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Article

The Effect of Hydrofluoric Acid Etching Duration on the Surface Micromorphology, Roughness, and Wettability of Dental Ceramics

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Abstract: The current laboratory study is evaluating the effect of hydrofluoric acid etching duration on the surface characteristics of five silica-based glass ceramics. Changes in the pore pattern, crystal structure, roughness, and wettability were compared and evaluated. Seventy-five rectangularly shaped specimens were cut from each material (IPS e-maxTM, Dentsply CeltraTM, Vita SuprinityTM, Vita mark IITM, and Vita Suprinity FCTM); the sectioned samples were finished, polished, and ultrasonically cleaned. Specimens were randomly assigned into study groups: control (no etching) and four experimental groups (20, 40, 80 and 160 s of etching). The etched surfaces' microstructure including crystal structure, pore pattern, pore depth, and pore width was studied under a scanning electron microscope, and the surface roughness and wettability were analyzed using a non-contact surface profilometer and a contact angle measuring device, respectively. The results were statistically analyzed using one-way analysis of variance (ANOVA) and the *post hoc* Tukey's test. The results showed a significant change in the pore number, pore pattern, crystal structure, surface roughness, and wettability with increased etching duration. Etching for a short time resulted in small pores, and etching for longer times resulted in wider, irregular grooves. A significant increase in the surface roughness and wettability was observed with an increase in the etching duration. The findings also suggested a strong association between the surface roughness and wettability.

Keywords: dental ceramics; lithium disilicate glass ceramics; acid etching; micromorphology; surface roughness; wettability

1. Introduction

Dental ceramics are biocompatible, natural-looking indirect restorative materials in modern restorative dentistry because of their aesthetic and biomechanical properties [1–3]. Ceramics are widely used, and there is a growing interest for their application in various disciplines of dentistry [4–6]. Development of computer-aided design/computer-aided machining (CAD/CAM) technology has enabled clinicians to deliver high-quality, precise ceramic restorations [4]. However, the lack of direct chemical bonding with natural enamel and low tensile strength has been a great concern over the years.

In dentistry, adhesion between two dissimilar materials may be enhanced by increasing the surface free energy [6,7]. Increasing the surface free energy improves the wettability of the surface for

resin cement bonding [8]. Thus, it is recommended to condition the internal surface of the ceramic restoration with hydrofluoric acid. According to several recent studies, etching of ceramic with 5% hydrofluoric acid for 2–3 min is enough to selectively dissolve the glassy phase [9,10] and make the surface porous for resin composite cement penetration [5,9,11,12]. This porous surface not only provides more surface area for resin bonding [8], but also exposes and generates hydroxyl groups on the ceramic surface that are responsible for chemical bonding via silane coupling agents [9,13,14].

After etching, the ceramic surface is treated with an activated silane coupling agent to improve chemical adhesion [8,15–20] and to provide reliable and durable chemical bonding with adhesive resin composite cement [13,21–23]. Silane coupling agents (silanes) are hybrid inorganic-organo-functional trialkoxysilane monomers and are capable of unifying organic and inorganic materials. In general, silanes have non-hydrolysable groups (such as methacrylate) and hydrolysable groups (such as ethoxy), which is why they are chemically bifunctional [8]. When reactive silanes are applied over the etched ceramic surface, the hydrolysable alkoxy groups react with exposed hydroxyl groups, and non-hydrolyzable organic groups polymerize with unset resin composite cement [6]. Hence, for reliable and durable chemical bonding, it is necessary that the ceramic surface should be conditioned. However, such chemical reactions are not applicable for non-silica containing zirconia-based ceramics [24].

Numerous studies have reported the effect of acid etching, etching duration, and acid concentration on the surface micromorphology, bond strength, and flexural strength of different ceramics, but none of the studies attempted to correlate altered surface topography to surface wettability. Furthermore, to the author's knowledge, none of the studies describe in detail the effect of acid etching duration on micro- and nano-scale parameters of the porosities. This is why the current study was aimed to (a) study the effect of acid etching duration on the pore pattern, pore width, and pore depth. and (b) study the effect of etching duration on surface roughness (S_a) and wettability of five selected silica-based glass ceramics.

The null hypothesis tested was that the etching duration has no effect on the micromorphology, surface roughness, or wettability of ceramic surfaces.

2. Results

Figures 1–5 shows the SEM images of control group and four experimental groups of all the tested materials. The control group specimens showed smooth and homogeneous surfaces without any porosity as a result of polishing. The control group specimen surfaces presented dark and light areas, which represented the glass matrix and crystals (Figures 1A, 2A, 3A and 4A), uniformly distributed fluorapatite and zirconia crystals in lithium disilicate and zirconia-reinforced lithium silicate ceramics (Figures 1A, 2A, 3A and 5A). The etched surfaces showed significant changes in the surface microstructure with an increase in the etching time. The etched surfaces of all specimens were irregular and were characterized by the presence of numerous micro porosities, grooves, and striations as a result of the dissolution of the glassy phase. The specimens etched for 20 s predominantly showed a glassy phase and isolated small pores with closed and irregular borders measuring 0.37 to 0.84 μm (Figure 6). With an increase in the etching duration to 40 s, a weaker glassy phase (SiO_2 , LiO_2 , K_2O , Al_2O_3 , P_2O_5 , ZrO_2 , and HfO_2) around the crystals that has higher solubility to acid action than lithium disilicate crystal phase dissolved at a faster rate than the crystals (Li_2SiO_5), resulting in an increase in the size of the pores, which appeared as elongated grooves. A further increase in the etching duration to 80 and 160 s resulted in specimens predominantly showing irregularly oriented crystals measuring 2.56 to 2.97 μm and scratch-like gaps because of an extensive loss of the glassy phase and areas with grain pullout (Figure 6) in particle filled ceramics (IPS e-maxTM, Dentsply CeltraTM, Vita SuprinityTM, Vita Suprinity FCTM). Specimens of Vita mark IITM (feldspathic porcelain) and Vita Suprinity FCTM (zirconia-reinforced lithium silicate, fully crystallized) showed large cavitations, the dimensions of which increased with an increase in the etching time (Figures 4 and 5). Images of Vita mark IITM typically showed a honeycomb-etched pattern because of the absence of crystal phase, which was different compared to other particle-filled samples (Figure 4). Figure 7 shows the pore width and

depth: the pore width and depth increased with an increase in the etching time, the depth ranged from 3.89 μm (Figure 7A) to 5.01 μm (Figure 7D), and the width ranged from 3.95 μm (Figure 7A) to 18.79 μm (Figure 7D).

