Zirconia Surface Treatments for Resin Bonding

George J. K. Cheung[a] / Michael G. Botelho[b]

Purpose: To evaluate the bond strength of resin to zirconia treated with different surface conditioning methods.

Materials and Methods: Sintered zirconia was surface treated to create 7 groups. Ceramic liner (L) was fired onto three groups of zirconia and subsequently received the following treatments: hydrofluoric acid etching (L/HFE), alumina particle abrasion (L/APA), and alumina particle abrasion with hydrofluoric acid etching (L/APA-HFE). All three groups were silane treated immediately prior to bonding. Two other zirconia groups received alumina particle abrasion with and without silane coupling (AP-S and AP). Another group underwent selective infiltration etching, in which the specimens received porcelain powder firing, ultrasonic etching with HF for 15 min, then rinsing under running water for 15 min, followed by silane treatment (SIE). The control group was zirconia as-sintered (ZAS). Twenty composite resin cylinders were luted to each group with a resin cement. Each group was divided into two subgroups (n=10) and subjected to 2 storage conditions: 24 h water storage or 21 days with 6000 thermocycles between 5°C and 55°C. Shear bond strength testing (SBS) was performed, followed by statistical analysis of the results using one-way ANOVA ($p < 0.05$).

Results: After 21 days of thermocycling, AP and ZAS groups spontaneously debonded prior to testing. The remaining groups showed a decrease in mean shear bond strength between 11.7% and 58.5% after thermocycling, except the L/HFE group, which increased by 11.7%. L/HFE showed the highest bond strength at both test intervals, and at 21 days was significantly higher than that of the AP-S and L/APA-HFE groups, which in turn were higher than that of the L/APA group, which was higher than that of the SIE group ($p < 0.05$).

Conclusion: The etched, fired ceramic liner with silane treatment provided the strongest and most durable bond under the conditions tested. Alumina particle abrasion degraded the durability of the ceramic liner. Alumina particle abrasion, as-sintered zirconia, and SIE did not provide durable bond strengths.

Keywords: zirconia, resin cement, shear bond strength.

J Adhes Dent 2015; 17: 551–558.
doi: 10.3290/j.jad.a35249

Submitted for publication: 20.01.14; accepted for publication: 22.10.15

Zirconia has become increasingly popular as a prosthetic material because of its favorable esthetic, mechanical, and biocompatible properties.[27] The stress-induced transformation toughening mechanism gives zirconia excellent flexural and fracture toughness compared to other dental ceramics.[23] The superior mechanical properties of this polycrystalline material in combination with CAD/CAM technology allows highly accurate fabrication of long-span and complex restorations with high success rates.[20] However, the chemical inertia of this material has stood as a challenge against the establishment of a strong, durable chemical bond with resin-based luting agents. To date, the most recommended method for bonding zirconia restorations has been a combination of airborne particle abrasion as a surface treatment with application of a phosphate-based monomer as a luting-cement adhesion promoter.[1,4,5,28,30]

In addition, chemical adhesion has been shown to occur when tribochemical silica coating is followed by application of silane coupling agents.[8,10,21] Silica-coated alumina particles are air blasted onto the zirconia surface, producing a silica coating onto which a silane coupling agent and an adhesive resin cement are applied. However, the durability of this surface treatment to resin bonding after artificial aging has been reported to decrease.[10,39]

The omission of particle abrasion can lead to a dramatic reduction in bond strength values, even when MDP monomer is used.[1,4,10,39] Therefore, surface roughness produced by particle abrasion appears to be important for adhesion to zirconia,[3] although it is not recommended by the manufacturers. Thus, the combination of microme-

[a] *AdvDipProsthodont Graduate, Discipline of Oral Rehabilitation, Faculty of Dentistry, the University of Hong Kong, the Prince Philip Dental Hospital, Hong Kong. Performed the experiments in partial fulfillment of requirements for an MDS degree, wrote manuscript.*

[b] *Associate Professor, Discipline of Oral Rehabilitation, Faculty of Dentistry, the University of Hong Kong, the Prince Philip Dental Hospital, Hong Kong. Hypothesis, experimental design, writing and editing manuscript.*

Correspondence: *Dr. Michael Botelho, Discipline of Oral Rehabilitation, Faculty of Dentistry, The University of Hong Kong, The Prince Philip Dental Hospital, 34 Hospital Road, Hong Kong. Tel: +852-2859-0412. e-mail: botelho@hkucc.hku.hk*

Table 1 Materials used in the study

Material	Batch number	Key chemical composition	Manufacturer
Cercon Base	18002494	92 wt% zirconium dioxide, 5 wt% yttrium trioxide, < 2.0 wt% hafnium dioxide	DeguDent; Hanau, Germany
Cercon Ceram Kiss Paste Liner	70564	Vitreous porcelain, butane-1,4-diol, hexane-1,2,6-triol	DeguDent
Cercon Ceram Kiss Glaze	597045	Vitreous porcelain, pigments	DeguDent
Ducera Stain Liquid	70629	N/A	DeguDent
Panavia F 2.0 Paste A	00022A	Methacrylate, MDP, quartz glass, microfiller, photoinitiator	Kuraray Noritake Dental; Tokyo, Japan
Paste B	00020A	Methacrylate, barium glass, sodium fluoride, chemical initiator	
Oxyguard II	00642A	Polyethyleneglycol, gel containing glycerine, sodium benzensulfinate	
IPS Ceramic Etching Gel	N71587	Hydrofluoric acid up to 5%	Ivoclar Vivadent; Schaan, Liechtenstein
Esthet•X HD Composite Resin	1201301	Resin matrix system: bis-GMA-adduct, ethoxylated bisphenol-A-dimethacrylate, triethelene glycol dimethacrylate (TEG/DMA) Photoinitiation system: diketone, camphoroquinone, ethyl-4-dimethylaminobenzoate Fillers: barium-alumino fluoroborosilicate glass with nano-sized silicon dioxide particles	Dentsply Caulk; Konstanz, Germany
Clearfil Ceramic Primer	0022AD	3-methacryloxypropyl trimethoxy silane, 10-methacryloyloxydecyl dihydrogen phosphate (MDP)	Kuraray Noritake Dental

