Effect of low-concentration hydrofluoric acid hot-etching on shear bond strength and biaxial flexural strength of zirconia after thermocycling

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Effect of low-concentration hydrofluoric acid hot-etching on shear bond strength and biaxial flexural strength of zirconia after thermocycling

Directed by Professor Jee-Hwan Kim

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먼저 저를 여기까지 이끌어 주시고 아낌없는 지원과 무한한 도움을 주신 김지환 지도교수님께 진심으로 감사드립니다. 학자로서의 냉철함과 열정뿐만 아니라 온화함과 따뜻함을 통해 교수님께 많은 부분을 배울 수 있었습니다. 교수님의 가르침을 본받아 연구자의 길을 계속 걷겠습니다. 또한 부족함 많은 저를 언제나 믿고 지켜봐 주신 심준성 병원장님께 존경과 감사를 전합니다. 언제나 따뜻한 가르침으로 학문의 길에서 인도해주신 신유석 교수님과 바쁘신 중에 논문 심사를 맡아 주시고, 유익한 말씀과 조언을 해주신 김종은 교수님 그리고 권재성 교수님께도 깊은 감사를 드립니다. 그리고 짧지만 긴 시간 동안 서로에게 의지하면서 옆에서 힘이 되어준 보철과 연구원 선생님들을 비롯한 모든 연구원, 수련의 선생님들과 힘들고 지칠 때마다 응원해준 친구들 모두에게도 감사의 마음을 전합니다.

공부하는 딸을 위해 사랑과 기도로 함께해주신 사랑하는 부모님과 넘치는 사랑으로 응원해주신 시댁 식구들에게 감사드리며, 늦게 공부하는 누나를 잘 따라준 동생 성현이 에게도 고마움과 깊은 사랑을 전합니다. 앞으로도 더욱 감사하며 겸손한 자세로 끊임없이 배우고 탐구하는 학자가 되도록 노력하겠습니다.

마지막으로, 변함없는 사랑으로 곁에서 묵묵히 지켜봐 주고, 언제나 큰 힘이 되어준 사랑하는 남편에게 진심으로 고마운 마음을 전합니다.

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ABSTRACT

Effect of low-concentration hydrofluoric acid hot-etching on shear bond strength and biaxial flexural strength of zirconia after thermocycling

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The present study aimed to evaluate the shear bond strength (SBS) and biaxial flexural strength (BFS) of zirconia before and after thermocycling according to the surface treatment methods using low-concentration hot-etching with hydrofluoric acid on the yttrium-stabilized tetragonal zirconia polycrystal (Y-TZP) surface.

Seventy-two Y-TZP cubes (5x5x5 ㎣) were classified into 3 groups for the SBS test according to the surface treatment methods. A total of 3 kinds of surface treatment methods were applied as follows: 1) airborne-particle with 50㎛ Al_2O_3 particles at 2 bar for 15 s at a distance of 10 ㎜ (group A), 3) hot-etching with hydrofluoric acid in 100 ℃ for 10 minutes (group E), 4) airborne-particle + hot-etching (group AE). The specimens for the SBS test were coated with a primer on the treated zirconia surface and followed by the application of resin cement with the aid of a plastic mold.

Ninety-six Y-TZP discs (25 ㎜ diameter by 15 ㎜ high) were divided into 4 groups for the BFS test according to surface treatment methods. Surface treatment methods were applied as follows: 1) no treatment (group C), 2) airborne-particle with 50㎛ Al_2O_3 particles at 2 bar for 15 s at a distance of 10 ㎜ (group A), 3) hot-etching with hydrofluoric acid in 100 ℃ for 10 minutes (group E), 4) airborne-particle abrasion + hot-etching (group AE). Half of the specimens in each group were stored in 37℃ distilled water for 24 hours, and the other half of the specimens underwent thermocycling between 5 ℃ and 55 ℃ with 1,000 cycles. The specimens of surface treatment groups were observed with the phase composition of Y-TZP was determined by an X-ray diffractometer, a scanning electron microscope, and the SBS, BFS, roughness (Ra) of the specimens were measured. All data were analyzed with analysis of variance or Kruskal-Wallis tests ($\alpha = 0.05$)

Regardless of thermocycling process, group E exhibited significantly higher SBS value than the other 2 groups ($p < 0.05$). Groups C and E exhibited significantly higher BFS values compared to groups A and AE after thermocycling ($p < 0.05$), whereas no significant differences were observed for the BFS values among the 4 groups before thermocycling ($p > 0.05$). For all groups, phase transformation occurred from tetragonal to monoclinic phase.

Low-concentration hot-etching for 10 minutes produced significantly higher SBS and BFS values compared to airborne-particle abrasion and simultaneous application of airborne-particle abrasion and hot-etching treatment.

Keywords: flexural strength; hot-etching; hydrofluoric acid; shear bond strength; surface treatment; zirconia

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I. INTRODUCTION

The use of partially stabilized zirconium dioxide ceramics in dental restorations has recently been increasing due to their excellent physical properties such as high hardness, high compressive strength, optimal biocompatibility in a variety of applications, and adequate optical properties (Manicone et al., 2007; Piconi and Maccauro, 1999). In particular, due to the development of computer-aided design and manufacturing (CAD/CAM) technology, these ceramics are increasingly being used as prosthetic restoration materials (Koutayas et al., 2009). Most dental zirconia is supplied in the form of pre-sintered zirconia blocks containing stabilized yttria, and the final prosthesis is obtained after sintering by milling with dental CAD/CAM equipment. According to in vitro studies, zirconia has a relatively high flexural strength of 900 to 1200 ㎫ and has an aesthetic similar to that of natural teeth therefore it is widely used as a single crown core material or as a fixed prosthesis(Christel et al., 1989).

Zirconia restorations are not silica-based ceramics; therefore, resin bonding is difficult. Numerous researchers have focused on characterizing the effects of zirconia surface treatment methods (STMs) on the adhesions between resin cement and zirconia (Abdullah et al., 2019; Casucci et al., 2009; Lee and Lee, 2017; Lv et al., 2015). STMs include the following five micro-mechanical and chemical bonding techniques: mechanical treatment, chemical treatment, lasers, silicon coatings, and coupling agents (Tzanakakis et al., 2016).

Among the mechanical treatment techniques, the most commonly used is airborne-particle abrasion. Several studies have found that the abrasion method contributes to the increase in the adhesive strength between the resin cement and zirconia. However, the effects of the surface treatment vary according to the specific type of abrasion method; particularly, there are uncertainties regarding the impact of its long-term use (Dantas et al., 2019; Yang and Liu, 2018). For example, airborne-particle abrasion using alumina particles (Al_2O_3), the positive effects of which have been evaluated and reported by several studies using meta-analysis (Blatz et al., 2010; Inokoshi et al., 2014; Okada et al., 2019a; Okada et al., 2019b; Ozcan and Bernasconi, 2015; Wongkamhaeng et al., 2019), eliminates impurities, induces surface modification, and increases surface roughness (known as Ra) on yttria-stabilized zirconia surfaces (Y-TZP). The resulting treatment features a rigid, durable micro-mechanical retention between the Y-TZP and resin cement, with significantly increased flexural strengths of the material; however, this method also induces phase transformation of the zirconia surface crystal structure from tetragonal to monoclinic. The formation of micro-cracks due to this transformation can negatively affect the long-term stability of the zirconia (Guazzato et al., 2004; Guazzato et al., 2005; Kosmac et al., 1999; Smielak and Klimek, 2015). In addition, airborne-particle abrasion is influenced by the particle size of the alumina, the pressure and distance at which air is applied, and the uniformity of abrasion on the surface; this is especially true in those cases in which excessive particle size and reduced application distance induce micro-crack formation. This is a disadvantage which not only reduces the long-term mechanical properties of the ceramic, but also makes it difficult to apply uniform surface treatment within dental clinics (Guazzato et al., 2005; Karakoca and Yilmaz, 2009; Kosmac et al., 1999; Sato et al., 2006). Due to these challenges, new methods of zirconia surface modification such as surface coating, laser irradiation, and acid etching, including a form of chemical etching known as “selective infiltration etching” (SIE), are being developed to improve the resin’s adhesion (Aboushelib et al., 2007; Akin et al., 2011; Akyil et al., 2010; Xie et al., 2013). Particularly, there have been studies that use chemical etching via different approaches to increase the adhesive strength (Thompson et al., 2011; Tzanakakis et al., 2016).

Zirconia was originally known as a material that is difficult to etch using hydrofluoric acid (HF) solution (Della Bona et al., 2007; Ural et al., 2010); however, it has now been shown that better adhesion to zirconia can be attained by changing the formulation and application of the etching solution (Akay et al., 2017; Casucci et al., 2010; Casucci et al., 2011; Casucci et al., 2009; Smielak and Klimek, 2015; Xie et al., 2013), thus improving the etching conditions. Previous studies have used various etching solutions of high to low concentrations, including HF, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3)(Casucci et al., 2010; Casucci et al., 2009; Liu et al., 2015; Xie et al., 2013). Lui et al. compared the shear bond strength (SBS) of the resin-zirconia bond after various surface treatments including those using high concentrations (above 9.5%) of HNO_3 and HF (Liu et al., 2015). The surface treatment involving the use of high-concentration HF solutions for 25 min at 100 ℃ and silica coating is effective in forming a micro-retentive structure, and has been reported to improve the reliability of the resin–zirconia bonding without phase transformation from tetragonal to monoclinic.