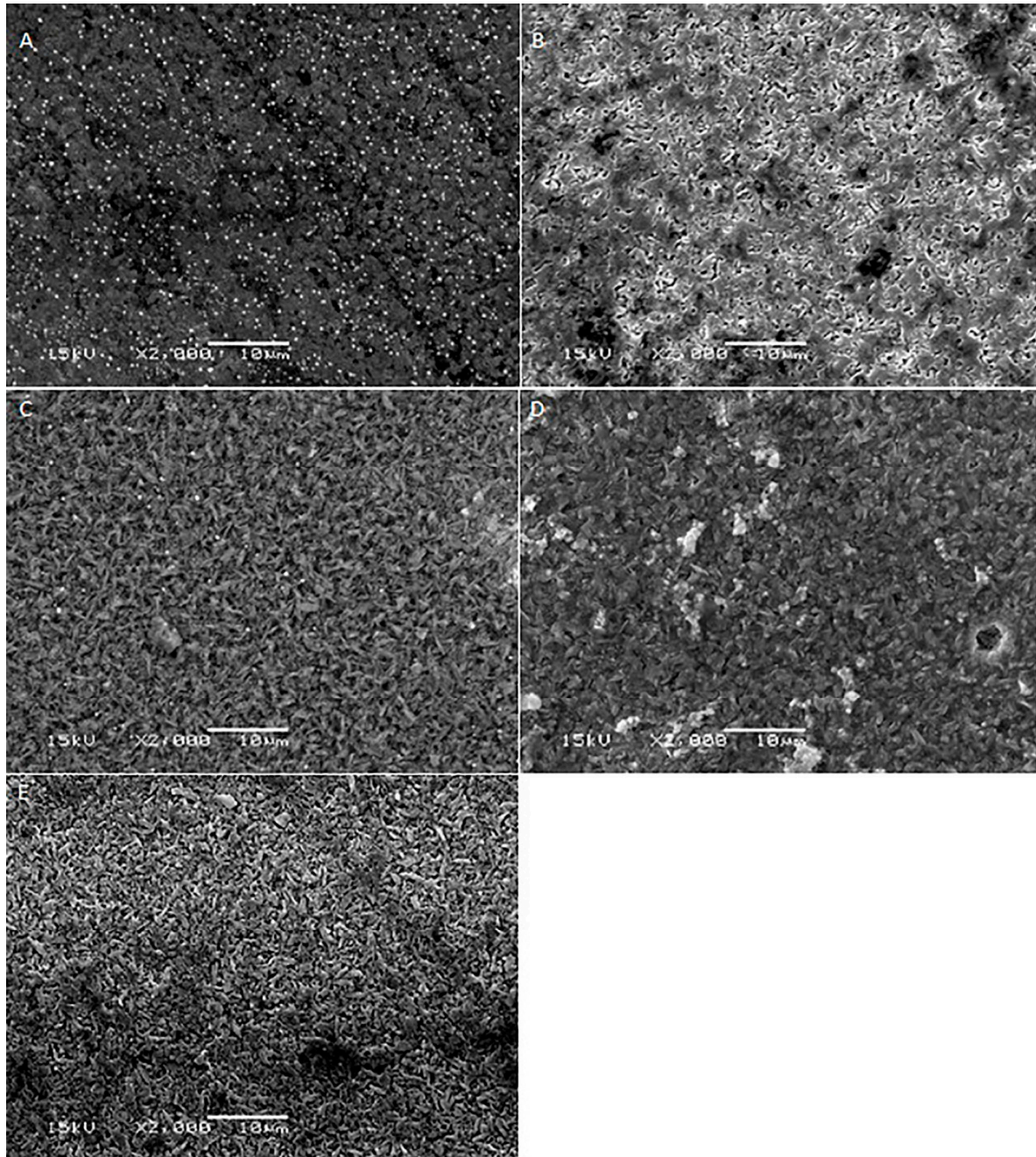


Figure 1. SEM photomicrographs of etched IPS e-max™ ceramic surfaces applied with different etching times. A: Control group; B: 20 s etching; C: 40 s etching; D: 80 s etching; E: 160 s etching. Original magnification: 2000 \times ; bar = 10 μm .

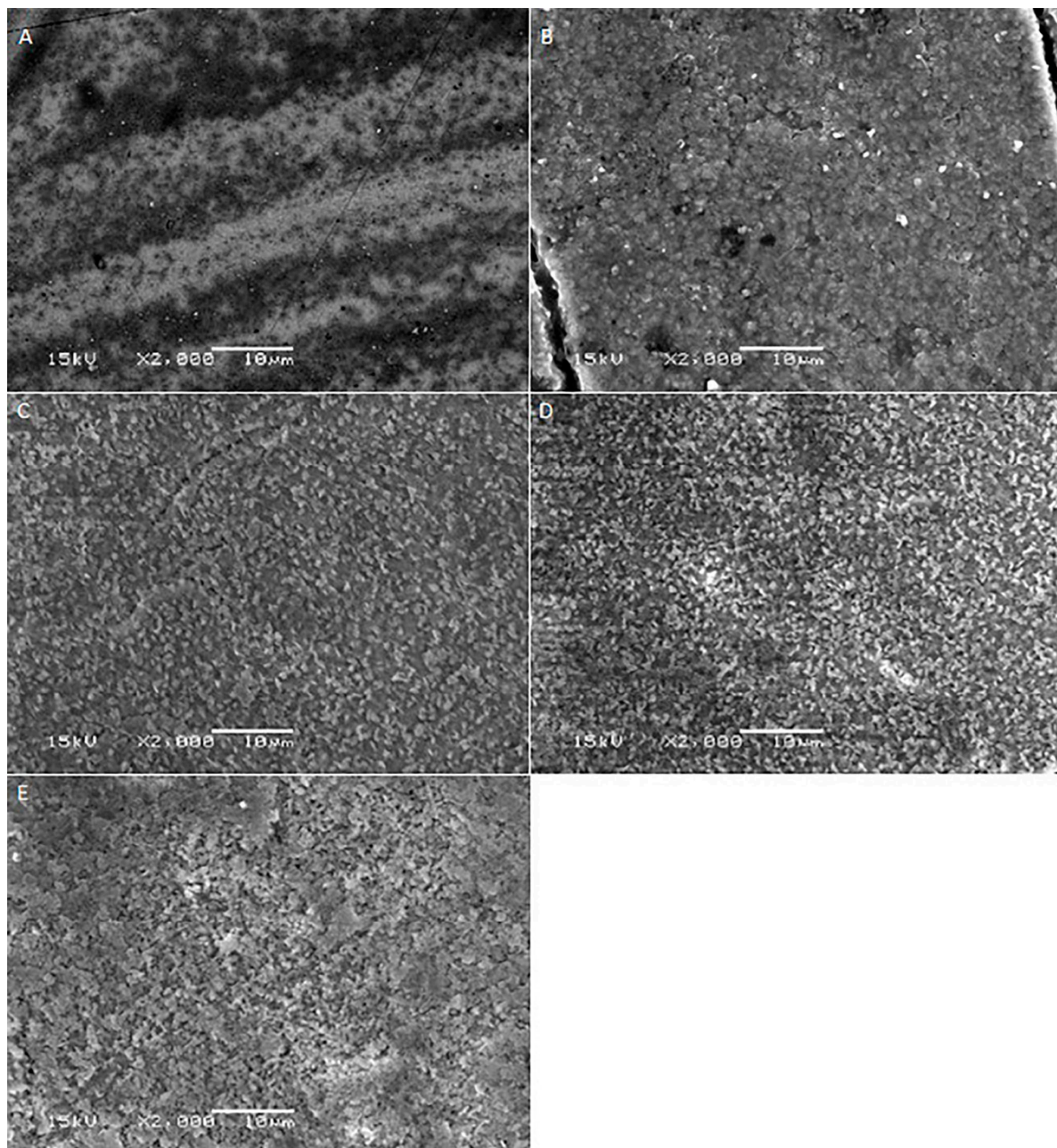


Figure 2. SEM photomicrographs of etched Dentsply Celtra™ ceramic surfaces applied with different etching times. **A:** Control group; **B:** 20 s etching; **C:** 40 s etching; **D:** 80 s etching; **E:** 160 s etching. Original magnification: 2000×; bar = 10 µm.

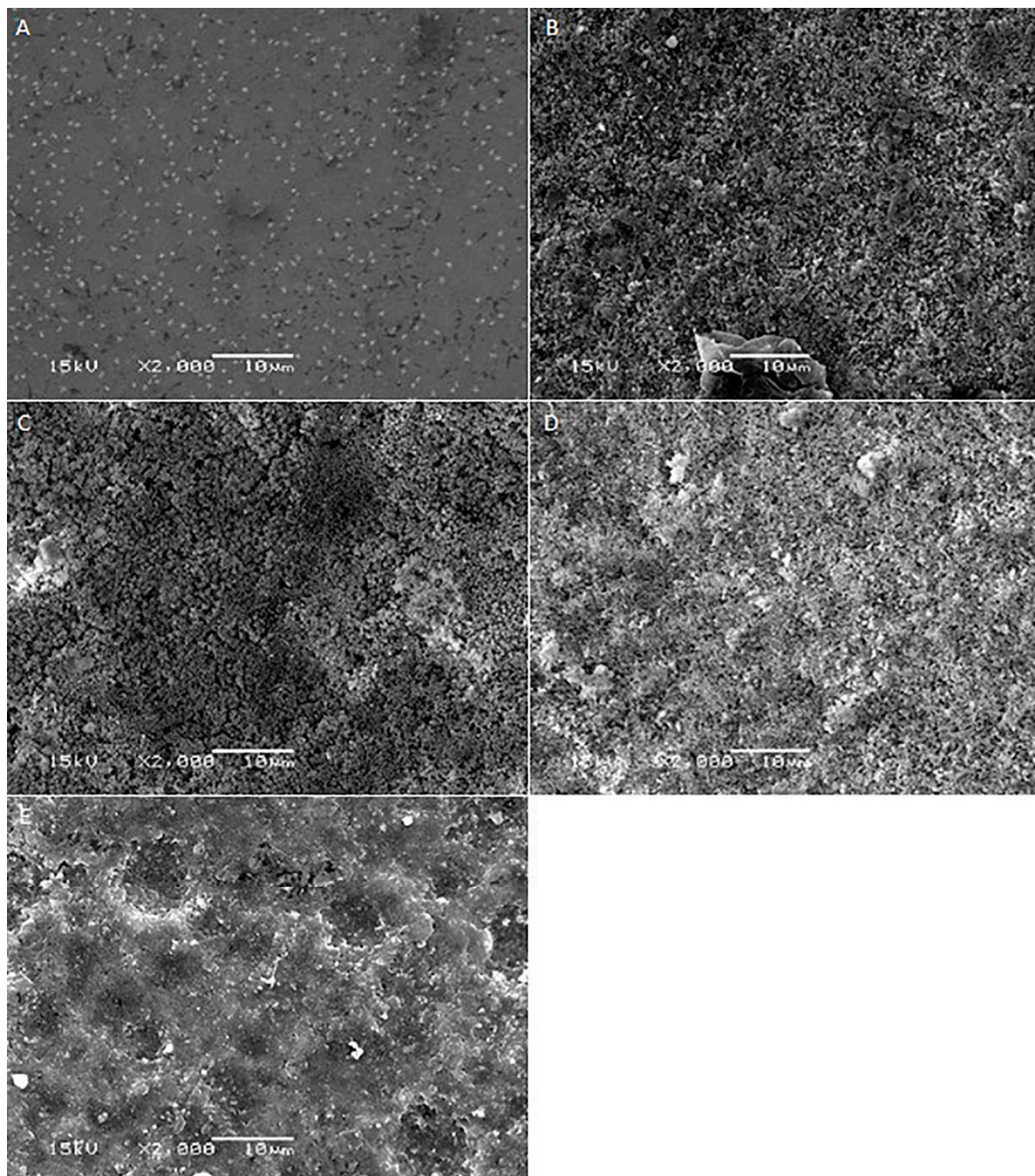


Figure 3. SEM photomicrographs of etched Vita Suprinity™ ceramic surfaces applied with different etching times. **A:** Control group; **B:** 20 s etching; **C:** 40 s etching; **D:** 80 s etching; **E:** 160 s etching. Original magnification: 2000×; bar = 10 µm.