chanical retention and adhesion promotion using phosphate monomer-containing resins has been performed for bonding to zirconia materials.[3] However, particle abrasion has been reported to have a damaging effect on the flexural strength of zirconia[40] and reduce bond strength.[17] Therefore, it may be desirable to develop alternative zirconia pre-treatments.

A selective infiltration etching technique has been developed to transform the dense, nonretentive surface of zirconia into a microporous surface capable of bonding with adhesive resins.[3] The procedure requires coating the surface with a special, silica-based glass of undefined formulation, and firing the glass to above its transition point, where it is said to diffuse at the grain boundary regions of zirconia and facilitates sliding and splitting of the surface grains. After removal of this glass by hydrofluoric acid, the surface reveals 3-dimensional microporosities between the surface grains into which the adhesive resin can penetrate and interlock, with the modified surface resulting in a strong bond.

Other studies have reported on the effects of low-fusing porcelain glass pearls to significantly improve the bond strength to composite cylinders in vitro, although thermocycling was not performed.[17,18] In another study, glazing ceramics were fired onto zirconia and etched, and were found to significantly increase shear bond strength compared to tribochemical coating.[19]

In this study, we build on previous investigations of a ceramic powder used to facilitate porcelain buildup onto the zirconia framework.[14] The aim of this study was to investigate the bond strength of an adhesive resin luting cement to zirconia that received a pre-treatment of a fired ceramic liner, which was subsequently treated with particle abrasion or not, or received HF etching alone. These were compared to: a "selective infiltration etching" technique, airborne particle abraded zirconia (with and without silane), and as-sintered zirconia (control). The null hypothesis was that the fired liner method would provide no difference in the shear bond strength between resin cement and the zirconia surface treatments described above. The aim of using the ceramic liner is that it is a simple procedure which is readily available with all zirconia ceramic systems, and therefore does not require special equipment or materials for application.

MATERIALS AND METHODS

The product names, manufacturers, chemical compositions, and batch numbers of the materials used in this study are listed in Table 1. The zirconia disks were surface treated as illustrated in Fig 1.

Specimen Preparation

Zirconia ceramic blanks (Cercon Base, DeguDent; Hanau, Germany) of 25 mm diameter were sectioned with a diamond disk (Micro-slice Metals TH25) to produce 3-mm-thick disk-shaped specimens. They were then wet ground with 1000-grit sandpaper to produce a smooth surface for bonding. The surface roughness

