

Comparison of Different Etching Agents and Repair Materials Used on Feldspathic Porcelain

Per Kristian Lundvall^a, Eystein Ruyter^{b,*}, Hans Jacob Rønold^a and Karl Ekstrand^a

^a Department of Prosthetic Dentistry, Faculty of Dentistry, University of Oslo, Boks 1109 Blindern, NO-0317 Oslo, Norway

^b NIOM, PO Box 70, NO-1305 Haslum, Norway

Abstract

When fractures of fixed partial dentures occur, they cause an aesthetic and functional dilemma both for the patient and the dentist. Re-make of the entire restoration is an option, but not always desirable. Previous studies have provided several options for ceramic reparation, but there is limited consensus about this issue.

The aim of this study was to test the shear bond strength due to four different etching agents for ceramic repair. The goal was to find a substitute for hydrofluoric acid as etching agent with less toxicity. Ideally, the repair of ceramics must meet both functional and aesthetic requirements.

A total of 70 square shaped feldspathic porcelain disks of dimensions 10 mm × 10 mm × 3 mm were produced and embedded in cylindrical polyethylene walled poly(methyl methacrylate) (PMMA) blocks (16 mm diameter and 12 mm thick). All specimens were wet-ground with silicon carbide papers down to P4000. For one of the groups ten cylindrical ceramic specimens (diameter 5 mm and 2.5 mm high) were made and wet-ground to P4000. The blocks were divided into 7 groups with 10 specimens for each group. In six of the groups composite cylinders were bonded to the porcelain with different pretreatments of the porcelain. As etching agents 9% hydrofluoric acid (HF), 35% phosphoric acid (PO), 15% hydrochloric acid (HCl) and 15% potassium fluoride/hydrogen fluoride (KF·HF) were tested. This study compared a one-part (activated) silane and a new two-part silane. In one group two porcelain specimens were bonded with composite veneer cement. All the specimens were thermocycled for 5000 cycles from 5°C to 55°C before shear bond test.

The best overall result was obtained in group 6 (two porcelain specimens bonded with veneer cement), and the mean shear bond strength was 24.5 MPa. The lowest values were obtained in group 4 with 35% phosphoric acid, and group 5 with 15% hydrochloric acid as the etching agent (6.5 and 0.8 MPa, respectively).

Pretreatment with either 9% HF or 15% KF·HF as the etching agent combined with two-part silane gave good adhesion for porcelain reparations.

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Keywords

Adhesion, ceramic, composite, etching, fluorides, shear bond strength, silane

* To whom correspondence should be addressed. Tel.: +4767512200; Fax: +4767512209; e-mail: eystein.ruyter@niom.no

1. Introduction

Crowns and bridges made of porcelain fused to metal or other core materials such as alumina and zirconia are widely accepted and used in clinical practice. Despite good long-term success rates they occasionally demonstrate fracture of the brittle ceramic veneer. Longitudinal studies have shown that failures resulting from porcelain fracture or chipping range from 2.4% to 8% [1, 2]. Walton *et al.* [3] described worn or lost veneers as the most frequent mechanical problem encountered with fixed partial dentures. Furthermore, failures occur most frequently in regions that are visible, compromising aesthetics in the anterior region. The fractures are mainly in the maxilla, and predominantly on the labial surface. Fractures of porcelain on crowns and bridges are multifactorial. Lack of a proper framework to support the porcelain, intraceramic defects, or parafunctional occlusion can cause this inconvenient problem [4]. Re-make of the restoration is possible, but it is not always the first choice for practical and economical reasons. The ability to repair a ceramic defect after chipping is more beneficial. The clinical success of the porcelain repair is almost entirely dependent on the integrity of the bond between the ceramic and the composite resin. The bond is achieved either by chemical or mechanical method, or both. Several studies have described different ceramic surface treatments to optimize bond strength at the ceramic–composite interface [5, 6]. In a study by Suliman *et al.* [7] the highest bond strength (19.7 MPa) was achieved with diamond roughening followed by hydrofluoric acid etching and Clearfil bonding agent. Leibrock *et al.* [8] claimed that hydrofluoric acid caused no increase in adhesion to porcelain when compared with phosphoric acid. The intra-oral application of the toxic hydrofluoric acid is very undesirable. Özden *et al.* [9] achieved 11.5 MPa bond strength with a diamond bur roughening and silane application only. The specimens were thermocycled for 100 cycles. There is evidence that thermocycling and hydration decreases the bond strength by weakening the interface due to different thermal expansion coefficients of materials involved [10–12]. Sun *et al.* [13] used a four-point bending test and showed a significantly higher bond strength after preparing the specimens with tribochemical sandblasting (Co-jet, ESPE, Bavaria, Germany) as compared with simple gritblasting.

