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Research Article

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Effect of hydrofluoric acid-based etchant at an elevated temperature on the bond strength and surface topography of Y-TZP ceramics

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Conflict of Interest
No potential conflict of interest relevant to this article was reported.

Author Contributions
Conceptualization: Yu MK, Lee KW; Data curation: Lim MJ, Na NR; Formal analysis: Lim MJ, Lee KW; Methodology: Lim MJ, Na NR; Project administration: Yu MK, Lee KW; Resources: Yu MK, Lee KW; Software: Lim MJ, Na NR; Supervision: Yu MK, Lee KW; Validation: Lim MJ, Lee KW; Writing - original draft: Lim MJ, Lee KW; Writing - review & editing: Yu MK, Lee KW.

ABSTRACT

Objectives: This study investigated the effects of a hydrofluoric acid (HA; solution of hydrogen fluoride [HF] in water)-based smart etching (SE) solution at an elevated temperature on yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics in terms of bond strength and morphological changes.
Materials and Methods: Eighty sintered Y-TZP specimens were prepared for shear bond strength (SBS) testing. The bonding surface of the Y-TZP specimens was treated with 37% phosphoric acid etching at 20°C–25°C, 4% HA etching at 20°C–25°C, or HA-based SE at 70°C–80°C. In all groups, zirconia primers were applied to the bonding surface of Y-TZP. For each group, 2 types of resin cement (with or without methacryloyloxydecyl dihydrogen phosphate [MDP]) were used. SBS testing was performed. Topographic changes of the etched Y-TZP surface were analyzed using scanning electron microscopy and atomic force microscopy. The results were analyzed and compared using 2-way analysis of variance.
Results: Regardless of the type of resin cement, the highest bond strength was measured in the SE group, with significant differences compared to the other groups ($p < 0.05$). In all groups, MDP-containing resin cement yielded significantly higher bond strength values than MDP-free resin cement ($p < 0.05$). It was also shown that the Y-TZP surface was etched by the SE solution, causing a large change in the surface topography.
Conclusions: Bond strength significantly improved when a heated HA-based SE solution was applied to the Y-TZP surface, and the etched Y-TZP surface was more irregular and had higher surface roughness.

Keywords: Y-TZP; HA-based etchant; Temperature elevation; Bond strength

INTRODUCTION

Conventional airborne aluminum particle abrasion has been widely used on yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics as a surface treatment. Additionally, the functional monomer 10-methacryloyloxydecyl dihydrogen phosphate (MDP) is known to chemically bond with zirconia ceramics [1-4]. The use of primers and resin cements containing 10-MDP has resulted in relatively high bond strengths to Y-TZP [5,6]. Therefore, the combination of an MDP-containing primer and resin cement following airborne

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aluminum particle abrasion of Y-TZP [7] enables the highest bond strength to be obtained; this technique is widely used for clinical Y-TZP cementation.

However, the microporosities induced by airborne particle abrasion may act as crack initiators and weaken the Y-TZP restoration [8,9]. Furthermore, airborne particle abrasion of Y-TZP may not yield stable results, with a significant reduction in bond strength after thermocycling [10]. It is therefore necessary to find new methods to obtain good long-term results without weakening the Y-TZP restoration.

Several studies [11,12] have reported that hydrofluoric acid (HA; solution of hydrogen fluoride [HF] in water) can be used to etch zirconia surfaces. On the basis of these studies, zirconia-etching solutions have recently been introduced to the market, with examples including an HA solution containing nitric acid [13] and a new version of an etching solution containing HA, phosphoric acid (PA; H_3PO_4), and hydrochloric acid (HCl). Some studies have explored the effects of nitrate-containing HA on zirconia surfaces, but little research has been done on the bond strength and surface changes of zirconia in response to the new HA-based zirconia etching solution. In particular, no studies have yet explored changes in the bond strength between Y-TZP and resin cement and alterations in surface morphology when an elevated temperature is used with the new HA-based etching solution.

This study was conducted to investigate the change in bond strength between resin cement and Y-TZP when a new HA-based smart etching (SE) solution was raised to 70°C–80°C and applied to a Y-TZP surface. This study also aimed to observe the morphological changes of Y-TZP surfaces etched with SE. The first null hypothesis was that there would be no difference in shear bond strength (SBS) values according to whether the SE solution was applied, and the second null hypothesis was that there would be no morphological change on the zirconia surface after SE etching.

