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Effect of Ceramic Etching Protocols on Resin Bond Strength to a Feldspar Ceramic

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Clinical Relevance

Acid neutralization following ceramic etching with hydrofluoric acid appears to not impair adhesion of resin cement to hot-pressed leucite-reinforced feldspar ceramic.

SUMMARY

This study sought to evaluate the resin microtensile bond strength (MTBS) stability of a leucite-reinforced ceramic after different ceramic etching protocols. The microtensile test had 40 ceramic blocks (5×5×6 mm) assigned to five groups (n=8), in accordance with the following surface etching protocols: NE non-etched (control); 9HF: hydrofluoric (HF) acid etching (9%HF)+wash/dry; 4HF: 4%HF+wash/dry; 5HF: 5%HF+wash/dry; and 5HF+N: 5%HF+neutralizer+wash/dry+ultrasonic-cleaning. Etched ceramic surfaces were treated with a silane agent. Next, resin cement blocks were built on the prepared ceramic surface and stored for 24 hours in distilled water at 37°C. The specimens were then sectioned to obtain microtensile beams (32/block), which were randomly assigned to the following conditions, nonaged (immediate test) and aged (water storage for 150 days plus 12,000 thermal cycles), before the microtensile test. Bond strength data were submitted to one-way analysis of variance and Tukey test (α=0.05). Additional ceramic samples were subjected to the different ceramic etching protocols and evaluated using a scanning electron microscope (n=2) and atomic force microscopy (n=2). Aging led to a statistically significant decrease in the MTBS for all groups, except the untreated one (NE). Among the groups submitted to the same aging conditions, the untreated (NE) revealed inferior MTBS values compared to the 9HF and 4HF groups. The 5HF and 5HF+N

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groups had intermediate mean values, being statistically similar to the higher values presented by the 9HF and 4HF groups and to the lower value associated with the NE group. The neutralization procedure did not enhance the ceramic/resin cement bond strength. HF acid etching is a crucial step in resin/ceramic bonding.

INTRODUCTION

Feldspar-based ceramic restorations, which can be etched by hydrofluoric (HF) acid, have shown high rates of survival.[1,2] According to the literature, these positive clinical outcomes seem to be associated with achieving a strong and stable bond between the tooth structure/resin cement as well as between the resin cement/ceramic surface.[1,3-7] Briefly, the bond between these restorations and the tooth structure is obtained through the application of phosphoric acid followed by the use of an adhesive system.[1,5] Meanwhile, the bond between resin cement and the ceramic is accomplished by HF acid etching followed by the use of a silane agent, which allows the establishment of both mechanical interlocking and chemical interaction between the materials.[4,5,8-11]

Typically, HF acid etching can appreciably alter the microstructure as well as the surface topography of feldspar-based ceramics, producing different pore sizes and geometries, depending upon the acid concentration and etching time.[12,13] Moreover, after these ceramics have been etched by HF acid and rinsed with water, precipitates are formed that remain on the surface and within its porosities and irregularities making resin bonding more challenging.[4,14-18] The use of neutralizing agents has been suggested[17] to solve this problem and to prevent the continuous etching effect of the acid, as well as the overall acidic environment that could affect resin cement polymerization.[15] Hence, acid precipitations are generated after the reaction between the HF acid and the salt used in the neutralization process, leading to the formation of sodium fluoride and unstable carbonic acid ($NaHCO_3 + HF \Leftrightarrow NaF + \langle H_2CO_3 \rangle$). These precipitates remain on the ceramic surface, hindering the penetration of resinous materials into the irregularities to obtain mechanical interlocking.[15] Taken together, the use of neutralizing agents prior to cementation is still debatable, given the lack of consensus in the literature about its real benefits. Therefore, the aims of this study were to 1) evaluate the bond strength between resin cement and a hot-pressed leucite-reinforced feldspar ceramic submitted to different etching protocols, a neutralizing agent, and aging conditions and 2) assess the changes in the ceramic microstructure and surface topography after the different etching protocols. The tested hypotheses were as follows: 1) the surface conditioning protocols and neutralizing agent would not influence the bond strength values; 2) the surface conditioning protocols would not alter the ceramic microstructure and surface topography; and 3) the thermal cycling aging would influence the bond strength values, independently of the etching protocol.