In a previous study (Ural et al., 2010), the SBS between zirconia and resin cement did not show significant improvement for treated zirconia with a low concentration of 9.5% HF. Other previous studies using 9.5% HF (Sriamporn et al., 2014) confirmed that the production of porosities as micro-morphological changes increased according to the time and temperature by comparing the 1-min treatment at 80 ℃ to 1h treatment at 25 ℃.

Some studies have found that hot chemical etching solutions can produce a significantly better Ra than that obtained with the SIE methods, and that hot-etching can improve the mechanical retention of zirconia and increase the mean arithmetic profile deviation roughness parameter (Ra_{mean}) (Akay et al., 2017; Casucci et al., 2009). For hot-etching, the etching effect was increased and the adhesion between the zirconia and resin was improved when heat was applied to the surface treatment of zirconia using the etching solution (Akay et al., 2017; Casucci et al., 2010; Casucci et al., 2011; Xie et al., 2013). It has also been demonstrated that hot-etching may result in a selective chemical etching of zirconia, which leads to the production of micro retention and increases the grain boundaries through the preferential removal of the less-arranged and high-energy peripheral atoms (Casucci et al., 2011). However, using high-concentration etching solutions in the clinic at high temperatures would be dangerous. According to author Sullivan JB, Krieger GR (as cited in Alex, 2008), although HF at concentrations of 4–10% was reported to be safe for dental use (Alex, 2008), few studies have been conducted on SBS and biaxial flexural strength (BFS) when hot-etching is performed for a short time with low-concentration HF at high temperatures.

Most of the experiments conducted in vitro studies do not reproduce the oral environment, however, the oral environment can cause physicochemical changes in dental materials. In particular, a change in temperature in an environment with moisture may cause a phase shift due to low-temperature degradation (LTD) of zirconia, which may cause micro-crack on the surface of zirconia and degrade physical properties. Therefore, it is very important to understand the change in the physical properties of zirconia in the thermal cycle. In previous studies, the shear bond strength of zirconia with the surface treatment with 48% of hydrofluoric acid at 100 ℃ for 25 min was no significant difference compared to sandblasting before and after thermocycling treatment (Liu et al., 2015). In another study with high-concentration acid, the shear bond strength on zirconia of various surface treatment decreased after thermal cycling compared to before thermocycling, and the shear bond strength of zirconia surface treatment with hot-etching using high-concentration acid was significantly higher compared to airborne-particle abrasion after thermocycling (Lee and Lee, 2017). There has been very little research on characterizing the properties of zirconia strength and surface changes about surface treatment with low-concentration HF acid hot-etching after thermocycling. Therefore, the development of a surface treatment that is safer for use in clinics while maintaining the integrity of the adhesive strength would appear to be necessary.

To address this need, this study aims to evaluate the effect of hot-etching surface treatment at 100 ℃ using low-concentration HF (9%) on the SBS between partially stabilized zirconia ceramic and resin cement and the BFS of zirconia. The null hypothesis of this study is that 1) there would be no significant difference in SBS of zirconia-resin cement and the BFS of zirconia in accordance to the different surface treatment of zirconia, 2) there would be no significant difference in mechanical properties according to the various surface treatments of zirconia after thermocycling.

II. MATERIALS AND METHODS

1. Sample Preparation

The primary material used for this study was pre-sintered yttria-tetragonal zirconia polycrystal (Dmax Natura Z-W9812, DMAX Co., Daegu, Korea), which was converted from block form into discs using a CAD/CAM process.

For the BFS test, the discs were sintered at 1530 ℃ for 2 h (heating rate: 3 h from 20 ℃ to 900 ℃, and 4 h from 900 ℃ to 1530 ℃, followed by natural cooling); subsequently, these were polished with a 1㎛ diamond paste to produce the final dimensions of 13.6 ㎜ diameter and 1.5 ㎜ thickness, yielding a total of 96 zirconia specimens (n = 96).

For the SBS preparation, zirconia block cubes (dimensions 5 × 5 × 5 ㎣) were fabricated using the same sintering method and were placed with the adhesive side down; the resin was then poured into the mold (25 ㎜ diameter by 15 ㎜ high), followed by self-curing for 24 h. The upper surface of each specimen was polished with silicon–carbon abrasive papers (grits #400, 600, and 1200); this was achieved by using a polishing machine under tap water irrigation to remove contaminants (Figure 1).

All specimens were then divided into four experimental study groups of 24 specimens each as follows: group C (control group), group A (abrasion group), group E (etching group), and group AE (abrasion-etching group). The specimens were then sonicated in water for 5 min according to the type of the surface treatment performed, as follows.

For C, no further treatment was applied; this group served as a control. For A, the zirconia surfaces were airborne-particle-abraded with 50 ㎛ aluminum oxide (Al_2O_3) particles (Cobra® 50 ㎛, white; Renfert GmbH, Hilzingen, Germany) applied perpendicular to the surface at 2 bar for 15 s at a distance of 10 ㎜. For E, after applying HF (Ceramic Etchant 9, Medifive Co., Ltd., Incheon, Korea) to the zirconia surfaces, the group was placed in a closed container that consisted of a triple-locking design with a heat-generating pack in 100 ℃ for 10 min. To neutralize the F ions and toxic substances emitted from the upper part of the closed vessel, a HF neutralizing agent was used (HF Neutralizer, Medifive Co., Ltd., Incheon, Korea). For AE, both airborne-particle abrasion and experimental hot-etching solution treatments were applied. After surface treatment using the same airborne-particle method as that applied to group A, and water rinsing with ultrasound and drying with an air syringe, the abraded zirconia surfaces were hot-acid-etched using the same method as that applied to group E. All the specimens were rinsed in an ultrasonic bath containing water for 5 min to remove the alumina particles or HF residue, and then dried using the air-water syringe. The specimen surface-treatment procedure is illustrated in Figure 1,2 and materials are suggested in Table 1. Groups C, A, E, and AE were included in the BFS test and Groups A, E, and AE were included in the SBS test.

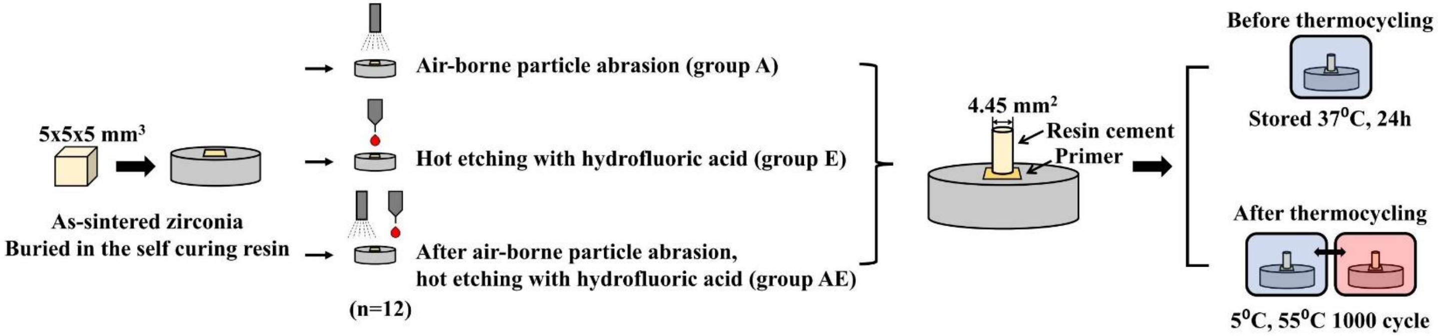


Figure 1. Specimen surface-treatment procedure of shear bond strength

Sample of shear bond strength (SBS) test and surface-treatment procedure (n=72, (group A, E and AE))

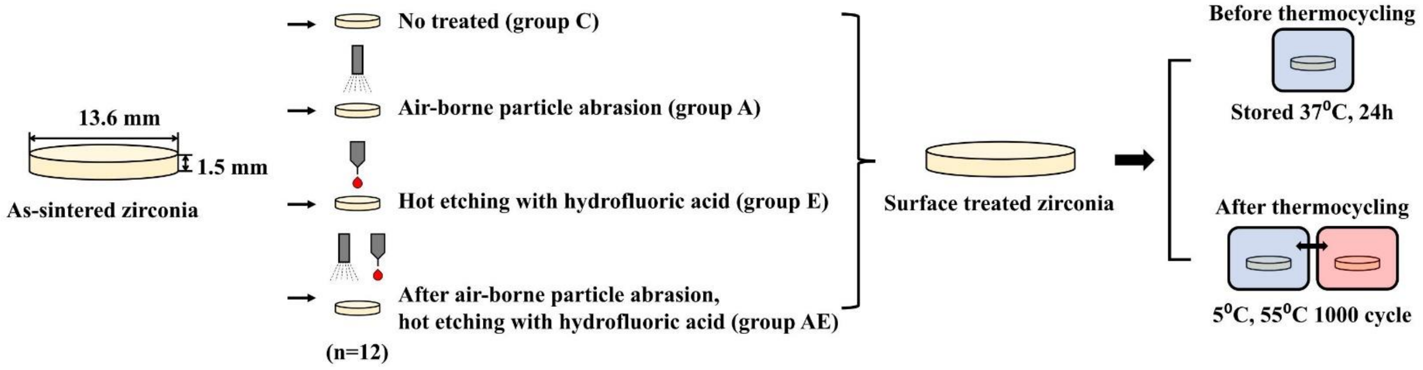


Figure 2. Specimen surface-treatment procedure of biaxial flexural strength

Sample of biaxial flexural strength (BFS) test and surface-treatment procedure (n=96, (group C, A, E and AE))

