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Effects of Surface-Etching Systems on the Shear Bond Strength of Dual-Polymerized Resin Cement and 3Y-TZP Zirconia

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Sang Hyun Kim

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This certifies that the Dissertation

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DEDICATION (감사의 글)

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2024년 12월

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ABSTRACT

Effects of Surface-Etching Systems on the Shear Bond Strength of Dual-Polymerized Resin Cement and 3Y-TZP Zirconia

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The long-term success of zirconia-based dental restorations is critically dependent on the bond strength between zirconia and resin cements. Conventional surface treatments, such as sandblasting, are widely used to enhance this bonding by increasing surface roughness and reactivity. However, recent developments in chemical etching systems have introduced alternative surface treatment methods that may provide superior adhesive strength. This study aims to perform a comparative analysis of the shear bond strength between dual-polymer resin cement and zirconia, with a focus on different etching systems in comparison to sandblasting, both before and after aging. A total of 100 zirconia specimens were divided into five groups, each subjected to different surface treatments. Of these, 20 blocks remained untreated, 20 blocks underwent sandblasting, and 60 blocks were acid-etched using three distinct zirconia etching systems: Zircos-E etching (strong-acid etching), smart etching (acid etching following air abrasion), and cloud etching system (acid etching under

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hot steam). Each group underwent a bonding procedure with dual-polymerized resin cement, including photopolymerization, after which 50 specimens were subjected to thermocycling. The shear bond strengths between the resin cement and zirconia were evaluated both before and after thermocycling. Surface analysis was conducted using X-ray diffraction, surface roughness measurements, and scanning electron microscopy. The results revealed that both acid-etching treated and sandblasted zirconia specimens exhibited a significant increase in bond strength compared to surface untreated zirconia. Among the non-thermocycled groups, specimens treated with etching solutions did not exhibit a significant increase in shear bond strength compared to sandblasted specimens ($p > 0.05$). However, in the thermocycled groups, the smart-etched specimens demonstrated the highest shear bond strength. While various etching agents did not significantly enhance bond strength compared to sandblasting in the short term, smart etching showed greater long-term stability, with less reduction in bond strength after aging($p < 0.05$).

Key words: Acid etching, Cementation, Ceramic bonding, Shear bond strength, Surface conditioning, Thermocycling, Zirconia

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1. INTRODUCTION

In contemporary restorative dentistry, zirconia has emerged as a material of choice due to its exceptional mechanical properties, biocompatibility, and esthetic potential. Its high fracture toughness and resistance to wear have made zirconia an ideal material for dental prostheses such as crowns and bridges[1]. However, achieving a durable and reliable bond between zirconia and resin-based cements remains a critical challenge, as zirconia's inherent chemical inertness and lack of surface reactivity hinder effective bonding.

Pure zirconia undergoes phase transitions with increasing temperature, shifting from a cubic phase to a monoclinic phase during cooling after the sintering process[2]. The addition of stabilizing oxides such as CaO, MgO, CeO_2, and Y_2O_3 to pure zirconia enables the formation of a multiphase material known as partially stabilized zirconia[3]. Among these, the addition of 2–3 mol% Y_2O_3 stabilizes the tetragonal phase at room temperature, enhancing the properties of zirconia and forming yttria-stabilized tetragonal zirconia

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polycrystals (Y-TZP). As a tetragonal phase, Y-TZP is stable at room temperature, and its physical properties, including its fracture toughness and strength, are superior to those of alumina[4].

To prevent the fallen out of zirconia restoration in clinical applications, achieving a strong and durable bonding is crucial[7]. Generally, hydrofluoric etching and silanization are used as pretreatment techniques to bond resin to conventional dental ceramic restorations[5,6]. However, they do not increase the strength of the bond between the resin and the zirconia[7]. Zirconia bonding is the most difficult type of ceramic bonding, and bond failure is common during clinical trials[8]. To address these limitations, surface treatment protocols have been developed to enhance the adhesion between zirconia and resin cements. According to a study on zirconia adhesion, when resin cements were used without an adhesive monomer, a combination of air abrasion and priming was needed to achieve durable long-term bonding to zirconia[9–16]. In addition, this treatment resulted in a high bond strength; several researchers have reported similar results[17–20]. Accordingly, several clinicians have performed zirconia adhesion using an adhesive resin cement containing 10-methacryloyloxydecyl dihydrogen phosphate after performing air abrasion during zirconia bonding.

Zirconia is subjected to air abrasion as a pretreatment to increase its bond strength with resin cement. In principle, air abrasion cleans the surface, removes impurities, increases the roughness of the surface, and changes the surface energy and wettability[21–28]. Furthermore, the silica nanoparticles that are emitted during the process not only loosely

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cover the abraded ceramic surface after the abrasion process but also cause the release of kinetic energy in the form of thermal energy, which results in the melting of the ceramic surface and the formation of zirconium silicate[29]. From this perspective, surface modifications of zirconia, including increased roughness and phase transitions, are critical factors that must be carefully considered.

Given the importance of these surface changes, their relevance extends beyond conventional restorations to more complex applications, such as implant dentistry. In particular, hybrid zirconia abutments are frequently employed in anterior implant prostheses, where superior aesthetics are paramount[8]. Achieving successful implantation with these abutments requires the use of adhesive cement at two critical interfaces: between the titanium base and zirconia abutment, and between the zirconia abutment and zirconia crown. Ensuring robust adhesion at these interfaces is vital for preventing adhesive failures, which could compromise the overall integrity and longevity of the prosthesis[9]. Thus, a deeper understanding of zirconia surface treatment methods is essential to achieving durable and reliable bonding in such high-stakes applications.

Despite the previous study on the effect of surface treatment with zirconia based on air abrasion, and efficacy of sandblasting, researchers continue to explore alternative surface treatment methods that may further enhance adhesive strength and long-term stability[19,36].

One of the most promising avenues for enhancing zirconia adhesion lies in the use of chemical etching systems. Etching aims to modify the zirconia surface chemically, increasing surface energy and reactivity without compromising the material's structural

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integrity. This approach is intended to offer a more effective bonding surface than mechanical treatments alone. However, the performance of these etching systems, particularly in comparison to the well-established sandblasting method, remains underexplored.