METHODS AND MATERIALS

Ceramic Block Preparation and Etching Protocols

Sixty (5×5×6 mm) blocks were made with vegetal wax (GEO, Renfert, Hilzingen, Germany). Then, using hot-pressed leucite feldspar-reinforced ceramic ingots (VITA PM9, VITA Zahnfabrik, Bad Säckingen, Germany), 60 ceramic blocks were obtained following the manufacturer's instructions. The ceramic bonding surface of each block was wet-finished with 600-1200 grit silica carbide paper (3M, St Paul, MN, USA) for 60 seconds in a polishing machine (EXTEC Labpol 8-12, Extec Corp, Enfield, CT, USA).

The ceramic blocks were allocated into five groups (N=12/group), in accordance with the ceramic etching protocol and aging conditions (Table 1). Forty blocks were used in the microtensile test (n=8/group); 10 blocks (n=2/group) were used for scanning electron microscopy (SEM) evaluation; and 10 blocks (n=2/group) were used for atomic force microscopy (AFM) evaluation. For the 5%HF+neutralizer+wash/dry+ultrasonic-cleaning (5HF+N) group, the neutralizing agent (Kit IPS Ceramic, Ivoclar-Vivadent, Schaan, Liechtenstein) was applied following the manufacturer's instructions. A 3-methacryloxypropyltrimethoxysilane (MPS)–based silane agent was applied onto the surface of all the etched ceramic blocks (Porcelain Primer, Bisco, Schaumburg, IL, USA).

Resin Cement Block Preparation

Upon ceramic surface etching, the blocks were inserted into an addition silicone mold (Elite HD, Zhermack, Badia Polesine, Italy) to a depth of 5 mm, keeping the etched surface up. A resin cement (Panavia F2.0, Kuraray, Okayama, Japan) was manipulated in a 1:1 ratio, applied on the etched surface, occupying all the space created in the silicone material, and photoactivated for 40 seconds with a quartz-tungsten-halogen unit (XL 3000, 3M,

Table 1: *Study Design*[a]

	Ceramic Etching Protocols	Aging	Groups
NE	Nonetched (control)	No	NE-dry
		Yes	NE-aged
9HF	9% Hydrofluoric acid during 1 min + washing[b] + drying[c]	No	9HF-dry
		Yes	9HF-aged
4HF	4% Hydrofluoric acid during 1 min + washing + drying	No	4HF-dry
		Yes	4HF-aged
5HF	5% Hydrofluoric acid during 1 min + washing + drying	No	5HF-dry
		Yes	5HF-aged
5HF+N	5% Hydrofluoric acid during 1 min + neutralizing agent (N) + washing/drying + sonic cleaning for 5 min	No	5HF+N-dry
		Yes	5HF+N-aged

Abbreviations: NE, nonetched; HF, hydrofluoric acid; N, neutralizer.
[a] *9% Hydrofluoric acid: Ultradent Porcelain Etch (Ultradent Products Inc, South Jordan, UT, USA); 4% hydrofluoric acid: Porcelain Etchant (Bisco, Schaumburg, IL, USA); 5% hydrofluoric acid and neutralizer (neutralizing powder): Kit IPS Ceramic (Ivoclar-Vivadent, Schaan, Liechtenstein).*
[b] *Washing with oil-free air-water spray for 20 seconds.*
[c] *Drying with air spray for 20 seconds.*

St Paul, MN, USA) through the upper surface. Next, the resin cement/ceramic block was removed from the silicone mold and the other bonded surfaces were photoactivated for 40 seconds. Finally, the assemblies were stored at 37°C in distilled water for 24 hours.

Sample Preparation, Aging, and Microtensile Bond Strength Test

The blocks were fixed with cyanoacrylate adhesive gel (Super Bonder Gel, Loctite, Dusseldorf, Germany) to a metallic device that was then attached to a sectioning machine (Labcut 1010, Extec, Enfield, CT, USA). The blocks were positioned perpendicularly to the diamond disc and four cuts of 1-mm thickness were made. The blocks were then rotated 90° and an additional four cuts of similar dimension were done to obtain microtensile beams with an adhesive area of 1 mm^2 and 10 mm in length. The beams located at the outer part of the blocks were discarded. Half of the specimens were submitted immediately to the microtensile bond strength test (without aging groups) in a universal testing machine (EMIC DL 2000, São José dos Pinhais, PR, Brazil) at a crosshead speed of 1 mm/min, while the remaining specimens were submitted to an aging protocol involving storage in distilled water at 37°C for 150 days followed by 12,000 thermal cycles of alternates baths at 5°C and 55°C, for 30 seconds each, with intervals of two seconds between them. After aging, the samples were tested as previously described.