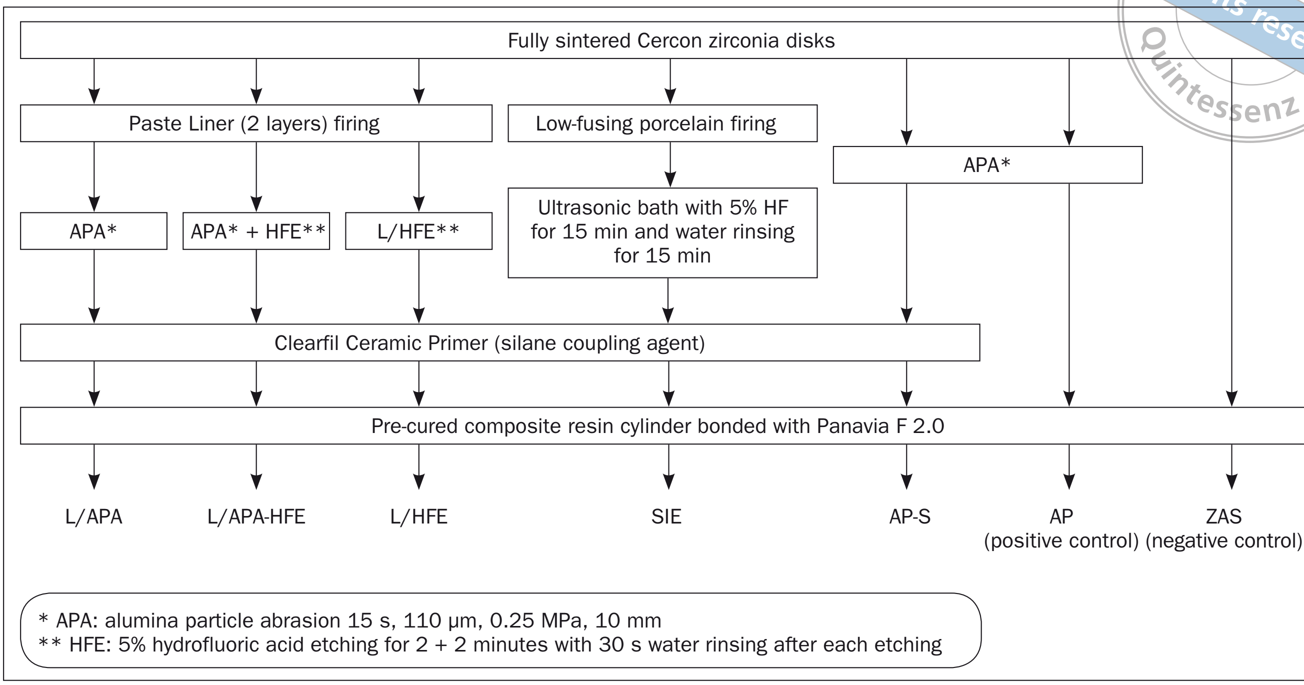

Fig 1 Different surface treatment groups.

of all samples was measured by a roughness gage (Surtronic 3+, Taylor Hobson; Leicester, UK). The specimens were ultrasonically cleaned in a water bath and then sintered in a Cercon heat furnace (Cercon heat, DeguDent) as programmed by the manufacturer, and then randomly divided equally into seven groups.

The 7 experimental groups (n = 10 each) were prepared as follows. In the first 3 groups, two layers of paste liners (Cercon Ceram Kiss paste liner, DeguDent) (L) were applied with a paintbrush and fired separately according to the manufacturer's recommendations. From this, three groups were created by different subsequent surface treatments on the fired paste liner: alumina particle abrasion with 110-µm aluminium oxide particles at 0.25 MPa pressure and a distance of 10 mm for 15 s (L/APA), alumina particle abrasion followed by 2-min hydrofluoric acid (5%) etching performed twice (L/APA-HFE), and 2-min hydrofluoric acid etching performed twice with no alumina particle abrasion (L/HFE). These surfaces received silane treatment with a silane coupling agent (Clearfil Ceramic Primer, Kuraray Noritake Dental; Tokyo, Japan) immediately prior to resin bonding.

In the fourth group, zirconia was treated with the selective infiltration etching technique (SIE) according to Aboushelib.[5] The substrate was coated with a thin layer of "glass conditioning agent," which was prepared by mixing the glass powder (Cercon Cera Kiss Glaze, DeguDent) with stain liquid (Ducera Stain Liquid, DeguDent) and applied with a paintbrush. Subsequently, specimens were heated in a ceramic oven in open air (Programat P500, Ivoclar Vivadent; Schaan, Liechtenstein) to 750°C for 3 min. After cooling to 450°C, they were removed from the oven to air cool. The ceramics were subjected to 15 min of ultrasonic cleaning in 5% hydrofluoric acid followed by washing the specimens under running water for 15 min to remove the glaze. These also received silane treatment prior to resin bonding.

The fifth and sixth groups only received alumina particle abrasion alone with no other treatment (AP) or with silane application (AP-S). The seventh group was a control, consisting of zirconia as-sintered surface (ZAS) with no other treatment.

Mounting and Cleaning Procedure

The sintered zirconia disks were placed on a glass slab and a 25-mm diameter ring was positioned around the disk to act as a specimen former. A 5-N weight in a loading apparatus was used to stabilize the disk on the glass slab. To embed the samples, cold-curing acrylic was filled incrementally into the ring to limit movement of the zirconia during setting. The ZAS specimens of the control group and the AP group were mounted after sintering, whereas the SIE and paste-liner groups were mounted after firing the ceramic powder.

Milling and polishing of zirconia may be associated with contamination and remnants of carbonaceous materials which might not be eliminated by ultrasonic cleaning in 99% isopropanol.[9,39] Therefore, after mounting, all specimens were ultrasonically cleaned in acetone, followed by 96% alcohol for 15 min, then ultrasonically washed in deionized water, and dried with oil-free compressed air.[9]

Cementation Technique

Composite resin buttons were prepared by incrementally filling a PTFE mold of 5 mm diameter and 3 mm height with composite resin (Esthet•X HD, Dentsply Caulk;

Table 2 Mean shear bond strength (MPa), standard deviation, and standard error of mean (Std.EM) of different subgroups and post-hoc multiple comparisons*

Test group	24 h			21 days + TC			n
	Mean	SD	Std. EM	Mean	SD	Std. EM	
L/APA	$9.6^{b,c}$	1.4	0.43	6.2^{c}	1.4	0.45	10
L/APA-HFE	8.8^{c}	1.2	0.39	7.8^{b}	1.3	0.42	10
L/HFE	11.3^{a}	1.5	0.46	12.7^{a}	1.8	0.57	10
SIE	$10.5^{a,b}$	1.8	0.57	4.3^{d}	2.0	0.65	10
AP-S	$10.2^{a,b,c}$	1.3	0.40	8.2^{b}	0.9	0.29	10
AP	5.5^{d}	1.1	0.34	0.06^{e}	0.04	0.01	10
ZAS	6.3^{d}	1.0	0.32	0.04^{e}	0.05	0.02	10

L/APA: liner + alumina particle abrasion, L/APA-HFE: liner + alumina particle abrasion and HF etching; L/HFE: liner + HF etching; SIE: selective infiltration etching; AP-S: alumina particle abrasion with silane coupling; AP: alumina particle abrasion without silane coupling; ZAS: zirconia as-sintered. TC: thermocycling. *Student-Newman-Keuls test, different superscript letters show significant difference.