The bond strength is achieved by the combination of mechanical and chemical bonds using surface roughening and silane coupling agents. It has recently been shown by Matinlinna and coworkers that different silanes show differences in their adhesion promotion properties [14–16]. It has been claimed that a silane provides chemical covalent as well as hydrogen bonding and also improves the wettability [17].

The aim of this study was to evaluate the shear bond strength due to four different etching agents, and compare a new two-part silane to a one-part (activated) silane. In addition to testing composite bond strength to ceramic, it was also important to test the strength of two ceramic specimens bonded with composite cement as a technique for porcelain repair.

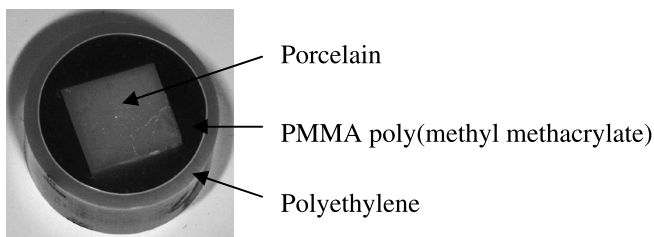


Figure 1. Specimen prior to bonding procedure.

2. Materials and Methods

A total of 70 square shaped feldspathic porcelain specimens (Hera-ceram[®], Heraeus Kulzer, Germany) of dimensions 10 mm × 10 mm × 3 mm were produced and embedded in cylindrical polyethylene walled PMMA blocks (16 mm diameter and 12 mm thick) (Fig. 1). All specimens were wet-ground with silicon carbide papers down to P4000 (<5 μm) on a rotating grinding machine (Struers, Denmark). Ten cylindrical ceramic specimens (diameter 5 mm and 2.5 mm high) (ISO 10477) [18] were made and wet-ground in the same manner. The blocks were divided into 7 groups with 10 specimens for each group and the production of the specimens was as follows.

Group 1 (HF–BS–C) $n = 10$. The porcelain surfaces were etched for 60 s with 9% hydrofluoric acid (Porcelain Etch[®], Ultradent, USA) followed by water rinsing for 30 s and air drying. A two-part silane (Bis-Silane, Bisco, USA) was activated by mixing equal parts of part A (3-methacryloyloxypropyltrimethoxysilane (5%) in ethanol) and part B (acetic acid), applied with a microbrush, and air blown for 60 s. Adhesive resin, PBR (Porcelain Bonding Resin, Bisco, USA), was applied and the excess resin removed with air. Finally the composite (Charisma, Heraeus Kulzer, Germany) was applied and light cured for 80 s (Demetron, VCL 400, Kerr, USA).

Group 2 (HF–C) $n = 10$. As group 1, but without silane coupling agent.

Group 3 (HF–S–C) $n = 10$. As group 1. The specimens were coated with a one-part silane (Silane, Ultradent Products, Inc., USA) for 60 s and air-dried.

Group 4 (PO–BS–C) $n = 10$. The porcelain surfaces were etched for 180 s with 35% phosphoric acid (Ultra-Etch[®], Ultradent Products, Inc., USA), water rinsed for 30 s and dried, followed by application of two-part silane, PBR, composite and light-cured as in previous groups.

Group 5 (HCl–BS–C) $n = 10$. The porcelain surfaces were etched for 300 s with 15% HCl (prepared in the laboratory), water rinsed and dried, followed by application of two-part silane, PBR, composite and light cured as in previous groups.

Group 6 (HF–BS–VC) $n = 10$. Porcelain was used as the repairing material and the cylindrical porcelain specimens were wet-ground (P4000 silicon carbide