Table 1. Materials used in this study

Material	Product name	Main composition[a]	Manufacturer
Zirconia block	D max Natura Z-W9812	< 95% ZrO_2+HfO_2 < 6% Y_2O_3,	DMAX Co., Daegu, Korea
Ceramic Primer	Z-Prime Primer	<90% Ethanol, <10% Biphenyl dimethacrylate, <20% 2-hydroxyethyl methacrylate (HEMA), <5% MDP	Bisco Inc. Schaumburg, IL, USA
Self-adhesive resin cement	TheraCem®	Base <50% Portland cement <50% Ytterbium w/ Barium Glass <5% Ytterbium Fluoride <5% BisGMA Catalyst paste <30% 10-Methacryloyloxydecyl Dihydrogen Phosphate, <5% 2-Hydroxyethyl Methacrylate	
Hydrofluoric acid	Zirconia Etchant	9% Hydrofluoric acid gel <10% hydrofluoric acid <2% thickening agent	Medifive Co., Ltd., Incheon, Korea

[a]Main composition was obtained from safety data sheets provided by manufacturers;

wt%, weight percent

The surface-treated zirconia specimens were then coated with primer (Z-Prime Plus; BISCO, Schaumburg, IL, USA) as directed by the manufacturer and dried with an air-water syringe for 5 s. The resin-zirconia bonding method was as follows. Resin cement (TheraCem, BISCO, Schaumburg, IL, USA) was applied to a plastic mold (Ultradent Jig; Ultradent Products, South Jordan, UT, USA), which was then placed on the zirconia surface (bonding area 4.45 ㎟) and light-cured with a 1200 mW LED light curing unit (DB-686 Cappu LED Curing Light; Bisco Asia, Seoul, Korea).

Finally, half of the specimens from each group (C, A, E and AE) were stored in distilled water at 37 ℃ for 24 h, and the other half of the specimens were thermally cycled for 1,000 cycles between 5 ℃ and 55 ℃ with a dwell time of 10 s.

2. Shear Bond Strength (SBS) Test

For the evaluation of SBS (n = 12), each specimen was fixed in a universal testing machine (Bisco, Schaumburg, IL, USA) using a metal jig. The maximum force load (recorded in N) was measured at a crosshead speed of 0.5 ㎜/min at a distance of 1 ㎜ from the bonding interface until the cement column was dropped. The bond strength for each specimen was calculated by dividing the peak load (in N) by the surface area (4.45 ㎟) to achieve the strength in ㎫ (Figure 2).

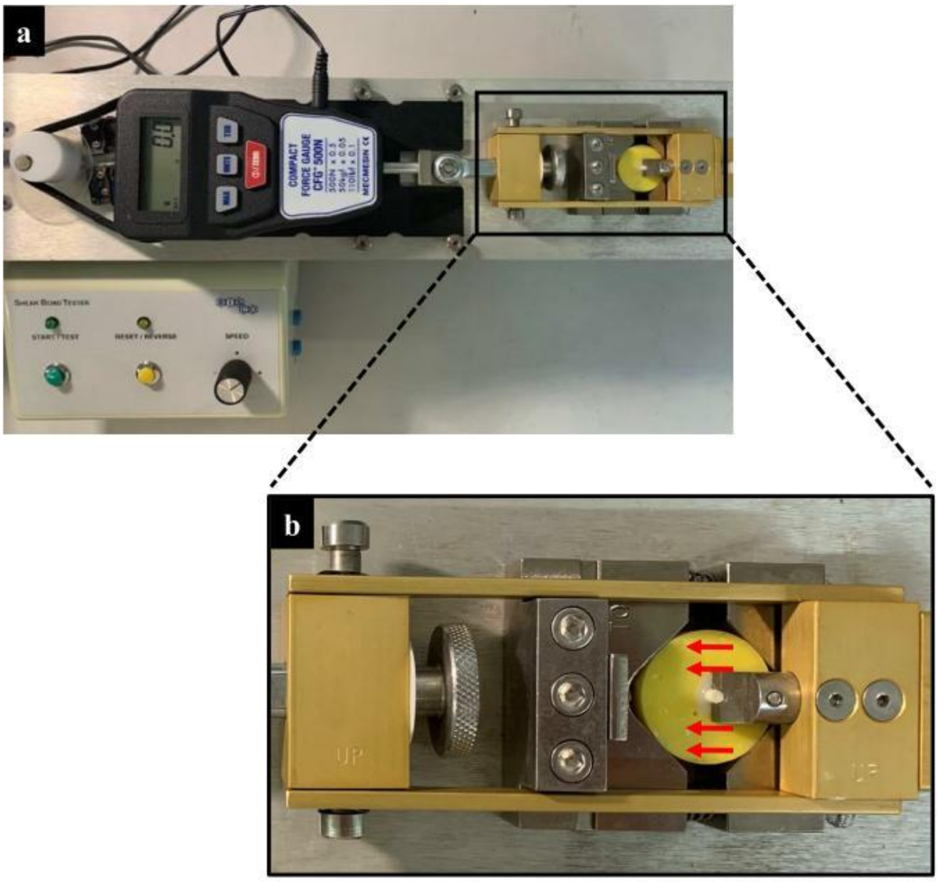


Figure 3. Shear bond strength machine

(A) A photograph of a specimen for shear bond strength test placed on a shear bond test machine.; (B) After fixing the specimen to the metal jig, when the force is transmitted in the direction of the arrow and the resin cement is removed, the shear bond strength value is output as Newton value.

3. Biaxial Flexural Strength (BFS) Test

The BFS (n = 12) tests were performed using the piston-on-three-ball technique in a universal testing machine (3366 Series, Instron Engineering, Norwood, MA, USA), which features three stainless-steel balls placed equidistant from each other on a support circle with a diameter of 9 ㎜ (Figure 4). The discs were placed centrally facing the steel balls. A thin plastic sheet (0.05 ㎜ thick) was positioned between the piston and the specimen to facilitate an even load distribution. The load was applied with a 1.5 ㎜ diameter piston at a crosshead speed of 1.0 ㎜/min. The BFS of each specimen was calculated using the following equation obtained from the International Organization for Standardization (ISO) Standard 6872 with Poisson's ratio value for dental ceramic as 0.25:

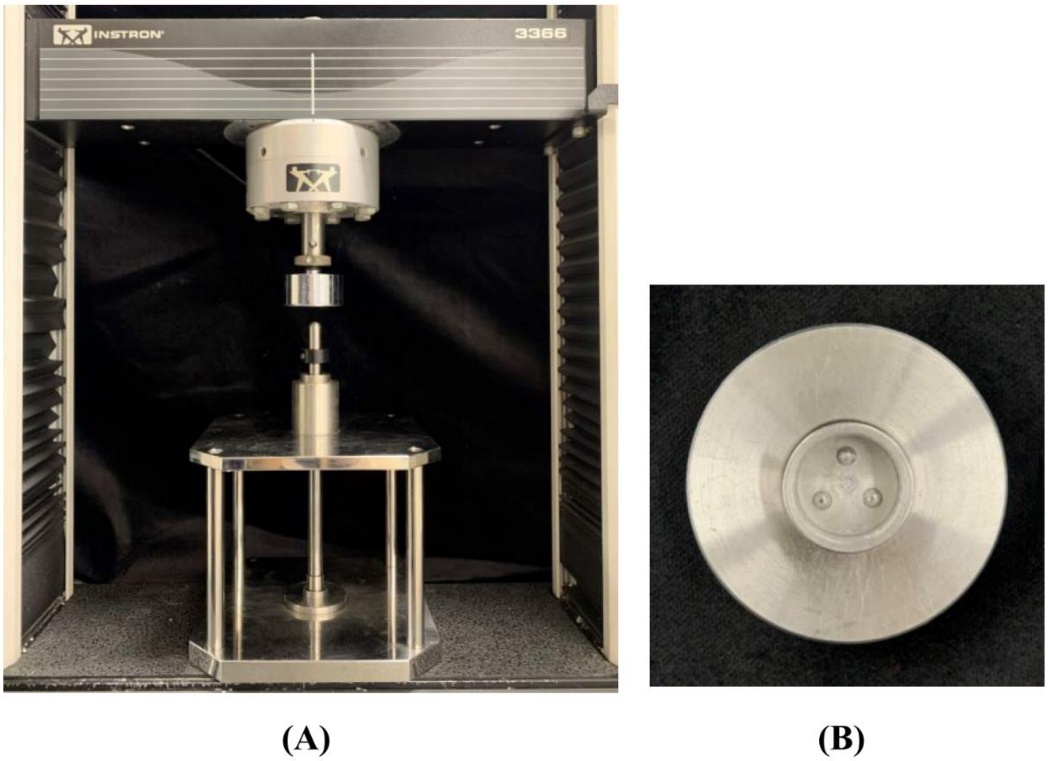
$$\sigma \;=\; -0.2387P \;\; (X - Y)/d^2 \qquad (1)$$

