Effect of air abrasion, acid etching, and aging on the shear bond strength with resin cement to 3Y-TZP zirconia

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보철과 수련시절부터 부족한 저를 언제나 믿고 지켜봐 주시고 인생에 있어서도 많은 조언을 해주시는 김선재 교수님 덕분에도 지치지 않고 여기까지 올 수 있었습니다. 아울러 연구진행에 큰 도움을 주신 남나은 선생님께도 깊은 감사를 드립니다.

마지막으로 항상 제 뒤에서 사랑과 정성으로 응원해주시고 도와주시는 부모님과 늦깎이로 공부하는 언니를 잘 따라주고 도와준 동생 미유와 영준이에게도 고마움과 깊은 사랑을 전합니다. 앞으로도 더욱 감사하며 겸손한 자세로 끊임없이 배움의 길을 갈 수 있도록 노력하겠습니다.

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ABSTRACT

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This study investigated the effect of acid etching treatment on the surface microstructure, surface roughness, and surface contact angle of zirconia and compared the effects of air abrasion, different etching times, and aging on the shear bond strength (SBS) of resin cement on the zirconia surface. 480 specimens (9 × 10 × 10 mm) were divided into as-sintered and air-abraded groups, and each group was further subdivided into six groups based on etching time (0, 3, 5, 10, 20, and 30 min). The etching solution comprised hydrofluoric acid 25%, sulfuric acid 16%, hydrogen peroxide, methyl alcohol, and purified water.

The shear bond strength (SBS), scanning electron microscopy, surface roughness, contact angle, and failure mode were measured. The results indicated that the mean SBS values increased and decreased significantly when the etching times increased to 20 min and 30 min, respectively, in both groups. Further, SBS after aging was lower than that before aging in all groups. Sandblasting, etching time, and aging all showed significant effects ($p<0.001$) in the three-way analysis of variance. In addition, the surface roughness increased and the contact angle decreased significantly with an increase in etching time. Thus, the acid-etching treatment induced significant changes on the zirconia surface and increased the SBS of the resin cement. The results of this in vitro study suggest that acid etching is a promising alternative for zirconia surface treatment.

Keywords : 3Y-TZP zirconia, Air abrasion, Acid etching, Aging, Resin cement, Shear bond strength(SBS)

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I. Introduction

Zirconia is widely used in dentistry as a material for crowns, cores for ceramic restorations, post, and implant abutment because of its excellent optical and mechanical properties and biocompatibility.[1] Further, there has been a recent increase in the demand for aesthetic dental restorations, and this has led to the application of zirconia for tooth-colored, metal-free ceramic restorations with great success and reliability.[2] New fabrication systems combined with computer-aided design and computer-aided manufacturing (CAD/CAM) systems have contributed to the increased popularity of zirconia restorations in dentistry.[3]

Although zirconia has good mechanical properties, the clinical applications of zirconia restorations remains limited because of its relatively weak adhesion with resin cement compared to other dental ceramics.[4] However, hydrofluoric acid etching and silane coupling agents commonly used in silica-based ceramics do not work effectively on zirconia surfaces because zirconia substrates are densely sintered and composed of a glass-free polycrystalline microstructure.[5]

Several studies suggest pre-treatments to condition the zirconia surface mechanically and chemically for improving the bond strength of the resin cement to zirconia. Mechanical pre-treatments such as grinding with abrasive paper or diamond rotary instruments, airborne-particle abrasion with Al_2O_3, tribochemical silica coating, selective infiltration etching (SIE), and laser etching, and they have been used to alter the zirconia surface to create a rough surface for micromechanical interlocking. Primers containing functional monomers such as 10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP), phosphoric acid acrylate, and anhydride have also been applied to the surface of zirconia for chemical treatments.[6]

However, there is no clear consensus on the most effective method for achieving durable adhesion between zirconia and resin cement. Although an increase in adhesion is observed with some surface treatments, other studies have reported the limitations of these methods.[7] Among these treatments, airborne-particle abrasion is most frequently used in clinical practice because of its ease of application. However, the surface roughness in air-borne particle abrasion depends on several variables such as the particle type and size, blasting pressure, application distance, and application time. Thus, the treatment is very subjective, and it may not always be possible to obtain consistent results because this process is performed manually.[8,9] Bonding strength between zirconia and resin cement increases when the surface roughness is limited to an appropriate depth.[10] However, airborne-particle abrasion creates irregular patterns of roughness on the zirconia surface and causes deep surface damage because of excessive surface treatment, which induces an unfavorable tetragonal-to-monoclinic phase transformation and makes zirconia more susceptible to cracking during function.[11,12] Tribochemical silica coating can produce a nonuniform silica layer on the zirconia surface, and therefore, it is difficult to expect a constant bonding strength.[13] Further, it has poor long-term stability because of the hydrolysis of the coated silica.[14] SIE is very complex and sensitive to all steps of the technique and remains inaccessible because of its high cost.[15] Laser etching is not as effective as airborne-particle abrasion in improving bond strength and temperature changes (heating and cooling) induced excessive monoclinic phase transformation.[16,17] 10-MDP presents a terminal functional group with phosphoric acid, and it enhances bond strength by reacting with zirconia to form P-O-Zr chemical bonds.[18] Although 10-MDP improves the initial adhesion between the resin cement and zirconia, it is not stable in water and suffers from hydrolytic degradation, which further results in a decrease in adhesion over time.[19,20]

Thus, there is a need to develop an alternative surface treatment method for improving the bond strength of resin cement to zirconia restorations while maintaining long-term stability without surface damage.

Although hydrofluoric acid (HF) is known to be inadequate for zirconia, recent studies reported that it can induce changes on the zirconia surface.

Sriamporn et al. showed that 9.5% and 48% HF used to etch dental zirconia resulted in micromorphological changes in the surface topography of zirconia. Further, the longer the immersion time, the higher was the etching-solution temperature, and the greater was the irregularity of the zirconia surface.[21] Elsaka reported that the roughness values (Ra) of zirconia treated with the hot etching solution for 60 min were higher than those of the untreated group and sandblasting treatment.[22] Chaiyabutr et al. reported that the shear bond strength with resin cements increased because of etching the zirconia surface with HF.[23] However, there are insufficient studies to conclude whether the change in the surface roughness of zirconia by acid etching treatment can lead to the strengthening of the adhesive strength of the resin cement. Moreover, there are few studies on the appropriate conditions for acid etching such as etching concentration, temperature, and application time, or on the long-term durability of the adhesion between resin cement and zirconia.

This study aims to investigate the effect of acid etching treatment on the surface microstructure, surface roughness, and surface contact angle of zirconia and to compare the effects of air abrasion, various etching times, and aging on the shear bond strength of resin cement to zirconia surfaces. The null hypothesis of this study is that air abrasion, various etching times, and aging does not significantly affect the zirconia surface and cause a difference in the shear bond strength between the resin cement and zirconia surface.