Konstanz, Germany) and compressed with a mylar strip followed by 60-s light polymerization with a halogen light-curing unit.

A silane coupling agent (Clearfil Ceramic Primer, Kuraray Noritake Dental) was applied to the prepared surfaces of all the test groups except AP and ZAS, left for 30 s, and then air dried. MDP-containing adhesive resin cement (Panavia F 2.0, Kuraray Noritake Dental) was mixed according to manufacturer's instructions and applied to the surface of the composite resin button that was in contact with the mylar strip during button preparation (the bonding surface), then placed onto the zirconia specimen. Excess cement was removed from the periphery of the disk with a foam pellet. A 5-N load was applied to the specimen using a seating apparatus, then Oxyguard II (Kuraray Noritake Dental) was applied to the setting cement to prevent formation of an oxygen inhibition layer, and then left untouched for 3 min during setting before its removal with water spray, as recommended by the manufacturer. Cementation of the specimens was performed immediately after ultrasonic cleaning and surface treatments to reduce the chance of surface contamination. While the use of pre-cured composite buttons does not simulate clinical use, it is a way to control some of the variables associated with direct placement of composite onto zirconia, including: control of the area for bonding, reduced likelihood of flash, air bubbles or defects that may influence stress concentrations during thermocycling and loading to failure.

Artificial Aging Technique and Shear Bond Strength Test

The specimens were subjected to two storage conditions: (1) deionized water storage at 37°C for 24 h, and (2) deionized water storage at 37°C for 21 days and 6000 cycles of thermocycling between 5°C and 55°C with a dwell time of 20 s.

The specimen block was inserted in the universal testing machine (ElectroPuls E3000, Instron; Norwood, MA, US), taking care to center the interface perpendicular to the load in the attachment unit. The specimens were loaded in the machine at crosshead speed of 1 mm/min until failure. A PTFE spacer of 0.5 mm thickness was placed between the ceramic bonding interface and the shear blade to ensure that a consistent space was present between the blade and the bonded interface. The shear bond strengths were calculated by dividing the load at failure by the cross-sectional area of the composite resin cylinder.

The tested specimens were observed under a stereomicroscope (Carl Zeiss; Jena, Germany) at 8X magnification to assess the failure mode.

SEM Analysis

Specimens were prepared for SEM analysis by sputter coating with gold (Fine Coat Ion Sputter, JEOL JFC-1100; Akishima, Japan), then examined in a Philips XL30 CP SEM (Philips; Eindhoven, the Netherlands) using an accelerating voltage of 10.0 kV. The surface roughness patterns produced by different treatments were examined at 500X magnification, and the thickness of the paste liner (Figs 3 and 4) in cross section was examined at 1000X magnification.

Statistical Analysis

Data were analyzed with SPSS (IBM SPSS Statistics 19.0.0, IBM; Armonk, NY, USA). The normality (Kolmogorov-Smirnov test) and the homoscedasticity assumptions (Levene test) of the data appeared valid. One-way ANOVA was used to compare means of the groups after 24 h and 21 days plus thermocycling. Post-hoc multiple comparisons were carried out using the Student-Newman-Keuls test (equal variances assumed) with statistical significance set at $\alpha = 0.05$.

RESULTS

The mean surface roughness of the fully sintered zirconia disks was Ra = 0.28 µm (SD 0.022). The bond strength values after 24-h water storage and after 21-day water storage plus thermocycling are given in Table 2.

After 24-h water storage, there were four groupings of bond strength results with no significant differences within each ($p > 0.05$) (Table 2). Between these 4 groupings, there were significant differences ($p < 0.05$), from highest to lowest: 1) L/HFE, SIE, AP-S (11.3-10.2 MPa); 2) SIE, AP-S, L/APA (10.5-9.6 MPa); 3) AP-S, L/APA, L/APA-HFE (10.2-8.8 MPa); 4) ZAS, AP (6.3 and 5.5 MPa). ZAS and AP showed approximately 44.3% to 50.7% lower strength than did the highest group, L/HFE, at 24 h (Table 2).

After thermocycling, greater differences were observed between the test groups. L/HFE (12.7 MPa) was the highest ($p < 0.05$) and actually experienced a 12.7% increase in the mean shear bond strength. The following groups each showed significant differences ($p < 0.05$) between them: AP-S (8.2 MPa), L/APA-HFE (7.8 MPa), L/APA (6.2 MPa), and SIE (4.3 MPa). These respectively experienced a reduction in bond strength after thermocycling of 20.3%, 11.7%, 35.9%, and 58.5%. Finally, the lowest groups were AP (0.06 MPa) and ZAS (0.04 MPa), which were statistically similar (Table 2). One ZAS specimen spontaneously debonded after thermocycling and 5 more before loading to failure. Three AP specimens also debonded before mechanical testing.

The mode of failure in the AP and ZAS groups was observed as totally adhesive in nature with the zirconia completely exposed. For the remaining groups, mixed modes of failure were observed, with co-occurrence of failure types as follows: cohesive failure of composite resin, interfacial adhesive failure between the liner and zirconia, and interfacial adhesive failure between resin and liner or between resin and zirconia in different proportions (Fig 2).