where σ is the biaxial flexural strength (㎫), P is the total load causing the fracture (N), and d is the specimen disk thickness at the fracture origin (㎜). X and Y were calculated as follows:

$$\mathrm{X} = (1 + v)\ln(r_2/r_3)^2 + [(1 - v)/2]\,(r_2/r_3)^2 \qquad (2)$$

$$Y = (1 + v)[1 + \ln(r_1/r_3)^2] + (1 - v)(r_1/r_3)^2 \qquad (3)$$

where v is Poisson's ratio (υ), r_1 is the radius of the support circle (4.5 ㎜), r_2 is the radius of the loaded area (0.75 ㎜), and r_3 is the radius of the specimen (6.8 ㎜) (Figure 5).



(A) (B)

Figure 4. Universal testing machine

Universal testing machine (UTM) for measuring biaxial flexural strength of zirconia ceramic disc after different surface treatments. (A) Biaxial flexural test device UTM, (B) Device with three stainless-steel balls to support the discs

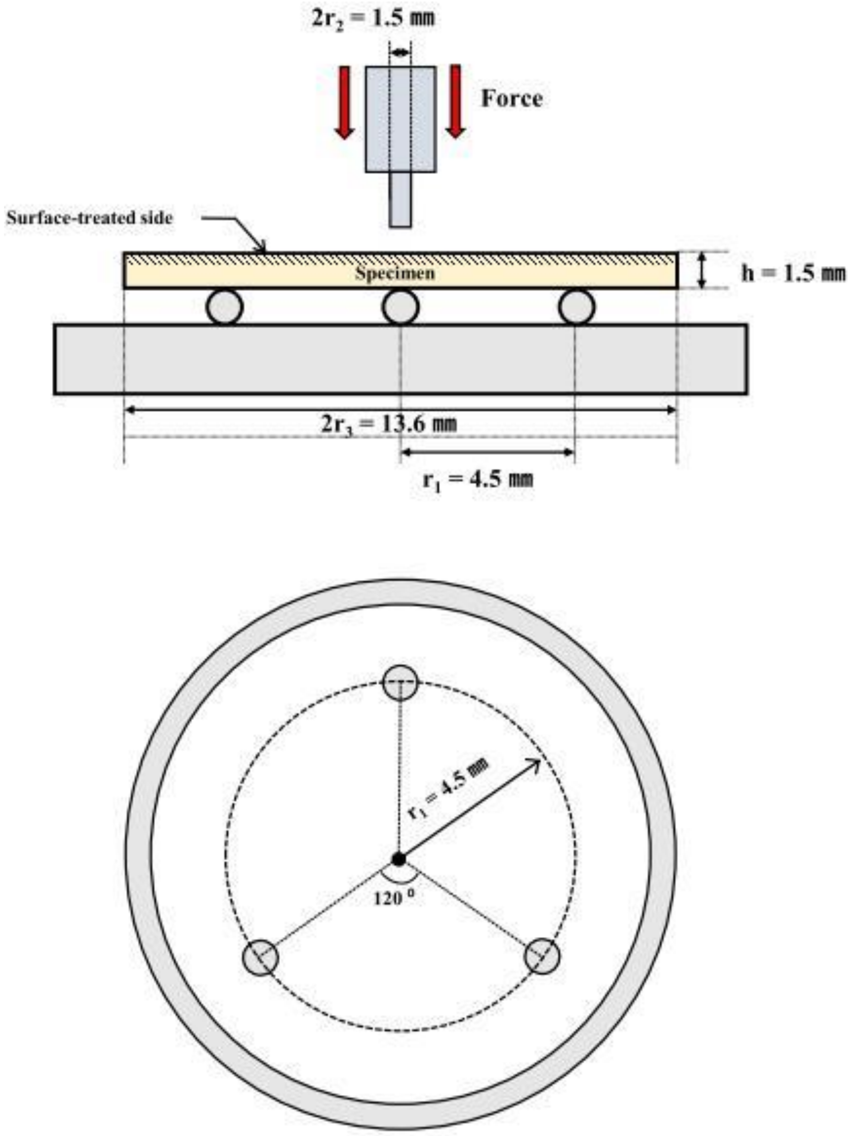


Figure 5. Schematic illustration of the piston-on-three ball biaxial flexural test

4. X-Ray Diffraction (XRD)

The percentages of monoclinic phase in each group (groups C, A, E, and AE both before and after thermocycling (n = 3 per group)) were calculated by high-resolution X-ray diffraction (HR-XRD; SmartLab, Rigaku, Tokyo, Japan). Scans were performed at 45 kV and 200 mA, from 25° to 36° with a 0.02° step size. The XRD patterns were analyzed using the Rietveld refinement methods; quantitative analyses by the reference intensity ratio method were performed using the PDXL software (PDXL V1.8.1.0, Rigaku, Tokyo, Japan). The monoclinic peak intensity ratio (X_m) was calculated using the equation reported by Garvie and Nicholsone(R C Garvie, P S Nicholson, 1972), as follows :

$$X_m = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(111)} \tag{4}$$

where I_t and $I_m$represent the integrated intensities of tetragonal (111)t peak and monoclinic (111)m and (−111)m peaks around 2θ = 30.2°, 31° and 28.2°, respectively. The monoclinic phase content (F_m) was calculated using the equation reported by Taraya et al.(Toraya et al., 1984), as follows:

$$F_m = \frac{1.311X_m}{1 + 0.311X_m} \tag{5}$$

5. Scanning Electron Microscopy (SEM)

To evaluate the difference between treatments, the representative surface morphology of each group (groups A, E, and AE before and after thermocycling) was observed with a field emission scanning electron microscope (JEOL-7800F Schottky, JEOL, Japan). The analysis procedures were performed after gold sputtering (Cressington High Resolution Sputter Coater 208HR, Cressington Scientific Instruments, UK) with × 20,000 and × 40,000 x magnification.

6. 3D Optical Microscopy

For the topographic analysis and determination of the Ra of the zirconia surfaces after different methods of treatment and thermocycling, representative specimens from each group were analyzed in this study (groups A, E, and AE before and after thermocycling) using a 3D optical microscope (Contour GT-X3 BASE; Bruker Co., Germany), in five areas per sample. Subsequently, the average Ra values were calculated.

7. Statistical Analysis

The results were analyzed by using statistical software (SPSS 25.0, SPSS Inc., USA) by separately observing the resulting SBS and BFS values of the groups. First, the data normality was tested using the Shapiro–Wilk tests. Based on the normality test, since both SBS (㎫), monoclinic phase content and Ra values of the test group were followed by normality distribution, they were analyzed using one-way analysis of variance (ANOVA), which was followed by a t-test and Tukey’s HSD test. The BFS data (㎫) followed non-normality distribution were analyzed by using the variance analysis provided by the Kruskal–Wallis and Mann-Whitney-U tests which are nonparametric test. Student’s t-test or Mann-Whitney-U test was used for data analysis of before and after thermocycling. Significance was set at α = 0.05.

III. RESULTS

1. Shear Bond Strength (SBS)

The mean bond strength values (mean ± SD) of the tested groups (A, E and AE before and after thermocycling) are summarized in Table 2. The one-way ANOVA test showed a statistical difference in each surface treatment group ($p < 0.05$). With regard to the groups observed before and after thermocycling, group E demonstrated a significantly higher SBS than those of the other two groups. There were no significant differences between the SBS values of A and AE. In all the groups, the adhesive strength after thermal cycling was significantly lower than that observed before cycling.

Table 2. Adhesion assessed by shear bond strength (㎫) before and after thermocycling on surface-treated zirconia (mean ± SD), (n=12)

Surface treatment	Group A	Group E	Group AE
Before thermocycling	$24.9 \pm 3.0^{A,a}$	$29.5 \pm 2.9^{B,a}$	$23.7 \pm 3.1^{A,a}$
After thermocycling	$11.4 \pm 4.7^{A,b}$	$15.5 \pm 3.8^{B,b}$	$11.5 \pm 3.3^{A,b}$

Superscript uppercase letters indicate the difference in shear bond strength between the different surface treatments within before and after thermocycling groups ($p < 0.05$). Superscript lowercase letters indicate the difference in shear bond strength between the before and after thermocycling within the different surface treatment groups ($p < 0.05$).