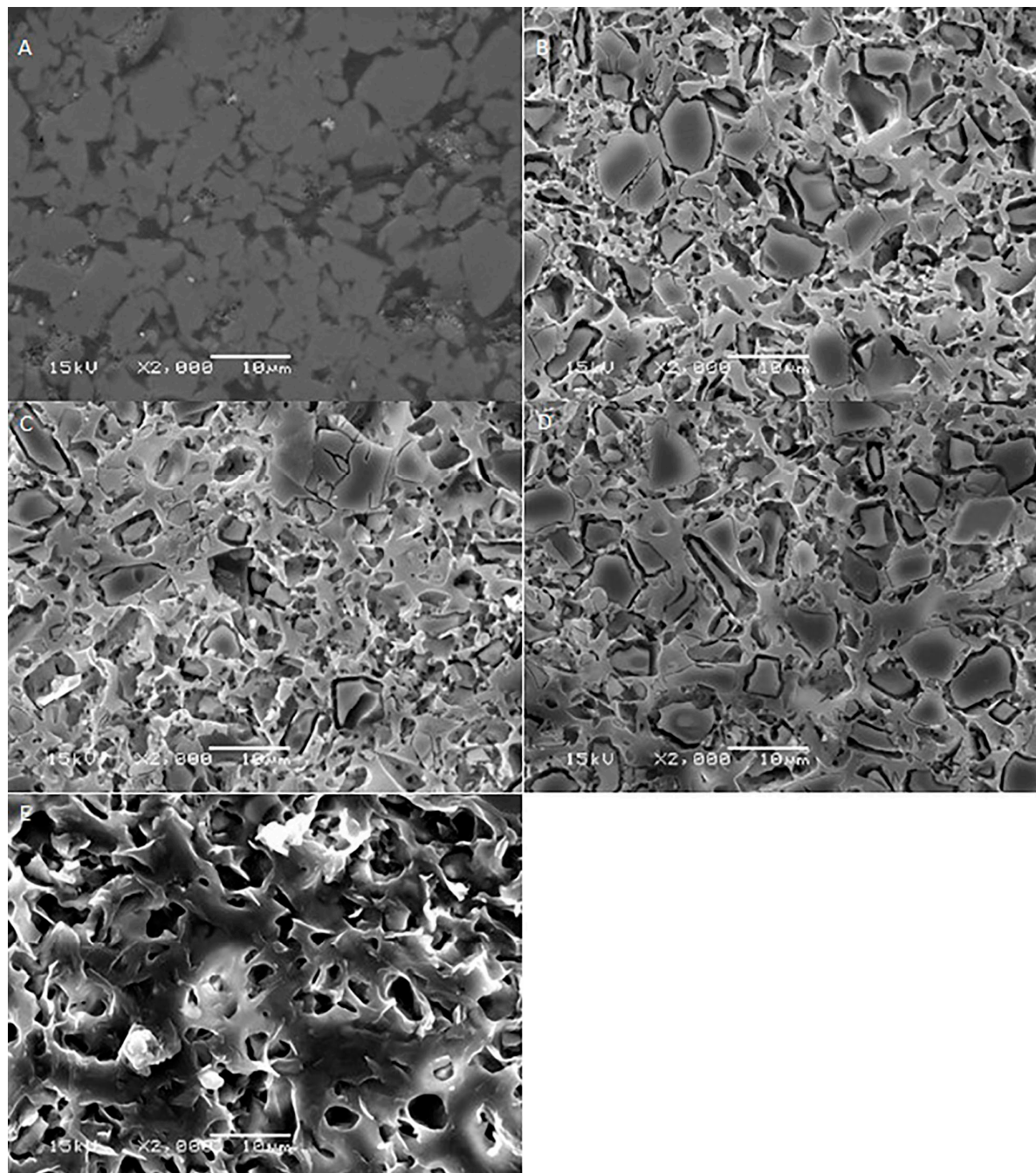


Figure 4. SEM photomicrographs of etched Vita mark II™ ceramic surfaces applied with different etching times. **A:** Control group; **B:** 20 s etching; **C:** 40 s etching; **D:** 80 s etching; **E:** 160 s etching. Original magnification: 2000×; bar = 10 µm.

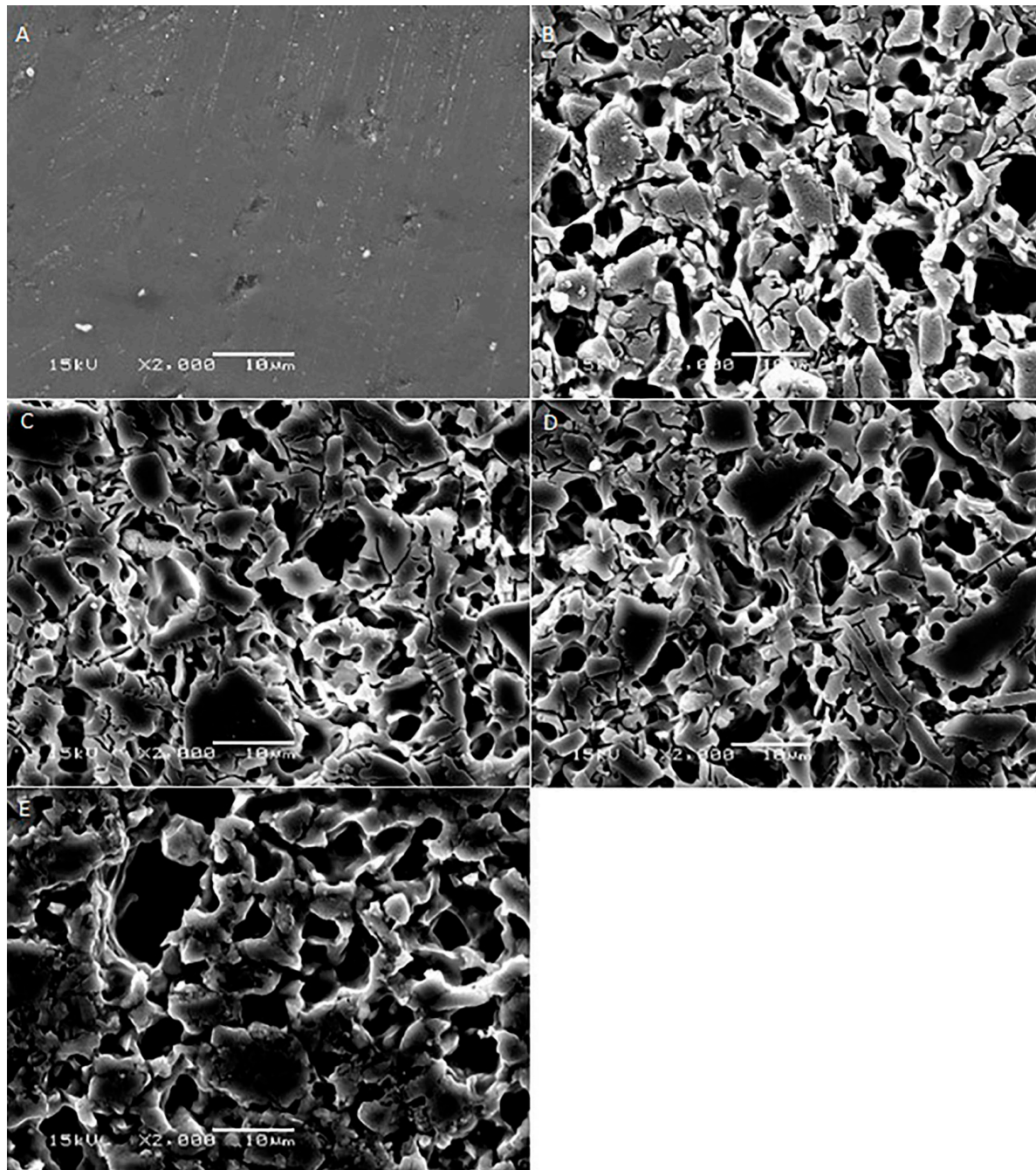


Figure 5. SEM photomicrographs of etched Vita Suprinity FC™ ceramic surfaces applied with different etching times. **A:** Control group; **B:** 20 s etching; **C:** 40 s etching; **D:** 80 s etching; **E:** 160 s etching. Original magnification: 2000×; bar = 10 µm.