Bond strength was calculated using the formula $\sigma = F/A$, where σ is the bond strength (MPa), F is the load to fracture (N), and A is the adhesive area (mm^2). The adhesive area of each specimen was measured prior to the test with a digital caliper (Starrett, Itu, SP, Brazil).

Failure Analysis

After the microtensile test, all specimens were examined under a stereomicroscope (Discovery V-20, Zeiss, Germany) at 50× magnification to determine the failure mode. The failures were classified as Adhesive (Adhes)—failure in the interface between resin cement and ceramic; Cohesive of resin cement (Cohes-cem)—cohesive failure of the resin cement; Cohesive of ceramic (Cohes-cer)—cohesive failure of the ceramic; and Mixed (Mix)—adhesive failure associated with a cohesive failure.

Statistical Analysis

For statistical analysis, the bond strength means of the samples (repetitions) from each block were calculated, considering each block (n=8) as the experimental unit.[19] The bond strength means of aged groups and not aged groups were compared by one-way analysis of variance (ANOVA) and Tukey tests using the software Statistix 8.0 (Analytical Software, Tallahassee, FL, USA). The comparison between nonaged (immediate) vs aged groups submitted to the same etching protocol was performed by Student *t*-test. All analyses were done at the 5% significance level. Specimens with cohesive failure were not included in the statistical analysis. Pretest failures received an arbitrary value of 2 MPa, which corresponds to half of the minimal bond strength value observed during the microtensile test.[7,20-22]

Table 2: *Means and Standard Deviations of the Bond Strength Data and Tukey and Student* t*-Test (5% Significance Level)*

Ceramic Etching Protocol	Aging: No[a]	Aging: Yes[b]	*p*-Value[c]
NE	3.4 ± 1.6 C	2.3 ± 0.5 B	0.0844
9HF	13.7 ± 2.1 A	8 ± 4.8 A	0.0077
4HF	15.2 ± 2.7 A	9 ± 4.1 A	0.0032
5HF	16.8 ± 2.2 A	6 ± 4.9 AB	0.0001
5HF+N	10.6 ± 2.2 B	5.2 ± 2.9 AB	0.0010

Abbreviations: NE, nonetched; HF, hydrofluoric acid; N, neutralizer.
[a] *Comparison for nonaged groups using one-way analysis of variance (ANOVA) and Tukey tests: different letters indicate statistically significant differences.*
[b] *Comparison for aged groups using one-way ANOVA and Tukey tests: different letters indicate statistically significant differences.*
[c] *Comparison for nonaged vs aged groups, for each etching method, using Student* t*-test:* $p < 0.05$ *indicates statistical difference.*

Micromorphological Analysis—SEM and AFM

After ceramic etching, four blocks from each group were analyzed by SEM (n=2) and AFM (n=2) to assess changes in surface topography. For SEM, the samples were mounted onto aluminum stubs, sputter-coated with gold, and evaluated under a SEM (JEOL, JSM-T330A, Jeol Ltd, Tokyo, Japan) at different magnifications. For AFM (Bruker BioScope Catalyst, Santa Barbara, CA, USA), the images (20 μm×20 μm) were collected in peak force tapping mode using RTESPA probes (Bruker, radius nominally 8 nm, k=40 N/m). AFM micrographs were analyzed using a scanning probe microscopy data analysis software (Gwyddion™, version 2.33, GNU, Free Software Foundation, Boston, MA, USA).

RESULTS

One-way ANOVA revealed a significant influence of the ceramic etching protocols for both immediately tested ($p<0.0001$) and aged groups ($p=0.0001$) (Table 2).

Among nonaged groups, all the etching protocols tested promoted higher bond values (10.6-16.8 MPa) than did the control (3.4 MPa). The group etched by 5HF+N (dry condition) presented lower (10.6 MPa) bond values than did its counterpart (without neutralization; ie, 5HF [16.8 MPa]). After aging, the group that was subjected to neutralization (5HF+N) had values (5.2 MPa) similar to that of the nonetched group (2.3 MPa).

When comparing the same etching protocols before and after aging, the Student *t*-test revealed that aging led to a significant decrease in the bond strengths of all the etching protocols, except the untreated (nonetched [NE]) group (Table 2). The failure analysis is depicted in Table 3. All of the pretest failures were adhesive (Table 3). SEM micrographs revealed very similar microstructures and topographical patterns, regardless of the HF acid concentration used (Figure 1). AFM three-dimensional topographical analyses further confirmed the morphological findings provided by SEM.