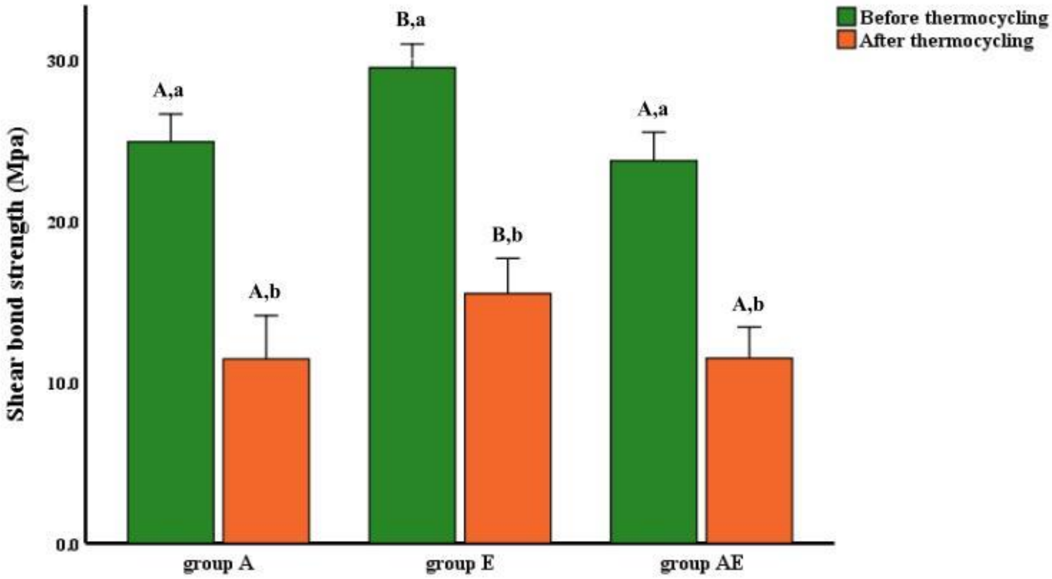


Figure 6. Shear bond strength (㎫) values of different surface treatment groups

Superscript uppercase letters indicate the difference in shear bond strength between the different surface treatments within before and after thermocycling groups ($p < 0.05$). Superscript lowercase letters indicate the difference in shear bond strength between the before and after thermocycling within the different surface treatment groups ($p < 0.05$).

2. Biaxial Flexural Strength (BFS)

Mean flexural strength values (㎫ ± SD) for each group (C, A, E, and AE before and after thermocycling) are listed in Table 3. There was no significant difference in the BFS values of all groups before thermocycling ($p > 0.05$). The Kruskal-Wallis test revealed a statistical difference in the thermocycling groups in each surface treatment group ($p < 0.05$). Groups C and E exhibit significantly higher BFS values than those of groups A and AE. There was no statistical difference between the BFS values of thermocycling groups C and E.

Table 3. Biaxial flexural strength (㎫) before and after thermocycling on surface-treated zirconia (n=12)

Surface treatment	Group C	Group A	Group E	Group AE
	median (Q1-Q3)			
Before thermocycling	1356.7^{A,a} (1324.6–1439.4)	1412.8^{A,a} (1308.3–1452.3)	1415.6^{A,a} (1371.3–1459.7)	1416.0^{A,a} (1294.6–1538.7)
After thermocycling	1289.0^{A,a} (1044.1–1355.0)	616.7^{B,b} (569.3–700.2)	1048.8^{A,a} (960.9–1455.6)	564.3^{B,b} (502.5–616.0)

Superscript uppercase letters indicate the difference in biaxial flexural strength between the different surface treatments within before and after thermocycling groups ($p < 0.05$). Superscript lowercase letters indicate the difference in biaxial flexural strength between the before and after thermocycling within the different surface treatment groups ($p < 0.05$).

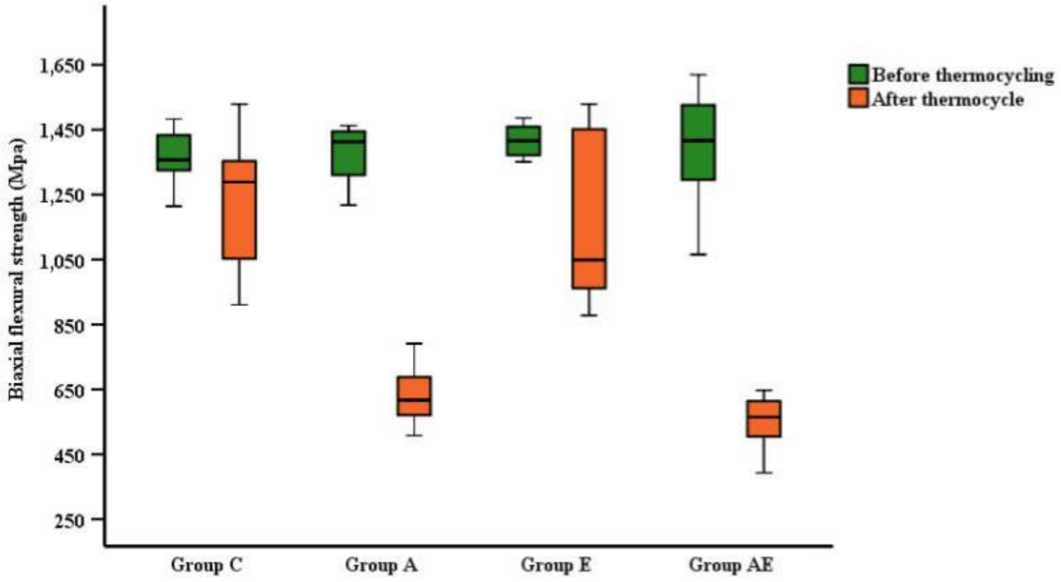


Figure 7. Biaxial flexural strength (㎫) values of different surface treatment groups

There was no significant difference in the BFS values of all groups before thermocycling ($p > 0.05$). Group C and E was significantly higher BFS than group E and AE after thermocycling ($p < 0.05$). There was a significant decrease in the BFS values of group A and AE after thermocycling compares to before thermocycling ($p < 0.05$).

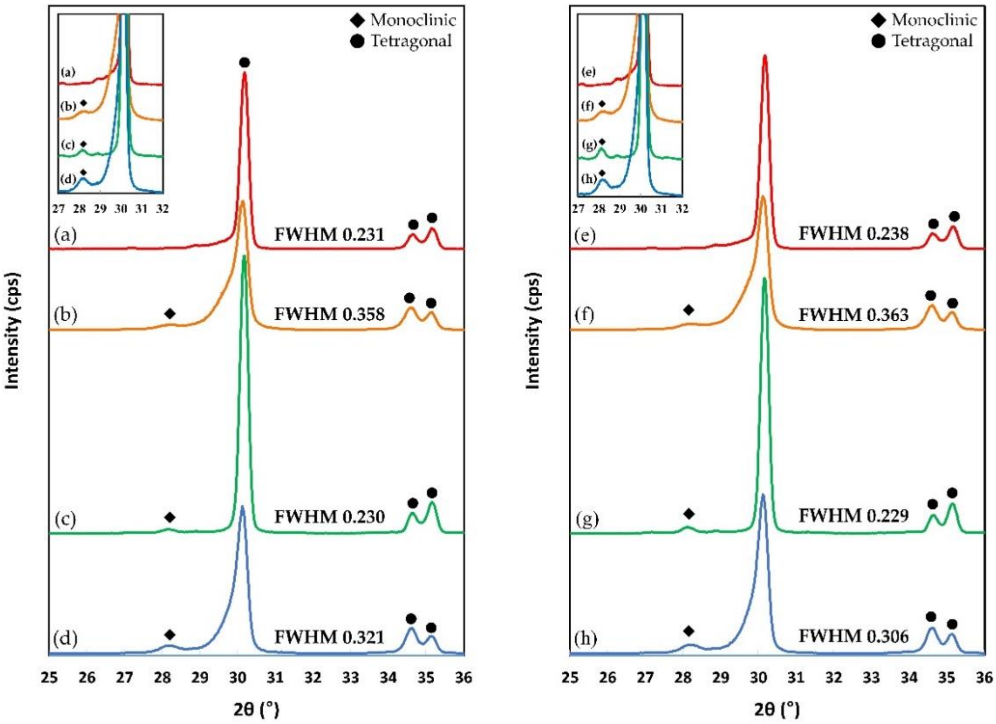
3. X-Ray Diffraction (XRD)

Representative XRD patterns obtained from the eight groups are presented in Figure 7. Table 4 reports the mean monoclinic phase content values with standard deviation of the zirconia in the groups before and after thermocycling. The monoclinic phase structure could be detected on the zirconia surface in all the groups, and the monoclinic (-111) peak was detected at a 2θ of 28.2°. The monoclinic crystal phase in group E was significantly lower among surface-treated groups and the corresponding value in group AE was significantly higher than those achieved in other groups; this was observed before and even after thermocycling. In all groups, the tetragonal (111) peak at a 2θ of 30.2° was detected. In group E, the tetragonal peak was narrow both before and after thermocycling, and the respective full width at half maximum (FWHM) was 0.230 and 0.229. In group A, the tetragonal (111) peak was broadened and the FWHM of the peak increased from 0.231 to 0.358 before thermocycling; further, the monoclinic content and FWHM increased up to 8.4% and 0.363, respectively, after thermocycling. Moreover, after thermocycling, the monoclinic phase peaks were observed to slightly increase in all the groups. The monoclinic phase content and FWHM of group AE decreased approximately by thermocycling. However, the monoclinic phase content was still higher than in other groups. However, in group E, the monoclinic phase content was lower than those of groups A and AE.

