Effect of hydrofluoric acid etching on bond strength of composite luting agent to lithium disilicate ceramic material

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Purpose: The purpose of the current study was to evaluate the effect of surface preparation on bond strength of a composite luting agent joined to a heat-pressed ceramic material.
Materials and Methods: Two sizes of disk specimens were made from a lithium disilicate-based ceramics (IPS Empress 2) and their surfaces were separately prepared with three methods: etching with phosphoric acid (PE), etching with hydrofluoric acid (HF), and air-borne particle abrasion with alumina (AA). Each group was further divided into two sub-groups: bonding with the Panavia F material (PF), and silane treatment followed by bonding with the Panavia F material. Shear testing was performed both before and after 20,000 thermocycles.
Results: Bond strength varied from 14.2 MPa to 46.6 MPa for the pre-thermocycling groups, whereas post-thermocycling bond strength ranged from 0.3 MPa to 37.5 MPa.
Conclusion: Hydrofluoric acid etching effectively enhanced bond strength of the Panavia luting agent to the ceramic material, regardless of the application of silane primer. **(Int Chin J Dent 2004; 4: 100-106.)**

Clinical Significance: Hydrofluoric acid etching roughened the IPS Empress 2 ceramic surface. The etched surface was suitable for adhesive bonding with the Panavia F composite luting agent.
Key Words: bonding, ceramics, composite, hydrofluoric acid, lithium disilicate.

Introduction

The IPS Empress glass-ceramics (Ivoclar Vivadent AG, Schaan, Liechtenstein) is a heat-pressed, leucite-reinforced material designed for tooth-colored restorations.[1,2] Mechanical properties of the material, however, are not sufficient for use in fixed partial dentures (FPDs). The IPS Empress 2 (Ivoclar Vivadent AG) glass-ceramics was introduced thereafter as an alternative material for single-unit restorations as well as for 3-unit FPDs limited to anterior and premolar areas.[3] The definitive restoration, made of a lithium disilicate framework ceramics and a fluoroapatite layering ceramics, offers clinical benefits in terms of machinability, polishability, and reduced wear of opposing tooth structure.[4]

Bonding ceramics to tooth structure with composite luting agent increases fracture resistance of the tooth and the restoration itself, and minimizes microleakage, which may be the determining factor in the success or failure of the restorative treatment.[5] Microleakage causes marginal discoloration of restorations and thus failure of restorations. Comparative bond strength studies were performed for evaluation of the characteristics of bonding of luting systems to the ceramic material. Due to the fact that lithium disilicate is a new composition for adhesive bonding, proprietary surface preparation is necessary prior to bonding restorations. Although the manufacturer recommends the use of a single-liquid silane primer for bonding the Empress 2 material, only limited information is available about surface preparation for mechano-chemical bonding. The purpose of the current study was to evaluate the effect of surface preparation on bonding of a dual-activated composite luting agent to the Empress 2 ceramics.

Materials and Methods

A lithium disilicate-based ceramic material (IPS Empress 2) was selected as the substrate material. A composite luting material with or without silane primer was evaluated. The material, identified as Panavia F

(Kuraray Medical Co., Ltd., Tokyo, Japan, PF), is a dual-polymerizing two-paste luting composite that contains 10-methacryloyloxydecyl dihydrogen phosphate (MDP) as a functional monomer. The Clearfil Porcelain Bond Activator material (Kuraray Medical Co., Ltd.) is a single liquid silane solution. The Clearfil Mega Bond Primer material (Kuraray Medical Co. Ltd.) is a self-etching primer for dentin bonding. The manufacturer claims that the Activator combined with the Mega Bond Primer is applicable, as a two-liquid primer (CP), for adhesive bonding of ceramic materials. Two etchants (K-etchant, Kuraray Medical Co., Ltd.; HF Gel, GC Corp., Tokyo, Japan) and 70 μm grain sized alumina (Hi-Aluminas, Shofu Inc., Kyoto, Japan) were used for ceramic surface preparation. Details of the materials are summarized in Table 1.

Table 1. Materials assessed.