II. Materials and methods

1. Specimen fabrication: zirconia block milling and acid etching

Pre-sintered zirconia disks (Zircos E Ace; Bioden Co., Seoul, Korea) were cut into square-shaped specimens (9 × 10 × 10 mm) using a dental milling machine (DWX-51D; Roland DGA Corp., Irvine, CA, USA) and sintered in a furnace (S-600; Add-in Co., Ltd., Goyang, Korea) at 1500 ℃ for 2 h according to the manufacturer's instructions. Each specimen was embedded in cold curing resin (Vertex Dental, Soesterberg, The Netherlands) using a polyethylene mold and wet-polished with silicon carbide abrasive paper up to 1200 grit.

A total of 480 specimens were prepared and randomly divided into 24 groups (n=20). First, the specimens were divided into two groups: as-sintered and air-abraded. Half of the specimens (n=240) received no sandblast treatment, and the other half was abraded with 50 μm Al_2O_3 particle at an air pressure of 3 bar from a distance of 10 mm for 15 s. Each group was subdivided into six groups according to etching time (0, 3, 5, 10, 20, and 30 min). The etching solution was the same as that used in a previous study; it comprised HF 25%, sulfuric acid 16%, hydrogen peroxide, methyl alcohol, and purified water. The HF, sulfuric acid, catalyst, and methyl alcohol were mixed in a volume ratio of 7:5:1:2, and the etchant composition and purified water were mixed in a 1:1 ratio to complete the preparation.[24] After the etchant was heated to 80 °C, it was applied to the zirconia surface for 0, 3, 5, 10, 20, and 30 min.

2. Surface treatment and resin cement cementation

10-MDP containing primer (Prime & Bond Universal^{TM}; DentsplySirona, Konstanz, Germany) was applied to the zirconia surface, and then, gentle air was applied using a 3-way syringe. Next, a dual-polymerizing self-adhesive resin cement (Smartcem$^{®}$2; Dentsply Sirona) was applied according to the manufacturer's instructions: A plastic mold (Ultradent Jig; Ultradent Products Inc., South Jordan, UT, USA) containing resin cement was placed on the zirconia surface and photopolymerized for 20 s in each of the four directions using a 1200 mW LED light curing unit (DB-686 Cappu LED Curing Light; Bisco Asia, Seoul, Korea). For each experimental group, half of the specimens were stored in a 37 °C water bath for 24 h as a non-aging group; the other half were artificially aged by immersion in 37 °C water for 6 months. The treatments for all experimental groups are summarized in Figure 1.

Table 1. Materials used in this study

Material	Product Name	Main Composition	Manufacturer
Zirconia block	Zircose-E Ace	ZrO_2, Y_2O_3, HfO_2, Al_2O_3	Bioden Co., Seoul, Korea
Primer	Prime & Bond Universal™	PENTA, 10-MDP, bi-and multifunctional acrylate, initiator, stabilizer, isopropanol, water	DentsplySirona, Konstanz, Germany
Dual polymerizing self-adhesive resin cement	Smartcem®2	UDMA, EBPADMA Urethane resin, di- and tri- functional diluents, PENTA, Proprietary photo-initiating system, Proprietary self-cure initiating system, fillers	DentsplySirona, Konstanz, Germany

As provided by the manufacturers.

PENTA (dipentaerythritol pentaacrylate phosphate), 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate), UDMA (urethane dimethacrylate), and EBPADMA (ethoxylated bisphenol A dimethacrylate)

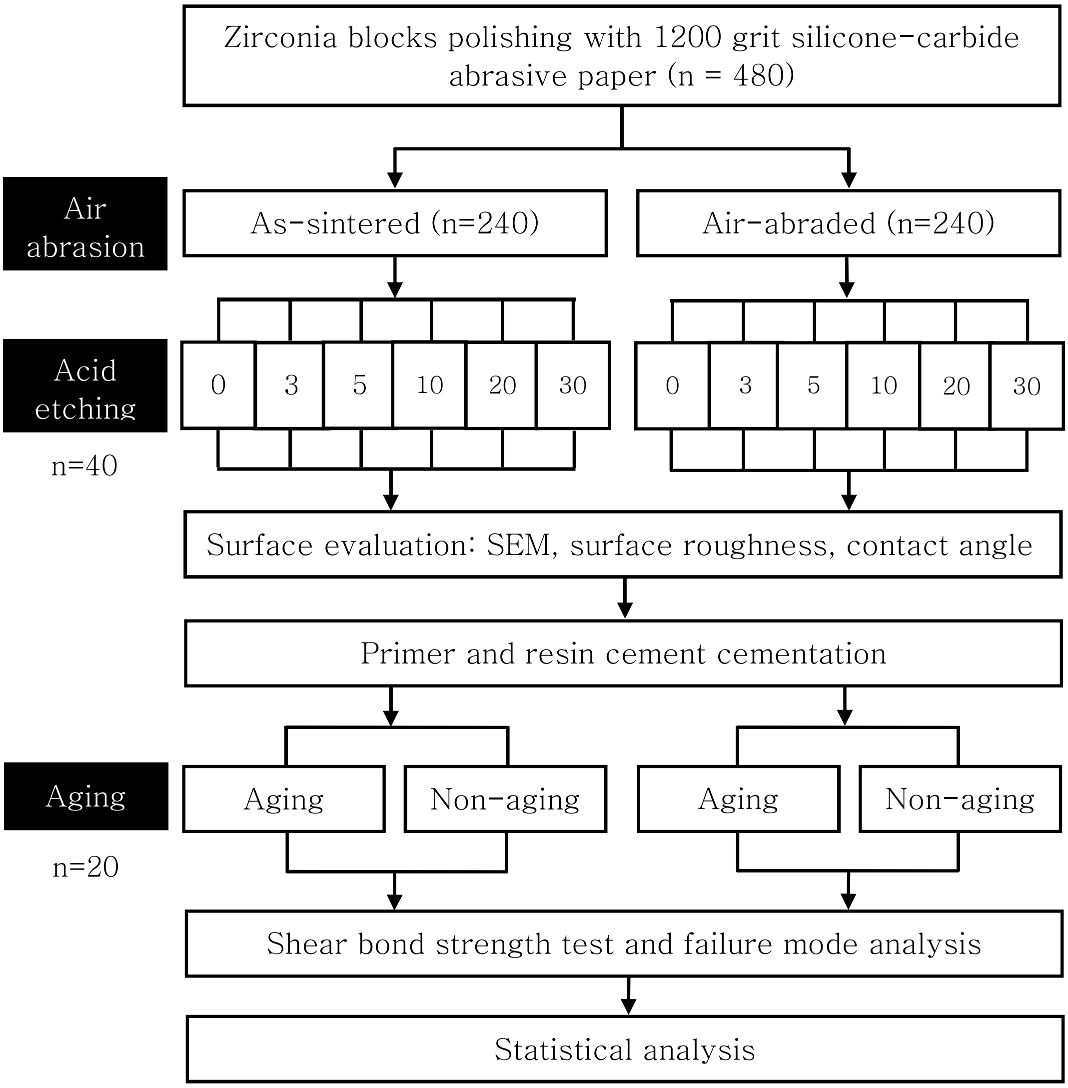

Figure 1. Flowchart of the surface treatments on the zirconia specimens.