Table 4. Monoclinic phase content (Fm.%) on zirconia of different surface treatment groups (mean ± SD), (n=3)

Surface treatment	Group C	Group A	Group E	Group AE
Before thermocycling	1.6 ± $0.7^{A,a}$	7.8 ± $0.2^{B,a}$	2.6 ± $0.2^{C,a}$	10.3 ± $0.5^{D,a}$
After thermocycling	1.7 ± $0.1^{A,a}$	8.4 ± $0.1^{B,b}$	4.2 ± $0.8^{C,b}$	9.5 ± $0.2^{D,b}$

Superscript uppercase letters indicate the difference in monoclinic phase content (Fm.%) between the different surface treatments within before and after thermocycling groups ($p < 0.05$). Superscript lowercase letters indicate the difference in monoclinic phase content (Fm.%) between the before and after thermocycling within the different surface treatment groups ($p < 0.05$).



(A) **(B)**

Figure 8. X-ray diffraction (XRD) pattern on zirconia surface treated before and after thermocycling

X-ray diffraction (XRD) pattern (A) before thermocycling of (a) group C, (b) group A, (c) group E, and (d) group AE. XRD pattern (B) after thermocycling of (e) group C, (f) group A, (g) group E, and (h) group AE. Both graphs show a difference in the monoclinic phase among the groups and contain the full width at half maximum (FWHM) of each group. The inset shows the magnified region.

4. Scanning Electron Microscopy (SEM)

Figure 9, 10 shows the morphological appearance of zirconia surface after being modified with the various methods used in this study. For group A, the zirconia appeared to have deep and rough abrasions. For E, an overall homogenous and fine rough surface was observed, while for AE, the deep areas due to abrasion formed fine rough surfaces, which was probably attributable to the hot-etching. For each of thermocycling groups A, E, and AE, the surfaces had smooth edges. It was also noted that the AE treatment resulted in signs of micro-crack formation.

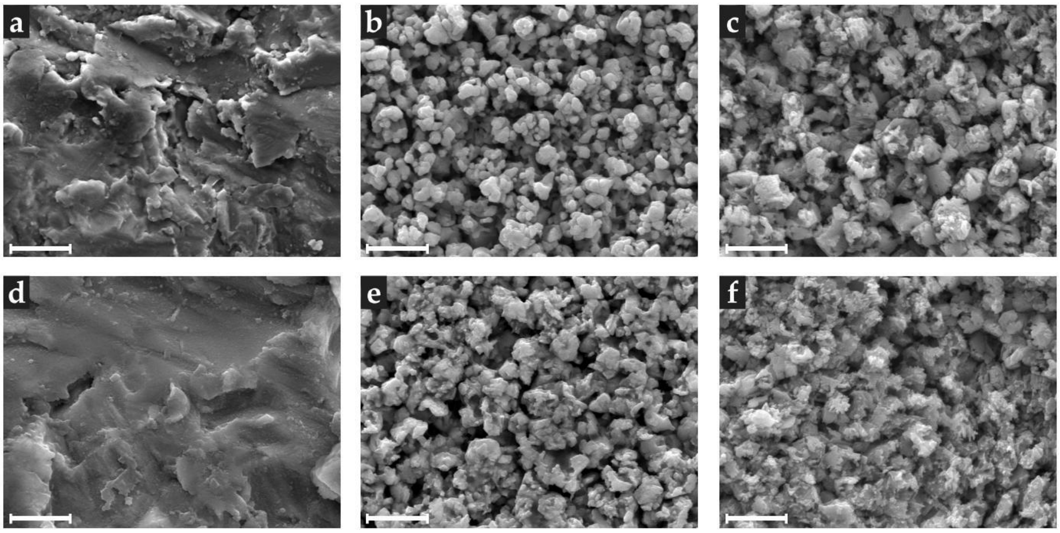


Figure 9. Scanning electron microscopy (SEM) photomicrographs (× 20,000 magnification) before and after thermocycling on surface-treated zirconia

Scanning electron microscopy photomicrographs of zirconia ceramic disc after different surface treatments: zirconia stored in distilled water at 37 ℃ for 24 h ((a), (b), and (c)) and thermocycled zirconia (1,000 cycles between 5 ℃ and 55 ℃ ((d), (e) and (f))); (a, d) airborne-particle abrasion (group A); (b, e) HF acid etching (heated up to 100 ℃, 10 min) (group E); (c, f) HF acid etching after airborne-particle abrasion (heated up to 100 ℃, 10 min) (group AE). (Scale: 1 ㎛; Magnification: × 20,000)

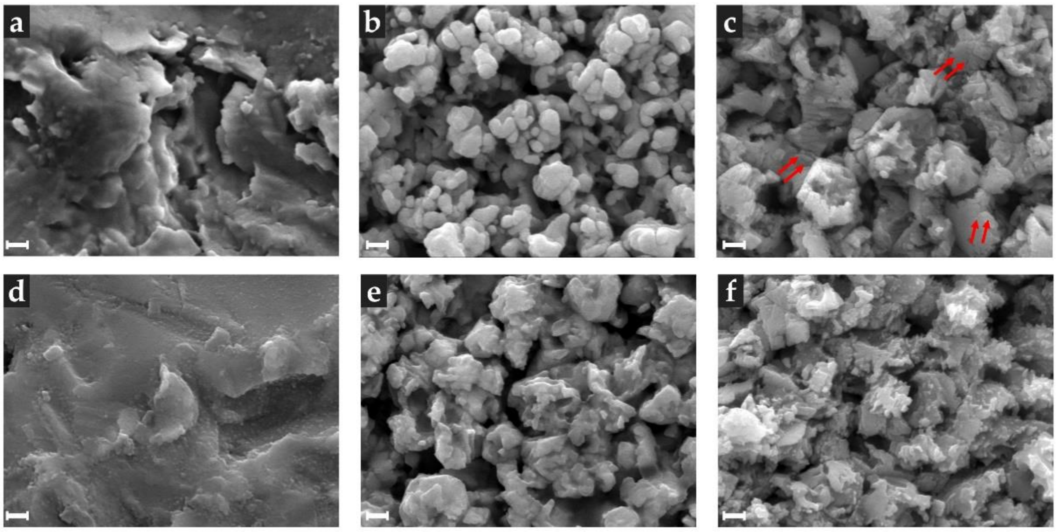


Figure 10. Scanning electron microscopy (SEM) photomicrographs (× 40,000 magnification) before and after thermocycling on surface-treated zirconia

Scanning electron microscopy photomicrographs of zirconia ceramic disc after different surface treatments. The surface morphology change of zirconia by surface treatment was observed at a higher magnification.: zirconia stored in distilled water at 37 ℃ for 24 h ((a), (b), and (c)) and thermocycled zirconia (1,000 cycles between 5 ℃ and 55 ℃ ((d), (e) and (f))); (a, d) airborne-particle abrasion (group A); (b, e) HF acid etching (heated up to 100 ℃, 10 min) (group E); (c, f) HF acid etching after airborne-particle abrasion (heated up to 100 ℃, 10 min) (group AE). Arrows indicate micro-crack formation. (Scale: 100 ㎚; Magnification: × 40,000)

5. Surface Roughness (Ra)

Figure 10 shows the outcomes of Ra after the initial surface treatment of each group, and after thermocycling following the initial treatment. Table 5 reports the mean Ra values with standard deviation of the zirconia in the groups before and after thermocycling.