Material	Trade name	Lot number	Composition
Ceramics	IPS Empress 2 Ingot 200	E41431	57-80% SiO_2, 11-19% Li_2O, 0.1-14% La_2O_3, 0-14% K_2O
Etchant	K-etchant(originally for enamel)	0307AA	40% Phosphoric acid
	HF Gel (for ceramics)	090721	5% Hydrofluoric acid
Abrasive	Hi-Aluminas	0703	70 μm Aluminum oxide
Silane primer	Clearfil Porcelain Bond Activator	00299A	γ-MPTS, Bis-GMA
	Clearfil Mega Bond Primer	00131A	MDP, HEMA, Water, Ethanol, etc.
Luting agent	Panavia F A paste	00067A	MDP, Bis-GMA, Silica, Photo initiator, Accelerator
	B paste (Brown)	00038A	Bis-GMA, Barium glass, Sodium fluoride, MDP, BPO

MDP, 10-methacryloyloxydecyl dihydrogen phosphate; Bis-GMA, Adduct of bis-phenol A and glycidylmethacrylate; BPO, Benzoyl peroxide; γ-MPTS, γ-methacryloxypropyl trimethoxysilane; HEMA, 2-hydroxyethyl methacrylate.

A total of 120 pairs of the Empress 2 ceramic disks (7 mm in diameter by 3 mm thickness; 5 mm in diameter by 2 mm thickness) were prepared according to the manufacturer's specifications. The surface to be bonded was ground with #2,000 silicon-carbide abrasive paper (New Maruto Lap ML-110, Maruto Instrument Co. Ltd., Tokyo, Japan) and divided into three groups: 1) phosphoric acid etching (PE), 2) hydrofluoric acid etching (HF), and 3) air-abrasion with alumina (AA) (n=40 pairs in each group). The phosphoric acid etchant was applied to the ceramic surface for 60 s, rinsed with tap water, and air-dried. The hydrofluoric acid etchant was applied to the ceramic surface for 20 s, rinsed with tap water, and air-dried. Air-borne particle abrasion was performed with a particle abrader (Multiblaster, AWS Co. Ltd., Tokyo, Japan) for 10 s. The pressure was 0.3 MPa and the distance of the orifice from the ceramic surface was approximately 20 mm. A piece of tape with a circular hole 3 mm in diameter was positioned on the 7-mm-diameter ceramic specimen to define the bond area and a consistent 50 μm thickness of the luting material.

The disks were divided into six system groups (Fig. 1). Silane primer was not used in three of these six systems and they were considered as controls (PF). For the remaining three groups, the two-liquid silane primer was applied to both 7-mm- and 5-mm-diameter specimens with a sponge pellet and gently air-dried (CPPF). The 120 pairs of disks were bonded with the Panavia F material. Thirty minutes after bonding, the specimens were immersed in 37˚C water for 24 hours. This state was defined as thermocycle 0. Six sets of ten pairs were subjected to shear testing at thermocycle 0 and 24-hour bond strengths were determined. The remaining six sets of 10 paired specimens were subsequently placed in a thermocycling apparatus (Thermal Shock Tester TTS-1 LM, Thomas Kagaku Co. Ltd., Tokyo, Japan) and cycled between 5˚C and 55˚C water with a one-minute dwell time per bath for 20,000 cycles. Post-thermocycling bond strengths were then determined. Before shear testing, each specimen was embedded in a steel mold and seated in an ISO/TR 11405 shear-testing jig. Bond strengths were determined on a mechanical testing device (Type 5567, Instron Corp., Canton, MA, USA) at a crosshead

speed of 1.0 mm per minute. For each condition, the average bond strength and standard deviation (SD) of 10 replications were calculated.

The values of each group were compared by analysis of variance (ANOVA). The three factors analyzed were surface preparation, bonding system, and thermocycling. After the three-way ANOVA, two-way ANOVA, one-way ANOVA, and post-hoc Tukey-Kramer tests were further performed with the value of statistical significance set at 0.05.

After the shear testing, debonded surfaces were observed through an optical microscope (SZX9, Olympus Corp., Tokyo, Japan) and failure mode was recorded as: A, adhesive failure at the luting agent-ceramic interface; C, cohesive failure inside the luting agent; and AC, combination of adhesive and cohesive failures. Selected specimens were sputter-coated with osmium, and observed with a scanning electron microscope (S-4300, Hitachi High-Technologies, Co., Ltd., Tokyo, Japan) operated at 15 kV.

