Effect of Hydrofluoric Acid Surface Treatments on Surface Roughness and Three-Point Flexural Strength of Suprinity Ceramic

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Article Info	A B S T R A C T
Article type: Original Article	**Objectives:** This study aimed to evaluate the effects of hydrofluoric acid (HF) concentration and etching time on the surface roughness (SR) and three-point flexural strength of Suprinity and to analyze the surface elements before and after etching.
	Materials and Methods: To measure the SR, 70 specimens of Suprinity ($2\times4\times5mm^3$) were assigned to seven groups (n=10). Six groups were etched for 20, 60, and 120 seconds with 5% and 10% HF and 7th group was the control group. Specimens were evaluated using atomic force microscopy (AFM). One specimen from each group was used to analyze the surface elements using scanning electron microscopy (SEM). For measuring the three-point flexural strength, 60 specimens were divided into six groups (n=10) and etched as previously described. The flexural strength was measured using a universal testing machine. T-test, one-way analysis of variance (ANOVA), and two-way ANOVA were used for statistical analyses (P<0.05).
* Corresponding author: Dental Materials Research Center, Babol University of Medical Sciences, Babol, Iran Email: halagheh@yahoo.com	**Results:** The 10% concentration of HF caused higher SR compared to the 5% HF. The effect of HF concentration on the flexural strength was significantly different in the 20- and 60-second etching groups. Different etching times had no significantly different effect on the SR. With 5% HF, the flexural strength was significantly higher for 20-second etching time than for the etching times of 60 and 120 seconds. With 10% HF, there was a significant difference in flexural strength between etching times of 20 and 120 seconds. The atomic percentage (at%) of silica was enhanced by increasing the etching time.
	Conclusion: The best surface etching protocol comprises 10% HF used for 20 seconds.
	Keywords: Glass Ceramic; VITA Suprinity; Hydrofluoric Acid; Surface Properties; Flexural Strength

INTRODUCTION

Dental ceramics are highly esthetic restorative materials that simulate the optical properties of natural tooth structure [1-3]. All-ceramic prostheses have been widely used in restorative treatments due to suitable physical and mechanical properties, natural-looking appearance, and biocompatibility. These

restorations can be made using computer-aided design and computer-aided manufacturing (CAD/CAM) systems. The traditional methods of ceramic fabrication are unpredictable, time-consuming, and technique sensitive because of the presence of several variables; CAD/CAM can be considered as a good alternative [1,3,4]. Moreover, the fabrication time of high strength ceramics may be decreased by 90% using CAD/CAM. The blocks manufactured by industrial methods are more consistent with minimal deficiencies [3,5].

Adequate retention can be obtained for lithium silicate ceramic restorations through the application of a silane coupling agent before cementation with a resin cement as well as ceramic surface treatment with acid etching [1,6].

In 1983, Horn [7] stated that the surface free energy (SFE), surface roughness (SR), and subsequently bond strength enhance when the surface of a porcelain veneer is etched with hydrofluoric acid (HF) [7].

All glass ceramic surfaces must be etched using HF before cementation to increase the SFE and SR. Generally, ceramic surfaces are inert and in need of SR and SFE for proper bonding [8].

In-vitro studies have suggested the positive effect of HF etching on the surface topography (increased SR), which provides micromechanical retention for the luting cement [1,9]. HF reacts with the silica-containing glass matrix and consequently forms hexafluorosilicates. Etching of the glassy matrix reveals the crystalline microstructure; therefore, the roughness of the ceramic surface enhances, which is advantageous for the micromechanical retention of resin cements [1,9,10].