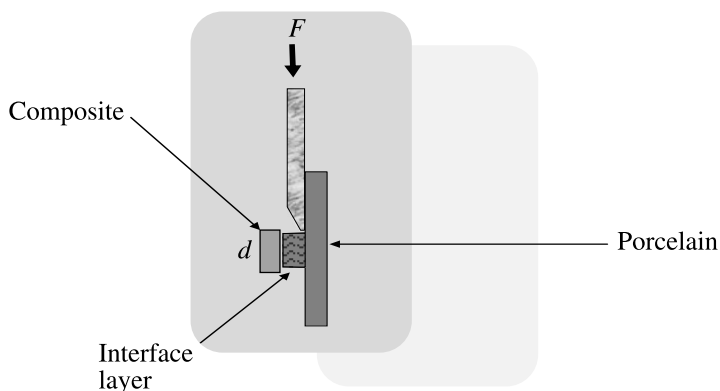


Figure 2. Schematic illustration of the setup for shear bond strength test. The specimen was loaded with a force, F , d is the diameter of the rod.

papers) before the bonding procedure. The following procedure was used for both porcelain plate and porcelain cylinder: 60 s etching with 9% HF (Porcelain Etch[®], Ultradent, USA), followed by water rinsing and air drying. Two-part silane (Bis-Silane, Bisco, USA) was activated, applied for 60 s and dried. PBR was applied on both specimens, and cemented with composite cement (Choice 2[®] light-cured veneer cement, Bisco, USA). Each specimen was light-cured for 80 s.

Group 7 (KF·HF–BS–C) $n = 10$. The porcelain surfaces were treated for 180 s with an aqueous solution of 15% KF·HF (potassium fluoride/hydrogen fluoride), and carboxymethylcellulose prepared in the laboratory. Then followed by application of Bis-silane, PBR and composite.

To ensure complete curing, all specimens were stored dry at $(22 \pm 1)^{\circ}\text{C}$ for 24 h before being thermocycled between 5°C and 55°C for 5000 cycles with a 30-s dwell time, according to ISO 10477 [18].

After thermocycling, the specimens were stored in distilled water before being subjected to shear load at a displacement rate of (1 ± 0.3) mm/min. The mean bonded area was measured for each specimen before mounting in the test machine (Lloyd LRX, Lloyd Instruments Ltd, Fareham, UK). The shear load at the point of failure was noted, and shear bond strength calculated according to ISO 10477 [18] (Fig. 2).

The abbreviations used, materials used, and production procedures for various groups are presented in Tables 1, 2 and 3, respectively.

3. Results

The statistical analysis showed that differences existed among the means: The statistical analyses were performed using one-way analysis of variance (ANOVA).

Table 1.

Abbreviations used in the text

HF	9 wt% hydrofluoric acid
HCl	15 wt% hydrochloric acid
PO	35 wt% phosphoric acid
KF·HF	15 wt% potassium fluoride/hydrogen fluoride
S	Silane, one-part
BS	Silane, two-part
PBR	Porcelain bonding resin
C	Composite veneer cement

Table 2.

Materials used in the study

Product	Composition	Manufacturer	Lot nr.
Hera-ceram	Feldspathic porcelain	Heraeus Kulzer, GmbH, Hanau, Germany	
Porcelain Etch	9 wt% hydrofluoric acid	Ultradent Products, Inc., South Jordan, Utah, USA	b3pkt
HCl	15 wt% hydrochloric acid	Laboratory prepared	–
UltraEtch	35 wt% phosphoric acid	Ultradent Products, Inc., South Jordan, Utah, USA	b3qet
KF·HF*	15 wt% potassium fluoride/ hydrogen fluoride	Laboratory prepared	–
Bis-silane	Silane, two-part	Bisco, Inc., Schaumburg, IL, USA	0600010784
Silane	Silane, one-part	Ultradent Products, Inc., South Jordan, Utah, USA	b3n6j
Porcelain bonding resin	Bonding resin, HEMA free	Bisco, Inc., Schaumburg, IL, USA	080009554
Charisma	Composite, hybrid	Heraeus Kulzer, GmbH, Hanau, Germany	010055
Choice 2	Veneer cement	Bisco, Inc., Schaumburg, IL, USA	0600010895

* KF·HF (15 wt% HF) was dissolved in an aqueous solution of carboxymethylcellulose (Sigma-Aldrich Norway AS).

The results of this study are presented in Table 4 and Fig. 3. For each group standard deviation and confidence interval were calculated.