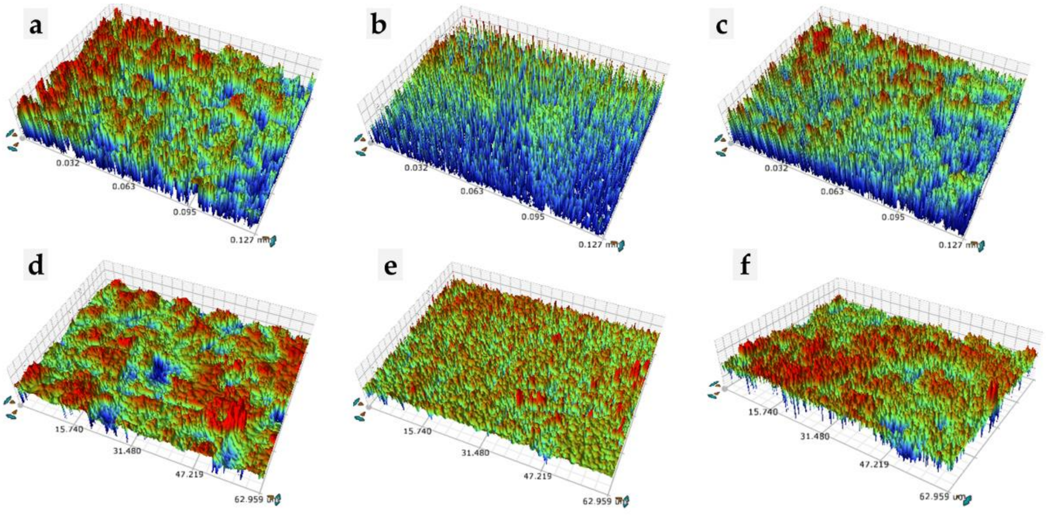


Figure 11. Roughness (Ra) on zirconia after surface treatment

Roughness (Ra) images of zirconia ceramic disc after different surface treatments: zirconia stored in distilled water at 37 ℃ for 24 h ((a), (b), and (c)) and those of thermocycled zirconia (1,000 cycles between 5 ℃ and 55 ℃ ((d), (e), and (f))); (a, d) airborne-particle abrasion (group A); (b, e) HF acid etching (heated up to 100 ℃, 10 min) (group E); (c, f) HF acid etching after airborne-particle abrasion (heated up to 100 ℃, 10 min) (group AE).

Table 5. Surface roughness (Ra, ㎛) on zirconia of different surface treatment groups (mean ± SD), (n=1, 5 points per specimen)

Surface treatment	Group A	Group E	Group AE
Before thermocycling	$0.439 \pm 0.02^{A,a}$	$0.247 \pm 0.04^{B,a}$	$0.428 \pm 0.02^{A,a}$
After thermocycling	$0.355 \pm 0.02^{A,b}$	$0.181 \pm 0.01^{B,b}$	$0.353 \pm 0.01^{A,b}$

Superscript uppercase letters indicate the difference in surface roughness between the different surface treatments within before and after thermocycling groups. ($p < 0.05$). Superscript lowercase letters indicate the difference in surface roughness between the before and after thermocycling within the different surface treatment groups. ($p < 0.05$).

IV. DISCUSSION

In previous studies, surface treatment of hot-etching using a low-concentration of hydrofluoric acid on zirconia mainly compared the surface morphology change and adhesive strength, and there were few studies comparing mechanical properties before and after thermocycling. Therefore, in this study, mechanical properties, phase transformation, and surface morphology change analyzed the effect in accordance with hot-etching surface treatment on zirconia before and after thermocycling in order to investigate the effect of chemical hot-etching using a low-concentration HF acid on zirconia before and after thermal cycling.

The comparison of the average adhesive strength in accordance with the surface treatment methods revealed that not only was the SBS of the HF etching group significantly higher than that two groups used airborne-particle abrasion before and after thermocycling but also the BFS not significantly different compared to initial zirconia before and after thermocycling. Additionally, the BFS did not decrease significantly after thermocycling compared to before thermocycling. The data in the present study rejected the first null hypothesis, as the SBS between zirconia and resin cement and BFS was affected by hot-etching using the low-concentration HF acid at 100 ℃. In addition, the second null hypothesis was rejected since it showed higher SBS and BFS in hot-etching using low-concentration HF compared to the other two surface treatment groups after thermocycling.

The method of surface treatment of zirconia can be an important factor in bonding strength (Table 2). The result in this study, the surface treatment of hot-etching with low-concentration HF acid showed higher SBS than airborne-particle abrasion before and after thermocycling ($p < 0.05$). Previous studies have reported that the zirconia with treated HF solution does not induce a surface change because it is a glass-free material; therefore zirconia cannot bond with the resin cement (Blatz et al., 2003; Thompson et al., 2011), and also have reported the bonding of nano-porosity and resin on HF-treated zirconia surfaces is difficult (Sriamporn et al., 2014). However, this study demonstrates that the hot-etching the hot-etching with low-concentration HF acid affected the SBS of zirconia with resin cement before and after thermocycling. This is attributable that HF acid with heat affected the transformation of the surface of zirconia. In previous studies, HF surface treatment of zirconia without heat treatment occurred lower results than SBS of airborne-particle abrasion (Saleh et al., 2019). However, since the SBS value obtained using hot-etching using low-concentration HF acid in this study was higher than that of airborne-particle abrasion, it can be assumed that heat treatment can increase the effect of HF. This result is based on the fact that temperature plays a very important role in molecular motion, as hot-etching renders the proton of the acid solution prone to ionization, and since it becomes even more acidic, thereby accelerating the removal of surface particles (Casucci et al., 2010; Casucci et al., 2011; Casucci et al., 2009; Liu et al., 2015; Xie et al., 2013). It could be speculated that the hot-etching treatment contributed to a micro-locking formation between the uniformed nano-structure of zirconia and the resin cement, which may have resulted in enhanced bond strength by the mechanical bonding effect of MDP contained in the resin cement. Due to the high bond strength observed after the hot-etching process, it can be speculated that, when the resin penetrates the surface of the zirconia, it could be more readily structurally bonded with the etched surface.

The BFS tested by loading the surface treated side. Previous studies have reported that the BFS test overcomes defects caused by edge and surface treatment of the specimen (Radford and Lange, 1978). However, clinically, because the surface-treated surface is in contact with the tooth, the untreated surface is exposed to the oral cavity, and the occlusal force is applied. Therefore, to give clinical significance, it is possible to consider measuring the BFS by applying a load to the untreated zirconia surface. In this study, there was no difference in the BFS between all the groups before thermocycling. However, the average BFS value of the group subjected to hot-etching treatment using low-concentration HF acid is significantly higher than that of the other treated groups after thermocycling ($p < 0.05$). In addition, the BFS of the two groups subjected to airborne-particle abrasion was significantly reduced after thermal cycling. The previous study of HF acid etching reported that zirconia treated with hydrofluoric acid for less than 1 hour does not show high sensitivity to hydrothermal degradation even after aging and that the biaxial flexural strength of the etched specimen can increase with aging (Flamant and Anglada, 2016). In this study, BFS a few decreased after thermocycling compared to before thermocycling, however, there was no significant difference with zirconia without any treatment. Therefore, it is considered that the thermal etching surface treatment using hydrofluoric acid has low sensitivity to low-temperature degradation and does not significantly affect the biaxial flexural strength.

The important factor in estimating clinically the long-term performance of the material is aging, since temperature, mechanical stresses, and humid environments can influence the degradation of the strength of zirconia (Chevalier, 2006; Denry and Kelly, 2008; Gale and Darvell, 1999). Thermocycling treatments were performed to compare SBS and BFS according to aging. In this study, thermocycling was used as the aging method. 1,000 cycles were performed between 5 ℃ and 55 ℃, which is about 50 days based on previous studies (Gale and Darvell, 1999; Xie et al., 2010) In the present study, the SBS value was significantly lower in all groups after thermocycling than that observed before thermocycling. The thermal stresses and wet environment may exhibit subcritical crack growth and hydrolysis of the resin at the bonded interface (Studart et al., 2007). According to previous research results, it was reported that SBS tended to decrease subsequently weakening due to the degeneration of material through thermocycling treatments (Lee et al., 2015). In the present study, it is presumed that the change of the surface and the material modification of the bonded area after thermal cycling treatment affect the bonding strength of resin cement and zirconia.

The phase transformation occurred before and after the thermocycling for all groups subjected to the surface treatment (Table 4, Figure 7), which is similar to previous studies; this suggests that airborne-particle abrasion and etching can lead to a phase transformation (Lee and Lee, 2017; Sriamporn et al., 2014; Subasi et al., 2014). This can be caused by pressure conditions, and wet conditions known as low-temperature degradation (LTD) (Flamant and Anglada, 2016; Hallmann et al., 2012; Kobayashi et al., 1981). First, Wet heat treatment using low-temperature degradation (LTD) (room temperature to 400 ℃) on zirconia can transform partially stabilized zirconia from the tetragonal to the monoclinic phase (Chevalier et al., 2009; Sriamporn et al., 2014). In particular, in this study, heat treatment with steam was carried out using an airtight container with a triple structure during the etching process. In group E, it can be assumed that the increased monolithic phase before and after thermal cycling is because of structural deformation due to heat treatment during etching with HF acid and thermocycling after surface treatment. However, in this study the integrity of the zirconia surface treated with hot-etching did not decrease; therefore, it is considered that the phase transformation by hot-etching does not degrade the mechanical properties. During airborne-particle abrasion treatment, a phase shift occurs from tetragonal phase to monoclinic phase, this phase transformation results in a 3-4% volumetric expansion inducing compressive stress in the area of the crack and theoretically prevents crack propagation (Piconi and Maccauro, 1999). However, it can be predicted that the microcrack affected the fracture strength as excessive phase shift occurred after thermocycling. Previous studies have reported that excessive phase transformation after thermocycling reduces the flexural strength (Okutan and Yucel, 2019). In this study, group A and AE treated with airborne-particle abrasion had a few higher BFS than initial zirconia before thermocycling, however, these group was significantly lower BFS after thermocycling. In the surface treatment with airborne-particle abrasion before thermocycling, the phase transformation to monoclinic might have an effect of increasing the strength of zirconia, however, excessive phase transformation after thermocycling might lead to an effect of decreasing the flexural strength.