On the other hand, HF etching can decrease the flexural strength of ceramics [1]. The flexural strength is an important mechanical property to evaluate the strength of brittle materials; ceramics are much weaker in tension compared to compression [11,12]. The zirconia particles reinforce the ceramic structure through crack interruption. The first zirconia-reinforced lithium silicate ceramic is Suprinity. This porcelain has been provided only for CAD/CAM technology. This modern glass ceramic is enriched with zirconia [8-12% zirconia (ZrO_2), 56-64% silicon dioxide (SiO_2), and 15-21% lithium oxide (Li_2O)]. It has been found that this recently extended generation of glass-ceramic materials incorporates the glass ceramic with positive properties of zirconia [12-14]. Some studies have investigated the effects of different HF etching concentrations or times on the flexural strength and SR of ceramic materials. However, no article has compared 5% and 10% HF concentrations and different etching times. To date, the optimal HF etching time and concentration have not been found for glass ceramic restoration [1,9]. Therefore, it is important to find the proper HF etching time and concentration that have no negative effect on the flexural strength [1]. Thus, this study aimed to evaluate the effects of different HF concentrations and etching times on the SR and three-point flexural strength of Suprinity and to analyze the surface elements before and after etching.

The null hypotheses of the current study were:
1- Increasing the etching time does not increase the SR.
2- Increasing the acid concentration does not increase the SR.
3- Increasing the etching time enhances the flexural strength.
4- Increasing the acid concentration enhances the flexural strength.
5- Changing the etching time and acid concentration does not alter the surface elements.

MATERIALS AND METHODS

Specimen preparation for SR and surface element analysis:

Firstly, 70 specimens of ceramic with dimensions of $2 \times 4 \times 5mm^3$ were prepared from 70 No.14 ceramic blocks ($12 \times 14 \times 18mm^3$; EC4SO10101, VITA Zahnfabrik, Germany) using a water-cooled diamond disk mounted on a low-speed saw machine (Delta precision sectioning machine, Mashhad, Iran) [9]. Secondly, 70 specimens were divided into seven groups (n=10), consisting of 6

experimental groups and one control group [15]. The ceramic surface was ground using a blue diamond bur (1013615103748615c, D&Z, Italy) to prepare the standard surface [3]. Then, all specimens were wet-finished using an 800-grit silicon carbide paper to remove the irregularities and scratches and to simulate the CAD/CAM-milled surfaces. The specimens were crystallized in a ceramic furnace (Vita SMART. FIRE, VITA Zahnfabrik, Germany) before etching according to the manufacturer's recommended temperatures (Table 1) [14].

Table 1. Crystallization cycle of Suprinity

Initial chamber temperature	400°C
Time at the initial temperature	8 minutes
Temperature rate increase	55°C/minutes
Crystallization temperature	840°C
Holding time	8 minutes
Ending temperature °C	680°C

The six experimental groups were divided into 2 main groups to be etched with concentrations of 5% and 10% handmade HF. Each group was further divided into 3 subgroups based on etching times of 20, 60 and 120 seconds [3]. Group 7 was left untreated. Handmade acids were used in order to eliminate possible interference from other compounds in the acid production of different factories.

This was done by adding 3cc and 6cc distilled water to 1cc of 40% HF (B0710538231; Merck KGaA, Darmstadt, Germany) for preparation of 5% and 10% acid concentrations, respectively. After etching for the specified time-spans, all specimens were rinsed with air-water spray for 30 seconds. Then, they were ultrasonically cleaned in distilled water for 5 minutes to remove the residual salts, placed in 99% alcohol, and then dried with air spray [3].

Next, the specimens were evaluated using atomic force microscopy (AFM, Nanosurf easyScan 2, Nanoscience Instruments Inc., Liestal, Switzerland). AFM images were obtained through measuring the force on a sharp tip, created by the proximity to the surface of the sample. After that, The SR was visualized (Fig. 1) [16], and the height of the highest point, the depth of the deepest point, and the mean of the SR (Ra) were determined with a precision of 10nm. One specimen from each group was used for surface element analysis using scanning electron microscopy (SEM; Rontec GmbH, Berlin, Germany) with energy-dispersive X-ray (EDX) analysis to identify the segregated and residual elements.

Specimen preparation for three-point bending test:

Sixty $2 \times 2 \times 15 mm^3$ ceramic specimens were prepared and grouped similar to the samples used for SR and surface element analysis, described above. Etching was performed on a selected surface of $2 \times 15 mm^2$ in each sample [9].

These specimens were then tested for three-point flexural strength in a universal testing machine (KOOPA TB-5T, Sari, Iran) connected to a 200-kg load cell. The etched surface of each specimen was faced downward and placed flat on a mounting jig with round supporting rods set 12mm apart [1,9].