Several companies have proposed etching agents that chemically treat the zirconia surface to increase the bond strength with resin cement. However, these manufacturers claim that these chemical surface treatments can effectively increase adhesive strength on the basis of their own experimental data, and independent experimental studies on such effects have not yet been reported. Therefore, this study aims to conduct a comprehensive comparative analysis of the shear bond strength between dual-polymer resin cement and zirconia, focusing on surface treatments using various etching systems and their effectiveness relative to the gold standard sandblasting method. Furthermore, the influence of aging on the bond strength will be evaluated to more accurately replicate intraoral conditions. By testing whether etching systems can surpass the adhesive strength achieved by sandblasting, this research seeks to provide insights into optimizing zirconia surface treatment protocols for improved clinical outcomes in restorative dentistry. The null hypothesis for this study is that there is no significant difference in the shear bond strength between dual-polymerized resin cement and zirconia, regardless of the surface treatment method (etching systems or sandblasting) or the effects of aging.

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2. MATERIALS AND METHODS

One hundred cubic blocks (12 mm × 12 mm × 12 mm) were fabricated from 3Y-TZP (Plus Zir Block; DMAX Co., Ltd., Daegu, Republic of Korea) using a milling machine (MAXX-5Z; Robots and Design, Pangyo, Republic of Korea) and computer-aided manufacturing software (GO2cam Dental V6.09; GO2cam Intl., Lyon, France) (overlap tool diameter: 0.0750%; overlap volume: 0.1500; XY scallop: 0.0028). The blocks were sintered at 1500 °C for 7 hours in a sintering furnace (Sintramat; Ivoclar Vivadent AG, Schaan, Liechtenstein) and randomly assigned to five groups; Group P, Group S, Group Z, Group M, Group C. The random surfaces of the blocks in each group were subjected to a different surface treatment before the bonding procedure. All milled surfaces were polished with 1500-grit sandpaper for standardization before testing. Each group of blocks underwent the same bonding process after surface treatment and was further divided into two subgroups based on whether thermocycling was performed (n = 10 per subgroup). In naming the specimens, these subgroups were distinguished using “T” for the specimens that underwent thermocycling and “N” for those that did not (Figure 1).

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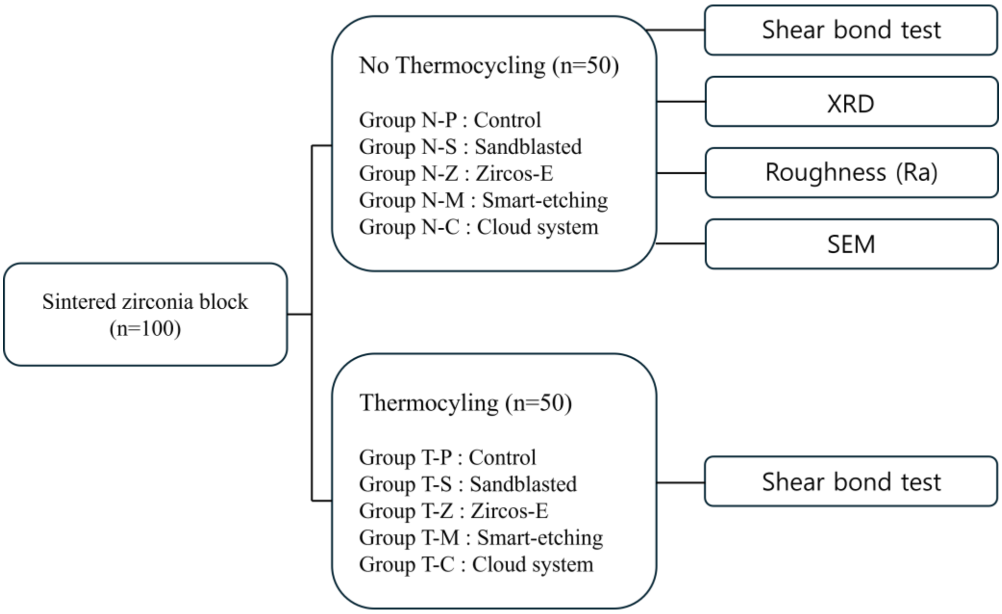

Figure 1. Overall experimental design

The control-group blocks (groups N-P and T-P) did not undergo additional mechanical surface treatment after sintering. The blocks from groups N-S and T-S were sandblasted with Al_2O_3 particles using a sandblasting unit (Basic Master; Renfert GmbH, Hilzingen, Germany). The blocks from groups N-Z and T-Z were acid-etched for 2 hours with Zircos-E etching solution (Zircos-E; Bioden, Seoul, Republic of Korea). The blocks from groups N-M and T-M were sandblasted for 15 s and then acid-etched using a smart etching solution (Smart-etching; YesBio, Seoul, Republic of Korea) for 10 min in a hot water bath. Lastly, the blocks from groups N-C and T-C were acid-etched for 10 min in a hot steam pot (Cloud system; MEDIFIVE Co., Incheon, Republic of Korea) (Table 1). The properties of the materials used in this study are presented in Table 2.

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Table 1. Classification of groups based on types of surface treatments for zirconia blocks

Group Names	Surface Treatment
N-P, T-P	As-sintered
N-S, T-S	Sandblasting for 15 s with Al_2O_3 particles (~25–70 μm, 4.83 bar, 1 cm apart)
N-Z, T-Z	Acid-etched for 2 h with Zircos-E etching solution
N-M, T-M	Sandblasted for 15 s and then acid-etched for 10 min in a hot water bath (80 °C)
N-C, T-C	Acid-etched for 10 min with steam

Table 2. Properties of the materials used in this study

Material	Product Name (Manufacturer)	Content
Zirconia block	Plus Zir Block (DMAX Co.)	ZrO_2, Y_2O_3, H_2O, Al_2O_3
Dual-cured resin cement	Panavia F2.0 paste (Kuraray)	10-Methacryloxydecyl dihydrogenphosphate photoinitiator Bis-phenol A polyethoxy dimethacrylate
	ED primer (Kuraray)	2-Hydroxyethyl methacrylate (HEMA), MDP (10-Methacryloyloxydecyl dihydrogen phosphate), NM-aminosalicylate acid, diethanol-p-toluidine, water
Zirconia etchant	Smart etching (YesBio)	HF, H_2SO_4, H_2O_2
	Zircos-E (Bioden)	HF, HCl, H_2SO_4, HNO_3, H_3PO_4
	Cloud system (MEDIFIVE)	2-Hydroxyethyl methacrylate 10-Methacryloxydecyl dihydrogen phosphate Hydrofluoric acid