3. Shear bond strength (SBS) test

The SBS was evaluated using a universal testing machine (Instron 3366; Instron Corp., Norwood, MA, USA) at a crosshead speed of 0.5 mm/min. A shear force was applied to the adhesion surface between zirconia and resin cement; the maximum load at failure was measured in N. The shear bond strength (MPa) was calculated by dividing the failure load (N) with the bonding surface area (mm^2). The Weibull characteristic strength ($σ_0$) and Weibull modulus (m) were calculated using

$$P_f = 1 - exp\left[-(\frac{\sigma}{\sigma_0})^m\right]$$

where P_f represents the probability of failure (between 0 and 1) at stress σ, which is the SBS in MPa. Further, $σ_0$ denotes the Weibull characteristic strength in MPa, which represents 63.2% of the specimen failure, and m denotes the Weibull modulus, which describes the shape of the strength distribution as a function of failure probability. The 95% confidence intervals (95% CI) were calculated, and a p-value of 0.05 was considered statistically significant. The higher the Weibull modulus, the more reliable is the treatment, the higher is the Weibull characteristic strength, and the higher is the bonding effectiveness.

4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM; JEOL-7800F, JEOL, Tokyo, Japan) was used to qualitatively analyze the morphological differences according to the zirconia surface treatment. Three specimens from each group were ultrasonically cleaned in distilled water and Pt coating (Cressington sputter coater 208HR, Cressington Scientific Instruments, Watford, UK) was applied for 60 s. Images were obtained at 20000X magnification with an operating voltage of 15.00 kV and a working distance of 10.0 mm.

5. Surface roughness evaluation

Five specimens were selected from each group for the evaluation of surface roughness using a surface profiler (DektakXT; Bruker, Hamburg, Germany). The average of the data was obtained using the calculation software based on the data peaks and valleys. Further, the arithmetic mean roughness (Ra, µm) data were obtained.

6. Contact angle evaluation

Five disc-shaped samples (diameter, 10 mm; thickness, 2 mm) were prepared per group to analyze the hydrophilicity between groups according to the zirconia surface treatment. 4 µL of distilled water was dropped into the center of each sample using a microsyringe with a video contact angle goniometer (SmartDrop, Femtobiomed Inc., Gyeonggi-do, Korea), and the contact angle was measured after 10 s. Each droplet image was immediately collected at 300X magnification, and the angles of the two opposite sides were measured and calculated as one value. The average of three measurements per specimen was used.

7. Failure mode analysis

Specimen surfaces were examined and photographed under a light microscopy at 25X magnification to determine the failure mode. The failure modes were classified as 1) adhesive failure, failure at the interface between zirconia and cement; 2) cohesive failure, failure within the cement layer; and 3) mixed failure, failure in which adhesive and cohesive are combined.

8. Statistical analysis

Statistical analyses were performed using SPSS v23.0 (SPSS Inc., Chicago, IL, USA). Shapiro-Wilk's test and Levene's test were performed to confirm data normality and variance homogeneity. The effect of three factors (sandblast, etching time, and aging) on the shear bond strength was evaluated using a three-way ANOVA test. The difference in the shear bond strength between groups was analyzed using one-way ANOVA, and the Bonferroni test was performed for post-hoc verification. The significance level was set at $P < 0.05$.

III. Results

1. SBS test

The mean and standard deviation of the SBS values of the as-sintered and air-abraded zirconia groups with respect to etching time and aging are listed in Table 2. The results showed that the SBS values increased significantly as the etching time increased to 20 min. In the as-sintered zirconia, the control group had a mean SBS of 23.78±12.98 MPa before aging. The SBS increased significantly with an increase in the etching time. The highest SBS value was observed at 20 min (59.16±12.85 MPa). However, the SBS decreased at 30 min and dropped to the value of the 10 min etching group. In the air-abraded zirconia, an increase in the pattern like that of the as-sintered zirconia was observed in the SBS values with an increase in etching time. The highest SBS value was obtained at 5 min of 60.64±16.50. Statistically similar SBS results were obtained when the etching time of 3–20 min were applied. The SBS decreased at 30 min, and this decrease was more pronounced than that of the as-sintered zirconia. Artificial water aging for 6 months reduced the SBS value. In all groups, the shear bond strength after aging was lower than that before aging. In the as-sintered zirconia, the control group achieved the lowest shear bond strength after aging, whereas the 20 min etching group had the highest SBS. In air-abraded zirconia, the SBS showed statistically similar values in all groups after aging.

Table 2. Mean and standard deviations of shear bond strength (MPa) of as-sintered and air-abraded zirconia specimens with etching time and aging ($p<0.05$). For the as-sintered and air-abraded groups, respectively, comparisons according to aging are shown in uppercase letters, and those according to etching time are shown in lowercase letters.

	As sintered		Air-abraded	
	Before aging	After aging	Before aging	After aging
0 min	23.78 ± 12.98^{Aa}	6.16 ± 4.00^{Ba}	36.54 ± 10.43^{Aa}	29.56 ± 13.09^{Aa}
3 min	44.52 ± 10.18^{Ab}	27.55 ± 14.54^{Bb}	55.97 ± 13.22^{Ab}	39.64 ± 9.67^{Ba}
5 min	42.46 ± 7.92^{Ab}	27.75 ± 10.65^{Bb}	60.64 ± 16.50^{Ab}	35.63 ± 9.30^{Ba}
10 min	53.50 ± 10.89^{Abc}	29.47 ± 11.52^{Bbc}	55.48 ± 11.07^{Ab}	41.13 ± 11.96^{Ba}
20 min	59.16 ± 12.85^{Ac}	47.58 ± 11.31^{Bd}	57.26 ± 13.93^{Ab}	41.33 ± 15.10^{Ba}
30 min	47.27 ± 13.85^{Abc}	40.58 ± 9.50^{Acd}	33.36 ± 7.27^{Aa}	31.94 ± 9.40^{Aa}

The results of the 3-way ANOVA are shown in Figure 2. and Table 3. They indicate that sandblasting, etching time and aging have significant impact ($p < 0.001$). The interaction between sandblasting and etching time ($p < 0.001$) and the interaction between etching time and aging were both significant ($p = 0.002$). However, there was no interaction between sandblasting and aging ($p = 0.438$); the interaction between these three factors was not significant ($p = 0.099$).