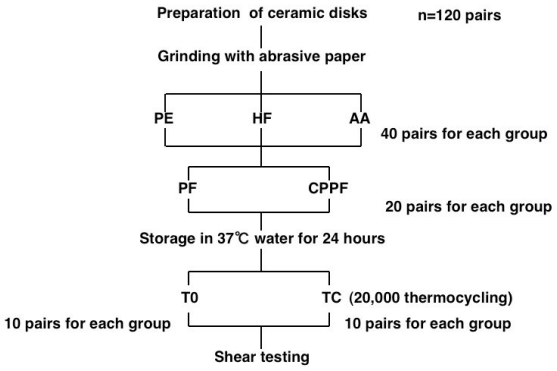


Fig. 1. Procedures for specimen preparation.

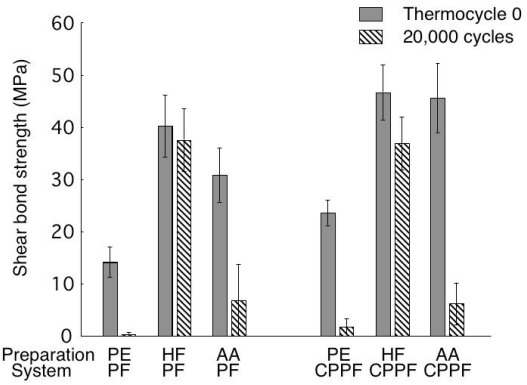


Fig. 2. Shear testing results.

Results

Table 2 shows the ANOVA results for shear bond strengths.

Table 2. Analysis of variance results.

Source	Degree of freedom	Sum of square	Mean square	F-value	p-value
Three-way ANOVA					
Luting system (LS)	1	780.3	780.3	33.9	0.0001
Surface preparation (SP)	2	18,627.2	9,313.6	404.5	0.0001
Thermocycling (TC)	1	10,378.8	10,378.8	450.7	0.0001
LSxSP	2	86.6	43.3	1.9	0.1573
LSxTC	1	784.4	784.4	34.1	0.0001
SPxTC	2	3,256.5	1,628.2	70.7	0.0001
LSxSPxTC	2	102.8	51.3	2.2	0.1123
Residual	108	2,486.8	23.0		
Two-way ANOVAs					
PF					
SP	2	10,227.1	5,113.5	199.4	0.0001
TC	1	2,728.4	2,728.4	106.4	0.0001
SPxTC	2	1,139.3	569.7	22.2	0.0001
Residual	54	1,384.7	25.6		
CPPF					
SP	2	8,486.8	4,243.4	207.9	0.0001
TC	1	8,434.8	8,434.8	413.3	0.0001
SPxTC	2	2,219.9	1,110.0	54.4	0.0001
Residual	54	1,102.1	20.4		

The table includes degree of freedom, sum of squares, mean squares, F-values, and p-values. Three-way ANOVA indicated that the following interactions were significant ($p<0.05$); 1) luting system and thermocycling, and 2) surface preparation and thermocycling. Among the three factors, thermocycling showed the highest F-value, followed by surface preparation, and cementing system. The bond strength results were analyzed by two-way ANOVA. The results showed that interaction between the two factors were significant ($p<0.05$) for both systems.

Fig. 2 demonstrates the bond strengths to the Empress 2 material before and after thermocycling. Table 3 shows the average bond strengths, standard deviations, and statistical categories. Bond strength varied from 46.6 MPa to 0.3 MPa. Surface preparations considerably affected bond strengths of both silanized and unsilanized groups. Specifically, the groups etched with the HF etchant exhibited greater post-thermocycling bond strength than those treated with other methods. Bond strength of one group (etched with HF but unsilanized) did not deteriorate after thermocycling. No significant difference in post-thermocycling bond strength was found between the silanized and unsilanized groups, when the ceramic surface was either alumina-blasted or etched with HF.

Table 3. Shear bond strengths in MPa and results of statistical analysis.

		Panavia F (PF)			Silane priming + Panavia F (CPPF)			
Preparation	Thermocyles	Mean	SD	Category	Mean	SD	Category	Difference between PF and CPPF
PE	0	14.2	2.9	C	23.6	2.4	G	Significant
HF	0	40.2	5.9	A	46.6	5.2	E	Significant
AA	0	30.8	5.2	B	45.5	6.7	E	Significant
PE	20,000	0.3	0.4	D	1.7	1.7	H	Significant
HF	20,000	37.5	6.0	A	36.8	5.0	F	Not significant
AA	20,000	6.8	6.9	D	6.1	4.0	H	Not significant

SD, Standard deviation; Category, Identical capital letters indicate that they are not statistically different ($p>0.05$).