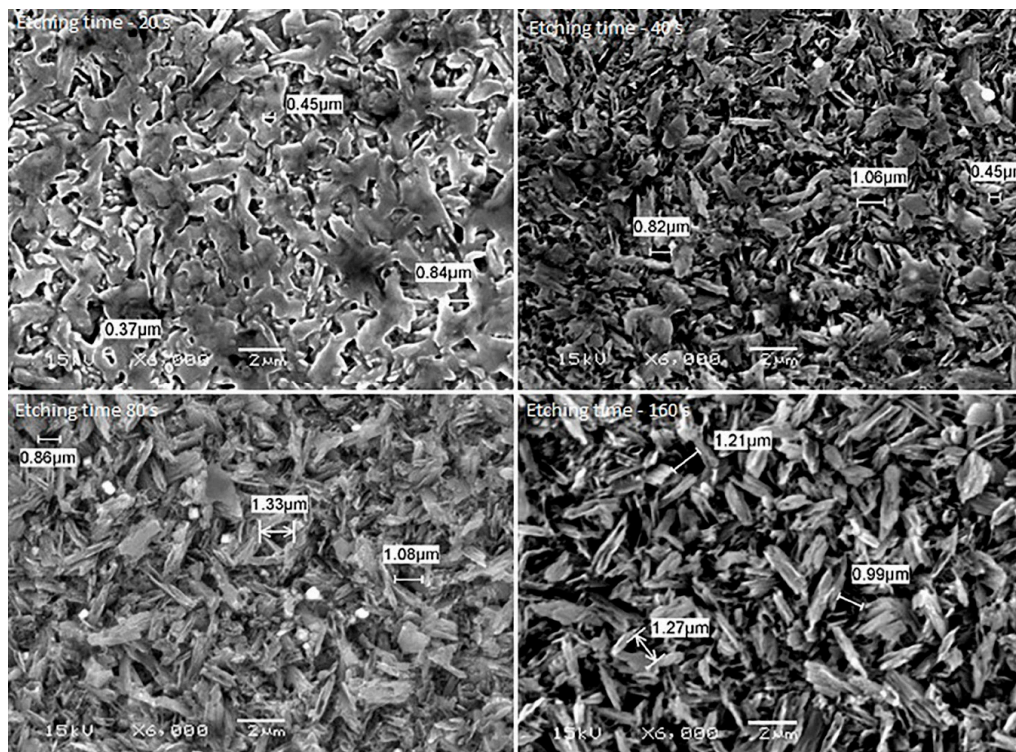


Figure 6. SEM photomicrographs showing microstructure of ceramics etched for different etching times (from the left, upper line: 20, 40, 80 and 160 s). Original magnification 6000×; bar = 2 μm.

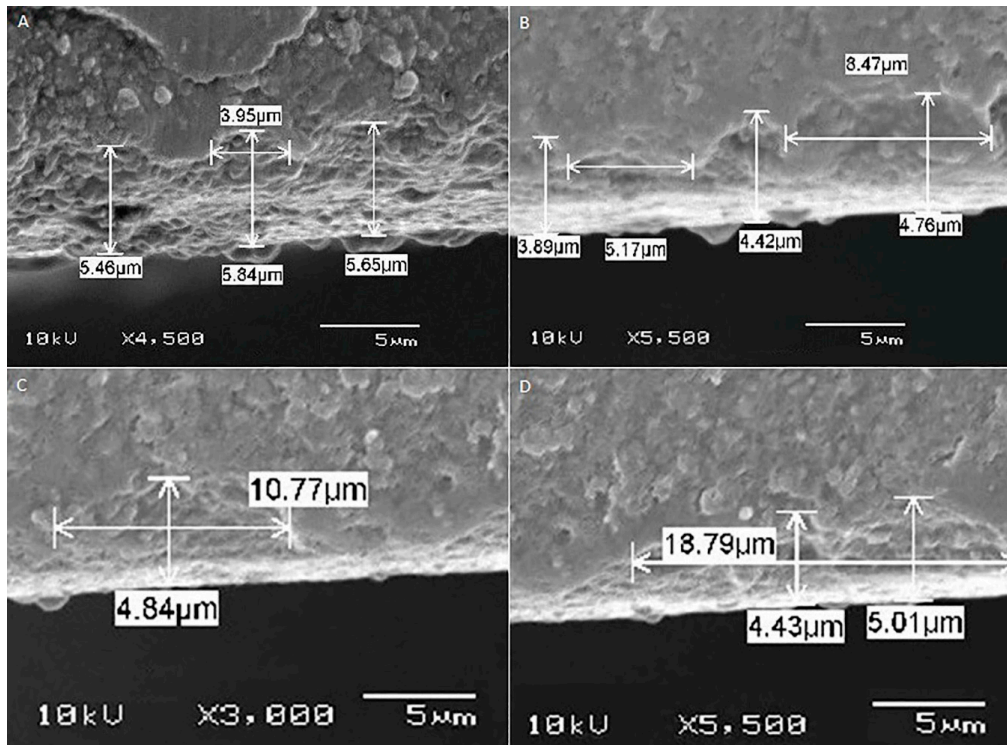


Figure 7. SEM photomicrographs of cross section showing width and pore pattern at different etching times. A: =20 s; B: =40 s; C: =80 s; D: =160 s; original magnifications: 4500×; 5500×; 3000×; and 5500×, respectively.

Tables 1 and 2 present the mean and standard deviation values of S_a and contact angle (CA), respectively.

Results of the one-way ANOVA for S_a showed a statistically significant difference among the groups (Table 1). The S_a increased with an increase in etching time in all the materials and experimental groups (Figure 8). Control group, Dentsply Celtra™ and Vita Suprinity FC™ specimens showed the lowest surface roughness (0.08 ± 0.008) and Vita mark II™ showed the highest surface roughness (0.14 ± 0.016). No significant difference was observed between Vita mark II™ and Vita Suprinity™ in 80, 160 s and 40 s, 80 s, respectively (values marked with similar superscripted letters in Table 1).

Table 1. Comparison of mean surface roughness (S_a) among different experimental groups.