Each group of blocks underwent the same bonding process after surface treatment. The surface-treated zirconia blocks were ultrasonically cleaned for 60 s and rinsed thoroughly with water. Subsequently, a primer (ED primer; Kuraray Noritake, Niigata, Japan) was applied to the blocks. Resin cement was applied to half of a size 5 gelatin capsule (PureCaps USA, Sudbury, MA, USA), which was then placed on the zirconia surface (bonding area: 12.56 mm2). Photopolymerization was performed using a 1000-mW light curing machine (LED.B; Guilin Woodpecker Medical Instrument CO Ltd., Guilin, China), applying light

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for 20 seconds from each side for a total of 40 seconds, while the specimens were pressed using a 1-N weight. The resin-bonded zirconia specimens were then stored in water at 37 °C for 24 h[30] (Figure 2).

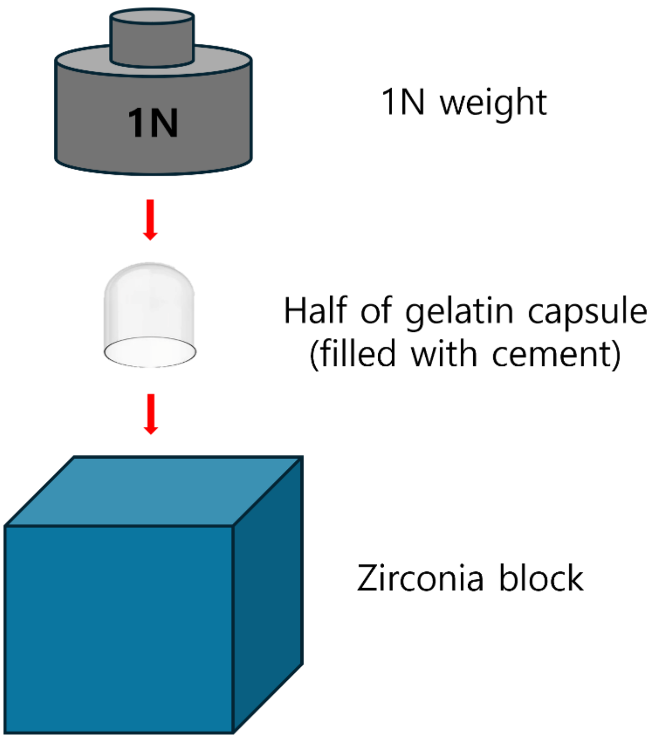

Figure 2. Bonding process of Zirconia block and resin-cement

Thermocycling was performed 10,000 times, corresponding to a 1-year aging process. The lowest and highest temperatures were set at 5 and 55 °C, respectively[31]. The dwell time and transfer time were set as 28 and 2 s, respectively[31]. Among the 100 specimens, only 50

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were subjected to the aforementioned aging process (the remaining samples were excluded from this aging process).

Shear bond testing was performed with a universal testing machine (Instron 5942; Instron Corp., Norwood, MA, USA) at a speed of 1 mm/min until the adhesion of the specimens failed (Figure 3); this adhesion failure was monitored using the testing machine software (Bluehill 2 software, Instron Corp., Norwood, MA, USA). The bond strength (MPa) of each specimen was calculated by dividing the peak load (in N) by the surface area (12.56 mm2)[32].

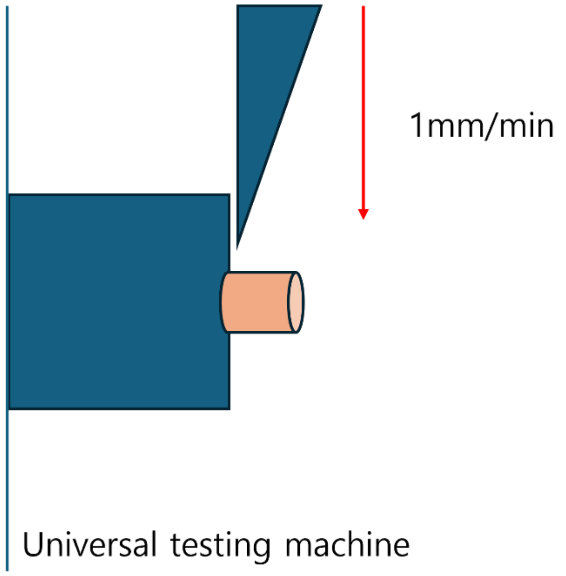

Figure 3. Shear-bond test using universal testing machine

All non-thermocycling groups were analyzed using X-ray diffraction (XRD). Phase transformation analysis was performed using an automated X-ray diffractometer (Ultima IV; Rigaku, Tokyo, Japan) emitting Cu Kα radiation at 30 mA and 40 kV. Phase

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identification was accomplished using a search-match software (JADE 9; Materials Data, Inc., Livermore, CA, USA), the data for which were provided by the International Centre for Diffraction Data (ICDD, Newtown Square, PA, USA)[33].

In addition, one randomly selected specimen from each group was assigned to surface roughness analysis. The roughness was measured at five points on each specimen with a three-dimensional (3D) optical profiler (Contour GT; Bruker, Billerica, MA, USA). Vision 64 software was used to calculate the surface roughness (Ra) and was implemented three-dimensionally.

In addition, surface characterization of the etched zirconia surfaces was performed with field-emission scanning electron microscopy (SEM; JEOL-7800F; JEOL Ltd., Tokyo, Japan). The surface-treated and control-group specimens were cleaned using a steam cleaner and an ultrasonic cleaner before being dried. The surface microstructures of the specimens were then observed and captured at different magnifications.

The normality test result showed a normal distribution. Statistical analysis was performed using a statistical analysis software program (SPSS version 22 SPSS Statistics, IBM, Armonk, NY, USA). The paired t-test was used to determine the groups with a significant difference in data before and after thermocycling. The differences among the mean results for the groups before thermocycling (N-P, N-S, N-Z, N-M, and N-C) and those for the groups after thermocycling (T-P, T-S, T-Z, T-M, and T-C) were subjected to a one-way analysis of variance (ANOVA). Finally, the data were subjected to a two-way

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ANOVA and the post hoc Tukey test to simultaneously analyze the effects of two factors: the type of surface treatment and whether aging was performed ($p = 0.05$ for all tests) [30].