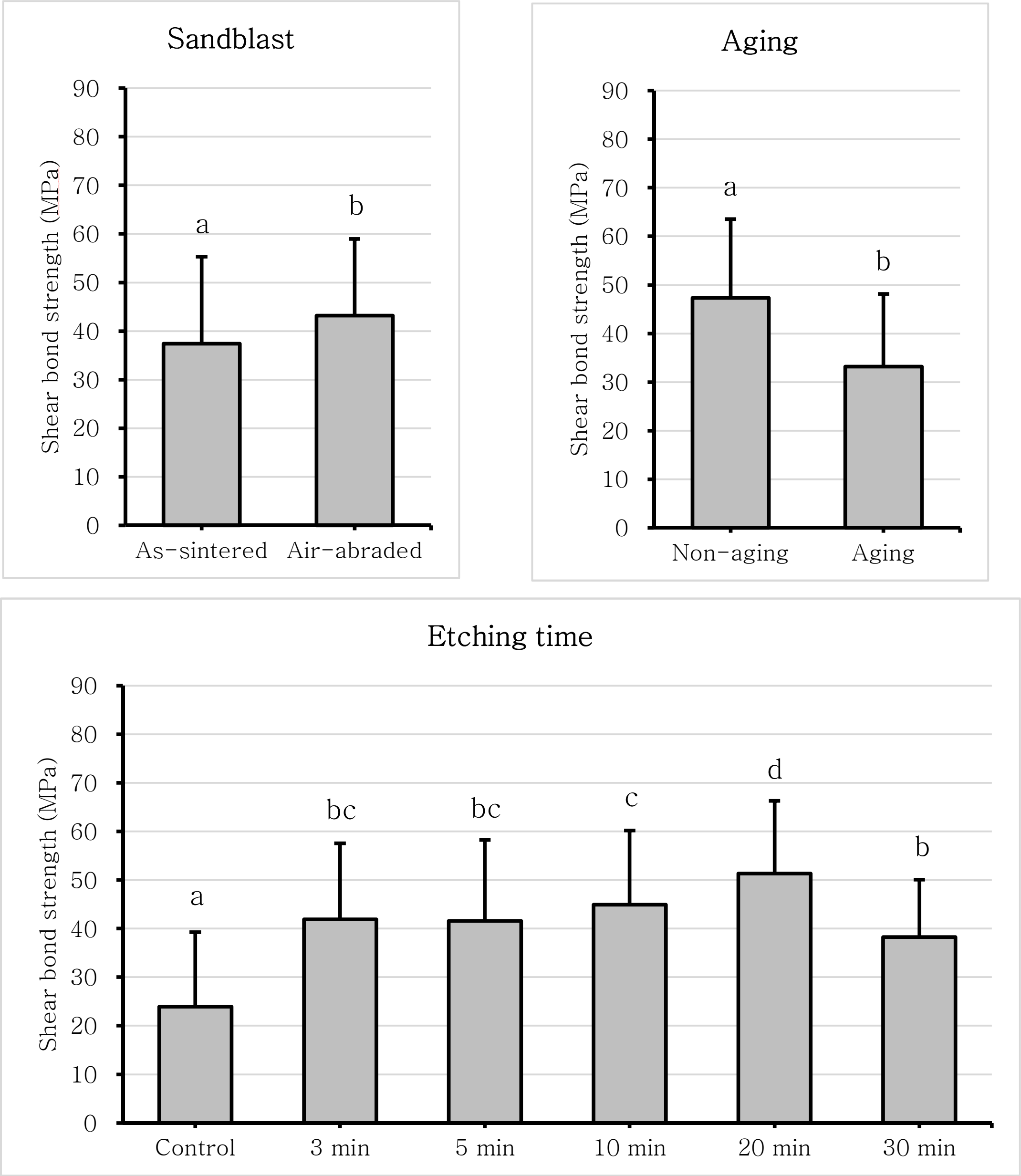

Figure 2. Shear bond strength according to the sandblast, etching time, and aging. Different superscript letters indicate statistically significant differences ($p < 0.05$).

Table 3. Summary of 3-way ANOVA

Source	Type III Sum Sq.	df	Mean Sq.	F	Sig
Sand(S)	2975.351	1	2975.351	22.116	.000
Etching(E)	25350.817	5	5070.163	37.687	.000
Aging(A)	18141.033	1	18414.033	136.875	.000
S*E	9505.117	5	1901.023	14.131	.000
S*A	81.162	1	81.162	0.603	.438
E*A	2552.363	5	510.473	3.794	.002
S*E*A	1258.639	5	251.728	1.871	.099

a. R Squared=.570(Adjusted R Squared=.541)

b. significance level=.05

The results of the Weibull analysis of the shear bond strength data are presented in Table 4. Two different Weibull parameters are listed: Weibull modulus (m) and Weibull characteristic strength (σ_0). All groups were compared at an unreliability level of 63.2%, which was considered actual bonding effectiveness. The control group (0 min) exhibited the lowest Weibull strength values. The Weibull strength was the highest at an etching time of 20 min in the as-sintered group. Similarly, high values were observed at 3, 5, 10, and 20 min in the air-abraded group. For the aging effect, the Weibull analysis confirmed that aging induced a decrease in the shear bond strength in both the as-sintered and air-abraded groups.

Table 4. Weibull modulus (m, 95% CI) and Weibull characteristic strength (σ_0, MPa) data for the zirconia specimens based on air-abraded, aging treatment, and etching times (min) ($p<0.05$). For the as-sintered and air-abraded groups, respectively, comparisons according to aging are shown in uppercase letters, and those according to etching time are shown in lowercase letters.

		Before aging		After aging	
		M	σ_0	M	σ_0
As-sintered	0 min	2.2 (2–2.4)	28.48509^{Aa}	1.5 (1.3–1.6)	6.93618^{Ba}
	3 min	5.1 (4.5–5.7)	48.45986^{Ab}	1.9 (1.6–2.2)	31.37552^{Bb}
	5 min	5.9 (5.1–6.7)	45.83827^{Ab}	3.2 (2.8–3.6)	30.95289^{Bb}
	10 min	5.5 (4.8–6.3)	57.94961^{Abc}	2.1 (1.7–2.5)	34.54445^{Bbc}
	20 min	4.6 (3.8–5.3)	65.03519^{Ac}	4.9 (4.1–5.7)	51.91877^{Bd}
	30 min	3.7 (3.4–4)	52.4659^{Abc}	5 (4.5–5.5)	44.16451^{Acd}
Air-abraded	0 min	4.3 (3.5–5)	40.16022^{Aa}	0.6 (0.4–0.9)	48.2764^{Aa}
	3 min	4.7 (4.2–5.3)	61.18386^{Ab}	4.5 (3.7–5.3)	43.5342^{Ba}
	5 min	4.3 (3.2–5.4)	66.79768^{Ab}	4.2 (3.6–4.9)	39.25373^{Ba}
	10 min	5.8 (5–6.6)	59.93942^{Ab}	4 (3.5–4.5)	45.41459^{Ba}
	20 min	4.7 (4.3–5.1)	62.59043^{Ab}	3.2 (2.8–3.6)	46.13053^{Ba}
	30 min	5.6 (4.5–6.6)	36.11556^{Aa}	3.9 (3.2–4.6)	35.33618^{Aa}

2. Scanning Electron Microscopy (SEM)

Morphological changes that occurred on the surface of the as-sintered zirconia following acid etching are shown in Fig. 3. The abrasive roughness created by the 1200-grit silicon carbide paper is shown in Figure 3A. An overall homogeneous surface structure with smooth and fine grains is observed. The smooth edges of the grain boundaries disappear with an increase in the etching time. The irregular surface roughness increases, which results in the appearance of the sharp edges of structures such as stars and needles. Further, the inter-grain space increases gradually (Figure 3B-F).