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

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

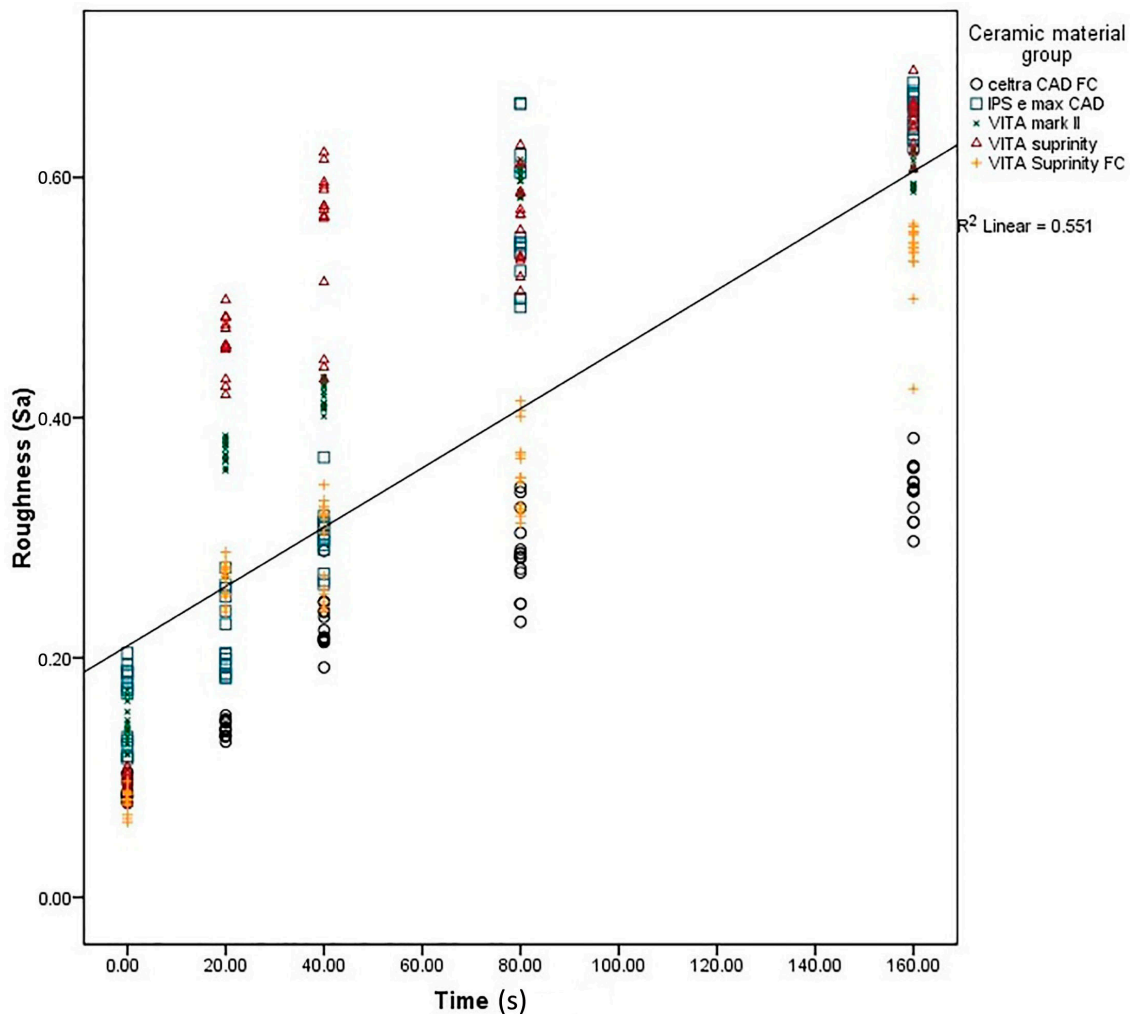


Figure 8. Regression analysis of surface roughness at different acid etching durations.

The results of wettability showed a statistically significant difference (a decrease) in CA (an increase in surface wettability) with an increase in the etching time (Figure 9). The samples etched for a longer time (160 s) showed the lowest mean CA, ranging between 6.86 ± 0.35 (Dentsply Celtra™) and 27.4 ± 0.5 (Vita Suprinity FC™) (Table 2). The S_a and CA values showed significant dependency on each other in all the materials and at all the intervals (Figure 10).

Table 2. Comparison of mean contact angle among different experimental groups.

Material	Mean Contact Angle (Mean ± SD)					p-Value
	Control Group	20 s	40 s	80 s	160 s	
Celtra	90.33 ± 0.81 ^a	54.94 ± 1.03 ^b	46.06 ± 0.45 ^c	24.86 ± 0.83 ^d	06.86 ± 0.35 ^e	0.001 *
e-max	45.80 ± 0.56 ^a	27.95 ± 0.52 ^b	24.06 ± 0.25 ^c	18.00 ± 0.37 ^d	17.53 ± 0.51 ^d	0.001 *
Mark II	91.27 ± 1.43 ^a	74.80 ± 0.56 ^b	49.87 ± 0.83 ^c	30.00 ± 1.73 ^d	22.20 ± 0.41 ^e	0.001 *
Suprinity	62.13 ± 0.74 ^a	39.13 ± 0.91 ^b	33.27 ± 0.79 ^c	27.07 ± 0.59 ^d	20.93 ± 0.25 ^e	0.001 *
Supri FC	72.20 ± 0.41 ^a	61.13 ± 0.18 ^b	48.67 ± 0.81 ^c	40.27 ± 1.33 ^d	27.40 ± 0.50 ^e	0.001 *

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

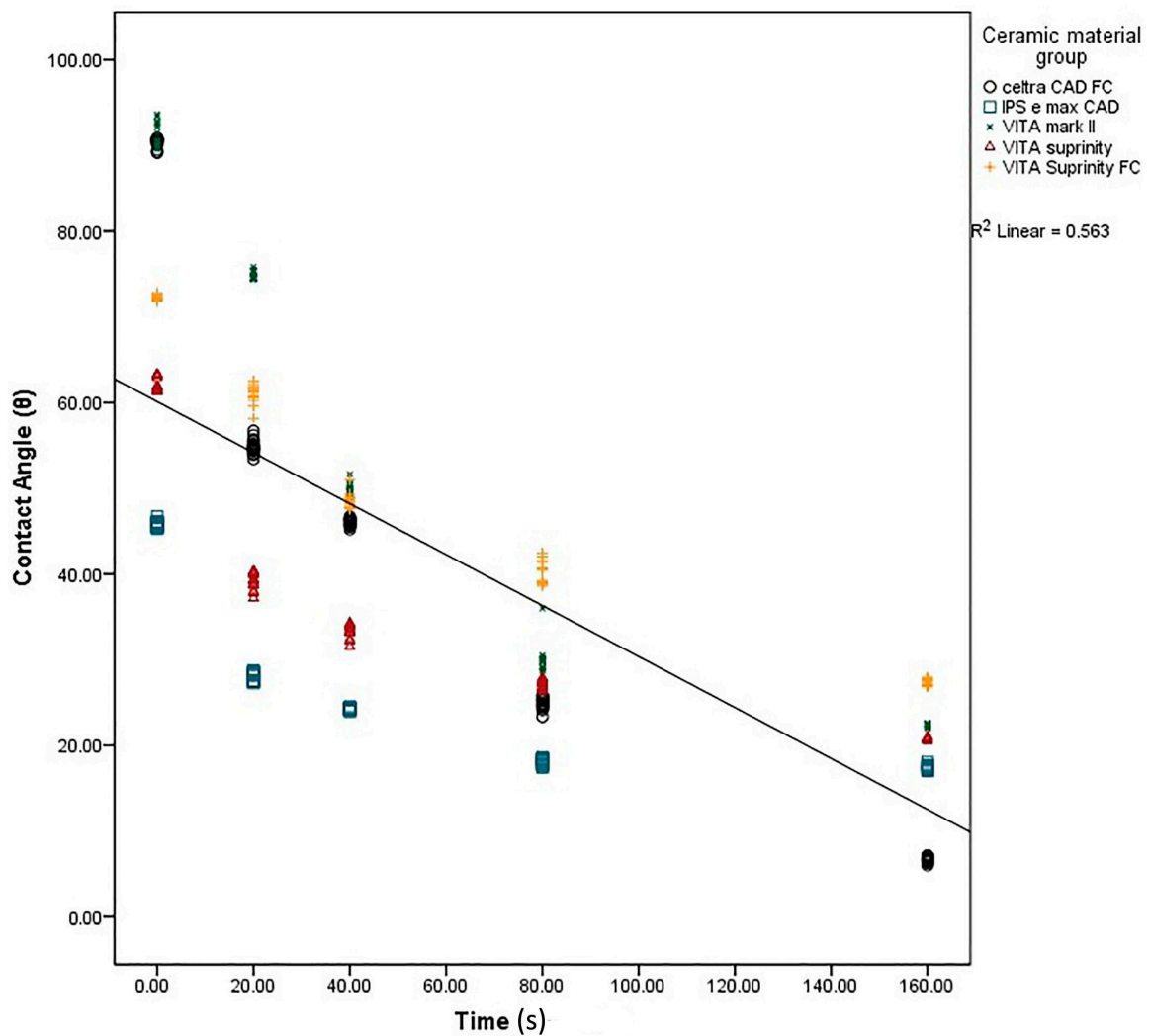


Figure 9. Regression analysis of contact angle at different acid etching durations.