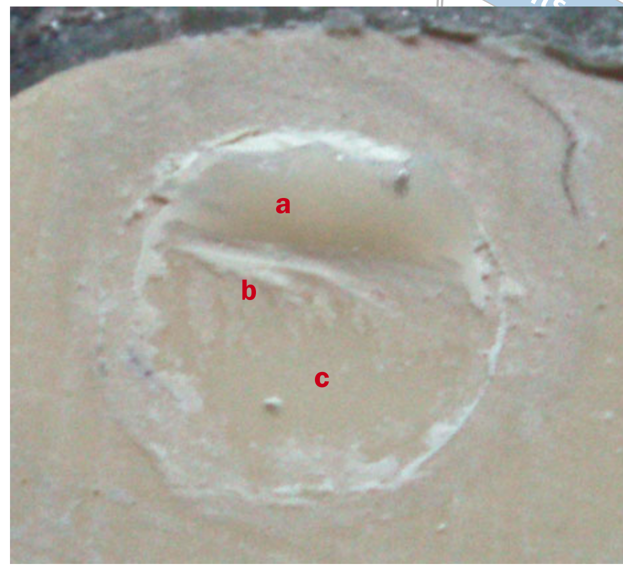

Fig 2 Mixed failure mode of a specimen of group L/HFE: a) cohesive failure of composite resin; b) adhesive failure at resin/liner interface; c) adhesive failure at liner-zirconia interface.

DISCUSSION

There were significant differences within the groups at both 24 h and after thermocycling, but the greatest were between the two test intervals. In this study, the firing of the paste liner and its subsequent HF etching yielded significantly higher bond strengths than all the other test groups at 24 h as well as after thermocycling; thus, the null hypothesis was rejected. The use of the paste liner modified the inert nature of zirconia by creating a more reactive and etchable glass surface. The HF selectively removed the glassy matrix, creating a microporous surface with high surface energy for the penetration of the adhesive resin cement, which both enables micromechanical interlocking and provides a silica-rich substrate for silane bonding.[15] A number of studies have used similar approaches to modify zirconia for bond strength enhancement.[17-19]

The initial bond strength achieved in the L/HFE group was resistant to artificial aging and even increased, suggesting a maturation of the setting cement and stability of the adhesive bond interface, which has been reported elsewhere.[19] The bond strength after artificial aging still satisfied the level of clinical acceptance of 10 to 13 MPa, as described by previous authors.[7,22,26,33] The effectiveness of the L/HFE surface treatment in obtaining a durable bond can be attributed to its intended use on the ceramic liner in fusing to the zirconia substrate or framework for laminating veneering porcelain. The fired ceramic powder is said to infiltrate into the superficial layer of the zirconia, leading to an intimate ultrastructural contact.[3,19] Subsequent etching of this layer creates a micromechanically retentive surface which forms a durable bond between resin and zirconia.[3,4]

Artificial aging has been considered an important aspect of bond strength testing.[24,32] Wegner and Kern concluded that thermocycling has a greater effect than water storage at a constant temperature alone.[36] Thermocycling may induce stress on the bonded interface due to different coefficients of thermal expansion of the substrate and test materials. In the current study, thermocycling adversely affected the bond strength of AP and ZAS groups, with both groups showing a final bond strength value approximately 99% lower than the 24-h results. Previous studies have shown a significant decrease in bond strength after artificial aging where air abrasion was not performed and phosphate-monomer–containing cements were used. Tsuo et al[34] reported a bond strength of zero and Aboushelib et al[1] reported a 69.5% reduction after 10,000 thermocycles. Particle abrasion has been suggested as a prerequisite for enhanced bonding to zirconia-based materials.[6,12,37,39] However, reductions in bond strength after thermocycling of zirconia treated with alumina particle abrasion have been reported in other studies. Tsuo et al[34] reported zero bond strength after 10,000 thermocycles. Likewise, Wegner et al[37] found moderate to relatively high initial bond strengths for zirconia treated with alumina particle abrasion, but spontaneous debonding occurred after 2 years of storage and 37,500 thermocycles. However, other studies have reported less severe reductions in bond strengths after thermocycling compared to 1- to 3-day bond strengths. Wolfart et al[39] showed only a 13% drop in alumina-particle abrasion-treated zirconia with Panavia F, but spontaneous debonding with two non-MDP resin cements after thermocycling. Aboushelib et al[1] found a 20% reduction after 10,000 thermocycles of artificial aging, and Blatz et al[12] reported alumina particle abrasion treatment to have caused a significant decrease of 46% in resin-zirconia bond strengths after 12,000 thermocycles. Currently, there are no guidelines for the optimum storage time of such bonded specimens, and longer storage times may be necessary.