Failure modes after shear testing are summarized in Table 4. Failure mode analysis revealed that PE-PF groups showed type A adhesive failure for all specimens, whereas HF-CPPF groups exhibited type AC failure for all specimens. The number of type A failures increased on the application of thermocycling for the AA-PF, PE-CPPF, and AA-CPPF groups.

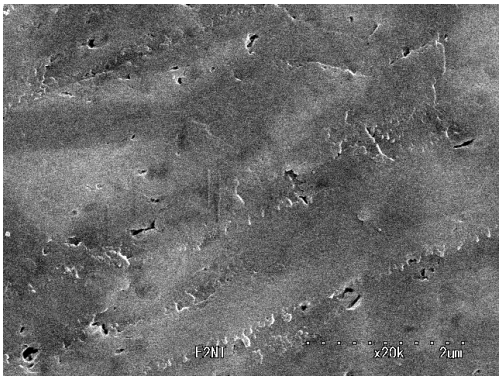
Table 4. Failure modes after the shear testing.

			Thermocycle 0			20,000 cycles		
Preparation	Luting system	Failure mode	A	CA	C	A	CA	C
PE	PF		10	0	0	10	0	0
HF	PF		1	9	0	1	9	0
AA	PF		6	4	0	10	0	0
PE	CPPF		3	7	0	9	1	0
HF	CPPF		0	10	0	0	10	0
AA	CPPF		2	8	0	9	1	0

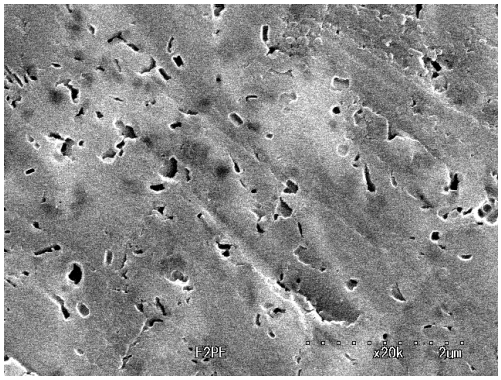
A, Adhesive failure at the luting agent-ceramics interface; C, Cohesive failure inside the luting agent; CA, Combination of cohesive and adhesive failures.

Fig. 3 shows scanning electron micrographs of ceramic disks after surface preparation including ground reference surface (Fig 3a). Phosphoric acid etching slightly roughened the ceramic surface (Fig. 3b), whereas

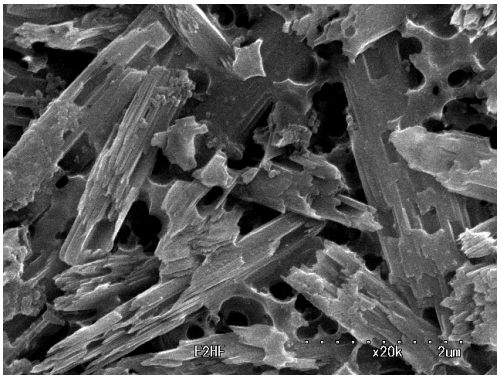
etching with hydrofluoric acid generated a splintery structure (Fig. 3c). An irregular relief pattern with loss of surface structure was generated after air-borne particle abrasion with alumina (Fig. 3d). Fig. 4 shows the sectioned micrographs of the composite-ceramic interface. The composite luting agent penetrated into the undercut of the etched ceramic surface and the polymerized material appeared to be mechanically retained in the etched ceramic material (Fig. 4b).