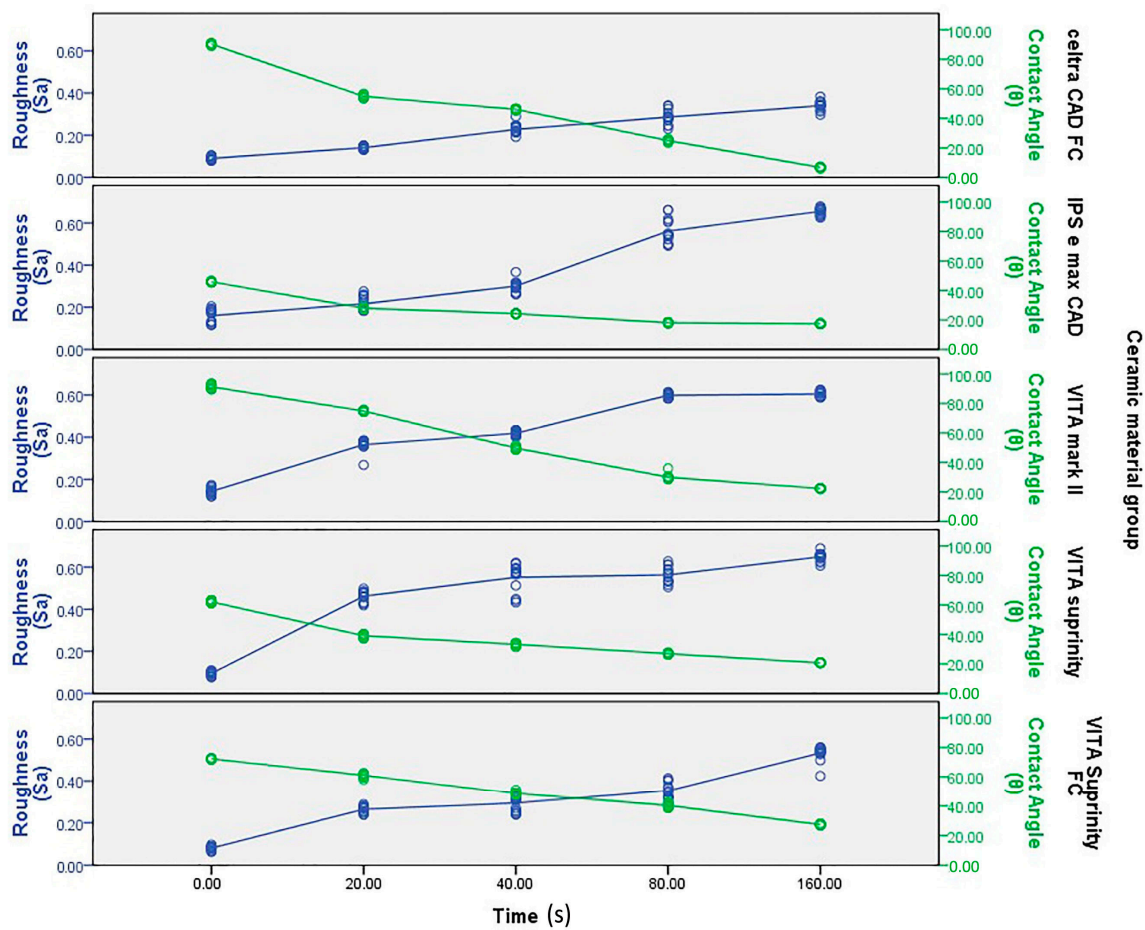


Figure 10. Regression analysis of surface roughness and contact angle at different acid etching durations.

3. Discussion

This laboratory study investigated the effect of the etching duration on the micromorphology, roughness, and wettability of five glass-ceramic based materials. The concentration of the etching acid, HF, has little to do in the clinical scenario because it is pre-determined by the manufacturer, whereas the etching duration is in operator control and can greatly vary, resulting in an increase in surface roughness. Etching of intaglio surface before cementation is an imperative step for better clinical performance of ceramic restorations [25], etching alters surface topography by creating micro- and nano-scale porosities of varying depth and width [26]. The resultant-altered topography increases the surface area for micromechanical bonding (interlocking, retention) with resin composites [27–29]. However, creating a desired surface topography for durable bonding depends on the concentration of etchant [4,5,12] and the etching duration [11,30]. Furthermore, the surface roughness also affects wettability of the ceramic surface and thereby the subsequently applied silanes coupling agent and resin composite. The results of this study displayed a significant change in the surface micromorphology, roughness, and wettability with an increase in the etching duration in all the materials tested; therefore, the tested null hypothesis is rejected. In other words, an increase in the etching time resulted in increased wettability or hydrophilicity. The CA values also showed a significant dependence on the values of S_a .

The current study showed a marked change in the surface micromorphology in terms of pores and grooves pattern, width, and depth. This is considered as critical for bonding ceramics to tooth structure with resin composites, and these observations are in agreement with some previous studies [4,5,27,31–34]. Nagai *et al.* studied the effect of hydrofluoric acid etching on the bond strength

of resin composites to lithium disilicate ceramics and reported improved bond strength. The study attributed the improved bond strength to the roughened surface after etching [35]. Zarone *et al.* [36] and Aboushelib *et al.* [37] also showed micro-morphological changes after the etching of ceramic samples, which improved bond strength. Some studies have stated that the correct choice of resin cement and surface treatment procedure suitable for the type of ceramic is a pre-requisite for improving bond strength [36,37]. Etching with hydrofluoric acid selectively dissolves the surface containing a glass matrix and crystals, resulting in the highest bond strength [12]. In the current study, etching for a short duration of 20 s resulted in the dissolution of the glassy phase predominantly around the crystals and creating small isolated pores and fissures. It is noteworthy that there is no real, serious alternative to HF etching [24]. Some other etching agents for porcelain, such as acidulated phosphate fluoride (APF) and ammonium hydrogen difluoride, have been attempted [26]. However, a study conducted by Poorzamani *et al.* showed higher bond strength with hydrofluoric acid-etched ceramic samples than APF gel-etched samples [38]. In the current study, the hydrofluoric acid treatment of ceramic surfaces for 40 and 80 s resulted in the further loss of the glassy phase around the crystals, which exposed the crystal structure. The SEM images presented topographies predominantly consisting of platelet shaped lithium disilicate and lithium orthophosphate crystals (Figure 6). Prolonged etching for 160 s dissolved the matrix around the crystals, which at this stage appeared as protruding out of the glass matrix. Figure 6 (80 and 160 s etching time) shows the typically elongated, randomly oriented pillars of plate-like lithium disilicate crystals measuring 2.56 to 2.97 μm . This suggests that the matrix dissolves at a faster rate than do crystals, and deeper and wider pores are formed when the surface was exposed for longer etching cycles.

Acid etching is the most commonly employed technique compared to grit-blasting to improve the bond strength (adhesion strength). Etching increases the surface area by creating micropores into which uncured flowable resin penetrates to provide durable micromechanical interlocking [39,40]. Etching also cleans the surface by removing debris and impurities. However, prolonged etching does not significantly increase the bond (adhesion) strength. Some studies have reported a reduction in the shear bond strength on prolonged acid etching, which may be due to the smaller pores and fissures that offer better mechanical interlocking sites than do the wider pores [26,41]. Creating an adequately porous surface is a vital step for durable cementation of the indirect restoration, and this can be achieved by etching the surface for shorter etching cycles. However, the etching duration is always governed by the composition of ceramics. Thus, in the present study, a desirable porous surface for lithium disilicate ceramics was achieved by etching for 20 s.

Etching porcelain with hydrofluoric acid is a gold standard because it creates a rough surface required for micromechanical retention with resin composites [11,12,42]. Posritong *et al.* showed an altered microstructure of IPS e-maxTM glass ceramic and ZirPressTM after etching the surface for different etching times and reported a significant change in flexural strength [43]. Similarly, Sato *et al.* found a significant increase in flexural strength of 5% hydrofluoric acid-etched lithium disilicate ceramics [44]. The surface roughness is a result of the formation of numerous porosities and grooves due to the acid action on the matrix and the crystal structure. The absolute amount of roughness required for ideal bonding is actually not known, but a positive correlation between roughness and etching duration as observed in the present study has been found [4,11,30,45]. Some studies have also found a positive correlation between roughness and bond strength [11,45]. However, over etching can lead to the formation of large and deep porosities (Figure 7) and may affect the bond strength [20,30,42]. Hooshmand *et al.* reported a significant reduction in biaxial flexural strength after etching the IPS empress and IPS empress 2 ceramics for 2 min [46]. Furthermore, the present study found that the width of the porosities increased at a faster rate than did the depth after having been exposed to longer etching cycles, which resulted in relatively large, wide, and shallow pores. The increase in the pore width is because of the dissolution and disintegration of the weaker glassy phase at a faster rate than the crystal phase. This significant loss of glassy phase weakens the ceramic and affects the bond

strength [20,30]. Etching for as low as 20 s resulted in higher mean S_a values than those for the control group specimens. SEM images showed small pores with a large amount of glassy phase (Figure 6).

Wettability is another important factor crucial for the ultimate bond strength of ceramics to resin composites. In a clinical scenario the fabricated ceramic restoration is bonded to natural dentin (or enamel) using resin composite cement, which is hydrophobic in nature. However, in the present study, the ceramic surface was tested for wettability using deionized water that is obviously hydrophilic. The rationale behind using hydrophilic water was that the etched ceramic surface is treated first with a hydrophilic activated silane coupling agent before it is bonded with hydrophobic resin composite cement. The present study suggests a positive correlation between the etching duration and wettability: wettability increased significantly with an increase in the etching time because of an increase in the surface free energy [6]. This is usually attributed to the fact that etching removes surface impurities such as oxides and other inorganic and organic debris which makes the surface readily wettable for the subsequently applied silane coupling agent and resin composite cement [26]. This laboratory study also showed a significant and positive correlation between S_a and wettability. A porous surface with improved wettability allows easy spreading and a reaction of silane and resin composites and thereby results in superior adhesion strength.

4. Materials and Methods

4.1. Materials and Study Design

The lot numbers and manufacturers' details of five silica-based glass ceramics used in this study are listed in Table 3. Ceramic surfaces were exposed to acid etching for four different time intervals with 5% hydrofluoric acid gel for dental use (IPS Ceramic etching gelTM, Ivoclar Vivadent, Schaan, Liechtenstein). The etched samples were examined under a scanning electron microscope (SEM) (JSM-6360LV, JEOL, Tokyo, Japan) to study the pore pattern, width, and depth. Furthermore, the effect of acid etching duration on S_a and wettability was evaluated.

Table 3. Ceramic materials used in the study.

