Shear Bond Strength of Lithium Disilicate to Resin Cement After Treatment with Hydrofluoric Acid and a Self-etching Ceramic Primer

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The aim of this work was to analyze the properties and shear bond strength (SBS) of lithium disilicate to resin cement before and after etching the glass-ceramic surfaces. Lithium-metasilicate samples were heat treated and characterized by Scanning Electron Microscopy, X-ray diffraction and roughness measurement. For the analysis of the shear bonding strength (SBS) of lithium disilicate to dental resin cement, three groups (n = 12) of $Li_2Si_2O_5$ were prepared: 1°)without treatment (NT); 2°)surface etching with hydrofluoric acid(HF), followed by silane agent and adhesive treatment; 3°) surface treatment with a self-etching ceramic primer (SECP). After the heat-treatment, the samples had $Li_2Si_2O_5$ crystalline phase dispersed in a residual amorphous phase. Roughness of the NT and SECP samples was smaller that of the HF samples. Samples without surface treatment (NT) had the lowest SBS (5.5MPa). HF(24.2MPa) and SECP(24.8MPa) samples has similar SBS. Weibull statistics showed that HF-samples are more reliable than NT and SECP. The SBS was significantly increased by either HF etching and SECP surface treatment. While the chemical characteristics of the surface submitted to SECP treatment are considered to be responsible for the SBS increase, the main adhesion mechanism after HF etching is the increase in surface roughness.

Keywords: *Lithium disilicate, $Li_2Si_2O_5$, shear bond strength, hydrofluoric acid, self-etching ceramic primer.*

1. Introduction

The development of new glass-ceramics with good mechanical properties combined with aesthetics results, allowed the manufacture of metal-free ceramic dental prostheses for the restoration of different tooth elements[1-3]. CAD-CAM (Computer-Aided Design / Computer-Aided Manufacturing) has several advantages over conventional manufacturing of prostheses, such as the ability to prepare the restoration in less time, uniform morphology, automation of the manufacturing process and better mechanical properties[4].

CAD-CAM blocks are available for aesthetic restorations, including yttrium tetragonal zirconia polycrystals, Y-TZP[5,6], feldspathic glass ceramics[7,8], lithium silicate glass ceramics[9,10], composite resins or hybrid ceramics[11,12]. The ceramic performance of adhesive cementation is influenced by variations in the chemical composition of these materials, which modify their mechanical properties[13].

Lithium disilicate glass-ceramic ($Li_2Si_2O_5$) has excellent optical properties and mechanical resistance, is used in many dental applications, such as veneers, inlays, onlays, single and full crowns[3,14]. This biomaterial has adequate mechanical properties to be used in dental restorations with thicknesses up to 0.5 mm and the results are equivalent to those obtained with zirconia covered with porcelain[6]. $Li_2Si_2O_5$ is available in blocks for CAD/CAM systems. After manufacture, a thermal treatment is necessary to promote the phase transformation to of lithium disilicate and a reduction of the volume fraction of amorphous material. After this procedure the flexural strength is about 400 MPa[10].

The mechanical properties of materials used in dentistry (ceramic restorations, resin cements, silane coupling agents, tooth structures) and the surface optimization of bonding

substrates influence the performance of prosthetic restorations. To have a good ceramic adhesion, it is essential to prepare the tooth structure and surface restoration. Insufficient bond strength between restoration and resin cement promotes an inhomogeneous stress distribution at the bonding interface, inducing the failure of the cement-restoration bond under the action of masticatory forces[15-17].

The surface treatment before cementation is very important for the success and longevity of ceramic restorations. In this treatment, a micro-roughness is created on the surface of the ceramic to promote bonding to the resin cement[18]. The protocol treatment varies according to the material used. Feldspathic glass-ceramic and leucite-reinforced glass-ceramic, for example, are treated for 60 s with hydrofluoric acid (5 - 10% HF), while lithium disilicate requires only 20 seconds[17,19,20]. However, ceramics based on alumina (Al_2O_3) and zirconia (ZrO_2-Y_2O_3) have high chemical stability and are commonly treated with airbone particle abrasion before adhesive cementation.

The protocol for treatment of glass ceramic is HF acid etching to create surface roughness. In the treatment, the glass matrix is selectively removed by controlling the time of exposure to a fatty acid with lower chemical than the $Li_2Si_2O_5$ crystals. The roughness created with HF etching is suitable for micromechanical retention on the ceramic surface[21]. This rough surface increases the surface energy and facilitates the subsequent treatment with silane. Silane has a bi-functional molecule, in which one end reacts with the glass phase of the ceramic surface and the other end copolymerizes with methacrylate groups in the organic matrix of resin cements through siloxane links. The mechanisms involved characterize adhesive cementation[22,23]. The use of silane in dentistry has been successful, improving the bond strength of the ceramic with the resin cement[24,25]. However, severe surface changes can decrease the flexural strength of materials due to surface defects that induce the formation of cracks. It is thus important to control the concentration and conditioning time to obtain surface changes without weakening the ceramic[22,24,26,27]. If the treatment is performed in the intraoral cavity, care must be taken in relation to the high toxicity of HF-solution, which can generate necrosis of the soft tissues and bones[28]. In addition, once one cannot use it in the mouth, an alternative treatment is desirable. These two deleterious mechanisms depend on the time of exposure and the concentration of the HF solution.

A self-etching ceramic primer[29] has been used as an alternative to the traditional HF acid etching procedure[30-33]. A self-etching ceramic primer is basically composed of ammonium polyfluoride[34], trimethoxypropyl methacrylate, solvents (alcohol and water) and a green pigment to provide visibility) in an all-in-one system (one-step etching technique). This procedure requires less time, does not weaken the glass ceramic because it is less aggressive and avoids the toxic risks of hydrofluoric acid[17,24,29,35-37].

The aim of this study was to evaluate the effect of the use of a self-etching ceramic primer (SECP) in the treatment of the surface of lithium disilicate samples, to determine the shear bond strength to resin cement and to compare the results with the conventional HF acid etching technique. The microstructural and crystallographic aspects

of lithium disilicate after heat treatment and its correlations with resistance to adhesion with resin cement are discussed.

2. Experimental Procedure

2.1. Materials

Lithium metasilicate (Li_2SiO_3) blocks used in the manufacture of dental prostheses were transformed by a heat treatment (840 °C - 7 min) into lithium disilicate ($Li_2Si_2O_5$) and, the surface was prepared for a bonding strength test with resin cement. The specifications of all materials are shown in Table 1.

2.2. Processing

Commercial blocks of lithium metasilicate IPS E-max CAD CAM (Ivoclar Vivadent Schaan, Liechtenstein) with dimensions of 14 x 18 x 12 mm were cut into approximately 10 x 10 x 3 mm plates using an Isomet-Buehler 1000 cutter (Buehler - Germany). The plates were ultrasonically cleaned with distilled water for 15 min and subjected to a heat treatment at 840 °C for 7 min under vacuum for phase transformation. The heat treatments were carried out in an Ivoclar P 5000 furnace (Ivoclar Vivadent Schaan, Liechtenstein), following the manufacturer's recommendations. After the phase transformation, the samples were polished with Al_2O_3 suspension, to standardize surfaces and facilitate comparative analysis, using Aropol polisher (Arotec, São Paulo - Brazil).