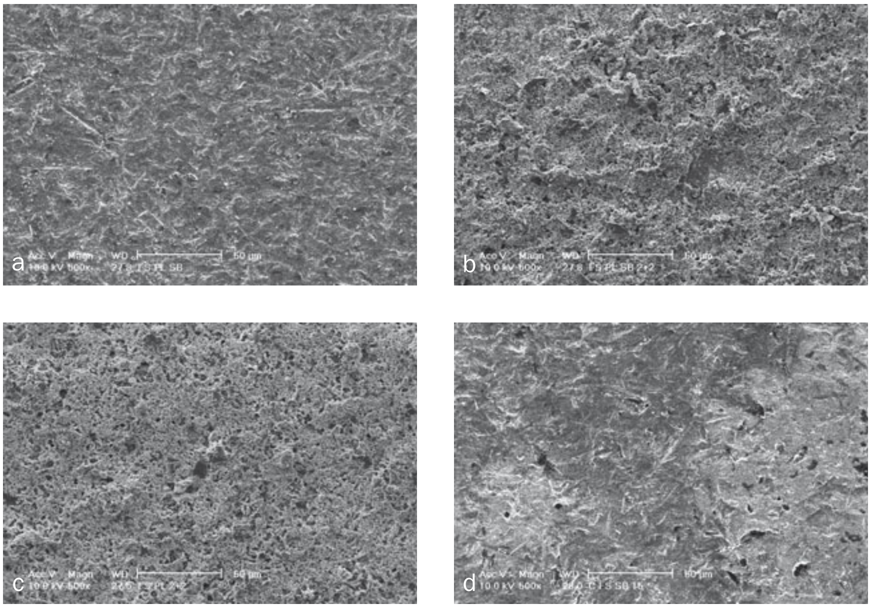

Fig 3 (a) Surface of ceramic liner after alumina particle abrasion (L/APA). Magnification 500X. (b) Surface of ceramic liner after alumina particle abrasion and 2-min HF etching, rinsing, and another 2-min HF etching (L/APA-HFE). Magnification 500X. (c) Surface of ceramic liner after 2-min HF etching, rinsing, and another 2-min HF etching (L/HFE). Magnification 500X. (d) Surface of zirconia surface after selective infiltration etching technique (SIE). Magnification 500X.

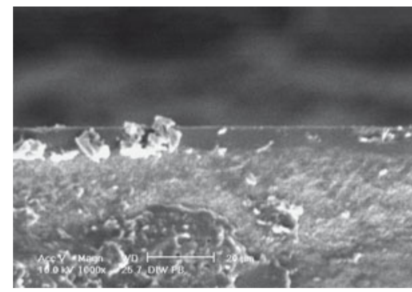

Fig 4 Cross-sectional view of a zirconia disk showing the thickness of 2 layers of paste liner. Magnification 1000X.

Although lower than the bond strengths mediated by L/HFE, the use of a silane coupling agent with an MDP cement with alumina particle abrasion (AP-S) gave a durable bond after thermocycling, as has been reported by other authors.[10,12,29,31,32] This can be explained by two possible different bonding mechanisms. The first is the chemical bonding between MDP and ZrO_2. The phosphate ester monomer of the MDP in the resin luting agent has been reported to bond directly to metal oxides, such as alumina and zircona. The second bonding mechanism is the formation of siloxane bonds formed by silane coupling agents. This bonding chemistry or its combination with MDP suggests why significantly higher bond strength was obtained when compared to alumina particle abrasion alone. From the current results, the benefit of a silane coupling agent when used with an MDP resin cement in achieving a durable bond is highlighted. However, it is not known whether this positive effect is silane-product specific or is provided by silanes in general. The advantage of silane is supported by other studies.[11,24]

Alumina particle abrasion has been variously reported to cause increased and decreased flexural strength of zirconia, depending on the surface damage induced by the abrasion method.[16] Wang et al[35] found that an increase in flexural strength may occur with 50-µm alumina particle abrasion, attributing it to the removal of weakly attached surface grains and the elimination of milling and grinding trace lines, thus reducing the irregularities. Conversely, air particle abrasion with 120-µm alumina results in a significant increase in surface roughness but a decrease in the flexural strength; this is attributed to the creation of sharp cracks and structural defects, resulting in susceptibility to radial cracking during function.[2,25,35] In the current study, while alumina powder of 110 µm was used for sandblasting, smaller sized particles should be investigated, which may produce critically sized defects but still provide sufficient surface area for durable bonding. Furthermore, roughness of the treated surfaces should be considered and recorded prior to bonding to understand its possible effects on bond durability.

These potential adverse effects of alumina particle abrasion were observed on the fired ceramic liner and can be seen when comparing the bond strength of L/APA and L/APA-HFE to L/HFE. The latter gave the highest bond strength, while the alumina particle abrasion of the ceramic liner reduced the bond strengths by 51.2% (L/APA) and 38.6% (L/APA-HFE). Therefore, the effects of grooves or scratches produced by alumina particle abrasion may act as stress concentration sites which could lead to premature crack initiation and propagation during aging and testing.[2,25,35] Although airborne particle abrasion is considered an appropriate treatment for improving bonding of zirconia ceramics,[6,37,39] it appears redundant or harmful when used on a ceramic liner. The reported high surface energy effects of alumina particle abrasion might cause surface or subsurface damage due to physical particle impact or thermal stresses to the paste liner, creating initiation sites for failure.[35] Therefore, alumina particle abrasion should be avoided on fired ceramic liners due to its degrading effect.

The selective infiltration etching technique (SIE) was first described by Aboushelib et al[3] in 2007 and by Casucci et al[13] in 2009. A special silica-based glass of unknown formulation was used to transform the non-retentive zirconia surface into a microporous surface by ultrasonically HF-acid etching the fired glass, thereby creating a microporous, 3-dimensional structure into which the adhesive resin can penetrate between the surface grains and interlock, resulting in a strong bond.[1] The current study attempted to follow the SIE protocol as described above using a porcelain glaze. However, durable bond strengths as demonstrated previously[1,3,13] were not achieved, with a 58.5% reduction after thermocycling. From the scanning electronic microscope investigation, the SIE-treated substrate showed a surface that appeared to be clear of the fired porcelain glaze. The lower bond strength of the SIE group after thermocycling in this study suggests this procedure may require use of the same ceramic formulation and/or a more detailed knowledge of the etching protocol, implying that this may be a technique-sensitive procedure. The present results suggest that prolonged ultrasonic etching of a ceramic liner to enhance bonding should be performed cautiously.