Group 6 had the best overall result (Mean: 24.5 MPa, SD: 7.0) and had significantly higher shear bond strength ($p < 0.001$) than the other groups except group 1 (Mean: 19.0 MPa, SD: 5.0) and group 7 (Mean: 18.4 MPa, SD: 7.1). The lowest

Table 3.
Materials and methods used for production of different groups

Materials and methods	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7
Specimens	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10	<i>n</i> = 10
Feldspathic porcelain (square) wet-ground to P4000	•	•	•	•	•	•	•
Feldspathic porcelain (cylindrical) wet-ground to P4000						•	
Composite, hybrid (C)	•	•	•	•	•		•
9 wt% hydrofluoric acid (HF) 60 s	•	•	•			•	
15 wt% hydrochloric acid (HCl) 300 s					•		
35 wt% phosphoric acid (PO) 180 s				•			
15 wt% potassium fluoride/hydrogen fluoride (KF·HF) 180 s							•
Silane, two-part (BS) 60 s	•			•	•	•	•
Silane, one-part (S) 60 s			•				
Porcelain bonding resin, HEMA free (PBR)	•	•	•	•	•	•	•
Composite veneer cement (C)						•	
Light-cured 80 s	•	•	•	•	•	•	•
Thermocycling 5°C–55°C for 5000 cycles	•	•	•	•	•	•	•
Shear bond test ISO 10477	•	•	•	•	•	•	•

shear bond strength was obtained in group 5. (Mean: 0.8 MPa, SD: 1.8). This was significant lower ($p < 0.0001$) than all groups except group 4 (Mean: 6.5 MPa, SD: 5.9). There was no significant difference ($p = 0.424$) in shear bond strengths between group 1 and group 2 (Mean: 13.4 MPa, SD: 2.2) nor between group 1 and group 3 (Mean: 13.8 MPa, SD: 5.4). During thermocycling 8 specimens in group 5 and 3 specimens in group 4 debonded. No significant difference was obtained between the best composite groups (groups 1 and 7), using HF and KF·HF as the etching agents, respectively.

Table 4.

Mean shear bond strength in MPa, standard deviation (SD), number of specimens per group (*n*) and confidence interval 95%

Groups	HF-BS-C (1)	HF-C (2)	HF-S-C (3)	PO-BS-C (4)	HCl-BS-C (5)	HF-BS-CS* (6)	KF·HF-BS-C (7)
Mean	19.0	13.4	13.8	6.6	0.8	24.5	18.3
SD	5.0	2.2	5.4	5.9	1.8	7.0	7.1
<i>n</i>	10	10	10	10	10	10	10

* Two porcelain specimens bonded with composite veneer cement.

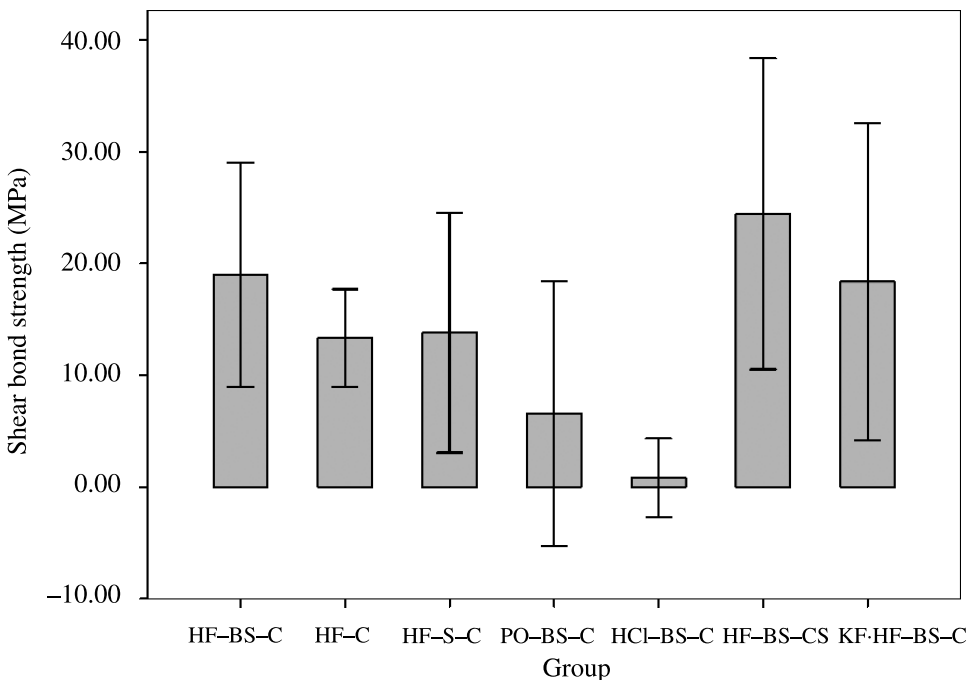


Figure 3. Results from the shear bond test for 7 experimental groups. Bars represent mean values $\pm$ 2SD.