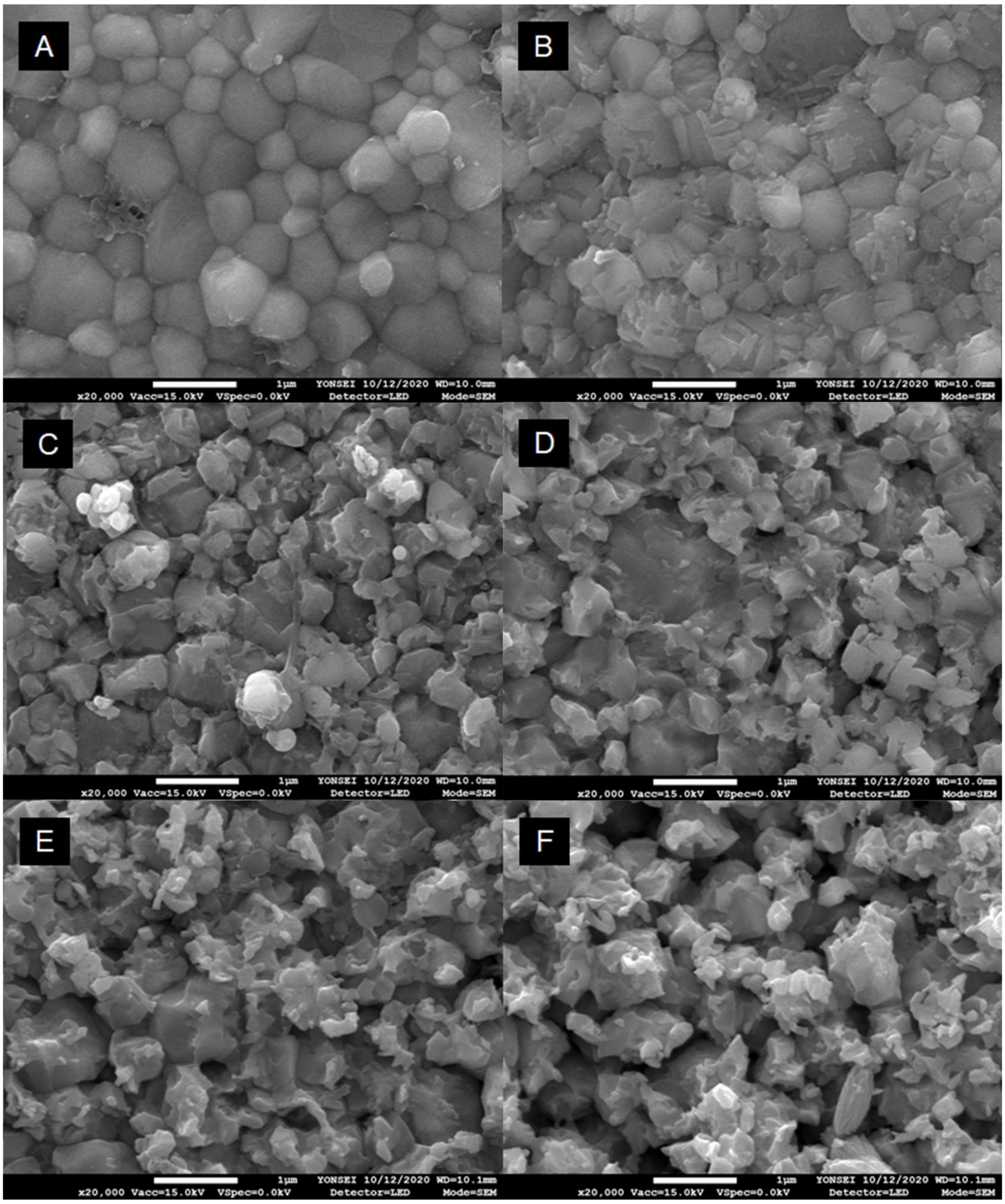

Figure 3. SEM photomicrographs at 20,000X magnification of as-sintered zirconia specimens following etching for various time periods. A) Control, B) 3 min, C) 5 min, D) 10 min, E) 20 min, F) 30 min

Morphological changes in the air-abraded zirconia surfaces at different etching times are shown in Figure 4. Figure 4A shows a relatively smooth surface with no irregularities. In contrast, the zirconia surface subjected to acid etching exhibited modified surface textures with an increased irregular surface roughness. The grain size decreased and became more compact with an increase in the etching time with smaller pits and pores. The irregularity of the air-abraded zirconia surface is more uniform and detailed than that of the as-sintered sample. However, the zirconia surface subjected to etching for 30 min was over-etched; the surface roughness was lower than that of the 20 min specimen.

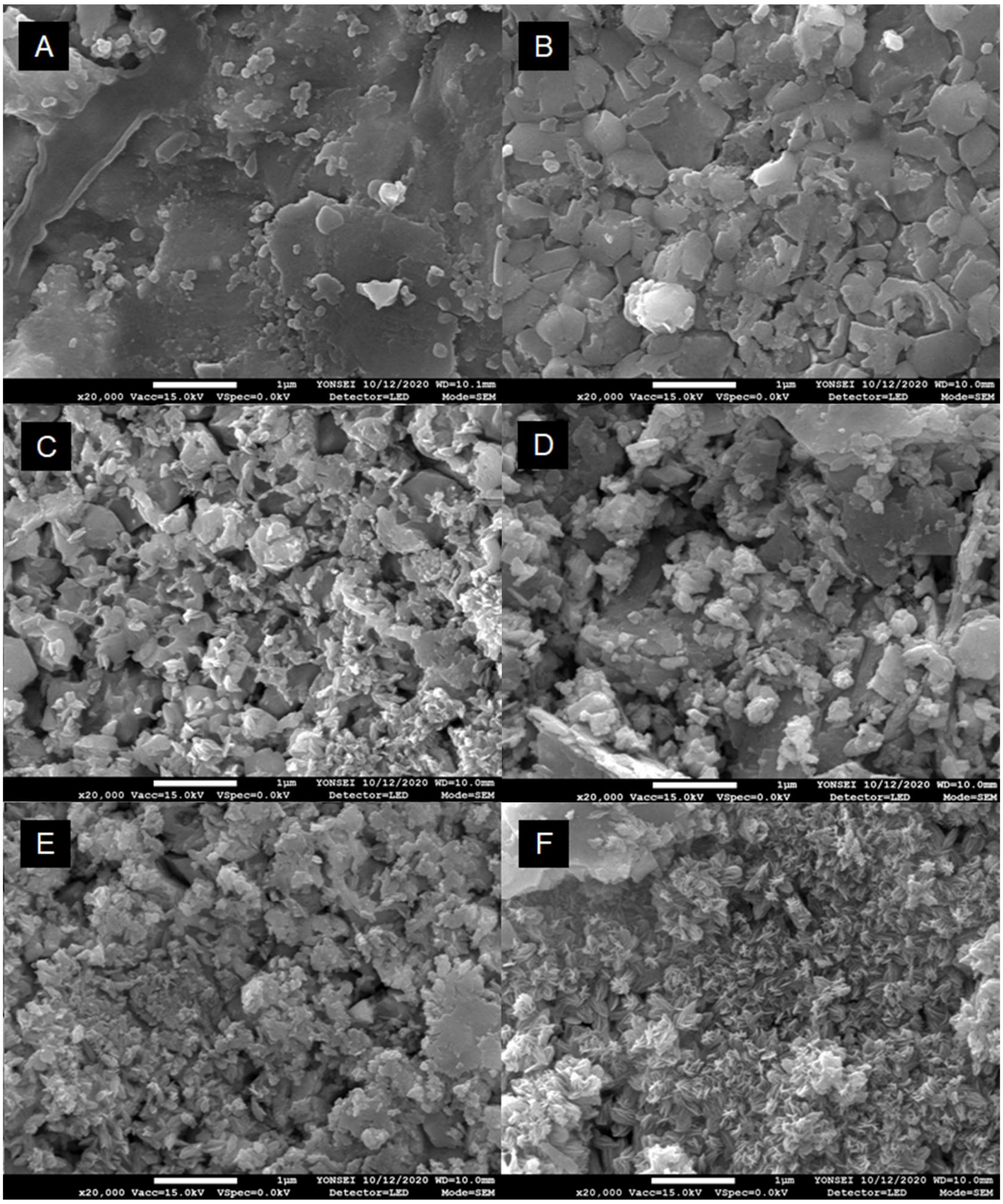

Figure 4. SEM photomicrographs at 20,000X magnification of air-abraded zirconia specimens following etching for various time periods. A) Control, B) 3 min, C) 5 min, D) 10 min, E) 20 min, F) 30 min