MATERIALS AND METHODS

Eight sintered Y-TZP test specimens and resin blocks were prepared for SBS testing. Y-TZP specimens in the form of standard cylinders (12 mm in diameter, 8 mm in height) were prepared using a pre-sintered Y-TZP block according to the manufacturer's instructions (NexxZr T, Sagemax, Federal Way, WA, USA). The resin block was prepared by packing the composite resin (Filtek Z350 XT, 3M ESPE, St. Paul, MN, USA) into a cylindrical plastic matrix (3 mm in diameter, 10 mm in height) and then light-cured with an LED curing unit (1,000 mW/cm^2, Bluephase, Ivoclar-Vivadent, Schaan, Liechtenstein) for 40 seconds.

The bonding surface of the Y-TZP specimens was treated with PA etching (ETCH-37, Bisco Inc., Schaumburg, IL, USA), HA etching (Porcelain Etchant, Bisco Inc.), or SE solution etching (Smart Etching, Yesbiogold Inc., Seoul, Korea). The specimens were classified into the following 4 groups:

1) Control (n = 20): not etched.
2) PA group (n = 20): 37% phosphate etchant was placed on the Y-TZP surface for 10 minutes at 20°C–25°C. The Y-TZP specimen was then rinsed with an air-water spray and dried.
3) HA group (n = 20): 4% porcelain etchant was placed on the Y-TZP surface for 10 minutes at 20°C–25°C. The Y-TZP specimen was then rinsed with an air-water spray and dried.

4) SE group (n = 20): the SE solution was heated to 70°C–80°C in a water bath. Following the manufacturer's instructions, the Y-TZP specimen was placed in a heated SE solution bath for 10 minutes. The Y-TZP specimen was then rinsed with an air-water spray and dried.

Zirconia primer (Z-prime Plus, Bisco Inc.) was applied to the bonding surface of Y-TZP for 10 seconds and air-dried for 15 seconds in all groups. Two types of resin cement were used in each group. One was an MDP-containing resin cement (G-CEM LinkAce, GC Inc., Tokyo, Japan) and the other was an MDP-free resin cement (Duo-link Universal, Bisco Inc.). The resin cement was applied to the adhesive surface of Y-TZP under a constant load of 5 N. Photocuring was performed for 3 seconds for tack curing, and the excess cement was carefully removed with an explorer. All surfaces were light-cured for 20 seconds while maintaining the load. The specimens that underwent the luting procedure were stored in water at 36°C for 24 hours before SBS testing. The materials used in this study are listed in **Table 1**.

Each specimen was mounted in a jig of a universal testing machine (Model 5543, Instron, Canton, MA, USA) and shear force was applied to the specimen using a chisel-shaped metal rod at a constant crosshead speed of 0.5 mm/min until failure. The load was measured as the force at which failure occurred, and SBS was calculated using the formula: SBS (MPa) = Load (N)/Area (mm^2).

The morphology of the etched Y-TZP surface was observed using scanning electron microscopy (SEM) (SU8230, Hitachi, Tokyo, Japan), and the surface roughness of the etched Y-TZP surface was measured using atomic force microscopy (AFM; Multimode-8, Bruker, Santa Barbara, CA, USA).

Statistical analysis was performed using SPSS version 18.0 (SPSS Inc., Chicago, IL, USA), and 2-way analysis of variance (ANOVA) was applied to identify significant differences in SBS among the groups. A *p* value less than 0.05 was considered to indicate statistical significance in all tests.

Table 1. Materials used, manufacturers, and major components

Material	Trade name	Manufacturer	Main components
PA etching	Etch-37	Bisco Inc., Schaumburg, IL, USA	37% PA gel w/benzalkonium chloride
HA etching	Porcelain Etchant	Bisco Inc., Schaumburg, IL, USA	4% buffered HA gel
SE solution etching	Smart Etching	Yesbiogold Inc., Seoul, Korea	40% HA (vol %) 59% PA (vol %) 1% HCl (vol %)
Zirconia primer	Z-prime Plus	Bisco Inc., Schaumburg, IL, USA	BPDM, HEMA, ethanol
MDP-containing resin cement	G-CEM LinkAce	GC Inc., Tokyo, Japan	Paste A: Fluoro-alumino-silicate glass, UDMA, dimethacrylate, silicon dioxide Paste B: PA ester monomer (MDP), silicon dioxide, UDMA, dimethacrylate
MDP-free resin cement	Duo-link Universal	Bisco Inc., Schaumburg, IL, USA	Base: Bis-GMA, TEGDMA, UDMA, glass filler Catalyst: Bis-GMA, TEGDMA, glass filler

PA, phosphoric acid; HA, hydrofluoric acid; SE, smart etching; HCl, hydrochloric acid; BPDM, biphenyl dimethacrylate; HEMA, hydroxyethyl methacrylate; UDMA, urethane dimethacrylate; MDP, methacryloyloxydecyl dihydrogen phosphate; Bis-GMA, bisphenyl A glycidyl methacrylate; TEGDMA, triethylene glycol dimethacrylate.