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3. RESULTS

The mean shear bond strengths of the specimens and their standard deviations are presented in Table 3.

Table 3. Shear bond strengths (MPa) of different surface treatment groups (Group P: as-sintered; Group S: sandblasted; Group Z: zircos-E; Group M: smart etching; Group C: cloud system) (*n* = 10 per subgroup); data are expressed as mean values

	Shear Bond Strength (MPa)	
	No Aging Procedure	**Aging Procedure**
Group P	3.66 ± 1.18[A]	0.01 ± 0.02[B]
Group S	9.57 ± 4.02[C,D]	0.19 ± 0.28[B]
Group Z	10.29 ± 4.35[C,D]	0.96 ± 1.05[B]
Group M	8.71 ± 1.46[D]	4.15 ± 3.43[C]
Group C	4.86 ± 1.20[A]	0.16 ± 0.27[B]

Analyzing the differences in shear bond strength before thermocycling through a one-way ANOVA revealed that the differences between groups N-C, N-M, N-P, N-S, and N-Z were all significant ($p < 0.001$). Meanwhile, post hoc analysis showed that groups N-S and N-Z had statistically significantly larger values than the N-C group, whereas groups N-M, N-S, and N-Z had statistically significantly larger values than the N-P group ($p < 0.05$). Analyzing the differences in shear bond strength after thermocycling through a one-way ANOVA showed that the differences between groups T-C, T-M, T-P, T-S, and T-Z were all significant ($p < 0.001$). Post hoc analysis showed that the T-M group had statistically significantly larger values than groups T-C, T-P, T-S, and T-Z. The results of

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a two-way ANOVA indicated that there were statistically significant interactions between the bond strength and surface treatment of the zirconia surface ($p < 0.001$). Additionally, statistical analysis using a two-way ANOVA suggested that the bond strength varied according to whether thermocycling was performed ($p < 0.001$).

Among the groups that did not undergo thermocycling, the bond strengths of the N-S, N-M, and N-Z groups were significantly higher than that of the control group (N-P) ($p < 0.05$), whereas the N-C group did not exhibit a statistically significant difference($p > 0.05$). Furthermore, the bond strength of the N-M group was similar to but slightly lower than that of the N-S group, whereas that of the N-Z group was higher than the latter. However, neither group showed a statistically significant difference from the N-S group ($p > 0.05$). Thus, the commercial surface-etching systems did not demonstrate a significant improvement in bond strength compared to sandblasting.

By comparing the shear bond strengths of each surface-treated group before and after thermocycling (such as N-P and T-P) using the paired t-test, it was found that the shear bond strengths of all the groups differed significantly before and after thermocycling ($p < 0.001$).

Following thermocycling, all groups exhibited a statistically significant reduction in bond strength. Groups S, P, Z, and C showed substantial decreases in both bond strength and adhesion failure rates after aging. In contrast, group M demonstrated no adhesion failures and only a minor reduction in bond strength compared to the other groups. (Figure 4).

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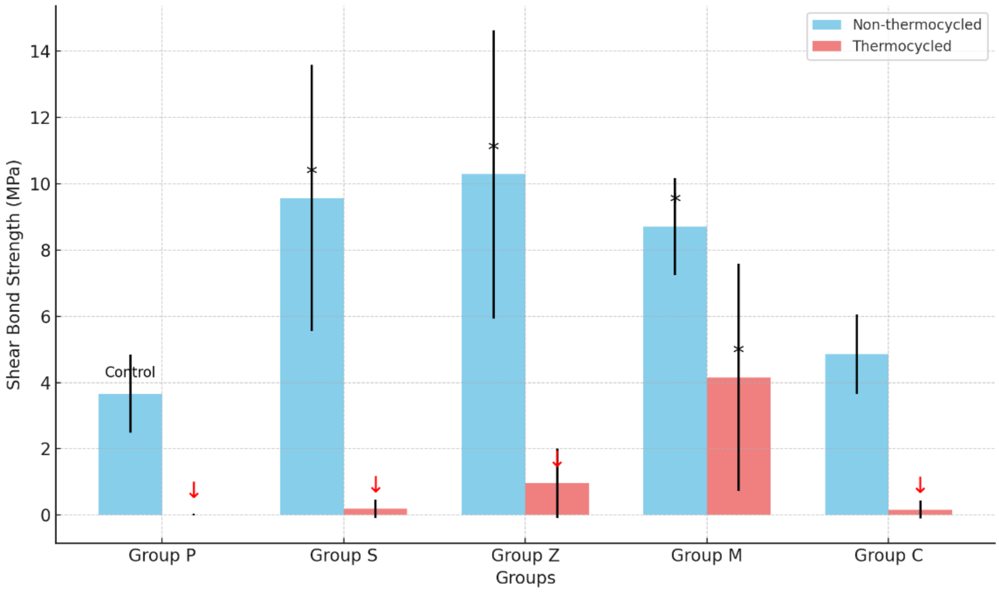

Figure 4. Shear bond strengths (MPa) of different surface treatment groups (*n* = 10 per subgroup). Data are expressed as mean and standard error values (The statistical significance is indicated with asterisks (*), and the significant reductions after aging are marked with downward arrows (↓))

The representative XRD patterns obtained from the five groups are presented in Figure 5. The tetragonal phase structure is the main structure in modern zirconia[29]. However, a monoclinic phase structure was detected in the N-S, N-M, and N-C groups. In contrast, the representative peak of the monoclinic phase was not observed in the XRD patterns of the N-P and N-Z groups.