DISCUSSION

HF acid application followed by a silane coupling agent has been recommended as the main conditioning protocol of the intaglio surface of feldspar-based ceramic restorations.[5,8-10,23] However, different HF acid concentrations can change both the pH and the

Table 3: *Number and Percentage of the Pretest Failures and Failure Types*

Groups	Aging	No. of Pretest Failures	Type of Failure (%)[a]: Adhesive	COHES[cem]	COHES[Cer]	Mixed
NE	No	13	13 (40.6)	1 (3.2)	0 (0)	18 (56.2)
9HF		0	0 (0)	0 (0)	0 (0)	32 (100)
4HF		0	0 (0)	0 (0)	0 (0)	32 (100)
5HF		0	0 (0)	2 (6.3)	1 (3.2)	29 (90.5)
5HF+N		0	0 (0)	0 (0)	3 (6.3)	29 (93.7)
NE	Yes	23	23 (71.8)	2 (6.3)	1 (3.2)	6 (18.7)
9HF		5	5 (15)	0 (0)	0 (0)	27 (85)
4HF		5	16 (50)	3 (9.4)	0 (0)	13 (40.6)
5HF		16	5 (15.60)	0 (0)	4 (12.5)	23 (71.8)
5HF+N		11	11 (34.3)	0 (0)	0 (0)	21 (65.6)
Total			73 (22.8)	8 (2.5)	9 (2.8)	230 (71.8)

Abbreviations: NE, nonetched; HF, hydrofluoric acid; N, neutralizer.
[a] *Adhesive: failure at the interface between resin cement and ceramic; COHES[cem]: cohesive failure of the resin cement; COHES[Cer]: cohesive failure of the ceramic; Mixed: adhesive failure combined with cohesive failure.*