RESULTS

The mean SBS values (with standard deviations) of all experimental groups are presented in **Table 2** and **Figure 1**. The SBS values were 8.50 MPa, 12.37 MPa, 12.60 MPa, and 16.15 MPa when using MDP-free resin cement in the control (etch-free), PA, HA, and SE groups, respectively. The experimental group with the highest bond strength was the SE group, followed by the HA group, PA group, and control group in descending order. The SBS values were 12.80 MPa, 16.17 MPa, 15.60 MPa, and 20.39 MPa when using MDP-containing resin cement in the control, PA, HA, and SE groups, respectively. The SE experimental group had the highest bond strength values, followed by the PA group, HA group, and control group in descending order.

Two-way ANOVA showed that the type of etching solution and resin cement had a significant effect on SBS. Regardless of the type of resin cement, the highest bond strength was measured in the SE group, with a significant difference compared to the other groups ($p < 0.05$). No statistically significant difference was found between the HA and PA group ($p > 0.05$), but these 2 groups showed significantly higher SBS values than the control group ($p < 0.05$). In all groups, MDP-containing resin cement yielded significantly higher bond strength values than MDP-free resin cement ($p < 0.05$).

Representative SEM images of specimens etched by different etchants on Y-TZP surfaces are shown in **Figure 2**. The SEM analysis showed no significant change compared to the control surface when the Y-TZP surface was etched with 37% PA or 4% HA. However, etching the Y-TZP surface with SE changed its shape, making the surface more irregular.

Table 2. Shear bond strength values of each experimental group according to the use of methacryloyloxydecyl dihydrogen phosphate (MDP)-free or MDP-containing resin cement after etching the yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) surface under various conditions

Etching condition	Resin cement, Mean ± SD (MPa)	
	MDP-free resin cement	MDP-containing resin cement
Control	8.50 ± 2.16^{Aa}	12.80 ± 0.81^{Ab}
37% PA at 20°C–25°C	12.37 ± 2.92^{Ba}	16.17 ± 0.99^{Bb}
4% HA at 20°C–25°C	12.60 ± 3.03^{Ba}	15.60 ± 2.55^{Bb}
HA-based SE at 70°C–80°C	16.15 ± 2.82^{Ca}	20.39 ± 2.29^{Cb}

SD, standard deviation; PA, phosphoric acid; HA, hydrofluoric acid; SE, smart etching.
Identical uppercase letters indicate no statistically significant differences ($p > 0.05$).

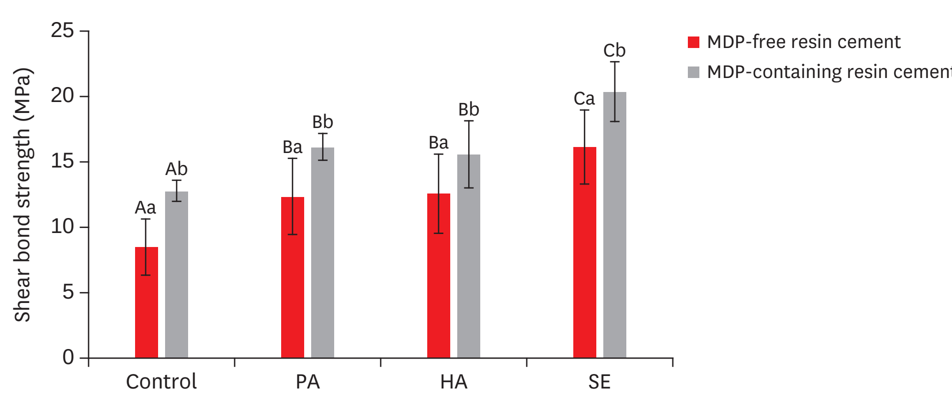

Figure 1. Shear bond strength values of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) in each group etched under various conditions with different resin cements.
MDP, methacryloyloxydecyl dihydrogen phosphate; PA, phosphoric acid; HA, hydrofluoric acid; SE, smart etching.
Identical uppercase letters indicate no statistically significant differences ($p > 0.05$).