The center of the specimen was loaded with a round chisel (radius of 3mm) at a crosshead speed of 0.5 mm/minute until fracture occurred [1,9]. Then, the width and thickness of the porcelain at the fracture line were measured using a digital caliper (Shinwa digital caliper; Niigata-ken, Japan). The resultant figure was in kiloNewton (kN), and the three-point flexural strength was calculated in megapascal (MPa) as follows:
$3 \times load \times length / 2 \times width \times thickness^2$

Statistical analysis:

T-test was used to compare the effect of different HF concentrations on the three-point flexural strength. In addition, one-way analysis of variance (ANOVA) was applied to compare the effect of different etching times on the three-point flexural strength and to compare the effect of various HF concentrations and etching times on the SR. Two-way ANOVA was used to evaluate the interactions among the factors.
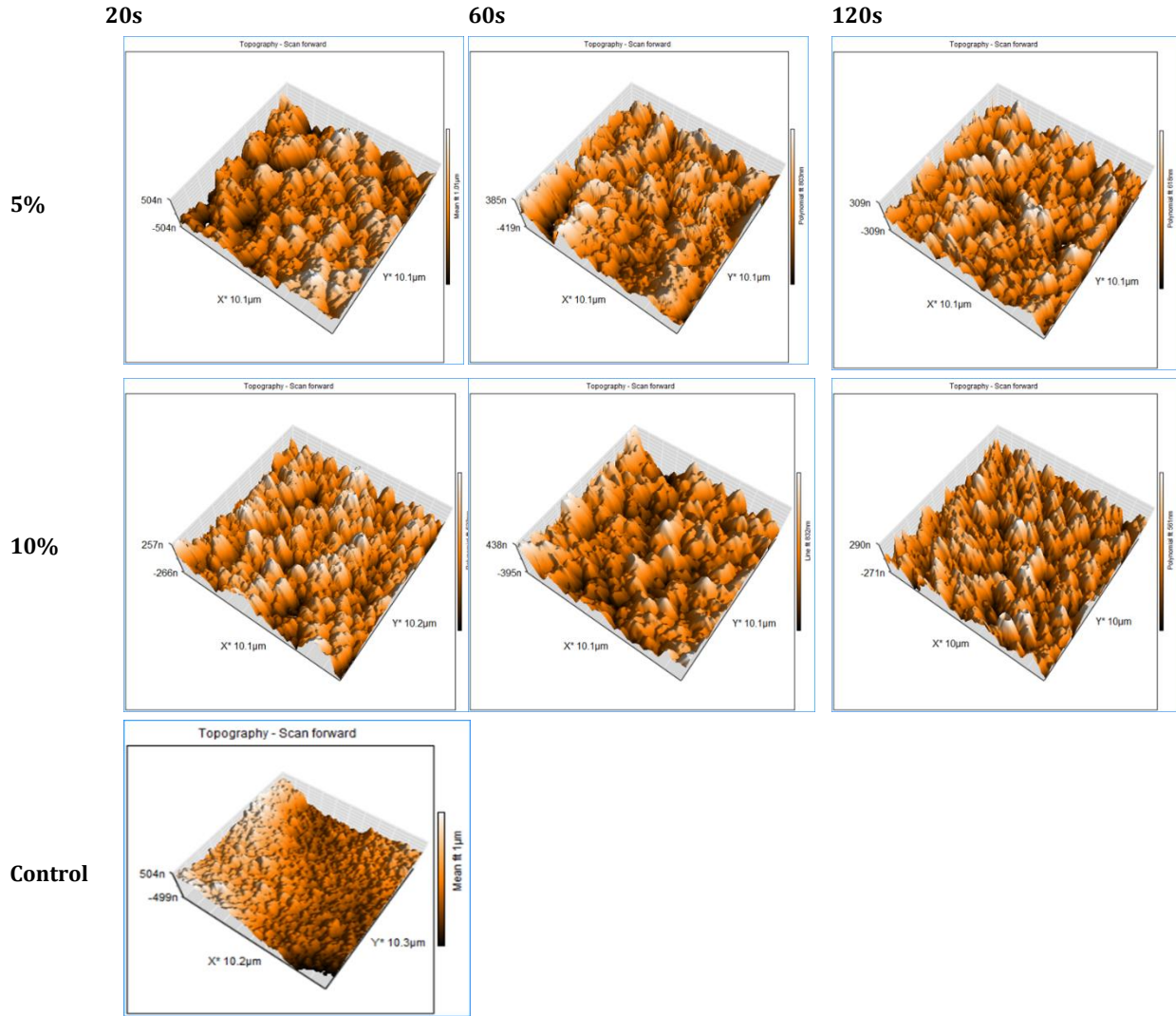
Fig. 1. Surface roughness (SR) atomic force microscopic (AFM) images before and after etching with different acid concentrations and etching times (second)

