramer N, Reich S, Braun A, et al. Adhesive luting of new CAD/CAM materials. *International Journal of Computerized Dentistry*. 2015;18(1):9-20.
26. Mokhtarpour F, Alaghehmand H, Khafri S. Effect of hydrofluoric acid surface treatments on micro-shear bond strength of CAD/CAM ceramics. *Electronic Physician*. 2017;9(10):5487.
27. Maruo Y, Nishigawa G, Irie M, Yoshihara K, Matsumoto T, Minagi S. Does acid etching morphologically and chemically affect lithium disilicate glass ceramic surfaces? *Journal of Applied Biomaterials & Functional Materials*. 2017;15(1):e93-e100.
28. Nagai T, Kawamoto Y, Kakehashi Y, Matsumura H. Adhesive bonding of a lithium disilicate ceramic material with resin-based luting agents. *Journal of Oral Rehabilitation*. 2005;32(8):598-605.
29. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. *Journal of Prosthetic Dentistry*. 2003;89(3):268-74.
30. Salvio LA, Correr-Sobrinho L, Consani S, Sinhorette MA, de Goes MF, Knowles JC. Effect of water storage and surface treatments on the tensile bond strength of IPS Empress 2 ceramic. *Journal of Prosthodontics*. 2007;16(3):192-9.
31. Kern M, Barlooi A, Yang B. Surface conditioning influences zirconia ceramic bonding. *Journal of Dental Research*. 2009;88(9):817-22.



## Chapter 6: Conclusion

The first objective of this study was to determine the chemical composition of the nanosurfaces of four different types of CAD/CAM LDGC before and after treatment with 5% hydrofluoric acid. The second objective was to evaluate and compare the effect of different surface treatments on the surface roughness and micromorphology of these four types of CAD/CAM LDGC. The third objective was to estimate and compare the bond strengths of resin cement and ceramic interface that was treated with different surface treatments and silane coupling agents.

In this project, we found that the chemical composition of the four types of LDGC changed after they were treated with hydrofluoric acid. Also, some of the chemical compositions dissolved on the surface of these types of ceramic after using hydrofluoric acid. That means the internal surface characteristics of CAD/CAM LDGC restoration will be different after hydrofluoric acid treatment application.

Surface treatments like sandblasting and hydrofluoric acid are important steps before the cementation process. Surface treatment creates mechanical retention between the resin cement and LDGC restorations which is fundamental to improve the bonding between CAD/CAM LDGC restoration and resin cement, The combination of surface treatments and silane coupling agents makes the bonding between resin cement and CAM/CAM LDGC is more predictable.

Future work will be required to further shed light on the bonding between resin cement and CAD/CAM LDGC restorations. In turn, this will support a better understanding of the relationship between the surface chemical composition of the ceramic surface and the actual chemical bonding between the resin cement and CAD/CAM LDGC.

## References

1. Babu PJ, Alla RK, Alluri VR, Datla SR, Konakanchi A. Dental ceramics: Part I—An overview of composition, structure and properties. *American Journal of Materials Engineering and Technology*. 2015;3(1):13-8.
2. McLean JW. Evolution of dental ceramics in the twentieth century. *Journal of Prosthetic Dentistry*. 2001;85(1):61-6.
3. El-Meliegy E, Noort Rv. *Glasses and glass ceramics for medical applications* 2012.
4. Gracis S, Thompson VP, Ferencz JL, Silva NR, Bonfante EA. A new classification system for all-ceramic and ceramic-like restorative materials. *The International Journal of Prosthodontics*. 2015;28(3):227-35.
5. Holand W, Beall GH. *Glass ceramic technology*: John Wiley & Sons; 2012.
6. Huang S, Zhang B, Huang Z, Gao W, Cao P. Crystalline phase formation, microstructure and mechanical properties of a lithium disilicate glass–ceramic. *Journal of Materials Science*. 2012;48(1):251-7.
7. Stookey, S.D *Catalyzed Crystallization of Glass in Theory and Practice*. *Industrial and Engineering Chemistry* 1959;51(7):805-808

8. Goharian P, Nemati A, Shabani M, Afshar A. Properties, crystallization mechanism and microstructure of lithium disilicate glass-ceramic. *Journal of Non-Crystalline Solids*. 2010;356(4-5):208-14.
9. Lad PP, Kamath M, Tarale K, Kusugal PB. Practical clinical considerations of luting cements: A review. *Journal of International Oral Health*. 2014;6(1):116-20.
10. Baratto SS, Spina DR, Gonzaga CC, Cunha LF, Furuse AY, Baratto Filho F, et al. Silanated Surface Treatment: Effects on the Bond Strength to Lithium Disilicate Glass-Ceramic. *Brazilian Dental Journal*. 2015;26(5):474-7.
11. Ozdemir H, Aladag LI. Effect of different surface treatments on bond strength of different resin cements to lithium disilicate glass ceramic: an in vitro study. *Biotechnology & Biotechnological Equipment*. 2017;31(4):815-20.
12. Sato T, Anami L, Melo R, Valandro L, Bottino M. Effects of surface treatments on the bond strength between resin cement and a new zirconia-reinforced lithium silicate ceramic. *Operative Dentistry*. 2016;41(3):284-92.