2.3. Characterization

Before and after the heat treatment, the samples were characterized by X-ray diffraction using an XRD-6100 diffractometer (SHIMADZU Corp. Japan), aiming to determine phase transformations that will occur in the investigated glass-ceramic during the dental prosthesis manufacturing protocol. Fragmented samples (particle size < 32 μm) were analyzed using Cu-Kα radiation, in the 2θ range from 20 to 90°, using a step width of 0.05° and a counting rate of 5 s/step. The XRD patterns were compared with those of the Crystalographica Search-Match software (Oxford Cryosystems). Phase quantification was performed using Rietveld refinement with the FullProf Suite 3.0 software.

Polished glass-ceramic bulk samples, before and after the heat treatment were imaged in a scanning electron microscopes Zeiss EVO LS15. In order to reveal the microstructural features, the polished surfaces were etched with a 5% HF solution for 20 s. After acid etching, the samples were coated with a thin layer of gold using an Emitech K550X Sputter Coater.

2.4. Sample preparation

To analyze the influence of the surface treatment on the shear strength to resin cement, the samples were divided in three groups (Table 2):

1) Group 1 - (NT) - Control group: Before adhesion, the disilicate samples (polished surfaces) were air dried for 15 seconds and treated with Prosil commercial silane (S) (FGM, Joinville-SC, Brazil) for 1 min. The adhesion of lithium disilicate to resin cement was carried out using the adhesive system

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Table 1. Technical specifications and main characteristics of the materials used (data from the manufacturers).

Material	Code	Composition (wt.%)	Application mode
IPS e.max CAD (*LDC*) (Ivoclar Vivadent- Schaan, Liechtenstein)	EM	SiO_2 (57 - 80%), Li_2O (11 -19%), K_2O (0 -13%), P_2O_5 (0 -11%), ZrO_2 (0 - 8%), ZnO (0 - 8%), Al_2O_3 (0 - 5%) MgO (0 - 5%), colouring oxides (0 - 8%)	
Condac Porcelana 10% FGM, Joinville, SC, Brazil	HF	10% hydrofluoric acid	Apply to the ceramic surface for the indicated time and wash with plenty of water
Prosil, FGM, Joinville, SC, Brazil	S	3 Methacryloxypropyltrimethoxysilane < 5%; ethanol >85%; water <10%	Apply a thin layer, wait for 1 min. No light curing required, just dry with light air jets
Allcem core, FGM, Joinville, SC, Brazil	–	Base paste: methacrylic monomers (such as TEGDMA, BisEMA and BisGMA), camphorquinone, co-initiators, barium aluminum silicate glass microparticles, silicon dioxide nanoparticles, inorganic pigments and preservatives; Catalyst Paste: metaacrylic monomers, dibenzoyl peroxide, stabilizers and glass microparticles of barium-aluminum-silicates. 1: 1 ratio presents 62% load	
Monobond Etch & Prime (*SECP*) (Ivoclar Vivadent-Schaan, Liechtenstein)	SECP	Butanol, tetrabutylammonium dihydrogen trifluoride, methacrylated phosphoric acid ester, bis (tretoxethoxysilyl) ethane, silane methacrylate, dye, ethanol, water	Actively apply to the ceramic surface for 20 s, let it react for 40 s, wash with water for 30 s
Adhesive Ambar, FGM, Joinville, SC, Brazil	A	Active ingredients: MDP (10-methacryloyloxidecyl dihydrogen phosphate), methacrylic monomers, photoinitiators, co-initiators and stabilizer, inactive ingredients: inert charge (silica nanoparticles) and vehicle (ethanol)	With the aid of a disposable microapplicator, apply Ambar Universal to the internal surface of the part (previously treated) under friction, wait 15s and then apply a light jet of air for 10s. Non-light-curing

Table 2. Experimental groups, according to IPS e-max CAD CAM ceramic surface treatment.

Group	Designation	Surface treatment
Control	NT	No treatment
Group 2	HF	hydrofluoric acid 10% + silane + adhesive
Group 3	SECP	Monobond Ecth & Prime

(A) Ambar (FGM) for 30 seconds, and dried for 15 seconds at a distance of approximately 30 cm for solvent evaporation.

2) Group 2 (HF) - Etching with 10% hydrofluoric acid: The disilicate samples (polished surfaces) were dried for 15 seconds and etched with HF solution (10%) Condac Porcelana FGM - Brazil, for 20 s. After etching, these surfaces were washed in water for 30 seconds. The sample surface was treated with Prosil silane (FGM) for 1 min before the the Ambar adhesive system was applied.

3) Group 3 (SECP) - treated with Monobond Ecth & Prime: The disilicate samples (polished surfaces) were air dried for 15 s and treated with the self-etching ceramic primer Monobond Etch & Prime (Ivoclar- Liechestein) by rubbing with a microbrush for 20 seconds. The primer was kept on the surface for 40 seconds before being removed by spraying with air and water for 30 seconds.

After the lithium disilicate surface polishing and HF acid etching or treated with self-etching ceramic primer, the surface roughness of the samples was measured using a Zygo New View 7100 Optical Profiler. The parameters of the roughness Ra, PV and Rz were measured. The test was performed according to the recommendations of the ISO 4288:2008[38] and ISO 4287:2002[39] standards. These surfaces were coated with a thin layer of gold and analyzed by SEM using a microscope model EVO-MA10- Zeiss.

Figures 1 and 2 show the different sample preparation steps to determine the shear bonding strength of lithium disilicate to resin cement.

Before acid etching (10% HF) and SECP, the lithium disilicate samples were embedded in acrylic resin and covered with a 2 mm thick silicone (Express 3M) plate, with four perforations with a diameter of 2 mm, which were filled with Allcem Core (FGM) dual resin cement. After removing excess resin cement, the samples were light-cured for 40 s, using an Ultradent VALO Cordless LED light curing device, simulating the clinical practice. The silicone mould was cut with a scalpel and removed from the sample. A second light cure for 40s was performed on the resin cylinders with the same light curing device. The samples (Figure 1) were stored in a container with 70% relative humidity. The shear strength test was made 24 h after sample preparation and bonding.