Initial studies were performed to determine the application and duration of hydrofluoric acid etching. Using the scanning electron microscope, a more uniform etching pattern was observed with the twice 2-min hydrofluoric acid etching protocol. The L/HFE group surface treatment as described gave the highest bond strengths, eliminating the need for alumina particle abrasion, which has been considered a technique-sensitive procedure and to have potentially adverse effects on zirconia.

If a paste liner is to be used on the fitting surface of a zirconia framework, such as for short clinical crowns or for resin-bonded fixed dental prostheses, the effects this ceramic layer may have on the fit of the restorations must be taken into account. Wettstein et al[38] measured the internal gap between abutment teeth and the zirconia bridge framework; mean values taken from different areas ranged from 121.3 µm to 192.0 µm. The SEM observations in the current study found the thickness of two layers of liner to be less than 10 µm, as measured by the SEM software (Fig 4). While a thickness of this magnitude appears acceptable, these measurements were only obtained on flat surfaces. The thickness at the internal angles and defects of tooth preparation may be higher. Further investigation with trial tooth preparations and fabricated copings should be performed to confirm the actual influence on restoration fit. If this is not found to adversely affect the fit of the restorations, this could become an effective, inexpensive, convenient, and predictable method of providing a strong, durable bond between zirconia frameworks and tooth tissue without the need for additional processing or methods. The procedure for applying and firing the liner is simple, and the extra time needed is mainly due to the duration of the firing cycles, which take about 15 to 20 min each. The airborne particle abrasion process can be omitted, so that surface damage or degradation will not be a concern.

CONCLUSION

The firing of the paste liner and its subsequent HF etching yielded significantly higher bond strengths than all the other test groups at 24 h as well as after thermocycling; thus, the null hypothesis was rejected. Based on the present results, the conclusion may be drawn that as-sintered zirconia used with an adhesive cement has limited bond strength compared to surface-treated zirconia, and that similarly cemented alumina-particle–abraded zirconia may have an unpredictable bond strength over time. A limitation of this study was the 21-day storage time, which may not have allowed full water saturation of the luting resin, and therefore the hydrolytic stability of the bonding interface may not have been tested.

ACKNOWLEDGMENTS

The authors would like to thank Mr. Tony Yuen, Mr. Simon Lee, Mr. Chui Y. Y., and Mr. Paul Lee for assisting in laboratory procedures and Mr. Shadow Yeung for assisting with the statistical analysis.

REFERENCES

1. Aboushelib MN. Evaluation of zirconia/resin bond strength and interface quality using a new technique. J Adhes Dent 2011;13:255-260.
2. Aboushelib MN, Feilzer AJ, Kleverlaan CJ. Bonding to zirconia using a new surface treatment. J Prosthodont 2010;19:340-346.
3. Aboushelib MN, Kleverlaan CJ, Feilzer AJ. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. J Prosthet Dent 2007;98:379-388.
4. Aboushelib MN, Matinlinna JP, Salameh Z, Ounsi H. Innovations in bonding to zirconia-based materials: Part I. Dent Mater 2008;24:1268-1272.
5. Aboushelib MN, Mirmohamadi H, Matinlinna JP, Kukk E, Ounsi HF, Salameh Z. Innovations in bonding to zirconia-based materials. Part II: Focusing on chemical interactions. Dent Mater 2009;25:989-993.
6. Akgungor G, Sen D, Aydin M. Influence of different surface treatments on the short-term bond strength and durability between a zirconia post and a composite resin core material. J Prosthet Dent 2008;99:388-399.
7. Appeldoorn RE, Wilwerding TM, Barkmeier WW. Bond strength of composite resin to porcelain with newer generation porcelain repair systems. J Prosthet Dent 1993;70:6-11.
8. Atsu SS, Kilicarslan MA, Kucukesmen HC, Aka PS. Effect of zirconium-oxide ceramic surface treatments on the bond strength to adhesive resin. J Prosthet Dent 2006;95:430-436.
9. Attia A, Kern M. Effect of cleaning methods after recduced-pressure air abrasion on bonding to zirconia ceramic. J Adhes Dent 2011;13:561-567.
10. Blatz MB, Chiche G, Holst S, Sadan A. Influence of surface treatment and simulated aging on bond strengths of luting agents to zirconia. Quintessence Int 2007;38:745-753.
11. Blatz MB, Sadan A, Kern M. Resin-ceramic bonding: a review of the literature. J Prosthet Dent 2003;89:268-274.
12. Blatz MB, Sadan A, Martin J, Lang B. In vitro evaluation of shear bond strengths of resin to densely-sintered high-purity zirconium-oxide ceramic after long-term storage and thermal cycling. J Prosthet Dent 2004;91:356-362.
13. Casucci A, Osorio E, Osorio R, Monticelli F, Toledano M, Mazzitelli C, Ferrari M. Influence of different surface treatments on surface zirconia frameworks. J Dent 2009;37:891-897.
14. Cheung GC, Botelho MG, Matinlinna JP. Effect of surface treatments of zirconia ceramics on the bond strength to resin cement. J Adhes Dent 2014;16:49-56.
15. Cura C, Özcan M, Isik G, Saracoglu A. Comparison of alternative adhesive cementation concepts for zirconia ceramic: glaze layer vs zirconia primer. J Adhes Dent 2012;14:75-82.