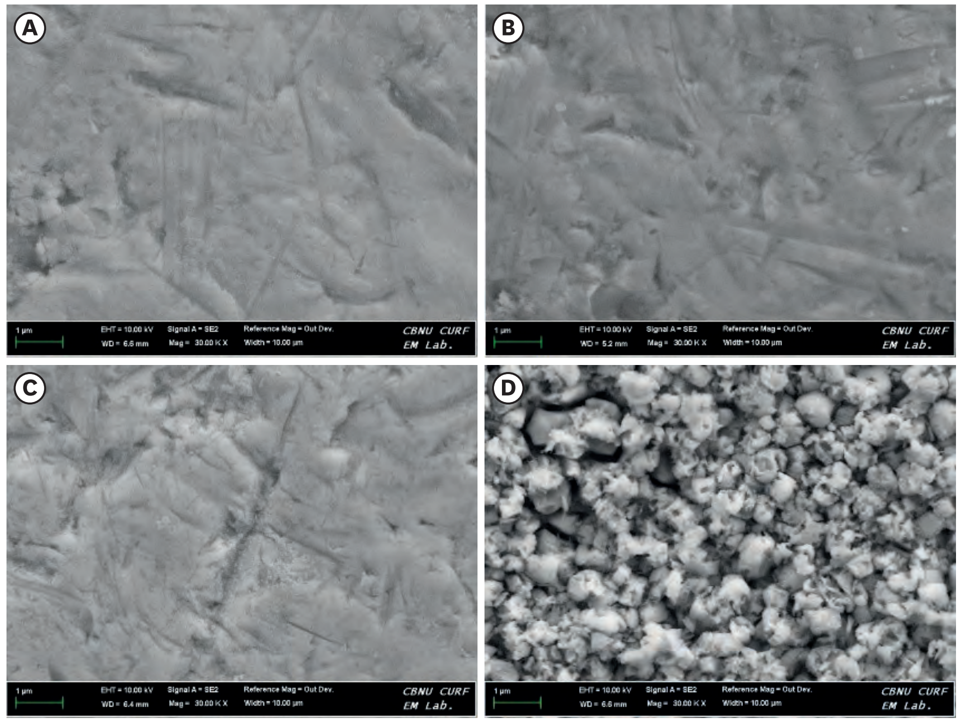

Figure 2. Scanning electron microscopy (SEM) images at 30,000 times magnification of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) surfaces etched under different conditions. (A) Etching-free specimen (control); (B) 37% phosphoric acid (PA)-etched specimen; (C) 4% hydrofluoric acid (HA)-etched specimen; (D) HA-based smart etching (SE)-etched specimen.

The surface roughness values of the control, HA, and PA groups were 0.014 μm, 0.015 μm, and 0.015 μm, respectively. In contrast, the surface roughness of the SE group was 0.098 μm. On AFM, the SE group showed the roughest surface (**Figure 3**).

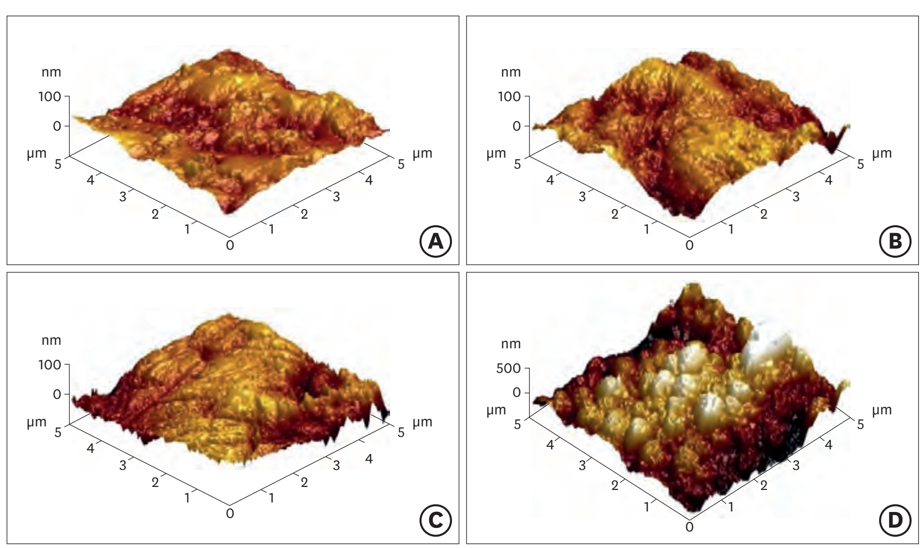

Figure 3. Atomic force microscopy images of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) surfaces etched under different conditions. (A) Etching-free specimen (control); (B) 37% phosphoric acid (PA)-etched specimen; (C) 4% hydrofluoric acid (HA)-etched specimen; (D) HA-based smart etching (SE)-etched specimen.