The cross sections of the glass-ceramic/resin cement interfaces were analyzed by SEM using the microscope model EVO-MA10-Zeiss. In this stage, the analyzed surfaces
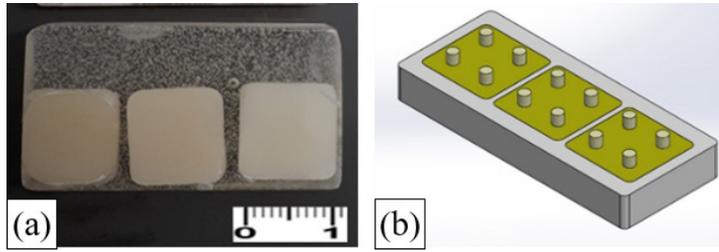
Figure 1. (a) Samples of lithium disilicate embedded in acrylic resin for shear test; (b) schematic drawing of lithium disilicate glass-ceramic samples with resin cement cylinders bonded on the surface.
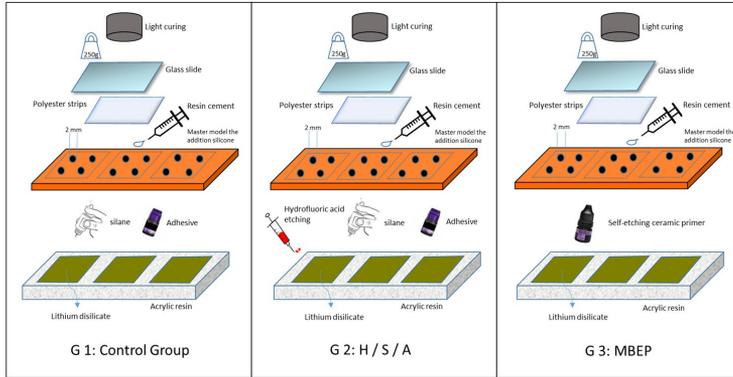
Figure 2. Sequence of sample preparation for shear test (G1: NT samples; G2: HF samples; G3:SECP).
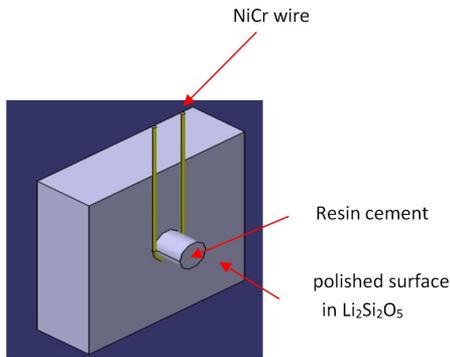
Figure 3. Schematic representation of the shear test using NiCr wire.

were also covered with a thin layer of gold to make them conductive.

2.5. Shear bond strength testing

The shear bond test was performed using the device shown in Figure 3, following procedures of previous works[40], using an EMIC DL10000 universal testing with a 20 N load cell. The loading speed was 1.0 mm/min.

The shear strength of the interface between lithium disilicate and resin cement was calculated using the equation

$$\sigma_{shear} = \frac{F}{A} \tag{1}$$

where σ_{shear} is the shear stress in MPa, F is the maximum failure load in N and A is the adhesion area in mm^2.

2.6. Statistical analysis

One-way ANOVA analysis was used to evaluate the mechanical properties, followed by a Tukey's Honestly

Significant Difference (HSD) post hoc test ($\alpha = 0.05$) to determine the difference between the means of roughness and shear strength. The statistical analysis was performed with the software ASSISTAT version 7.7 beta.

The complementary statistical evaluation of shear strength was carried out using Weibull statistics[41]. The bi-parameterized Weibull distribution function was used according to Equation 2. The Weibull parameters m and σ_0 are obtained transforming

Equation 2 into Equation 3 and plotting $ln\left[\dfrac{1}{(1-P)}\right] versus ln\sigma$.

$$P = 1 - exp\left\{\left[\frac{-\sigma}{\sigma_0}\right]^m\right\} \tag{2}$$

$$ln ln\left[\frac{1}{\left(\frac{1}{P}\right)}\right] = m ln\sigma - m ln\sigma_0 \tag{3}$$

where P is the failure probability, m is the Weibull modulus, σ_0 is the characteristic stress in MPa and σ is the average bonding strength in MPa.

3. Results

3.1. Substrate characterizations

Figure 4a, b presents the results of X-ray diffractograms of the samples before and after thermal treatment. The volume fractions of the phases are shown in Figure 4c. The as-received blocks have 38.64% lithium metasilicate (Li_2SiO_3), small percentages of $Li_2Si_2O_5$ and SiO_2 and a considerable amount of the amorphous phase (54.5%). The amorphous phase is
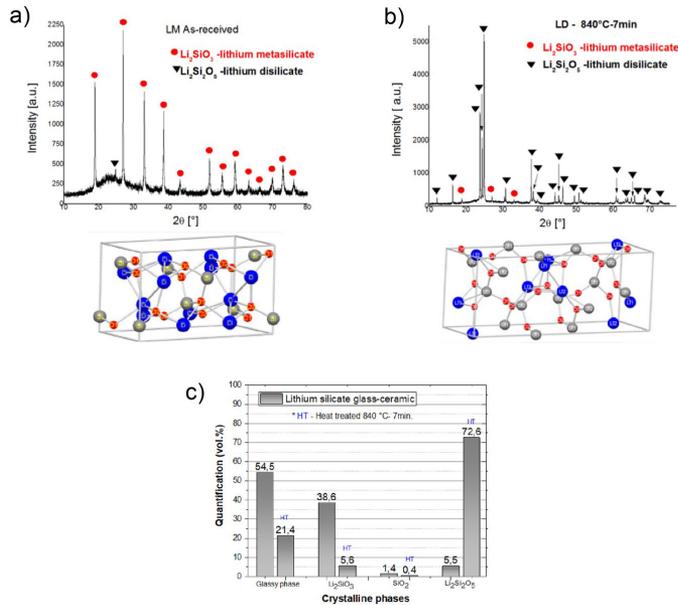
Figure 4. X-ray pattern of glass-ceramics, a) Before heat treatment and Li_2SiO_3 unit cell b) after heat treatment and $Li_2Si_2O_5$ unit cell. c) Quantitative phase analysis of lithium silicate glass-ceramics, as-received and heat treated (HT) at 840 °C - 7 min.
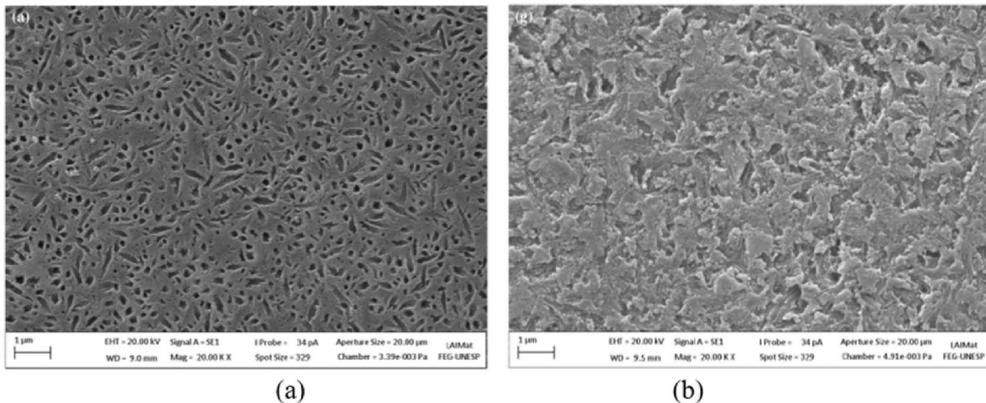
Figure 5. SEM micrographs of the lithium silicate glass-ceramics: (a) Microstructure before heat treatment (Li_2SiO_3 crystals); (b) after heat treatment at 840 °C - 7 min, (elongated $Li_2Si_2O_5$ crystals).

responsible for by the halo observed in the XRD pattern, Figure 4a. After the heat treatment, Figure 4b, the percentage of $Li_2Si_2O_5$ increased to approximately 72.6% with 5.6% of Li_2SiO_3 and 21.4% of the amorphous phase.