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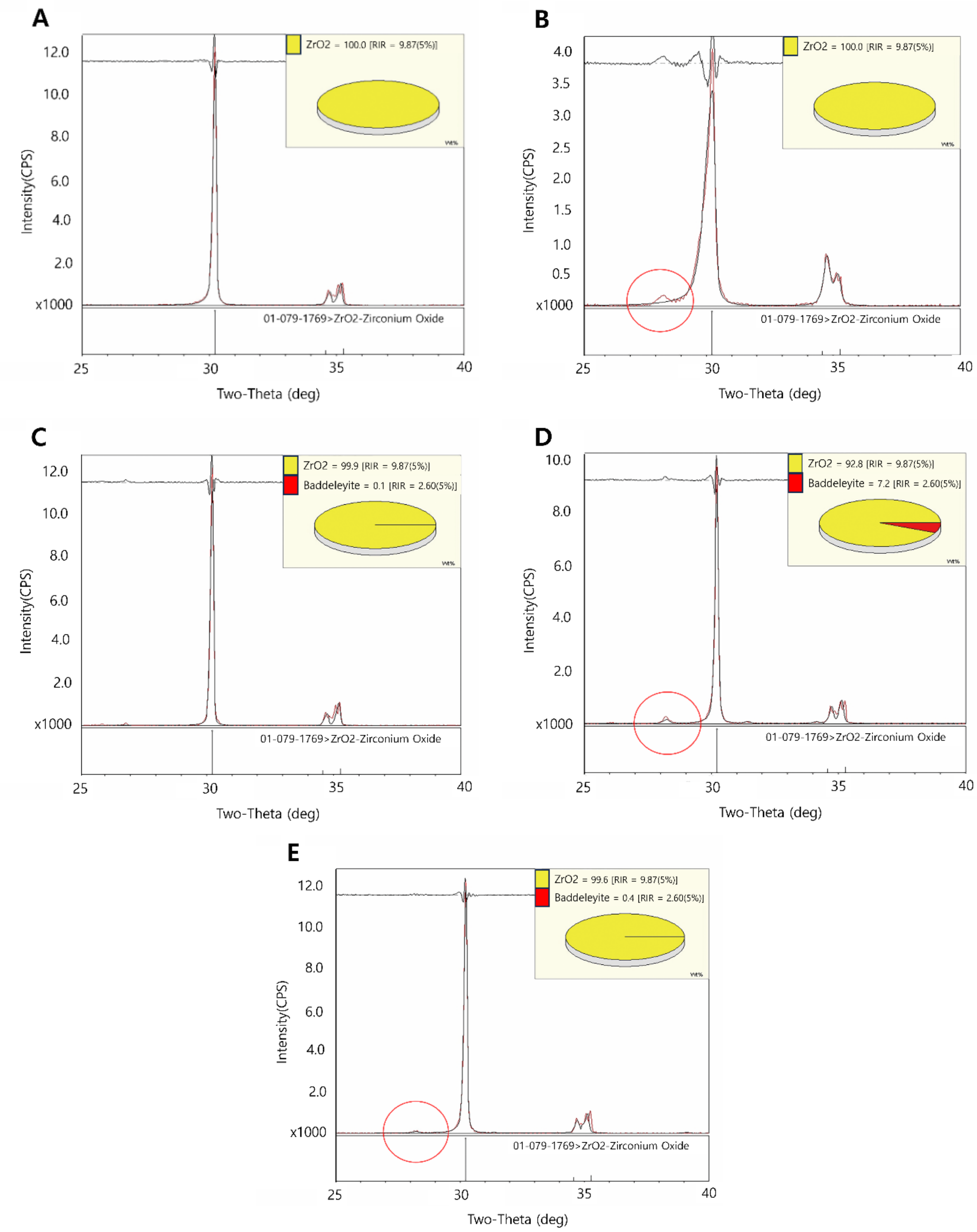
A
ZrO2 = 100.0 [RIR = 9.87(5%)]
Intensity(CPS)
12.0
10.0
8.0
6.0
4.0
2.0
x1000
01-079-1769>ZrO2-Zirconium Oxide
25
30
35
40
Two-Theta (deg)
B
ZrO2 = 100.0 [RIR = 9.87(5%)]
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
C
ZrO2 = 99.9 [RIR = 9.87(5%)]
Baddeleyite = 0.1 [RIR = 2.60(5%)]
D
ZrO2 = 92.8 [RIR = 9.87(5%)]
Baddeleyite = 7.2 [RIR = 2.60(5%)]
E
ZrO2 = 99.6 [RIR = 9.87(5%)]
Baddeleyite = 0.4 [RIR = 2.60(5%)]

Figure 5. Representative XRD patterns of non-aged groups: (A) N-P, (B) N-S, (C) N-Z, (D) N-M, and (E) N-C. The red circles indicated the peaks of monoclinic zirconia structures

The three-dimensional image of the surface of each zirconia group is presented in Figure 6. The surface topography of the N-S group was more pronounced compared to the other groups, which is consistent with the higher Ra value observed for the N-S group. The average Ra value and its standard deviation are shown in Table 4. The N-S group, which was treated with sandblasting, exhibited the highest Ra value, while the N-C group, treated with acid etching, demonstrated a reduction in Ra value compared to the control group.