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DISCUSSION

Zirconia has a high crystallinity and no glass phase. Thus, for traditional ceramics, surface pretreatment such as HA etching or silane primer application was established not to increase the bond strength to zirconia surfaces [14-16]. However, this was because the conditions under which HA was applied to silica-based ceramics, such as feldspathic porcelain or lithium disilicate, were the same as those used for zirconia. By adjusting the conditions in which the HA solution is applied, zirconia surfaces can be etched. HA (9.5%) solution can etch zirconia surfaces if the immersion time is extended (up to 24 hours) or if the application temperature is increased (up to 80°C). In addition, high-concentration (48%) HA solutions can be used to etch zirconia [11,17,18].

The SE solution used in this study consisted of HA, PA, and HCl. HA is known to be a weak acid because the HA solutions generally used in industry contain low concentrations. However, we used a high concentration of HA in this study, at which point it becomes a strong acid with a very high acid dissociation constant (K_a). By volume, PA was the most predominant component of the SE solution, but considering the acidity of the components of the SE solution, it can be seen that HA provided it with the ability to serve as an etchant. In fact, this experiment found that PA did not etch the Y-TZP surface. SEM and AFM images showed that the Y-TZP surface treated with SE solution was more irregular and had higher surface roughness than the other groups. In other words, the SE solution could etch Y-TZP surfaces. According to Ansari *et al.* [19], an HA-based zirconia etching solution did not adversely affect the surface hardness of the tested zirconia specimens, unlike airborne particle abrasion. The SE solution, with a with similar composition, is also expected to have no adverse effect on surface hardness, but further study is needed.

Etching for 10 minutes with the SE solution significantly increased the SBS compared to other groups. This result is thought to have occurred because the SE etching induced more changes in the surface morphological characteristics of the Y-TZP surface. PA is known to be unable to etch zirconia surfaces, and this was also confirmed by SEM and AFM images in this study. However, although the morphological characteristics of the Y-TZP surface did not change significantly in the PA group, the SBS was significantly higher in the PA group than in the control group. It is generally known that cleaning with PA can remove residual organic matter, which readily dissolves in acid. A previous study of saliva contamination on zirconia showed that PA removed almost all organic contaminants [20]. Therefore, the result obtained in this study for PA is thought to be due to the excellent surface cleaning ability of PA on Y-TZP surfaces.

As expected, when MDP-containing resin cement was used, all groups showed significantly higher bond strength than when MDP-free resin cement was used. This is because 10-MDP can chemically bond to zirconia. Many studies [1-4,21,22] have reported the bonding efficacy of 10-MDP to zirconia, and some have presented theoretical proposals for this behavior. Nagaoka *et al.* [3] found that the chemical interaction of 10-MDP depended on the ionic interactions of 10-MDP with partially positive zirconium and intermolecular hydrogen bonding.

Commercially available zirconia etching solutions are generally applied at room temperature. Zeta Etching Solution (Eunjin Chemical Co., Gunsan, Korea) [19] is applied to zirconia for 60 minutes in an ultrasonic bath at room temperature. The Zircos E etching system [13] (Eunjin Chemical Co.) is applied to zirconia for 3 hours at 25°C. In this experiment, SE solution was applied to Y-TZP for 10 minutes at 70°C–80°C. The SE etchant had a higher application temperature and shorter application time than the other zirconia etchants. It is believed that a higher application temperature increases the molecular activity of the etchant so that the zirconia surface can be etched quickly and efficiently in a short time.

As a result of this study, when the surface of Y-TZP was etched by raising the HA-based SE solution to 70°C–80°C, the SBS between resin cement and Y-TZP was significantly higher than in the other experimental groups. It was also shown that the Y-TZP surface was etched by the SE solution, causing a large change in the surface topography. Based on these results, both the first and second null hypotheses proposed in the introduction were rejected. However, further research is needed to obtain a more detailed understanding of the effects of long-term water storage and thermal cycling on the bonding surface and the problems encountered in clinical applications.

CONCLUSIONS

The SBS between Y-TZP and resin cement significantly improved when an HA-based SE solution was raised to 70°C–80°C and applied to the Y-TZP surface. In addition, the Y-TZP surface treated with the SE solution was more irregular and had higher surface roughness.

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