Figure 5 shows typical SEM micrographs of the sample surface before and after heat treatment. One can see in Figure 5a a large amount of amorphous phase surrounded by equiaxial crystals of lithium metasilicate (Li_2SiO_3) before the heat treatment. These observations are consistent with the XRD results. After the heat treatment, as shown in Figure 5b, there are elongated and interlaced grains of $Li_2Si_2O_5$ surrounded by the residual amorphous phase partially extracted by the HF-solution chemical etching.

Table 3 and Figure 6 show the results of the roughness tests of the samples. Table 3 shows the average values of Ra, PV and Rz without superficial acid etching (NT), after treatment with hydrofluoric acid (HF) and after treatment with Monobond Ecth & Prime (SECP).

Figure 6 shows that the samples of lithium disilicate after hydrofluoric acid etching (HF) have a surface with inhomogeneous morphology, with several peaks and valleys. The samples of the control group (NT) and the samples treated with a self-etching primer (SECP) had a much more homogeneous surface. The surfaces (HF) etched with hydrofluoric acid had a larger mean surface roughness (Ra = 0.591 ± 0.35 μm, PV = 12.863 ± 7.576 μm and Rz = ± 7.58 ± 2.6 μm) than the surfaces (SECP) treated with MEP (Ra = 0.02 ± 0.003 μm, PV = 0.545 ± 0.07 μm e Rz = 0.387 ± 0.005 μm). Figure 7 shows representative micrographs of the surfaces of samples of the control group and subjected to treatments with HF and MEP. The morphological aspects are consistent with the results of 3D roughness presented in Figure 6. The surfaces treated with SECP (group 3) show less topographic change, shallower conditioning and less pronounced modification, while surfaces treated with HF are rough and inhomogeneous.

Table 3. Surface roughness parameters (Ra), maximum peak value (Peak) and minimum valley value (Valley) of lithium disilicate samples - no surface treatment (NT), hydrofluoric acid etching (HF) and pre-treatment with Monobond Etch and Prime (SECP).

Group	Sample	Ra (μm)	PV (μm)	Rz (nm)
(NT)	1	0.017	0.249	179.18
	2	0.022	1.062	355.00
	3	0.016	0.289	186.88
	4	0.022	1.386	423.35
Average		0. 019 ± 0.003	0. 746 ± 0.762	286. 10 ± 122.28
(HF)	1	0.770	23.662	10727.55
	2	0.844	11.707	7911.82
	3	0.674	9.978	7335.15
	4	0.077	6.087	4383.82
Average		0. 591 ± 0.35	12. 863 ± 7.57	7589. 585 ± 2600.79
(SECP)	1	0.017	0.634	409.84
	2	0.016	0.454	313.61
	3	0.017	0.569	393.37
	4	0.022	0.523	433.96
Average		0. 018 ± 0.003	0. 545 ± 0.075	387.69 ± 51.127
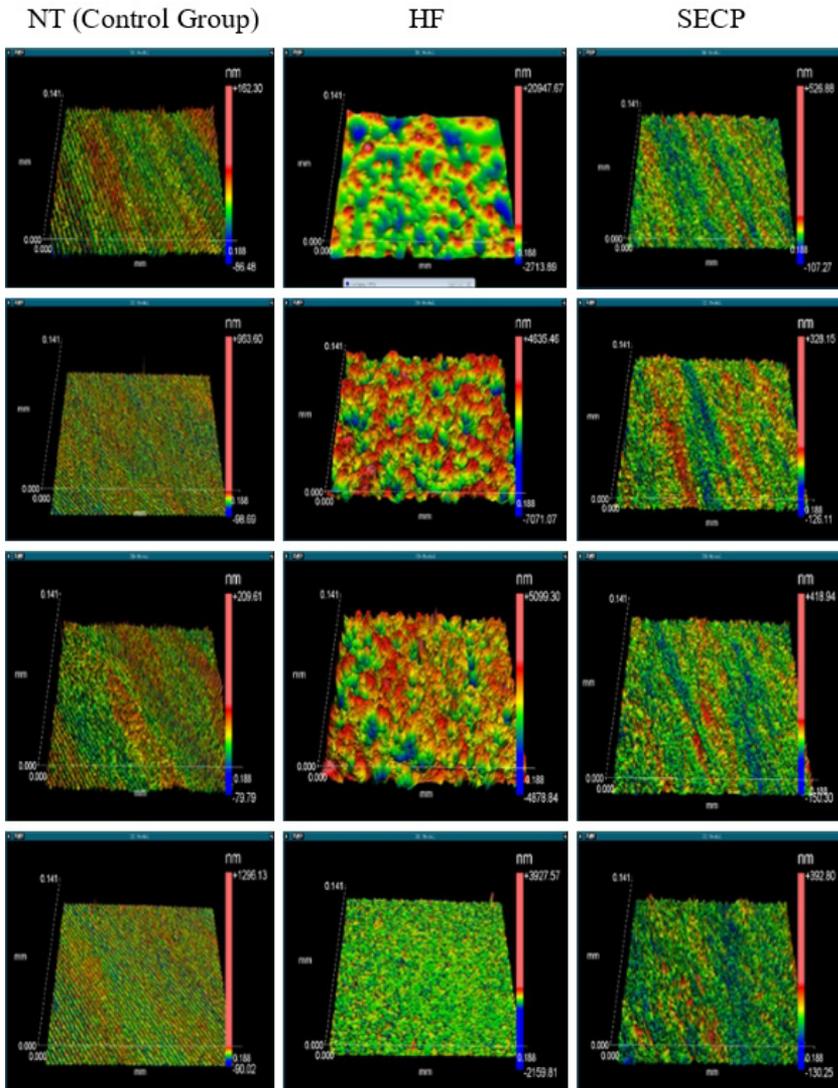
Figure 6. 3D roughness profile of the sample surfaces: Left - control group - no treatment (NT); Middle - after hydrofluoric acid etching (HF) and, Right - pre-treatment with Monobond Etch and Prime (SECP).
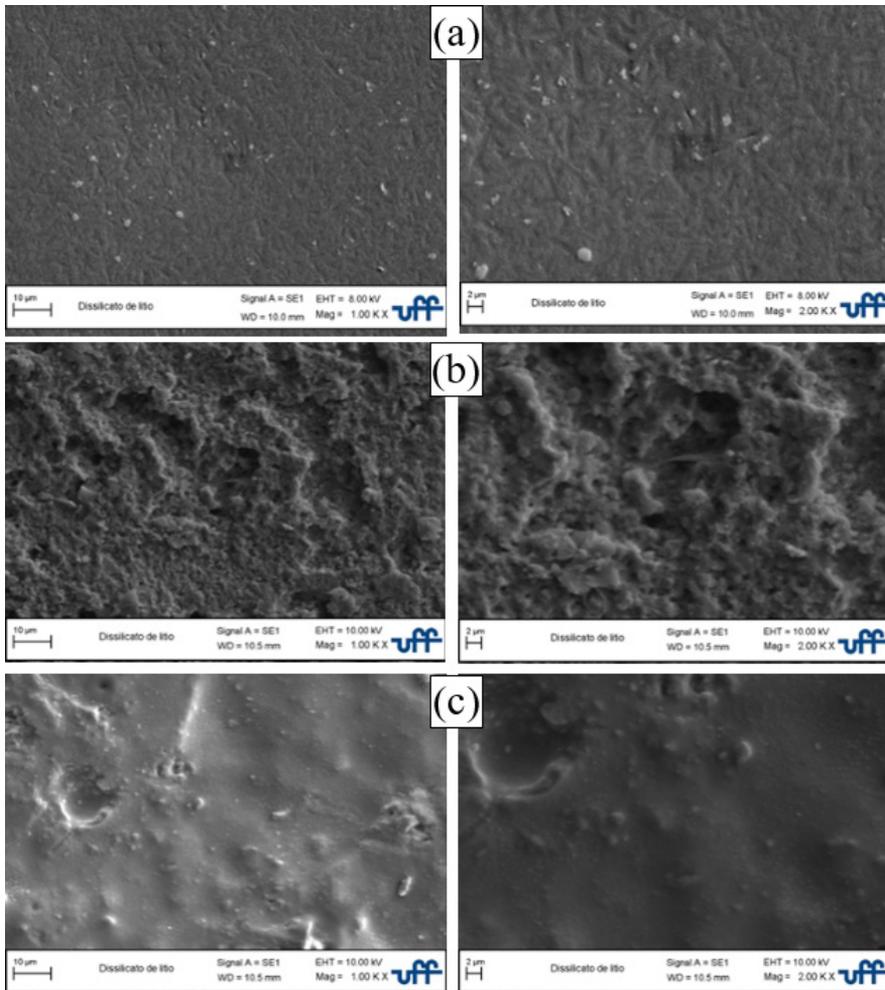
Figure 7. Surface morphology of the sample surfaces: a) without surface treatment (NT); b) after conditioning with hydrofluoric acid (HF); c), after conditioning with self-etching ceramic primer (SECP).