16. Curtis AR, Wright AJ, Fleming GJP. The influence of surface modification techniques on the performance of a YTZP dental ceramic. J Dent 2006;34:195-206.
17. Derand T, Molin M, Kleven E, Haag P, Karlsson S. Bond strength of luting materials to ceramic crowns after different surface treatments. Eur J Prosthodont Restor Dent 2008;16:35-38.
18. Derand T, Molin M, Kvam K. Bond strength of composite luting cement to zirconia ceramic surfaces. Dent Mater 2005;21:1158-1162.
19. Everson P, Addison O, Palin WM, Burke FJ. Improved bonding of zirconia substructures to resin using a “glaze-on” technique. J Dent 2012;40:347-351.
20. Guazzato M, Albakry M, Ringer SP, Swain MV. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics. Dent Mater 2004;20:449-456.
21. Heikkinen TT, Lassila LV, Matinlinna JP, Vallittu PK. Effect of operating air pressure on tribochemical silica-coating. Acta Odontol Scand 2007;65:241-248.
22. Kappert HF, Krah M. Keramiken– eine Ubersicht. Quintessenz Zahntech 2001;27:668-704.
23. Kelly R, Denry I. Stabilized zirconia as a structural ceramic: An overview. Dent Mater 2008;24:289-298.
24. Kumbuloglu O, Lassila LV, User A, Vallittu PK. Bonding of resin composite luting cements to zirconium oxide by two air-particle abrasion methods. Oper Dent 2006;31:248-255.
25. Lawn BR, Deng Y, Lloyd IK, Janal MN, Rekow ED, Thompson VP. Materials design of ceramic-based layer structures for crowns. J Dent Res 2002;81:433-438.
26. Lindgren J, Smeds J, Sjögren G. Effect of surface treatments and aging in water on bond strength to zirconia. Oper Dent 2008;33:675-681.
27. Manicone PF, Iommetti PR, Luca Raffaelli L. An overview of zirconia ceramics: Basic properties and clinical applications. J Dent 2007;35: 819-826.
28. Matinlinna JP, Heijkkinen T, Özcan M, Lassila LV, Vallittu PK. Evaluation of resin adhesion to zirconia ceramic using some organosilanes. Dent Mater 2006;22:824-831.
29. Phark JH, Duarte S, Blatz M, Sadan A. An in vitro evaluation of the long-term resin bond to a new densely sintered high-purity zirconium-oxide ceramic surface. J Prosthet Dent 2009;101:29-38.
30. Piwowarczyk A, Lauer JC, Sorensen JA. The shear bond strength between luting cements and zirconia ceramics after two pre-treatments. Oper Dent 2005;30:382-388.
31. Qeblawi DM, Munoz CA, Brewer JD, Monaco EA. The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement. J Prosthet Dent 2010;103:210-220.
32. Rosentritt M, Behr M, Ven der Zel JM, Feilzer AJ. Shear bond strength of cement to zirconia. J Adhes Sci Technol 2009;23:1125-1132.
33. Thurmond JW, Barkmeier WW, Wilwerding TM. Effect of porcelain surface treatments on bond strengths of composite resin bonded to porcelain. J Prosthet Dent 1994;72:355-359.
34. Tsuo Y, Yoshia K, Atsuta M. Effects of alumina-blasting and adhesive primers on bonding between resin luting agent and zirconia ceramics. Dent Mater J 2006;25:669-674.
35. Wang H, Aboushelib MN, Feilzer AJ. Strength influencing variables on CAD/CAM zirconia frameworks. Dent Mater 2008;24:633-638.
36. Wegner SM, Gerdes W, Kern M. Effect of different artificial aging conditions on ceramic-comosite bond strength. Int J Prosthodont 2002;15:267-272.
37. Wegner SM, Kern M. Long-term resin bond strength to zirconia ceramic. J Adhes Dent 2000;2:139-147.
38. Wettstein F, Sailer I, Roos M, Hammerle CH. Clinical study of the internal gaps of zirconia and metal frameworks for fixed partial dentures. Eur J Oral Sci 2008;116:272-279.
39. Wolfart M, Lehmann F, Wolfart S, Kern M. Durability of the resin bond strength to zirconia ceramic after using different surface conditioning methods. Dent Mater 2007;23:45-50.
40. Zhang Y, Lawn BR, Malament KA, Van Thompson P, Rekow ED. Damage accumulation and fatigue life of particle-abraded ceramics. Int J Prosthodont 2006;19:442-448.

Clinical relevance: The etched ceramic liner provided a durable bond that may have benefit for short clinical crowns or resin-bonded fixed partial dentures. Although silane application increased the bond strength of alumina particle abraded zirconia, alumina particle abrasion had an adverse effect on the fired ceramic liner. Alumina particle abrasion alone and as-sintered zirconia are not recommended if a durable adhesive bond is required. Selective infiltration etching appears to be sensitive to the conditions of preparation.