The surface treatment of the hot-etching using a low concentration of HF caused a uniform and fine morphological change (Figure 9,10). The airborne-particle abrasion group showed a rough and irregular surface, whereas the hot-etching group showed that the space between the grains was increased due to the decrease in particle size and the uniform application of the treatment. These results are similar to Sriamporn et al. (Sriamporn et al., 2014). The formation of such a uniform and fine space might be an element that can increase the adhesive strength, and it is suggested that micro-cracks generated by thermocycling during surface treatment of airborne-particle abrasion can degrade mechanical properties after a long time.

In order to observe the change in surface roughness before and after the thermocycling of zirconia according to various surface treatments, the roughness of the specimens of surface-treated three groups was measured. The Ra value of zirconia was significantly lower in the hot-etching group than in the abrasion group (Table 5). It is speculated that this result could be due to the formation of rough structures and cracks caused by uneven and concentrated pressure during the abrasion surface treatment, and the formation of the nano-porosity structure that is uniformly treated during the hot-etching surface treatment. In previous studies, a lower Ra value than that observed in the abrasion group was measured in the etching surface treatment; however, the SBS value before and after thermocycling was significantly higher than that of the abrasion group (Lv et al., 2015). It suggests that although the average surface roughness was improved when treated with airborne-particle abrasion, hot-etching is more appropriate for zirconia and cement bonding since microporous roughness. Ra values after the thermocycling were significantly reduced in all groups ($p < 0.05$). This can be associated with a decrease in SBS. Resin cement absorbs moisture under the influence of moisture and dissolves to weaken the adhesive layer (Saade et al., 2020; Valandro et al., 2007), it may reduce SBS.

There have been many studies on the change of the surface and mechanical properties in accordance with the various surface treatment of zirconia. Various studies of chemical treatment methods have been attempted in previous papers, however, mainly high-concentrations of HF acid have been used, which is actually a dangerous method for clinical use. In other studies, using low-concentrations of HF acid, few studies measured the properties and surface changes of zirconia, and the stability, and persistence after aging were conducted. In this study, changes in surface and physical properties of zirconia that were hot-etching using a low-concentration of HF acid were analyzed. Hot-etching with a low-concentration of HF acid showed excellent SBS of zirconia with resin cement and BFS of zirconia and showed higher SBS and BFS results than the mechanical surface treatment method even after thermal cycling treatment. In addition, it is expected to have high clinical application potential as it showed a result of fine and uniform surface change and low phase transformation even before and after thermocycling. In the future, it is necessary to study the change of mechanical properties of zirconia and the adhesion between zirconia and resin cement for a long time for clinical usefulness.

V. CONCLUSION

Within the limitations of this study, the data in the present study rejected the null hypothesis based on the following conclusions.

1) Hot-etching surface treatment with low concentrations of HF on zirconia had a higher SBS than other groups regardless of thermocycling.

2) SBS after thermocycling was significantly decreased in all groups than before thermocycling.

3) All groups of BFS were not significantly different before thermocycling. After thermocycling, the control group and hot-etching group was significantly higher BFS than other groups.

5) The BFS after thermocycling of the control group and hot-etching group with low-concentration HF acid caused not significantly decreased than before thermocycling. However, the groups using the airborne-particle abrasion was significantly reduced BFS than before thermocycling.

6) Hot-etching using the low-concentration HF acid on zirconia induced lower phase transformation from tetragonal to monoclinic before and after thermocycling than other

surface treatment groups.

7) Hot-etching using low concentration HF acid transformed the zirconia surface morphology into a uniform and fine nanoporous structure.

8) The roughness value (Ra) of treated zirconia with hot-etching using the low-concentration HF acid before and after thermocycling was the lowest among the treatment groups.

Based on these results, this study concluded the following. 1) Hot-etching using low-concentration HF acid on zirconia has higher mechanical properties of zirconia and bonding strength with resin cement than airborne-particle abrasion surface treatment regardless of the thermocycling process. 2) Hot-etching using low-concentration HF acid forms a uniform and microstructure on the surface and affected stable strength due to less phase transformation before and after thermal cycling. further in-vitro studies concerning the long-term thermocycling will be necessary to thoroughly evaluate the effects of the hot-etching surface treatment with low concentrations of HF. These studies will complement the hot-etching methods that are available in clinics.

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ABSTRACT (KOREAN)

저농도 불산 에칭이 열순환 후 지르코니아의 전단 결합 강도 및 이축 굴곡 강도에 미치는 영향

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강 유 정

부분적으로 안정화된 이산화 지르코늄 세라믹은 우수한 물리적 특성과 최적의 생체적합성 및 적절한 광학적 성질을 가진 재료로 최근 사용이 증가해 왔다. 그러나 지르코니아 수복물은 레진 시멘트와 접착이 어렵다는 한계가 있어 기계적인 표면처리 방법으로 알루미나 입자를 분사하는 방법인 airborne-particle abrasion 또는 샌드블라스팅(sandblasting)방법을 가장 많이 사용하고 있다. 이 방법은 지르코니아의 표면에 거칠기를 형성하여 레진시멘트와 견고하고 내구성 있는 미세한 기계적 결합을 얻을 수 있는 반면 상변이에 의한 표면

미세균열은 장기간의 안정성에 영향을 미칠 수 있고 입자 크기, 압력, 분사 거리, 균일한 표면 처리에 영향을 받을 수 있다. 이에 최근 다양한 농도의 산처리로 지르코니아 표면에 거칠기를 제공할 수 있음이 확인된 바 있다. 지르코니아는 불산으로 표면처리하기 어려운 물질이나 고농도의 불산에서 장기간 고온 처리를 하면 지르코니아 산처리가 가능하다. 그러나 위험한 고농도의 불산을 고온에서 처리하는 것은 임상에서 사용하기에 많은 위험이 따를 수 있다.

따라서 본 연구는 저농도의 불산을 사용한 hot-etching 표면 처리 방법이 지르코니아와 레진 시멘트 사이의 전단결합강도에 미치는 영향과 지르코니아의 이축굴곡강도에 미치는 영향을 평가하고자 하였다. 또한 열순환 처리 후 지르코니아 강도와 표면의 변화를 비교 분석하고자 하였다.

전단결합강도 측정을 위한 지르코니아 시편은 완전히 소결 후 5x5x5 ㎜ 크기의 정육면체 형태로 제작하였고, 레진 몰드에 매몰하여 72 개의 시편을 제작하였다. 제작된 지르코니아 시편은 airborne-particle abrasion 표면처리 군, 저농도의 불산을 사용한 hot-etching 표면처리 군, airborne-particle abrasion 후 저농도 불산을 사용한 hot-etching 표면처리 군으로 분류하였다.

이축굴곡강도 측정을 위한 지르코니아 시편은 완전히 소결 후 지름 13.6 ㎜ 및 두께 1.5 ㎜ 원판의 형태로 96 개를 제작하였다. 제작된 지르코니아 시편은 아무 처리하지 않은 군, airborne-particle abrasion 표면처리 군, 저농도의 불산을 사용한 hot-etching 표면처리 군, airborne-particle abrasion 후 저농도 불산을 사용한 hot-etching 표면처리 군으로 분류하였다.

각 군을 24 시간 동안 37C 에서 보관한 군과 열순환 처리한 군으로 나누어 전단결합강도는 총 6 개의 군(n=12), 이축굴곡강도는 총 8 개의 군(n=12)으로 분류하여 전단결합강도와 이축굴곡강도를 측정하였고, 표면 분석, X 선 회절분석, 표면 거칠기 분석 후 통계 분석을 시행하였다.

열순환처리에 관계없이 저농도 불산을 사용한 hot-etching 표면처리 군은 다른 두 군보다 전단결합강도가 유의하게 높았다 ($p < 0.05$). 열순환처리 전 4 개의 군 사이의 이축굴곡강도는 유의한 차이가 없었지만($p > 0.05$), 열순환처리 후 아무 처리하지 않은 군과 저농도 불산을 사용한 hot-etching 표면처리군은 다른 두 군에 비해 유의하게 높은 이축굴곡강도를 보였다($p < 0.05$). 모든 군에서 정방정상에서 단사정상으로 상변이가 관찰되었으며, 열순환처리 전과 후 저농도 불산을 사용한 hot-etching 표면처리 군에서 다른 두 군 보다 미세하고 균일한 표면이 관찰되었다.

이 연구의 한계 내에서, 지르코니아 표면에 저농도 겔타입의 불산을 사용한 hot-etching 표면처리는 airborne-particle abrasion 표면처리 군 과 airborne-particle abrasion 후 저농도 불산을 사용한 hot-etching 표면처리 군 보다 전단결합강도와 이축굴곡강도가 높았다.

핵심되는 말: 불산; 상변이; 열순환처리; 열에칭; 이축굴곡강도; 전단결합강도; 지르코니아