Table 4. Average of the bond strength values (MPa), standard deviation and statistical analysis (equal letters means without statistical difference) of the e.max CAD CAM glass ceramic, without conditioning (NT), etched with hydrofluoric acid solution (HF) and with SECP .

	Group 1 - NT	Group 2 - HF	Group 3 - SECP
Average (μm)	5.31 [b]	24.25 [a]	24.80 [a]
Standard deviation	0.94	1.21	1.82

3.2. Shear strength and statistical analysis

The results of shear strength and statistical analysis are shown in Table 4. Figure 8 shows the Weibull distributions of the shear tests. Groups NT, HF and SECP had shear strengths of 5.31 ± 0.94 MPa, 24.25 ± 1.21 MPa e 24.80 ± 1.82 MPa, respectively. Statistical analysis showed that there was no significant difference between groups HF and SECP. These groups have significant differences in shear strength from control group (NT).

The Weibull moduli of HF group ($m_{HF} = 19$) and SECP ($m_{SECP} = 13$) were higher than the control group NT ($m_{NT} = 6$). The lower value of the Weibull modulus of the group without surface treatment (NT) indicates greater dispersion of shear strength, which is associated with a lack of chemical and / or mechanical adhesion, between the lithium disilicate and the resin cement, allowing the parts involved in the interface, and consequently in the shear strength, are strongly associated with the surface characteristics and the standardization of the surface preparation protocol. These results confirmed change in topography and in the surface roughness of the ceramic material due the surface treatment with 10% HF. The HF etching increased the micromechanical interlock and the bond strength between the resin cement and the glass ceramic. The self-etching ceramic primer promotes changes in the surface of the lithium disilicate sample and adhesive strength similar to Group HF even with a less pronounced conditioning pattern.

Figures 9a-c shows the resin cement-lithium disilicate interfaces for the three groups of samples. It is observed in Figure 9a (NT, control group) the presence of empty spaces at the interface, showing a deficient bonding between the resin cement and the lithium disilicate ceramic. There is no resin cement infiltration and heterogeneous mechanical
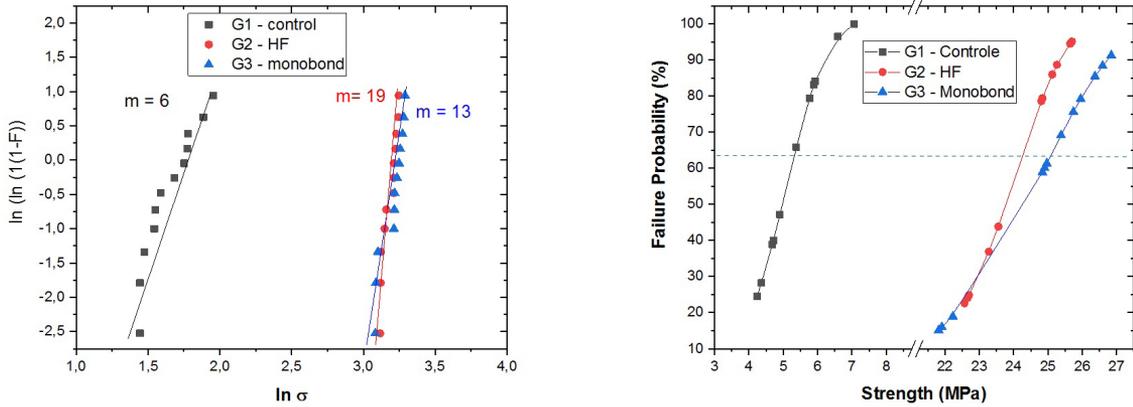
Figure 8. Weibull diagram and probability of failure of the ceramic-resin bonds.
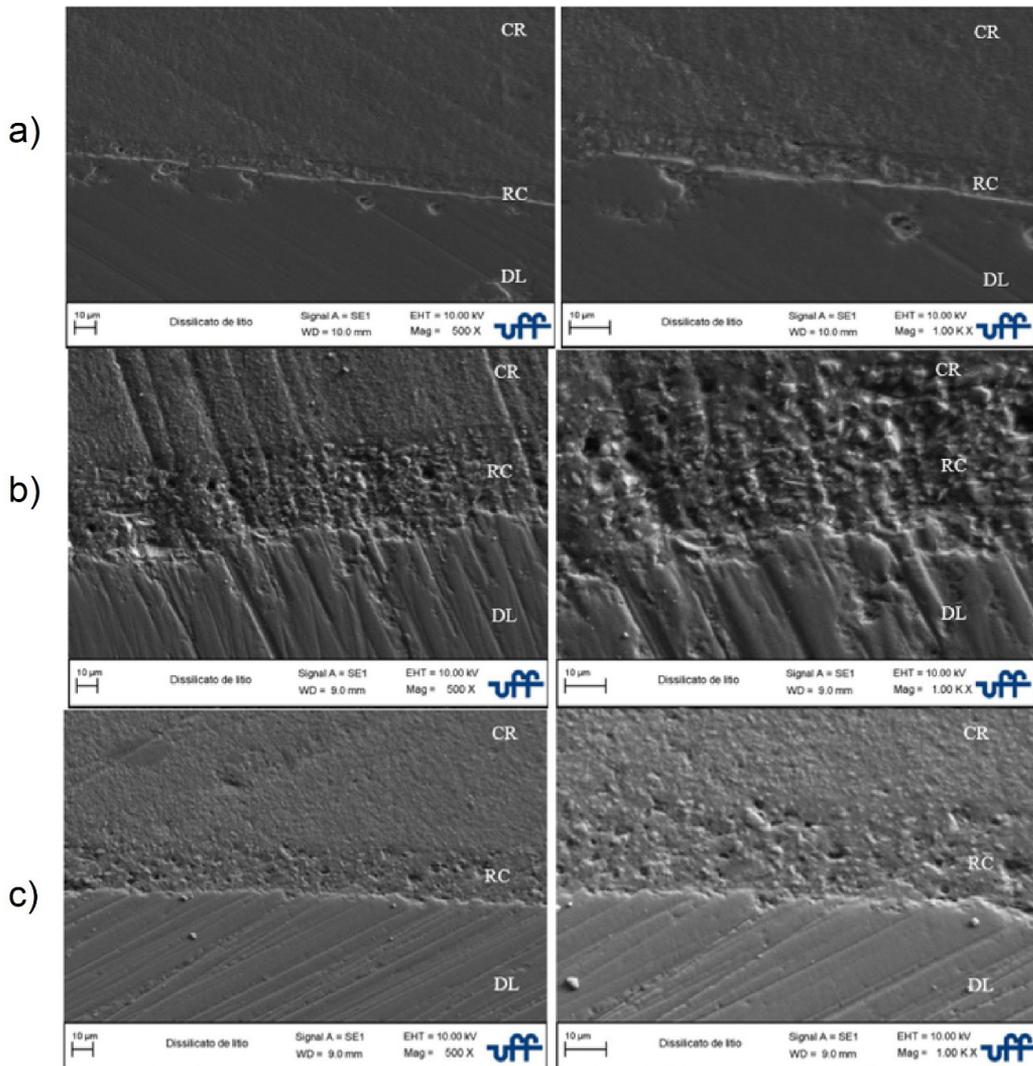
Figure 9. a) Micrograph of the cross section of the bond interface of lithium disilicate and resin cement (Group 1 without surface treatment - NT). It is observed incomplete penetration of the resin cement on the surface of the lithium disilicate; b) Group 2 (after HF etching). The figures show complete penetration of the resin cement on the surface of the lithium disilicate in the irregularities created by hydrofluoric acid. The mechanical interlocking of the resin cement is observed with the surface of the lithium disilicate glass ceramic. c) Group 3 (SECP). complete penetration in the irregularities created by the self-etching ceramic primer. The mechanical interlocking of the resin cement whit lithium silicate is observed. * CR: composite resin; RC: resin cement; DL: lithium disilicate.