RESULTS

Tables 2 and 3 show the mean, standard deviation (SD) of SR and flexural strength in the tested groups. SR showed a significant difference between 5% and 10% HF (P<0.001). At all time points, the 10% acid caused a higher SR compared to the 5% acid concentration (P<0.05).

At the other time points, except for the 120-second etching group, HF concentration had a significant effect on the flexural strength of the samples (P>0.05). Various etching times had no significant effect on the SR of the specimens (P>0.05).

Table 2. Mean and standard deviation (SD) of surface roughness (SR) in 5 and 10% hydrofluoric acid (HF) with different etching times

Time (s)	5% HF	10% HF
20	58.40±27.07 [aA]	112.92±56.78 [aB]
60	64.24±25.15 [aA]	137.81±80.78 [aB]
120	63.48±14.07 [aA]	150.45±70.90 [aB]
Control	16.47±6.70 [b]	

Different lowercase letters indicate a significant difference (P<0.05) among etching times with the same acid concentration. Different capital letters show a significant difference (P<0.05) among acid concentrations at the same time point

Table 3. Mean and standard deviation (SD) of flexural strength (MPa) in different hydrofluoric (HF) concentrations and etching times

Time (s)	5% HF	10% HF
20	347.53±43.63 [aA]	300.57±33.64 [aB]
60	302.27±30.85 [bA]	268.54±29.67 [abB]
120	271.99±22.29 [bA]	244.95±34.66 [bA]

Different lowercase letters indicate a significant difference (P<0.05) among etching times with the same acid concentration. Different capital letters indicate a significant difference (P<0.05) among acid concentrations at the same time point

Acid etching significantly increased the SR of the specimens regardless of the etching time and acid concentration. Different etching times significantly affected the flexural strength in some groups. With the 5% concentration of HF, the flexural strength was significantly higher for the 20-second etching time compared to the 60-second (P=0.014) and 120-second (P=0.00) etching times. Nevertheless, there was no significant difference between the 60- and 120-second acid etching (P>0.05). With the 10% HF concentration, there was a significant difference in flexural strength only between etching times of 20 and 120 seconds (P=0.002). According to the two-way ANOVA, the combined effect of acid concentration and etching time on the flexural strength and SR was not significant (P>0.05). The highest level of SR was observed in the 120-second etching group with 10% HF. The highest level of three-point flexural strength was found in the 20-second etching group with 5% HF.

DISCUSSION

The results of AFM demonstrated a significant difference between etched and non-etched groups, but there was no significant difference in the SR with different etching times; therefore, the first null hypothesis was proven. The SR results were significantly different with different HF concentrations; thus, the second null hypothesis was rejected. The three-point flexural strength results represented significant differences in the flexural strength with different etching times and HF concentrations; therefore, the third and fourth null hypotheses were rejected.

A combination of chemical and mechanical retention should be present for a reliable bonding between ceramics and resin cements. Porcelain surface treatments cause a change in the SR, increasing the micromechanical retention of resin cements [1,9,17,18]. HF etching generates undercuts, micro-porosities, and grooves through the exposure of the crystalline phase and selective dissolution of the glassy matrix, thereby increasing the surface area for bonding and micromechanical retention when combined with a resin cement [1,2]. Therefore, HF was used to produce SR in the present study.