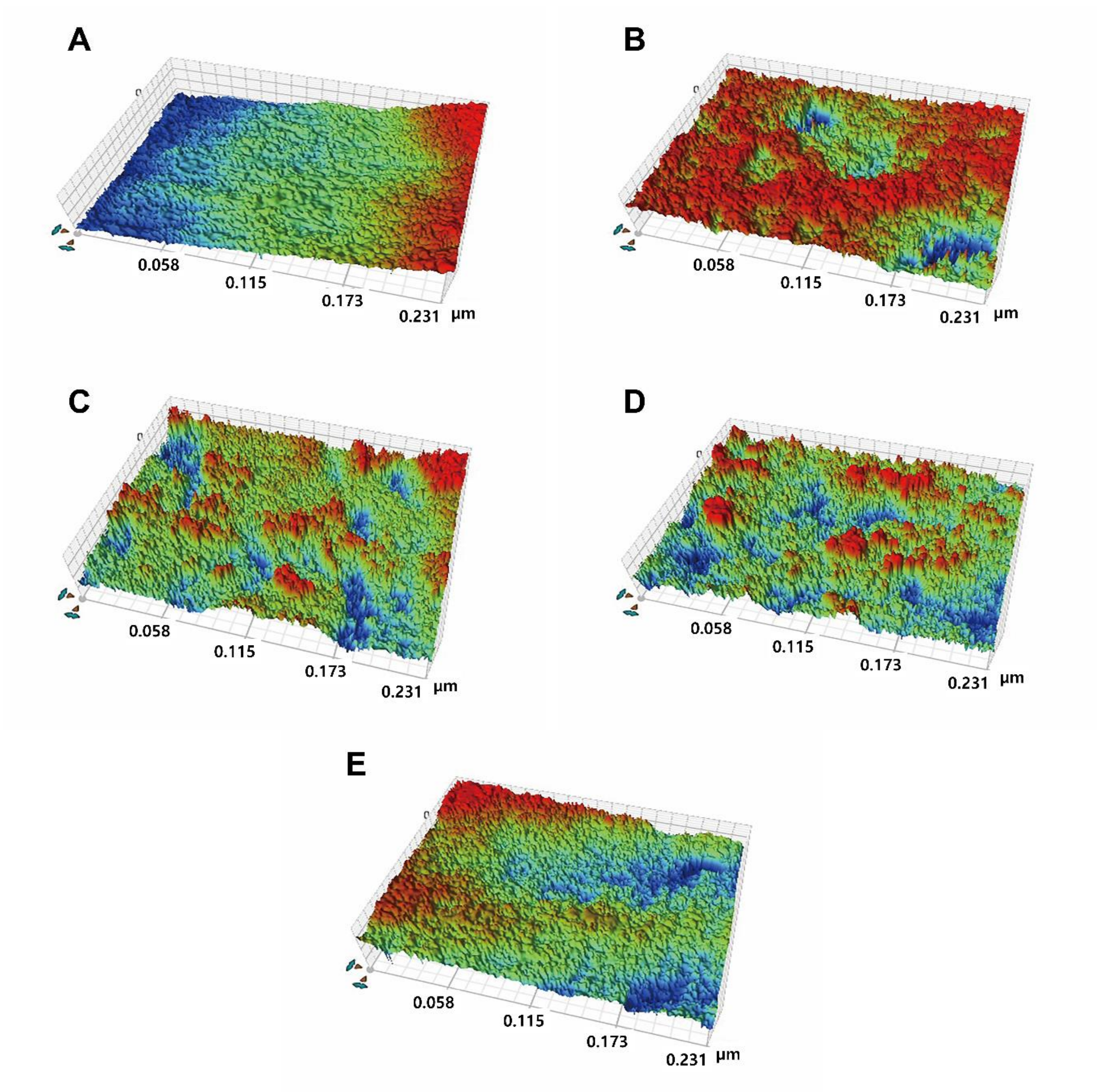

Figure 6. Representative roughness images of non-aged groups: (A) N-P, (B) N-S, (C) N-Z, (D) N-M, and (E) N-C (Red: highest points of surface, Green: intermediate points of surface, Blue: lowest points of surface)

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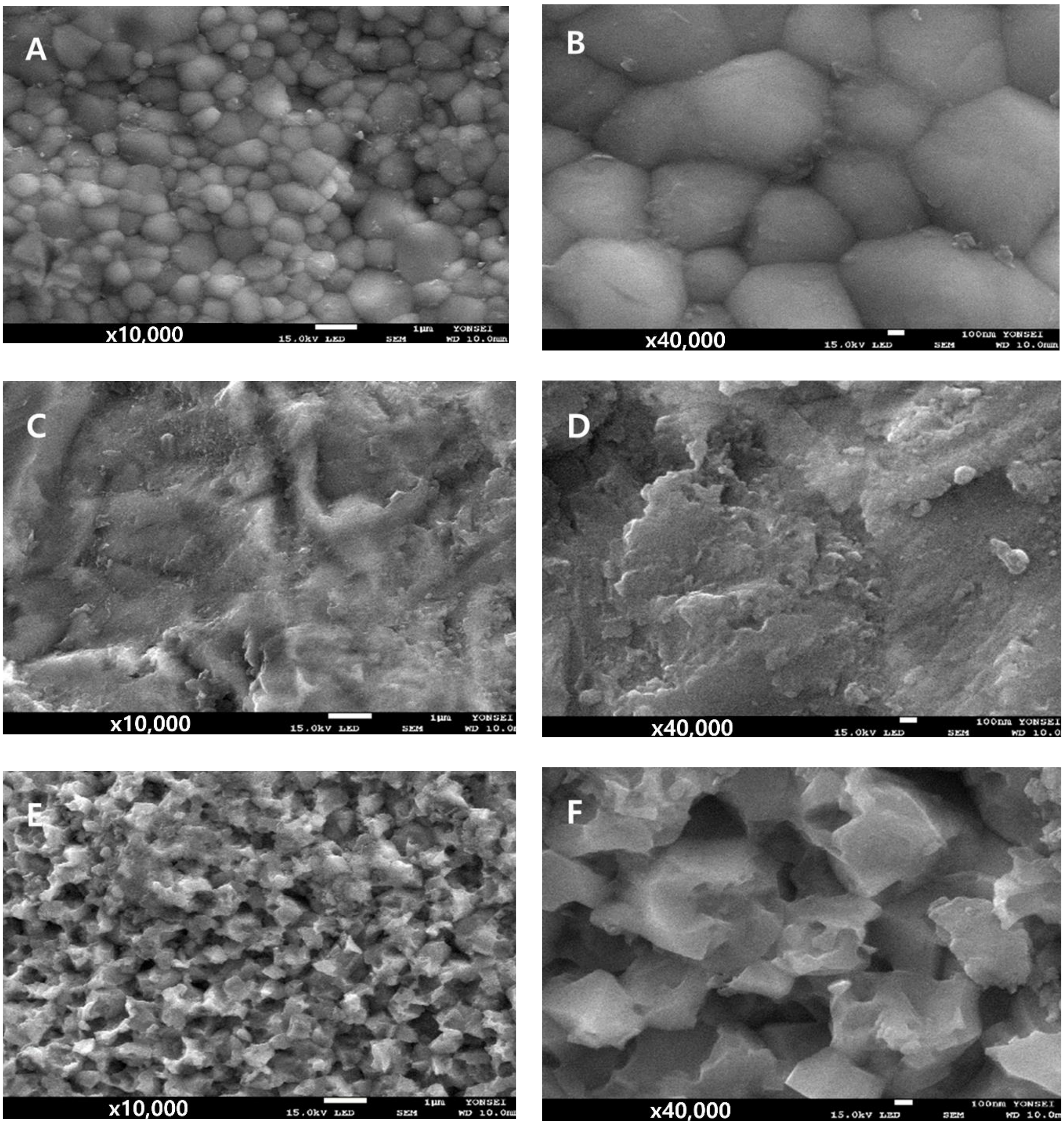
Table 4. Roughness of surface treated zirconia block surface (Different letters (A, B, C) indicate statistically significant differences between groups ($p < 0.05$).)