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interlock. Figures 9b and 9c show a homogeneous layer on the cement-glass-ceramic interface after hydrofluoric etching (HF) and treatment with the self-etching ceramic primer (SECP). The irregularities caused by HF etching or SECP and mechanical interlock were completely filled out.

4. Discussion

The phase transformations of the lithium silicate, resulting from the heat treatment proposed by the manufacturer (840 °C-7min), are well known. and studied[42]. Based on the chemical composition of the glass informed by the manufacturer (SiO_2:60-80% Li_2O:11-19%, K_2O:13%, P_2O_5:11%, ZrO_2:0-8%, ZnO:0-8%, Al_2O_3: 0-5%, MgO: 0-5%, and pigments), and from the XRD analyzes performed on the as-received lithium metasilicate, Figures 4a and 4b, it can be inferred that the formation of $Li_2Si_2O_5$ crystals that occur at 840 °C - 7min, come mainly from two simultaneous chemical reactions, and are based on the presence of Li_2SiO_3 crystals (metastable above 700 °C), and the presence of 54.5% of residual amorphous phase, rich in SiO_2 and Li present in Li_3PO_4 nuclei dissolved in this residual glass of the crystallized samples.

$$SiO_{2(amorphous)} + Li_2SiO_{3(crystalline)} \rightarrow Li_2Si_2O_{5(crystalline)} \text{ (4)}$$

$$2SiO_{2(amorphous)} + Li_2O_{(amorphous)} \rightarrow Li_2Si_2O_{5(crystalline)} \text{ (5)}$$
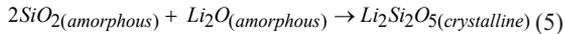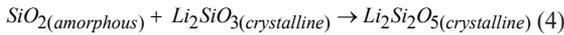
As identified in Figure 4c, the crystallization occurred at 840 °C-7min. In addition to elongated crystals of $Li_2Si_2O_5$, Figure 5b, the heat-treated material presents an amount of residual amorphous phase in the order of 21%. The microstructural aspects indicate that the grains of $Li_2Si_2O_5$ are elongated (high aspect-ratio) and with an average size of 1 to 2 μm, which increases the atomic roughness of the surface of these crystals. This information is important, since this 21% of residual glass, basically contains silica (SiO_2) in addition to ions of such as K, P, Al, Zn, Mg. The silica matrix present in the residual glass is responsible for the activation of chemical reactions that allow chemical bonding and anchoring between the glass ceramic matrix and the resin cement, and the increase in the atomic roughness of the elongated crystals helps in the anchoring between the two layers.

The lack of these chemical and topographic interactions between the surfaces are the main reasons for lowering the bond strength presented by the control group (NT), in comparison to the HF and SECP groups.

The cementation defects of dental prostheses occur at the ceramic-resin interface. Adhesion plays an important role in long-term success, since it improves marginal adaptation of the restoration, decreases microleakage and increases fracture resistance when the prosthesis is subjected to masticatory loads[14,15]. The acid etching surface treatments of ceramics dental prostheses before cementation creates micro-porosities due the removal of the glass phase. Microporosities increase the surface area, increase the surface energy and favour chemical bonding. The bonding agent during the silanization process improves the adhesion. Once adhesive cementation is completed, the formation of a tooth-restoration monoblock

is sought to increase the longevity and durability of indirect adhesive restorations[23-25,43,44].

The 3D roughness analysis (Figure 6) showed that the surface treatment increased the roughness of the samples relative to the control group. This result is consistent with the SEM micrographs (Figure 7) and previous results reported in the literature[17,24,35,45]. HF etching acts dissolves the amorphous component, exposing the lithium disilicate crystals and yielding a rough surface suitable for cementation. In this work, HF 10% treatment was performed for 20 s, followed by water jet removal, but one must be careful, because small increases in the treatment time and/or HF concentration can promote significant changes in the microstructure that are detrimental to its clinical performance.

The surface treatment with the one-step self-etching ceramic primer yields a smoother conditioning pattern (Figure 6). Tetrabutylammonium dihydrogen trifluoride in SECP is Table 3 shows that the SECP treated samples have a surface profile with shallower valleys and fewer stress sites than HF treated ones, as also observed by Tribst et al.[45]. This morphology improves the mechanical behavior under cyclic loading of lithium disilicate. In a practical way, SECP is a simple process for glass-ceramics surface treatment that decreases damage to the microstructure of adhesive restorations, improve mechanical interlocking and provides enough adhesive resistance to t minimize the risk of handling accidents by the dentist and his assistants The conventional surface treatment protocol is HF etching and silanization. Silanes are mediators and provide stable resistance between resin cement and glass ceramic. The silane used in this work is 3-methacryloxypropyltrimethoxysilane, a bifunctional molecule with an organofunctional group containing methyl methacrylate that copolymerizes with resin cements and hydrolyzable alkoxyl groups (silanol) that react with Si-OH on the ceramic surface[24]. The alkoxyl group activates the condensation reaction with the hydroxyls present in the residual amorphous phase and in the glass ceramic, releasing water and products. The 3-methacryloxypropyltrimethoxysilane forms siloxane bonds resulting in a cross-linking tri-dimensional layer. The formation of this layer results in the adhesion of resin cements[34,44].