Product	Lot No.	Description	Manufacturer
Celtra	18017131	Zirconia-reinforced (10% by weight) lithium silicate ceramic	DeguDent, Hanau, Germany
e-max	T10332	Lithium disilicate glass ceramic	Ivoclar Vivadent, Schaan, Liechtenstein
Mark II	43660	Feldspathic ceramic	VITA Zahnfabrik, Bad Sackingen, Germany
Suprinity	45960	Zirconia-reinforced (10% by weight) lithium silicate ceramic	VITA Zahnfabrik, Bad Sackingen, Germany
Suprinity FC	47860	Zirconia-reinforced (10% by weight) lithium silicate ceramic	VITA Zahnfabrik, Bad Sackingen, Germany

4.2. Specimen Preparation

Seventy-five rectangular slices measuring 15 ± 0.25 mm \times 11 ± 0.25 mm \times 2 ± 0.25 mm were cut from each material using a low-speed diamond wheel saw (Model 650, Ladd research industries, Williston, VT, USA). The sectioned specimens were polished with various, up to 1000 grit silicon carbide papers in a sequential manner and polished with a polishing liquid in order to remove gross surface scratches and irregularities using Labpol 8-12 (Extex, Enfield, CT, USA). Finally, the specimens were ultrasonically cleaned in distilled water for ten minutes using Qantex 140 (L and R, Kearny, NJ, USA) and then stored in sealed plastic containers.

4.3. Specimen Organization and Etching Procedure

Specimens requiring crystallization (IPS e-max™, and Vita Suprinity™) were crystallized in a ceramic furnace before etching. Fifteen samples from each material were randomly assigned to one control group and four experimental groups ($n = 75$). Control group received no etching, the remaining samples of experimental groups were etched for 20, 40, 80 and 160 s with 5% hydrofluoric acid. All the specimens were etched in well in a fume hood in a ventilated laboratory environment with all safety measures to avoid any acid hazard. The acid was rinsed with copious amount of water for 30 s and neutralized using a neutralizing agent for five min (IPS Ceramic Neutralizing Powder™, Ivoclar vivadent, Schaan, Liechtenstein). The specimens were washed in running water for 30 s and ultrasonically cleaned for 5 min using distilled water. All 15 specimens from each group were tested for roughness and wettability. SEM analysis was done for one sample from each group of respective material.

4.4. Analysis

To study the surface micro-structure of the pores, the samples were examined under a scanning electron microscope (SEM; JSM-6360LV, JEOL, Tokyo, Japan) at $\times 2000$ and $\times 6000$ magnification, respectively. To measure the pore depth and width, etched samples were fractured vertically from the edge of an un-etched surface using a sharp knife with a single hammer impact. The junction of etched surface and the fractured edge was examined, and the depth and width of the pores were measured directly in SEM using image measurement software after tilting the specimen by 45 degrees.

The S_a was measured using a non-contact optical profilometer [47] (Bruker Contour GT-K, Bruker, Berlin, Germany). This system utilizes a nano lens AFM module with a fully automated turret and platform which is programmable in the X, Y and Z directions. The profilometer delivers a laser light in order to guide the operator to select the test area on the specimen. Measurements on four randomly selected areas on each sample were taken, and their mean was calculated and considered as the final S_a value. To perform the measurement, the sample was placed on the platform in such a manner that the measuring surface was perpendicular to the optical beam. The measurement area of $1.261 \text{ mm} \times 0.946 \text{ mm} \times 500 \text{ }\mu\text{m}$ in the X-, Y-, and Z-axes were scanned with a resolution of 100 points/mm after the application of a Gaussian regression filter with a short wavelength pass. The long cutoff wavelength was 0.08 mm (X and Y), the short cutoff wavelength was 0.25 mm (X and Y), and the images were captured in $3\times$ optical zoom using integrated "Vision64" software (Bruker Corporation: Billerica, MA, USA). Several areal surface texture parameter values were measured to characterize the surface topography, which includes S_a (surface roughness), S_p (the maximum surface peak height), S_v (maximum valley or pit depth), S_z (the sum of largest peak height value and largest pit or valley depth), S_q (root mean square value of the sampling area), S_{sk} (the measure of skewness or symmetry in roughness), and S_{ku} (kurtosis of topography height distribution)/(the spread of height distribution). Mean S_a was considered in this study because this parameter gives the arithmetic mean of the heights and depths of the sampling surface.

The surface wettability was evaluated by CA measurement using sessile drop technique [47] (Oneattention, Biolin Scientific, Espoo, Finland). One reading was taken per sample from each group. In the analysis, a 2- μL drop of deionized water was dispensed on to the test surface, and the CA measurements were taken. The dynamic CA was measured with built-in software from the time of initial contact of the water droplet, and the images were captured using a built-in digital camera.

4.5. Statistical Analysis

The mean S_a and CA were analyzed using the one-way ANOVA and the *post hoc* Tukey's test, and the level of significance was 0.05. The linear regression analysis was used to determine the correlation between the etching duration and S_a , the etching duration and CA, and the S_a and CA.

5. Conclusions

The following conclusions were drawn:

(a) An increase in the hydrofluoric acid etching duration significantly alters the surface microstructure and increases the surface roughness and wettability of silica based ceramics;

(b) etching for longer times results in an increased number and width of the pores (Figure 6), and the width of the pores increases at a faster rate than does the depth (Figure 7);

(c) there is a positive correlation between the surface roughness and wettability: an increase in the surface roughness improves wettability.

Further research to perform and analyze the adhesion of ceramics that are etched for different time durations to enamel is recommended.

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Author Contributions: Ravikumar Ramakrishnaiah, Pekka K. Vallittu, Jukka P. Matinlinna, and Abdulaziz A. Alkheraif conceived and designed the experiments; Ravikumar Ramakrishnaiah performed the experiments; Ravikumar Ramakrishnaiah, Abdulaziz A. Alkheraif, and Darshan Devang Divakar analyzed the data; Ravikumar Ramakrishnaiah wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CAD/CAM	computer-aided design/computer-aided machining
SEM	scanning electron microscope
S _a	surface roughness
CA	contact angle
ANOVA	analysis of variance

References

- Ozkurt, Z.; Kazazoglu, E. Zirconia dental implants: A literature review. *J. Oral. Implantol.* **2011**, *37*, 367–376. [[CrossRef](#)] [[PubMed](#)]
- Kohal, R.J.; Klaus, G. A zirconia implant-crown system: A case report. *Int. J. Periodontics. Restorative. Dent.* **2004**, *24*, 147–153. [[PubMed](#)]
- Ho, G.W.; Matinlinna, J.P. Insights on ceramics as dental materials. Part I: Ceramic material types in dentistry. *Silicon* **2011**, *3*, 109–115. [[CrossRef](#)]
- Chaiyabutr, Y.; McGowan, S.; Phillips, K.M.; Kois, J.C.; Giordano, R.A. The effect of hydrofluoric acid surface treatment and bond strength of a zirconia veneering ceramic. *J. Prosthet. Dent.* **2008**, *100*, 194–202. [[CrossRef](#)]
- Ayad, M.F.; Fahmy, N.Z.; Rosenstiel, S.F. Effect of surface treatment on roughness and bond strength of a heat-pressed ceramic. *J. Prosthet. Dent.* **2008**, *99*, 123–130. [[CrossRef](#)]
- Matinlinna, J.P.; Vallittu, P.K. Silane based concepts on bonding resin composite to metals. *J. Contemp. Dent. Pract.* **2007**, *8*, 1–8. [[PubMed](#)]
- O'Brien, W.J. *Dental Materials and Their Selection*, 2nd ed.; Quintessence: Carol stream, IL, USA, 1997; pp. 259–265.
- Lung, C.Y.; Matinlinna, J.P. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. *Dent. Mater.* **2012**, *28*, 467–477. [[CrossRef](#)] [[PubMed](#)]
- Qeblawi, D.M.; Muñoz, C.A.; Brewer, J.D.; Monaco, E.A., Jr. The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement. *J. Prosthet. Dent.* **2010**, *103*, 210–220. [[CrossRef](#)]
- 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. *J. Biomed. Mater. Res.* **2000**, *53*, 297–303. [[CrossRef](#)]