Ra					**(Units: µm)**
Specimen	Group N-P	Group N-S	Group N-Z	GroupN-M	Group N-C
Average	19.2^{C}	22.9^{B}	19.7^{C}	19.7^{C}	17.7^{A}
Standard Dev	1.5	1.6	0.4	1.2	1.1

SEM images of the surface-treated zirconia specimens at two different magnification was presented in Figure 7. In the N-S and N-Z groups, which exhibited high bond strength, undercuts were observed on the surface, contributing to a microstructure capable of mechanical interlocking with the resin cement. Group N-M appeared to be a combination of the SEM forms of Group N-S and Group N-Z. This was consistent with this surface treatment method. Group N-C appeared to have relatively less surface roughness or undercut compared to other groups.


A
x10,000
B
x40,000
C
x10,000
D
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E
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F
x40,000

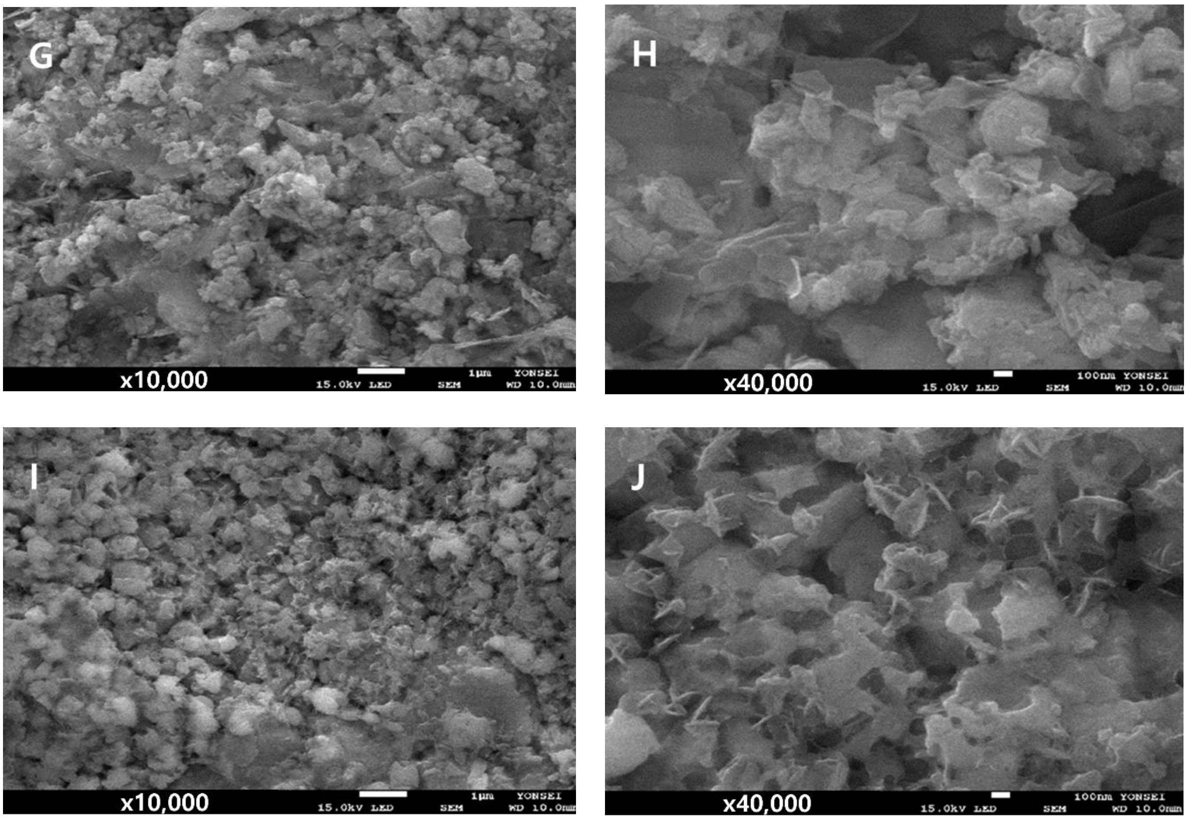

Figure 7. Representative SEM images of surface-treated sites of zirconia specimens at two magnifications (×10,000 and ×40,000): (**A**,**B**) N-P, (**C**,**D**) N-S, (**E**,**F**) N-Z, (**G**,**H**) N-M, and (**I**,**J**) N-C

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4. DISCUSSION

From the results of this study, the null hypothesis that there is no significant difference in the shear bond strength between dual-polymeried resin cement and zirconia, regardless of the surface treatment method (etching systems or sandblasting) or the effects of aging was rejected. The results indicated significant differences in shear bond strength between the various surface treatment methods. Among these, sandblasting and strong acid etching demonstrated notable increase in bond strength with dual-polymerized resin cement[34, 35, 36]. Additionally, most groups exhibited a substantial reduction in bond strength following the aging process.

The bond strength between untreated zirconia and surface-treated groups was compared, and a significant difference in bond strength was observed between the etched systems and those treated with sandblasting alone. Additionally, the results demonstrated a statistically significant difference in bond strength between untreated zirconia and acid-treated zirconia ($p < 0.001$).

The shear bond test results suggested that the bond strengths of the sandblasted, smart-etched, and Zircos-E-treated specimens were significantly increased compared to those of the control-group specimens; this result agrees well with that of a previous post-zirconia shear bond test study[38]. These results do not mean that the other pretreatment methods tested are better than conventional sandblasting, but they can be applied in various clinical situations (for example, zirconia is too thin to sandblast). However, upon acid etching with

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the cloud system, there was no statistically significant increase in bond strength compared to that of the control group because the cloud system heated the zirconia in the presence of a weak acid and water vapor, causing insufficient modifications to the surface structure of zirconia.

It would have been beneficial to analyze the fractured specimens following the shear bond test to examine various modes of adhesive failure, including adhesive and cohesive failures. Such an analysis could provide deeper insights into the failure mechanisms and bonding integrity between zirconia and resin cement. Unfortunately, this study did not include a detailed failure mode analysis, which is a limitation. Future studies incorporating fractographic analysis of failure modes could contribute to a more comprehensive understanding of the bonding performance and durability of different surface treatment methods.