The adhesive bond strongly depends on the irregularities created in the ceramic surface, which increases the free surface energy and improves the dispersion of silane and resin cement. The 3-methacryloxypropyltrimethoxysilane molecules present in the silane bind to the hydroxyl groups in the ceramic and decreases surface energy[34]. According to Prado et al.[24], cleaning with water and drying with air after applying SECP leaves a thin layer of silane on the ceramic surface, promoting the removal of ammonium polifluoride and the reaction by products forming siloxane bonds. The results of the shear test show an increase in the bond strength in samples treated with HF acid (Group 2) and self-etching primer (SECP) relative to those of the control group (NT), in which there is no considerable mechanical interlocking or silanization. In this study, the bond strength of SECP treated samples is statistically similar to that of HF treated ones.

Although the results of shear strength are statistically similar for groups HF and SECP, with average values of 24.25 MPa and 24.8 MPa respectively, the Weibull moduli

are different the three groups (Figure 8). The group without conditioning (NT) had a Weibull modulus $m_{NT} = 6$, which shows the scattering of results due to the lack of a uniform adhesive layer. Groups HF and SECP have Weibull moduli of $m_{HF} = 19$ and $m_{SECP} = 13$, respectively. The difference in terms of reliability and spreading of the results reveals that the HF group has less bonding variation among samples. This result is due to the efficient creation of surface roughness and increased surface area. HF etching improves glass phase dissolution, increases the wettability of silane that fills in the roughness and promotes a homogeneous surface layer, but also improves the wettability of the adhesive system.

The combination of acid and silane in a single bottle brings advantages such as saving time, decreasing the risks of acid in handling and avoiding the weakening effect on ceramics due to the action of ammonium polyfluoride, which promotes a less severe dissolution of the glass phase of the ceramic, while silanizing the conditioned surface *in situ*[24,34,45-47].

According to Moreno et al.[34], positive results were obtained with the use of SECP. The self-etching ceramic primer was able to transform the hydrophilic surface of the ceramic into a hydrophobic substrate by decreasing the free surface energy and the contact angle between the liquid and substrate. Contaminant removal increases cross-linking in the silane layer and the amount of reactive binding sites available. SECP produced a highly hydrophobic silane layer that favours the hydrolytic stability of the cement-resin interface, forms siloxane bonds with the ceramic surface of the lithium disilicate and improves the penetration of the resin cement by promoting mechanical interlocking. The analysis of the bonding interface in *in vitro* studies carried out by Murillo-Gomez *et. al.*[36] showed similar performances of SECP and acid conditioning. The authors attribute this similar efficiency to the silane contained in SECP, which forms a water-resistant layer, providing a chemical bond between the glass phase and the resin cement. The single-stage primer cleaning step appears to remove the contaminants left by the acid on the surface better than the air jet after applying silane separately in the standard protocol because, due to chemical affinity, water eliminates such by products.

The pattern shown in the SEM micrographs of the cross sections, of the bonding interface between resin cement and lithium disilicate glass-ceramic, Figure 9a-c, are consistent with the similarity of statistical results for both techniques. The bonding interface formed with conventional and simplified surface treatment proved to be homogeneous, showing that there was complete filling of the irregularities created by conditioning for both techniques, promoting mechanical interlocking between resin cement and ceramic. This condition has a positive influence on the quality of the bond and is in accordance with the values obtained in the bond strength tests. The ceramic-resin interface after application of silane and adhesive was deficient because the resin cement did not penetrate the ceramic surface, as shown in the image (Figure 9a) the unfilled spaces. The unfilled spaces generate areas of stress concentration leading to the failure of adhesive cementation and decreasing the longevity of adhesive ceramic restorations.

5. Conclusions

Based on the results obtained in the present study and within the inherent limits of the experimental techniques used, one comes to the following conclusions: The surface treatment with hydrofluoric acid etching (HF) yielded higher roughness parameters than the control group without surface treatment (NT) and the self-etching ceramic primer group (SECP). Furthermore, the HF and self-etching ceramic primer surface treatments increased the bond strength between the cementing agent and the ceramic surface. The simultaneous action of conditioning and silanizing provided by the self-etching ceramic primer promoted micro-retention and adhesive resistance with minor topographic changes in the microstructure, offering a simplified technique without the risks of hydrofluoric acid.

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7. References

1. Kelly JR, Benetti P. Ceramic materials in dentistry: historical evolution and current practice. Aust Dent J. 2011;56(1):84-96.
2. Li RW, Chow TW, Matinlinna JP. Ceramic dental biomaterials and CAD/CAM technology: state of the art. J Prosthodont Res. 2014;58(4):208-16.
3. Willard A, Gabriel Chu T-M. The science and application of IPS e.Max dental ceramic. Kaohsiung J Med Sci. 2018;34(4):238-42.
4. Giordano R. Materials for chairside CAD/CAM-produced restorations. J Am Dent Assoc. 2006;137:14S-21S.
5. Luthardt RG, Holzhuter M, Sandkuhl O, Herold V, Schnapp JD, Kuhlisch E, et al. Reliability and properties of ground Y-TZP-zirconia ceramics. J Dent Res. 2002;81(7):487-91.
6. Guess PC, Zavanelli RA, Silva NR, Bonfante EA, Coelho PG, Hompson VP. Monolithic CAD/CAM lithium disilicate versus veneered Y-TZP 71 crowns: comparison of failure modes and reliability after fatigue. Int J Prosthodont. 2010;23(5):434-42.
7. Guerra CN, Neves CAF, Almeida ECB, Valones MAA, Guimarães RP. Current stage of dental ceramics. Int J Dent. 2007;6(3):90-5.
8. Denry I, Holloway JA. Ceramics for dental applications: a review. Materials. 2010;3(1):351-68.
9. Guess PC, Schultheis S, Bonfante EA, Coelho PG, Ferencz JL, Silva NR. Allceramic systems: laboratory and clinical performance. Dent Clin North Am. 2011;55(2):333-52.
10. Lien W, Roberts HW, Platt JA, Vandewalle KS, Hill TJ, Chu T-MG. Microstructural evolution and physical behavior of a lithium disilicate glass-ceramic. Dent Mater. 2015;31(8):928-40.
11. Della Bona A, Corazza PH, Zhang Y. Characterization of a polymer-infiltrated ceramic-network material. Dent Mater. 2014;30(5):564-9.
12. Elsaka SE. Bond strength of novel CAD/CAM restorative materials to self-adhesive resin cement: the effect of surface treatments. J Adhes Dent. 2014;16:531-40.
13. Piwowarczyk A, Lauer H-C, Sorensen JA. In vitro shear bond strength of cementing agents to fixed prosthodontic restorative materials. J Prosthet Dent. 2004;92(3):265-73.