3. Surface roughness evaluation

The average surface roughness values for the as-sintered and air-abraded zirconia samples are shown in Figure 5. The surface roughness showed no significant change after 3 min of etching; however, the roughness increased significantly after 5 min and tended to increase with an increase in the etching time. The surface roughness value increased to 6.36±1.26 μm for the air-abraded zirconia and to 2.48±0.65 μm for the as-sintered zirconia at 30 min of etching time. The roughness of the air-abraded zirconia was always higher than that of the as-sintered zirconia.

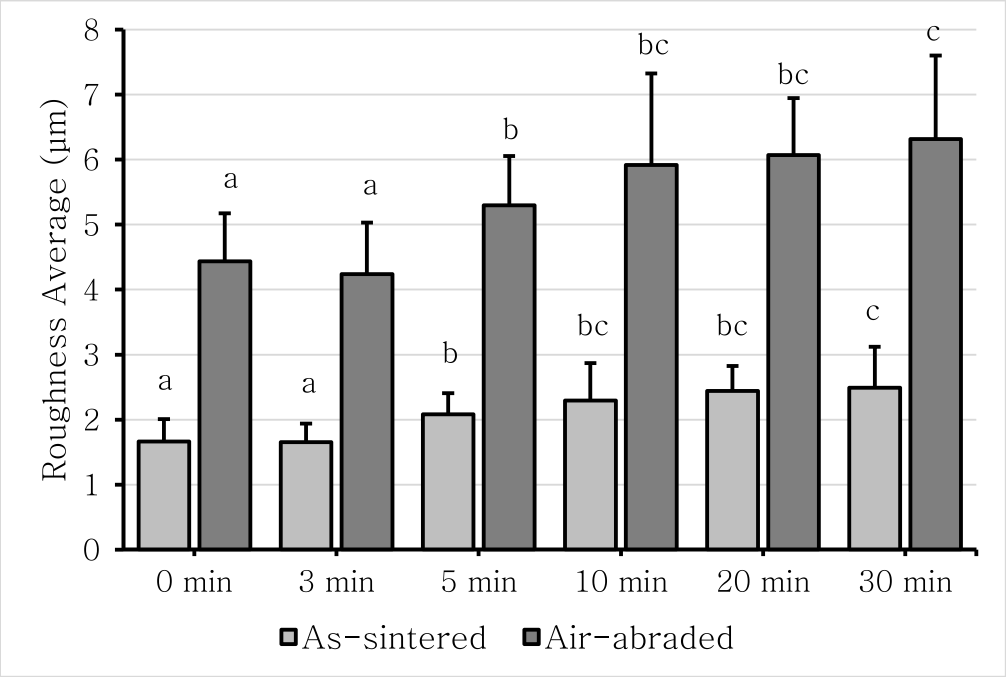

Figure 5. Surface roughness(μm) for as-sintered and air-abraded zirconia surfaces. Different superscript letters indicate statistically significant differences ($p<0.05$).

4. Contact angle evaluation

The average contact angles of the as-sintered and air-abraded zirconia surfaces are shown in Figure 6. The as-sintered zirconia, whose surface was modified with a 1200-grit silicon carbide abrasive paper, showed the highest water contact angle of 61.72±6.01. However, acid etching affected the surface properties of zirconia and rendered the surface hydrophilic. All surface treatments significantly reduced the contact angle compared to the control. The lowest water contact angle was observed at 20 min for the as-sintered zirconia, and 30 min for the air-abraded zirconia.

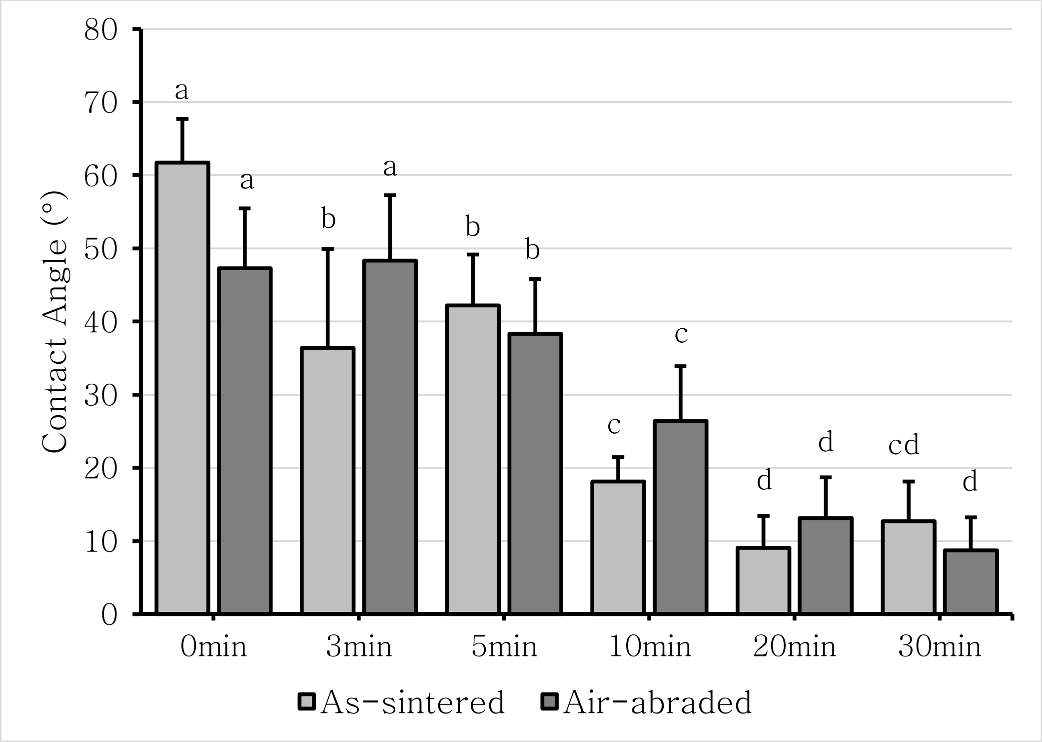

Figure 6. Contact angle(°) for as-sintered and air-abraded zirconia surfaces. Different superscript letters indicate statistically significant differences ($p<0.05$).