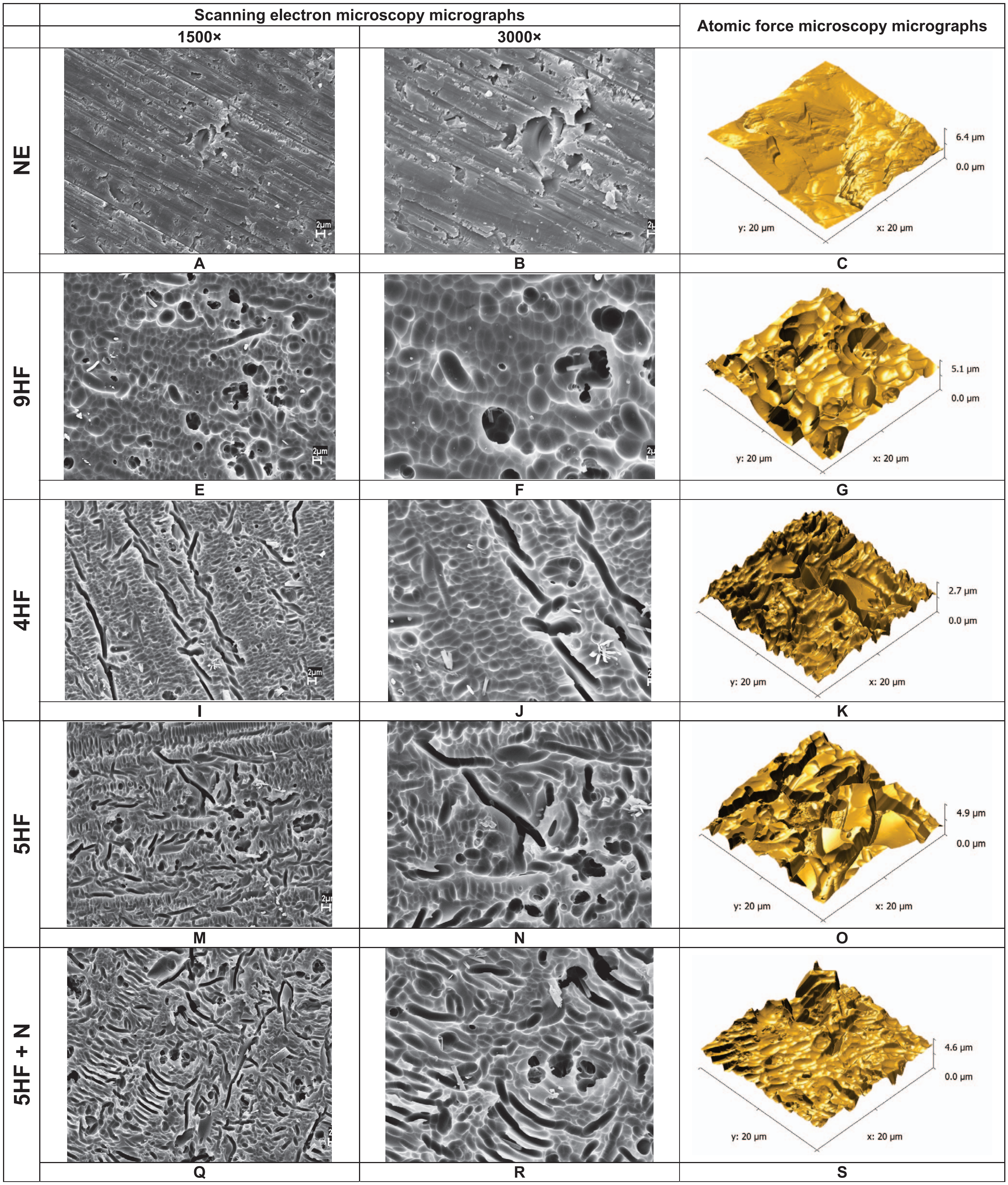

Figure 1. *Representative SEM micrographs and AFM 3D topography images of the ceramic surfaces submitted to the different acid etching protocols. The A, B, and C images show the control group with no surface alteration topography after etching protocol. The other images (E-S), correspond to different acid etching protocols, presenting similar surface topography modification.*

ceramic surface energy, affecting the bonding process.[13,14] In addition, the use of products for neutralizing the pH of the ceramic surface after etching is still a very debatable topic.[14,15]

Our data revealed a significant influence of the different ceramic etching protocols on the resin/ceramic bond strength (Table 2), counter to the first hypothesis of the study. Based on the results, the nonaged groups 4HF, 5HF, and 9HF showed higher bond strength values than did the NE and 5HF+N groups. Meanwhile, after aging, those groups were statistically similar: in other words, the neutralization procedure did not enhance ceramic/resin cement bond strength. The improved results obtained after ceramic etching relate to the fact that the HF acid selectively attacks the glassy phase of the ceramic, changing its surface topography, which in turn provides sites for mechanical interlocking between the resin cement and the ceramic.[5,9-11,23] Furthermore, HF acid etching increases the surface energy of the ceramic, augmenting its adhesive potential.[5,9,10] Additionally, silane agents based on MPS present molecules that react with water, forming silanol groups (–Si–OH) from the methacryloxy groups (–Si–O–CH_3). Silanol groups react to form a siloxane network (–Si–O–Si–O–) with silicon oxide present in the ceramic, forming a chemical bond between the materials.[5,11,24-28] The monomeric ends of the silane molecule react with the methacrylate groups of the resin cement.

The higher bond strengths associated with the etched group compared to the group etched and neutralized are in agreement with the findings of other studies.[14,15] These previous studies showed that the use of neutralizing products decreases the ceramic surface energy and creates precipitates within the etched region, damaging the bonding capability between resin cement and ceramic.[14,15] Taken together, the neutralization process appears not to impair adhesion for the cementation of a hot-pressed leucite-reinforced feldspar ceramic.

The ceramic microstructure imaged through both SEM and AFM (Figure 1) showed no apparent difference in surface topography after the different ceramic etching protocols, in agreement with the second hypothesis of the study. The very similar topographical changes observed among the etched groups may have contributed to the statistical similarity of the bond strength values between groups (Table 2), similar to the findings of Amaral and others.[14] However, when comparing the etched groups vs the nonetched, significant differences were apparent in terms of surface topography. An unappreciable surface modification was seen in the nonetched group, supporting the lower bond strength values.[9,17] Indeed, the failure analysis (Table 3) showed a higher number of pretest failures associated with the aged groups, confirming that the adhesive interface was affected.

CONCLUSIONS

Within the limitations of this study, the following conclusions were drawn: 1) the neutralization process did not improve the bond strength or stability between resin cement and ceramic; and 2) HF acid etching of hot-pressed leucite-reinforced feldspar ceramic is indispensable to enhance resin bonding.

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Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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