It has been suggested that acid concentrations and etching times must be determined for each specific porcelain type to achieve optimal bonding; the manufacturer's recommendation is 20 seconds. [10,18-20]. It is important to find proper HF concentration and etching time needed to produce the SR required for micromechanical retention without any negative effect on the flexural strength [1,9]. Flexural strength is one of the most important mechanical properties for evaluating brittle ceramic materials [11,12]. Several studies have been conducted to evaluate the appropriate HF concentration or etching time for various ceramics types.

In 1993, Yen et al [15] evaluated the effect of etching with HF on the three-point flexural strength of feldspathic and cast glass ceramics. They concluded that etching increases the retention of porcelain veneer without reducing the flexural strength, which is different from the results of the current study. Similar to the present study, Addison et al [21] stated that enhancing the etching time and acid concentration causes defects in the porcelain surface, leading to a clear decrease in the flexural strength of ceramics [21].

Zogheib et al [1] stated that after HF etching, the flexural strength of lithium disilicate-based glass ceramics declines, which might be due to the glass phase of lithium disilicate crystals. In this study, etching with HF increased the SR of all groups, even in the time group of 20 seconds recommended by the manufacturer.

Numerous studies have evaluated different ceramics and have confirmed that HF etching weakens glass ceramics as the etching time and HF concentration increase [1,21,22]. Prochnow et al [9] reported that three-point flexural strength and SR are not affected by etching with different acid concentrations. Nevertheless, the highest SR was obtained using 10% HF for 120 seconds; this protocol significantly reduces the flexural strength. If the aim is to achieve the highest flexural strength, the best result can be achieved with 5% HF used for 20 seconds.

However, if the aim is to provide the best bond with the highest flexural strength, it is necessary to measure the ceramic bond. Researchers have expressed that etching mechanisms vary based on the type of acid and etching time as well as the ceramic microstructure and composition [1]. Accordingly, it is difficult to compare the present results to those of previous studies that applied different types of ceramics and etching protocols. In this study, the energy dispersive X-ray analysis (EDAX) was used to measure the surface elements of ceramics.

Table 4. Surface element analysis of Suprinity before and after etching with different acid concentrations and etching times (second)

Elements (at%)*	5% hydrofluoric acid				10% hydrofluoric acid		
	0s	20s	60 s	120s	20s	60s	120s
O$_2$	76.83	73.80	74.78	72.18	72.44	68.20	74.52
F	0.03	0.03	0.03	0.03	0.05	0.02	0.05
Al	1.03	1.03	0.84	1.00	0.89	1.27	0.84
Si	18.85	21.37	20.79	22.65	22.51	25.55	20.86
P	0.59	1.03	1.11	1.21	1.41	1.31	0.95
Zr	2.48	2.62	2.41	2.76	2.64	3.48	2.75
La	00.00	0.12	0.03	0.17	0.06	0.15	0.03

*at%: atomic percentage

O$_2$: Oxygen; F: Fluoride; AL: Aluminium; Si: Silisium; P: Phosphor; Zr: Zirconium; La: lanthanum

Though the energy-dispersive spectrometers can be applied down to atomic number 6 (carbon), they usually are appropriate for all elements down to atomic number 11 (sodium) [23]. Hence, the EDAX is not applicable for detection of lithium with atomic number 3. The atomic percentage (at%) of silica slightly increased with the enhancement of etching time; thus, the fifth hypothesis was accepted. Fluoride percentage was approximately equal before and after etching, indicating that the procedure used in the current study to clean the etched surfaces has been successful (Table 4). One limitation of the present study that should be taken into consideration is that the three-point bending test does not reflect the actual strength in the clinical situation because of the different environmental and loading conditions. Hence, it is recommended to consider the clinical conditions such as wet and cyclic nature of the oral environment in

further studies [1,9].

CONCLUSION

According to the findings of the present study, it can be concluded that the proper surface etching protocol, which provides adequate SR without jeopardizing the porcelain flexural strength, comprises 10% HF used for 20 seconds.

CONFLICT OF INTEREST STATEMENT

None declared.

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