5. Failure mode analysis

The distribution of the failure types is shown in Figure 7. The visual examination of the failure mode showed mixed and adhesive failure, and it did not show any cohesive failure. In the as-sintered zirconia, an adhesive failure of up to 86% was observed in the control group. The adhesive failure decreased to approximately 13% at 20 min with an increase in etching time, and then, they slightly increased to 40% at 30 min. In the air-abraded group, in most cases, mixed failure was dominant, accounting for about 80%; however, in just 30 minutes, adhesive failure was dominant and accounted for more than 70%.

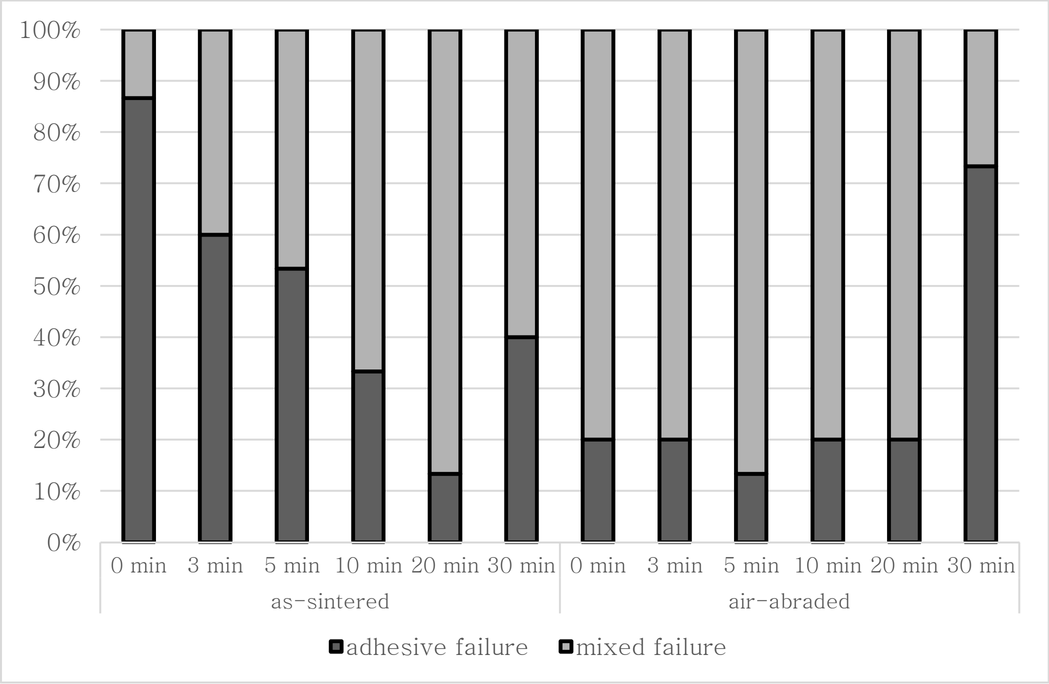

Figure 7. Failure mode percentage for as-sintered and air-abraded zirconia surfaces.

IV. Discussion

This study investigated the effect of the acid-etching treatment on the surface microstructure, surface roughness, and surface contact angle of zirconia; further, the effects of the air-borne particle abrasion, various etching times, and aging on the shear bond strength of resin cement to zirconia surfaces were compared. We found that acid etching altered the surface topography and increased the surface roughness of the zirconia. All surfaces showed a change in their wettability from hydrophobic to hydrophilic. The shear bond strength of the resin cement to zirconia significantly increased with an increase in the etching time, and sandblasting, etching time, and aging all showed significant effects. These results show that the null hypothesis of this study was rejected.

In the current study, the acid etching treatment can etch the zirconia surface by corroding the zirconia particles. The acid appeared to chemically dissolve the particles on the zirconia surface, as indicated in the SEM micrographs in Figure 3. and 4. The particle size decreased and the interparticle space widened. The grain structure changed to a rough and irregular pattern, which increased the bonding area and microretentive structure. This phenomenon can be explained by the fact that the acid promotes the destruction of atoms around the superficial border of grain on the zirconia surface and it initiates localized corrosion through the preferential removal of less arranged and more chemically reactive peripheral atoms.[21,25-27] Further, our findings revealed that no surface defects or microcracks were detected in the as-sintered or air-abraded specimens; this is in line with previous studies that demonstrated no significant effect on the monoclinic or flexural strength of zirconia.[24,28]

The surface roughness increased with an increase in the etching time (Figure 5). Further, the contact angle also decreased (Figure 6) and the SBS values increased significantly (Table 2). The change in the surface roughness and surface contact angle of zirconia by acid etching treatment seems to strengthen the adhesion of the resin cement.[29] The surface roughness of the air-abraded specimens was higher than that of the as-sintered ones. Likewise, the SEM micrograph confirmed that the irregularity of the air-abraded zirconia surface was more uniform and detailed than that of the as-sintered group. This is probably because the air-abrasion process roughened the surface and created more space for the etching solution to penetrate.

Thus far, the clinically sufficient bond strength between resin cement and zirconia has not been known. Several studies suggested that at least 10 MPa is the clinically sufficient level of bonding strength.[30-33] According to the results of this study, the SBS values increased significantly as the etching time increased and remained at an acceptable level, even after artificial water aging.

Most studies performed artificial aging through water storage and/or thermocycling to simulate oral conditions and estimate long-term stability. According to the meta-analyses, water storage simulates aging due to water absorption and hydrolytic degradation, whereas thermocycling represents hydrothermal aging in vitro; water storage presented a greater bond degrading effect.[34,35] In this study, artificial water aging was performed by immersion in water at 37 °C for six months. A significant decrease in the shear bond strength over six months of water storage was observed; this can be attributed to the hydrolytic degradation of the interface through water absorption.[6,36,37]

Weibull analysis was performed to determine the predictability and reliability of the shear bond strength data. In the Weibull analysis, the characteristic strength and Weibull modulus can be considered equal to the mean strength and standard deviation of the normal distribution; the Weibull modulus represents the reliability. The higher the value of the Weibull modulus, the closer is the observed values are grouped; therefore, the characteristic strength values are more reliable when determining the true bond strength.[38] In this study, the results of the Weibull analysis were in line with the findings from the one-way ANOVA, and they showed that air abrasion, etching time, and aging caused significant changes. However, because of the limited number of samples, caution should be exercised when interpreting the Weibull modulus. Further, clinical trials are required to confirm this result.

When analyzing the failure mode, the adhesive failure occurred when the bonding strength between the resin cement and zirconia was not strong. The failure mode was mixed when the bonding strength reached a relatively high level.[31,39] As shown in Figure 7, the adhesive failure occurred initially in the as-sintered specimens; however, adhesive failure decreased with an increase in the etching time. In the air-abraded group, the overall failure mode was predominantly a mixed failure. The adhesive failure was predominant only at an etching time of 30 min. Similarly, in the SEM micrograph of the air-abraded group, the zirconia surface was etched excessively at the etching time of 30 min. Similarly, the surface roughness at 30 min was lower than that at 20 min, and the SBS was also lower than 20 min at 30 min. This is attributed to the irregularities remaining on the surface after air abrasion were over-etched and removed after 30 min of etching.