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Self-etching Ceramic Primer

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14. Della Bona A, Kelly JR. The clinical success of all-ceramic, restorations. J Am Dent Assoc. 2008;139:S8-13.

15. Tian T, Tsoi JK-H, Matinlinna JP, Burrow MF. Aspects of bonding between resin luting cements and glass ceramic materials. Dent Mater. 2014;30(7):147-62.

16. Fabião MM, Stape THS, Yanikian CRF, Lima AF, Pizi ECG, Baron GMM, et al. Influence of different adhesive protocols on ceramic bond strength and degree of conversion of resin cements. Int J Adhes Adhes. 2015;62:7-13.

17. El-Damanhoury HM, Gaintantzopoulou MD. Self-etching ceramic primer versus hydrofluoric acid etching: etching efficacy and bonding performance. J Prosthodont Res. 2018;62(1):75-83.

18. Valandro LF, Della Bona A, Bottino MA, Neisser MP. The effect of ceramic surface treatment on bonding to densely sintered alumina ceramic. J Prosthet Dent. 2005;93(3):253-9.

19. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. J Prosthet Dent. 2003;89(3):268-74.

20. Kalavacharla VK, Lawson NC, Ramp LC, Burgess JO. Influence of etching protocol and silane treatment with a universal adhesive on lithium disilicate bond strength. Oper Dent. 2014;40(4):372-8.

21. 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. J Biomed Mater Res B Appl Biomater. 2017;105(4):885-91.

22. Della Bona A, Anusavice KJ. Microstructure, composition, and etching topography of dental ceramics. Int J Prosthodont. 2002;15(2):159-67.

23. Moro AFV, Ramos AR, Rocha GM, Perez CR. Effect of prior silane application on the bond strength of a universal adhesive to a lithium disilicate ceramic. J Prosthet Dent. 2017;118(5):666-71.

24. Prochnow C, Venturini AB, Grasel R, Gundel A, Bottino MC, Valandro LF. Adhesion to a lithium disilicate glass ceramic etched with hydrofluoric acid at distinct concentrations. Braz Dent J. 2018;29(5):492-9.

25. Matinlinna JP, Lung CYK, Tsoi JKH. Silane adhesion mechanism in dental applications and surface treatments: a review. Dent Mater. 2018;34(1):13-28.

26. Canay S, Hersek N, Ertan A. Effect of different acid treatments on a porcelain surface. J Oral Rehabil. 2001;28(1):95-101.

27. Xiaoping L, Dongfeng R, Silikas N. Effect of etching time and resin bond on the flexural strength of IPS e.max Press glass ceramic. Dent Mater. 2014;30(12):330-6.

28. Ozcan M, Allahbeickaraghi A, Dundar M. Possible hazardous effects of hydrofluoric acid and recommendations for treatment approach: a review. Clin Oral Investig. 2012;16(1):15-23.

29. Ivoclar Vivadent. Monobond Etch & Prime Material Safety Data Sheet according to 1907/2006/EC, 21/09/2016 version 3.

30. Lopes GC, Perdigão J, Baptista D, Ballarin A. Does a self-etching ceramic primer improve bonding to lithium disilicate ceramics? Bond strengths and FESEM analyses. Oper Dent. 2019;44(2):210-8.

31. Maier E, Bordihn V, Belli R, Taschner M, Petschelt A, Lohbauer U, et al. New approaches in bonding to glass-ceramic: self-etch glass-ceramic primer and universal adhesives. J Adhes Dent. 2019;21(3):209-17.

32. Prado M, Prochnow C, Marchionatti AME, Baldissara P, Valandro LF, Wandscher VF. Ceramic surface treatment with a single-component primer: resin adhesion to glass ceramics. J Adhes Dent. 2018;20(2):99-105.

33. Román-Rodríguez J-L, Perez-Barquero J-A, Gonzalez-Angulo E, Fons-Font A, Bustos-Salvador J-L. Bonding to silicate ceramics: conventional technique compared with a simplified technique. J Clin Exp Dent. 2017;9:e384-6.

34. Moreno MBP, Murillo-Gómez FDE, Goes MF. Physicochemical and morphological characterization of a glass ceramic treated with different ceramic primers and post-silanization protocols. Dent Mater. 2019;35(8):1073-81.

35. Wille S, Lehmann F, Kern M. Durability of resin bonding to lithium disilicate and zirconia ceramic using a self-etching primer. J Adhes Dent. 2017;19:491-6.

36. Murillo-Gómez F, Palma-Dibb RG, De Goes MF. Effect of acid etching on tridimensional microstructure of etchable CAD/CAM materials. Dent Mater. 2018;34(6):944-55.

37. Scherer MM, Prochnow C, Venturini AB, Pereira GKR, Burgo TAL, Rippe MP, et al. Fatigue failure load of an adhesively-cemented lithium disilicate glass-ceramic: conventional ceramic etching vs etch & prime one-step primer. Dent Mater. 2018;34(8):1134-43.

38. ABNT: Associação Brasileira de Normas Técnicas. NBR ISO 4288: especificações geométricas do produto (GPS): rugosidade: método do perfil: regras e procedimentos para avaliação de rugosidade. Rio de Janeiro; 2008.

39. ABNT: Associação Brasileira de Normas Técnicas. NBR ISO 4287: especificações geométricas do produto (GPS): rugosidade: método do perfil: termos, definições e parâmetros da rugosidade. Rio de Janeiro; 2002.

40. DeHoff PH, Anusavice KJ, Wang Z. Three-dimensional finite element analysis of the shear bond test. Dent Mater. 1995;11(2):126-31.

41. Quinn JB, Quinn GD. Review: a practical and systematic review of Weibull statistic for reporting strengths of dental materials. Dent Mater. 2010;26(2):135-47.

42. Alves MFRP, Simba BG, Campos LQB, Ferreira I, Santos C. Influence of heat-treatment protocols on mechanical behavior of lithium silicate dental ceramics. Int J Appl Ceram Technol. 2019;16(5):1920-31.

43. Belli RS, Geinzer E, Muschweck A, Petschelt A, Lohbauer V. Mechanical fatigue degradation of ceramics versus resin composites for dental restorations. Dent Mater. 2014;30(4):424-32.

44. Aguiar TR, Barbosa WFS, Di Francescantonio M, Giannini M. Effects of ceramic primers and postsilanization heat treatment on bond strength of resin cement to lithium disilicatebased ceramic. Applied Adhesion Science. 2016;4(1):20.

45. Tribst JPM, Monteiro JB, Venturini AB, Pereira GKR, Bottino MA, Melo RM, et al. Fatigue failure load of resin-bonded simplified lithium disilicate glass-ceramic restorations: effect of ceramic conditioning methods. J Adhes Dent. 2019;21:373-81.

46. Murillo-Gómez FDE, Goes MF. Bonding effectiveness of tooth-colored materials to resin cement provided by self-etching silane primer after short- and long-term storage. J Prosthet Dent. 2019;121(4):713.e1-e8.

47. Siqueira FSF, Alessi RS, Cardenas AFM, Kose C, Pinto SCS, Loguercio AD, et al. New single-bottle ceramic primer: 6-month case report and laboratory performance. J Contemp Dent Pract. 2016;17(12):1033-9.