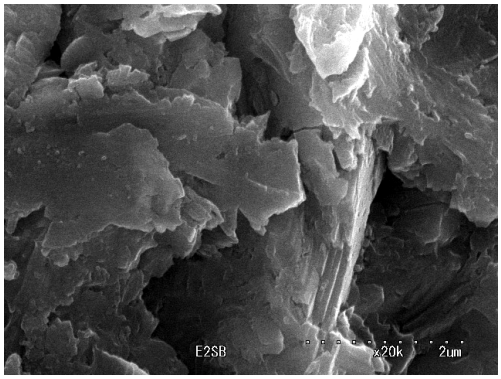
3a Ground



3b Etched with phosphoric acid

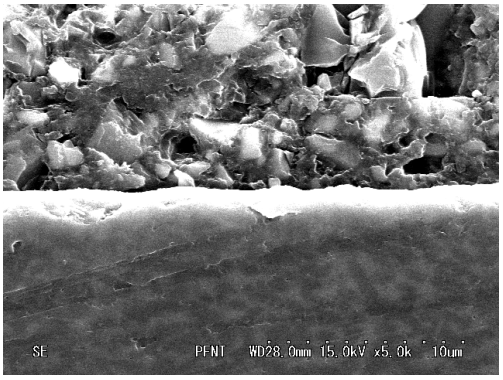


3c Etched with hydrofluoric acid

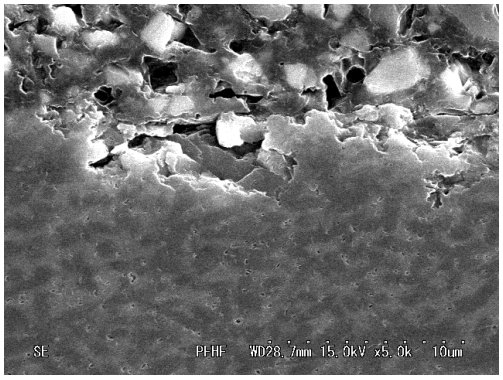


3d Air-borne particle abraded with alumina

Fig. 3. Scanning electron micrographs of the Empress 2 ceramics after surface preparations.



4a Bonded to ground surface



4b Bonded to the surface etched with HF

Fig. 4. Sectional micrographs of the Empress 2 ceramics after bonding with the Panavia F material.

Discussion

Micromechanical retention is an important factor for durable bonding of resin-based luting agents to ceramics. When the Empress 2 material was treated with phosphoric acid, the surface was not particularly etched (Fig. 3b) and mechanical retention appeared to be insufficient. Bond strength after phosphoric acid etching was 23.6 MPa

or lower. This result suggests that phosphoric acid etching is inadequate to achieve mechanical retention between the ceramic and luting agent.

When the Empress 2 was treated with hydrofluoric acid, an etched relief pattern composed of elongated crystals was clearly observed (Fig. 3c). According to a report concerning microstructure of the Empress 2 material, the crystal phase is formed by elongated lithium disilicate ($Li_2Si_2O_5$) and lithium orthophosphate (Li_3PO_4), both of which are surrounded by glass matrix.[6] Hydrofluoric acid is able to remove the glass matrix and lithium orthophosphate crystalline phase, thus creating irregularities within the lithium disilicate crystals. The micrograph of the present study (Fig. 3c) suggests that hydrofluoric acid attacked both lithium orthophosphate crystalline phase and glass matrix. This is confirmed by the fact that the etched surface displays both attacked crystals and etched glass matrix. This irregularity is considered to be suitable for adhesive bonding, and the speculation is supported by the shear testing results as well as the sectional micrograph (Fig. 4b). After HF etching, bond strengths greater than 30 MPa were recorded regardless of the use of the silane agent as well as application of thermocycling.

Air-borne particle abrasion with alumina was also evaluated because this procedure is performed to remove investment material after mold processing. As shown in Fig. 3d, alumina abrasion considerably roughened the Empress 2 surface. However, reduction in bond strength after thermocycling was remarkable. This is probably due to the lack of undercut on the abraded surface. Similar results have been reported for sintered porcelain.[7,8] Clinicians should therefore keep in mind that a particle-abraded surface is not mechanically retentive, although the surface may appear more retentive than polished or glazed surfaces.

The effect of silane primer was not apparent in the current research. One of the problems associated with the two-liquid silane primer is that the Clearfil Mega Bond Primer material contains water and 2-hydroxyethyl methacrylate (HEMA). Although these are indispensable for bonding dentin as a self-etching primer, they may act as inhibitors of silane coupling as well as interlocking within the etched ceramic material. Silane agents should contain neither water nor HEMA for proper polymerization reaction, but should contain an acidic monomer like MDP separated from the silane monomer. Also, an initiator should be added to the silane coupling agent. The ineffectiveness of the current two-liquid silane agent is probably explained by the presence of water that was originally included in the Mega Bond Primer liquid. Also, lack of an initiator in the two-liquid silane agent may also be responsible for the undesirable curing and bonding characteristics.[9]

On the basis of the current experiments, it can be concluded that hydrofluoric acid etching effectively enhanced bond strength of Panavia F luting agent to Empress 2 ceramic, regardless of the use of the two-liquid silane primer.

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