4. Discussion

In this *in vitro* study shear bond strengths were measured for different combinations of materials and methods used for porcelain repair after fracture within the porcelain.

Several studies [19–21] dealing with porcelain repair suggest etching of porcelain with hydrofluoric acid (HF) to generate the micromechanical retention necessary for the porcelain–composite bond. Chen and coworkers [22] studied the

importance of the etching time of porcelain in obtaining higher bond strengths. They reported the highest shear bond strength when the porcelain surface was etched for 120 s with 5% HF. Yen and coworkers [23] reported altered surface topography, but no significant effect on flexural strength of feldspathic porcelain after etching with hydrofluoric acid up to 5 min. In the present study there was higher shear bond strengths using two-part silane (group 1), in comparison with one-part silane (group 3), 19.0 MPa and 13.8 MPa respectively. One-part silane (group 3) showed similar bond strengths as the group without silane (group 2).

Hydrofluoric acid (HF) is widely used in the industry for etching glass. HF produces dehydration and etching of tissues, but unlike other halogen acids, hydrogen fluoride is a weak acid. However, unlike other acids, the dissociated fluoride ion, F^- , produces severe toxicity. It interferes with calcium metabolism in the underlying soft and bony tissue and the result is severe pain and cell destruction. Death has been reported from burns involving concentrated acid with as little as 2.5% body surface area (BSA). Topical and parenteral calcium salts have proven effective therapy for both dermal and systemic manifestations [23]. In this study the goal was to find an alternative to HF as the etching agent for clinical use. No significant difference was obtained between the best composite groups (groups 1 and 7), using HF and KF·HF as the etching agents, respectively.

In group 7 the use of 15% KF·HF (potassium fluoride/hydrogen fluoride) as the etching agent showed almost similar results to those obtained with the hydrofluoric acid (group 1).

Biological tests on KF·HF are not available yet, but we believe it to be less toxic because the solution does not produce free hydrofluoric acid [24].

Comparison of HF with the other etching agents 15% HCl (hydrochloric acid) and 35% PO (phosphoric acid) showed significantly lower bond strengths ($p < 0.0001$).

Silane coupling agents are capable of forming chemical bonds with porcelain surfaces and bonding to the resin occurs by an addition polymerization reaction between methacrylate groups of the matrix resin and the silane molecule during curing of the composite. The bond with ceramics may occur *via* a condensation reaction between the silanol group (Si–OH) of the ceramic surface and the silanol group of the hydrolyzed silane molecule, creating a siloxane bond (Si–O–Si) and producing a water molecule (H_2O) as byproduct [15, 25]. More importantly, silanes enhance resin–porcelain bonds by promoting wetting of the ceramic surface and thus making the penetration of the resin into the microscopic porosities of the acid conditioned porcelain [17]. Hooshmand *et al.* [26] concluded that, when using an appropriate silane application technique, the effectiveness of a pre-activated silane solution based on 3-MPTS (3-methacryloyloxypropyltrimethoxysilane), acetic acid and ethanol will not deteriorate when stored for up to 1 year at room temperature. In this study we found higher bond strength using a two-part inactivated silane compared to the one-part activated silane. It is reasonable to suggest that the pre-

activated silane, i.e., the one-part silane contained partly polymerized polysiloxane prior to the bonding procedure, thus preventing optimal adhesion.

Several of today's dentin–enamel bonding agents contain HEMA (2-hydroxyethyl methacrylate). HEMA has hydrophilic properties and enables the bonding agent to penetrate dentin tubules for higher bond strengths [27]. For the purpose of repairing fractured porcelain, this property is not necessary. Being hydrophilic, HEMA will absorb water, discolor and weaken the bonding over time. In this study, a HEMA-free bonding agent was used.

One of the aims of this study was to achieve a reparation technique with a good aesthetic result. Group 6 with two porcelain specimens bonded with composite cement showed best shear bond strength in the present study (24.5 MPa).

5. Conclusions

Within the limits of this study the following conclusions are drawn.

- Pretreatment with either 9% HF or 15% KF·HF as the etching agent combined with a two-part silane gives good adhesion for porcelain reparations.
- 15% KF·HF as the etching agent gives good adhesion and may be a better alternative than 9% HF because of less toxicity.
- Porcelain fractures repaired with bonded porcelain showed in this study the best shear bond strength, and should be the first technique of choice considering aesthetic demands.

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