11. Zogheib, L.V.; Bona, A.D.; Kimpara, E.T.; McCabe, J.F. Effect of hydrofluoric acid etching duration on the roughness and flexural strength of a lithium disilicate-based glass ceramic. *Braz. Dent. J.* **2011**, *22*, 45–50. [[PubMed](#)]
12. Bona, A.D.; Anusavice, K.J. Microstructure, composition, and etching topography of dental ceramics. *Int. J. Prosthodont.* **2002**, *15*, 159–167. [[PubMed](#)]
13. Ozcan, M.; Volpato, C.A. Surface conditioning protocol for the adhesion of resin-based materials to glassy matrix ceramics: How to condition and why? *J. Adhes. Dent.* **2015**, *17*, 292–293. [[PubMed](#)]
14. Matinlinna, J.P.; Vallittu, P.K. Bonding of resin composites to etchable ceramic surfaces—an insight review of the chemical aspects on surface conditioning. *J. Oral. Rehabil.* **2007**, *34*, 622–630. [[CrossRef](#)] [[PubMed](#)]
15. Matinlinna, J.P.; Choi, A.H.; Tsoi, J.H. Bonding promotion of resin composite to silica-coated zirconia implant surface using a novel silane system. *Clin. Oral. Implants. Res.* **2013**, *24*, 290–296. [[CrossRef](#)] [[PubMed](#)]
16. Matinlinna, J.; Ozcan, M.; Lassila, L.; Kalk, W.; Vallittu, P. Effect of the cross-linking silane concentration in a novel silane system on bonding resin-composite cement. *Acta. Odontol. Scand.* **2008**, *66*, 250–255. [[CrossRef](#)] [[PubMed](#)]
17. Rosen, M.R. From treating solution to filler surface and beyond: the life history of a silane coupling agent. *J. Coatings. Technol.* **1978**, *50*, 70–82.
18. Matinlinna, J.P.; Lassila, L.V.; Vallittu, P.K. The effect of three silane coupling agents and their blends with a cross-linker silane on bonding a bis-GMA resin to silicized titanium (a novel silane system). *J. Dent.* **2006**, *34*, 740–746. [[CrossRef](#)] [[PubMed](#)]
19. Matinlinna, J.P.; Lassila, L.V.; Vallittu, P.K. The effect of a novel silane blend system on resin bond strength to silica-coated Ti substrate. *J. Dent.* **2006**, *34*, 436–443. [[CrossRef](#)] [[PubMed](#)]
20. Della Bona, A.; Anusavice, K.J.; Hood, J.A. Effect of ceramic surface treatment on tensile bond strength to a resin cement. *Int. J. Prosthodont.* **2002**, *15*, 248–253. [[PubMed](#)]
21. Matinlinna, J.P.; Tsoi, J.K.; de Vries, J.; Busscher, H.J. Characterization of novel silane coatings on titanium implant surfaces. *Clin. Oral. Implants. Res.* **2013**, *24*, 688–697. [[CrossRef](#)] [[PubMed](#)]
22. Kern, M.; Thompson, V.P. Effects of sandblasting and silica-coating procedures on pure titanium. *J. Dent.* **1994**, *22*, 300–306. [[CrossRef](#)]
23. Anusavice, K.J. *Phillips' Science of Dental Materials*, 11th ed.; W.B. Saunders Co: Philadelphia, PA, USA, 1996; pp. 445–458.
24. Matinlinna, J.P. Processing and bonding of dental ceramics. In *Non-Metallic Biomaterials for Tooth Repair and Replacement*, 1st ed.; Vallittu, P., Ed.; Woodhead Publishing Limited: Philadelphia, PA, USA, 2013; pp. 129–160.
25. Della Bona, A.; van Noort, R. Ceramic surface preparations for resin bonding. *Am. J. Dent.* **1998**, *11*, 276–280. [[PubMed](#)]
26. Ho, G.M.; Matinlinna, J.P. Insights on ceramics as dental materials. Part II: Chemical surface treatments. *Silicon* **2011**, *3*, 117–123. [[CrossRef](#)]
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*, 330–336. [[CrossRef](#)] [[PubMed](#)]
28. Ren, D.F.; Luo, X.P. Effect of hydrofluoric acid etching time and resin bonding on the flexural strength of lithium disilicate glass ceramic. *Zhonghua Kou Qiang Yi Xue Za Zhi* **2013**, *48*, 462–466. (In Chinese) [[PubMed](#)]
29. Colares, R.C.; Neri, J.R.; Souza, A.M.; Pontes, K.M.; Mendonça, J.S.; Santiago, S.L. Effect of surface pretreatments on the microtensile bond strength of lithium-disilicate ceramic repaired with composite resin. *Braz. Dent. J.* **2013**, *24*, 349–352. [[CrossRef](#)] [[PubMed](#)]
30. Addison, O.; Marquis, P.M.; Fleming, G.J. The impact of hydrofluoric acid surface treatments on the performance of a porcelain laminate restorative material. *Dent. Mater.* **2007**, *23*, 461–468. [[CrossRef](#)] [[PubMed](#)]
31. Stawarczyk, B.; Hristova, E.; Sener, B.; Roos, M.; Edelhoff, D.; Keul, C. Effect of hydrofluoric acid etching duration on fracture load and surface properties of three CAD/CAM glass-ceramics. *Oral. Health. Dent. Manag.* **2014**, *13*, 1131–1139.
32. Kang, S.H.; Chang, J.; Son, H.H. Flexural strength and microstructure of two lithium disilicate glass ceramics for CAD/CAM restoration in the dental clinic. *Restor. Dent. Endod.* **2013**, *38*, 134–140. [[CrossRef](#)] [[PubMed](#)]
33. Sakaki, T.; Fukushima, T.; Kawai, S.; Matsumoto, M. Effect of physical properties of direct bonding adhesives on bonding to etched enamel. *J. Prosthet. Dent.* **1994**, *71*, 552–559. [[CrossRef](#)]

34. Stacey, G.D. A shear stress analysis of the bonding of porcelain veneers to enamel. *J. Prosthet. Dent.* **1993**, *70*, 395–402. [[CrossRef](#)]
35. Nagi, T.; Kawamoto, Y. Effect of hydrofluoric acid etching on bond strength of composite luting agent to lithium disilicate ceramics material. *Int. Chin. J. Dent.* **2004**, *4*, 100–106.
36. Zarone, F.; Sorrentino, R.; Vaccaro, F.; Traini, T.; Russo, S.; Ferrari, M. Acid etching surface treatment of feldspathic, alumina and zirconia ceramics: A micro-morphological SEM analysis. *Int. Dent. S. Afr.* **2006**, *8*, 1–5.
37. Aboushelib, M.; Ghoniem, M.; Mirmohammadi, H.; Salameh, Z. General principles for achieving adequate bond to all-ceramic restorations. *J. Dent. Oral. Hyg.* **2009**, *1*, 36–41.
38. Poorzamani, M.; Sanaye, V.M.; Alizadeh, S.E.; Kohkan, S. Effect of acidulated phosphate fluoride (APF) etching duration on the shear bond strength between a lithium disilicate-based glass ceramic and composite resin. *J. Res. Dent. Sci.* **2015**, *12*, 1–5.
39. Chen, T.M.; Brauer, G.M. Solvent effects on bonding organo-silane to silica surfaces. *J. Dent. Res.* **1982**, *61*, 1439–1443. [[CrossRef](#)] [[PubMed](#)]
40. Stangel, I.; Nathanson, D.; Hsu, C.S. Shear strength of the composite bond to etched porcelain. *J. Dent. Res.* **1987**, *66*, 1460–1465. [[CrossRef](#)] [[PubMed](#)]
41. Calamia, J.; Vaidyanathan, J.; Vaidyanathan, T.K.; Hirsch, S.M. Shear bond strength of etched porcelains. *J. Dent. Res.* **1985**, *64*, 296.
42. Della Bona, A.; van Noort, R. Shear vs. tensile bond strength of resin composite bonded to ceramic. *J. Dent. Res.* **1995**, *74*, 1591–1596. [[CrossRef](#)] [[PubMed](#)]
43. Posritong, S.; Borges, A.L.S.; Chu, T.G.; Eckert, G.J.; Bottino, M.A.; Bottino, M.C. The impact of hydrofluoric acid etching followed by unfilled resin on the biaxial strength of a glass-ceramic. *Dent. Mater.* **2013**, *29*, e281–e290. [[CrossRef](#)] [[PubMed](#)]
44. Prado Sato, T.; Cotes, C.; Yamamoto, L.T.; Rossi, N.R.; Macedo, V.C.; Kimpara, E.T. Flexural strength of a pressable lithium disilicate ceramic: influence of surface treatments. *Appl. Adhesion Sci.* **2013**, *1*, 1–5.
45. Wolf, D.M.; Powers, J.M.; O'Keefe, K.L. Bond strength of composite to etched and sandblasted porcelain. *Am. J. Dent.* **1993**, *6*, 155–158. [[PubMed](#)]
46. Hooshmand, T.; Parvizi, S.; Keshvad, A. Effect of surface acid etching on the biaxial flexural strength of two hot-pressed glass ceramics. *J. Prosthodont.* **2008**, *17*, 415–419. [[CrossRef](#)] [[PubMed](#)]
47. Ramakrishnaiah, R.; Al kheraif, A.A.; Mohammed, A.; Darshan, D.D.; Kotha, S.B.; Celu, S.L.; Hashem, M.I.; Vallittu, P.K.; Rehman, I.U. Preliminary fabrication and characterization of electron beam melted Ti–6Al–4V customized dental implant. *Saudi. J. Biol. Sci.* **2016**. [[CrossRef](#)]



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