The results of this study contrasted with those of previous studies in that HF had no effect on the zirconia surface. However, most studies used a low concentration of HF (4.5–9.5%) at room temperature and applied a short etching time (1–2 min); this is similar to the conventional etching process used in silica-based ceramics.[19,40,41] Under such etching conditions, the HF did not significantly change the surface topography and surface roughness of zirconia. However, the corrosion activity of the HF solution is influenced by etching conditions such as the etching temperature, concentration of the HF solution, and etching duration. According to Casucci et al., 9.5% HF did not change the surface of zirconia. However, in the experimental etching solution at 100 °C, the surface roughness increased after etching for 10 min, 30 min, and 60 min.[25] Further, a study by Sriamporn et al. revealed that the concentration and temperature of HF could affect the reaction rate; the surface irregularities increased with longer immersion times and higher etching-solution temperatures.[21]

In this study, the experimental design and study parameters were set based on the results of the prior studies on the HF etching of zirconia. A preceding study was designed as a 15-min etching group (ET15), a 30-min etching group (ET30), a sandblasting alone group (SB), and a 15-min etching group after sandblasting (SBET). The SBET and ET15 showed significantly higher shear bond strengths than ET30 and SB. Further, ET 30 exhibited a higher shear bond strength than SB.[42] Therefore, it was necessary to further subdivide the time setting within 30 min to determine the optimal HF etching conditions; thus, 0, 1, 3, 5, 10, 20, and 30 min were designed.

Another study evaluated the effects of the application time of an acid mixture solution on the biaxial flexural strength of zirconia specimens. Samples were divided into 11 subgroups based on the etching time (0, 1, 2, 3, 5, 8, 10, 12, 15, 20, and 30 min). The results showed that acid treatment of as-sintered and air-abraded zirconia increased the surface roughness without having a negative impact on the flexural strength.[24] Following the previous study, this study evaluated the effects of the HF etching treatment on the shear bond strength between resin cement and zirconia surface.

The etching solution comprised hydrofluoric acid, sulfuric acid, hydrogen peroxide, methyl alcohol, and purified water. Hydrofluoric acid was used to increase the surface roughness of the zirconia. Sulfuric acid was used to stabilize the catalytically active tetragonal phase of zirconia without increasing its surface roughness.[43] Hydrogen peroxide does not contribute to the increasing surface roughness, and it helps maintain the surface treated state by forming a mixture with sulfuric acid (known as piranha solution).[39] Water and alcohol were used as solvents to dissolve the solute.

In current study, MDP-containing universal adhesive was used, and the self-adhesive resin cement contained non-MDP phosphate ester monomer(Table 1). These two phosphate ester monomers have been proven to enhance the bond strength with zirconia.[18,44] The pretreatment with MDP-containing primer showed improvement in both initial and long-term bond strength of resin cement to zirconia compared to the unprimed control.[45,46] The zirconia surface is easily covered with a passive oxide film(ZrO_2). Therefore, hydroxyl groups may exist on the zirconia surface, and there may be a chemical interaction between the hydroxyl groups on the zirconia surface and the phosphoric acid ester of the MDP monomer.[13,47] Because acid etching break downs the oxide film on the zirconia surface, the reaction between zirconia and MDP monomer becomes less significant as the etching time increases.[26] Similar to the implications of our results, the MDP monomer increased bond strength when acid etched zirconia specimens for 10 min, but it did not have a significant impact when applied for 30 min.[48].

In this study, the effect of the acid-etching treatment on as-sintered and air-abraded zirconia surfaces was investigated in terms of surface topography, surface roughness, surface contact angle, and shear bond strength. The surface roughness and surface contact angle increased and decreased with the etching time in all groups. The shear bond strength increased with an increase in the etching time; the etching effect was better in the air-abraded group and it decreased with aging.

The results of this in vitro study suggest that acid etching is a promising alternative for zirconia surface treatment. However, it is still insufficient to draw conclusions on the effect of the acid etching treatment on the resin cementation of zirconia; this study has several limitations. First, only one type of acid mixture and one set of temperature conditions were used. The tendency of the change based on the increase in etching time was different at 20 and 30 min; however, the time interval between 20 and 30 min was not further subdivided. No results were obtained after more than 30 min. After six months of immersion in water, it was difficult to fully reproduce the actual oral situation to evaluate long-term stability.

Further investigation and optimization that includes comparisons of different etching conditions such as the formulation of the etching solution, etching temperature, and etching duration, need to be performed prior to clinical applications. Further studies concerning long-term aging are necessary to confirm long-term durability.

V. Conclusion

The following conclusions were drawn within the limitations of this study:

1. The acid etching treatment on the as-sintered and air-abraded 3Y-TZP zirconia surfaces significantly increased surface roughness and wettability ($p < 0.05$).
2. The acid etching treatment on the as-sintered and air-abraded 3Y-TZP zirconia surfaces significantly increased the shear bond strength of the resin cement to the zirconia surface ($p < 0.05$).
3. Sandblasting, etching time, and aging had significant effects on the SBS between the resin cement and 3Y-TZP zirconia surface ($p < 0.05$).

This study demonstrated that acid etching treatment can induce micro-morphological changes on the zirconia surface and increase shear bond strength. The results of this in vitro study suggest that acid etching treatment of the zirconia surface can help improve the adhesion of resin cement in clinical applications.

VI. References

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ABSTRACT(KOREAN)

공기마모, 산부식, 노화가 3Y-TZP 지르코니아에 대한 레진시멘트와의 전단결합강도에 미치는 영향

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서송희

본 연구의 목적은 산부식 처리가 지르코니아의 표면 미세구조, 표면 거칠기 및 표면 접촉각에 미치는 영향에 대해 조사하고 레진 시멘트와의 전단 결합 강도에 공기마모, 산부식 시간 및 노화가 미치는 영향을 비교하는 것이다.

총 480 개의 시편을 제작하여(9 × 10 × 10 mm) 각각 20 개씩 24 개의 그룹으로 나눴다. 공기마모 여부에 따라 소결군과 공기마모군으로 나누고 산부식 시간(0, 3, 5, 10, 20, 30 분)에 따라 6 개의 그룹으로 세분화했다. 산부식액은 불산 25%, 황산 16%, 과산화수소, 메틸알코올, 정제수로 구성했다. 전단결합강도, 표면 미세구조, 표면 거칠기, 표면 접촉각을 측정하고 실패양상을 평가했다.

평균 전단결합강도는 소결군과 공기마모군 모두에서 산부식 시간이 20 분까지 증가함에 따라 유의적으로 증가했고 산부식 시간이 30 분으로 늘어나자 감소했다. 모든 군에서 노화 후 전단결합강도는 노화 전보다 낮았다. 3-way ANOVA 결과 공기마모, 산부식 시간, 노화 모두 유의한 효과를

보였다($p<0.001$). 또한 산부식 시간이 증가함에 따라 표면 거칠기가 증가하고 접촉각이 감소했다. 이번 연구의 결과 지르코니아 표면에 대한 산부식 처리는 지르코니아와 레진시멘트의 결합강도를 향상시키기 위한 좋은 대안이 될 것으로 보인다.

핵심이 되는 말 : 공기마모, 노화, 레진 시멘트, 산부식, 전단결합강도, 지르코니아