In previous studies, there is a lot of literature on whether sandblasting is helpful for the adhesion of zirconia and resin cement. However, comparisons between the effects of sandblasting and acid pretreatments have not been discussed in detail. This study aimed to include a broad range of commercially available etching agents. In the literature, only the adhesion strengthening effect of air abrasion has been confirmed, or experiments have been conducted using a single etching agent[35]. In contrast, in the present study, we compared three etching agents and confirmed the bond strength after artificial aging. Several etching systems were proposed for the pretreatment of zirconia before the bonding process; they are based on methods such as etching by applying heat[37], using an acid with appropriate

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acidity[38], and using a strong acid for an extended period[35]. Zircos-E etching is a strong-acid etching method; thus, it is crucial to set an appropriate etching time. If the etching time is excessive, the adhesive strength may be reduced. Cho et al. reported that the R_a values of zirconia specimens, as observed from SEM images, were higher after etching for 2 hours than after etching for 1 and 3 hours[38]. Therefore, an etching time of 2 hours, as recommended by the manufacturer, is appropriate.

In conventional ceramics, both sandblasting and hydrofluoric (HF) acid etching increase surface roughness, thereby enhancing adhesion. However, these methods can simultaneously reduce flexural strength, with sandblasting in particular causing a substantial decrease in material strength. Clinicians must consider these effects when selecting surface treatment methods for dental ceramic restorations, balancing the improvement in adhesion with the potential compromise in structural integrity[40]. For zirconia, sandblasting can effectively enhance surface roughness and bonding potential, but it may also introduce surface flaws and residual stresses that adversely impact flexural strength. The extent of these effects depends on factors such as sandblasting pressure, particle size, angle, and duration. Therefore, when treating zirconia with sandblasting, it is crucial to carefully control the process to avoid excessive weakening of the material. Moderation in sandblasting application is essential to ensure that the improvements in adhesion do not come at the expense of flexural strength, thus preserving the long-term durability of zirconia-based restorations[41-43].

Determining an appropriate sample size is critical in ensuring the validity of

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experimental results. In this study, 100 zirconia specimens were prepared, with 10 specimens assigned to each group. A review of prior literature indicated that typical sample sizes range from 10 to 15 specimens per group, suggesting that the chosen number of specimens would meet the minimum statistical standards. Including untreated and sandblasted zirconia as control groups further strengthens the reliability of the study's findings, providing a robust basis for comparison among the surface treatments.

In the current experimental design using a universal testing machine, bond strength is measured by applying force to a single point, making it difficult to claim that the measurement reflects uniform force across the entire specimen. Additionally, separating the material and adhesive specimens under uniformly applied force poses a challenge. A key limitation of this study is the inability to replicate the multidirectional forces experienced during mastication in the oral cavity. Forces applied from various directions are expected to reduce bond strength. Future studies that incorporate forces mimicking the oral cavity or employ designs replicating multidirectional forces are necessary for more accurate and detailed results.

The most commonly used method for artificial aging is thermocycling[22]. However, estimating the number of cycles that correspond to one year of physiological aging in the oral cavity is challenging[39]. Therefore, clear criteria for the number of thermal cycles required are yet to be defined. Gale and Darvell postulated that approximately 10,000 thermal cycles correspond to one year of clinical function, even though most authors have applied fewer cycles[39]. To ensure at least one year of aging, the highest number of thermal

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cycles, i.e., 10,000, was applied in this study. Only 50 of the 100 specimens were subjected to thermocycling. The specimens were divided thus to compare the simple bond strength without aging and to confirm the stability of the bond strength by checking the change in bond strength after aging.

A comparison between the bond strengths before and after thermocycling revealed that the S and Z groups exhibited the largest reduction in bond strength after aging. The bond strength of group M (i.e., comparing N-M with T-M) decreased to a lesser extent (group T-M showed the highest bond strength after thermocycling). Therefore, the bond strength of the aged smart-etched specimens was more stable than that of the other groups. We assume that increasing the roughness of the fine surfaces that could not be reached by the sandblasting particles, removing foreign substances, and increasing surface energy resulted in the observed stability of the bond strength with smart etching over time. Also, looking at group M in the SEM image of figure 7, it looks like a combination of the shapes of group Z and group S, as mentioned earlier in result section. It can be said that this combines the advantages of both methods to some extent, showing relatively stable adhesive strength even after aging.

Following thermocycling, the substantial reduction in bond strength across all groups could be attributed to several factors. One possibility is human error or inconsistencies during the bonding process, which may have introduced variability. Additionally, the high number of thermocycling repetitions could have exaggerated the aging effects, leading to an excessive degradation of bond strength. During thermocycling, zirconia and resin

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cement, which typically do not come into contact with water in clinical settings, were exposed to water for experimental purposes. This water exposure may have significantly impacted the adhesive strength, as water can contribute to hydrolytic degradation of the bonding interface. Clinically, it is likely that this effect would be less pronounced than in the experiment, as the materials would not be subjected to such extensive water exposure in natural oral conditions. Therefore, the observed reduction in bond strength may not fully reflect the long-term performance in clinical intraoral environments.

From the XRD results, the monoclinic phase structure was detected in the N-S, N-M, and N-C groups. However, no monoclinic phase was observed in the N-Z group. This result suggests that either air abrasion or heat treatment induced the phase change of zirconia. In contrast, the phase change of zirconia did not occur when the surface was treated with the Zircos-E etchant—a strong acid. Moreover, in this study, only the particle transformation from the tetragonal phase to the monoclinic phase was examined through trend analysis of the XRD graph; spectroscopic characterization was not performed through surface analysis via ATR-FTIR or Raman spectroscopy. It is unfortunate that only the tendency of phase change was observed and surface analysis such as Raman spectroscopy mentioned above was not performed in more detail.

The highest average R_a was obtained for the N-S group. Zircos-E and smart etching resulted in a minimal increase in surface roughness compared to that of the specimens of the N-P group. The R_a value of the specimens decreased after treatment using the cloud etching system. These results confirmed that commercially available etchants did not

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significantly increase the average R_a or form irregularities on the surfaces of the specimens (Figure 6). Of course, it is difficult to determine the bonding strength only with the roughness value, but through the Ra value, we can think about why the cloud system showed the lowest bonding strength.

The SEM results suggest that the surface roughness increased in all the groups that were subjected to pretreatment before bonding. The N-S (Figure 4B) and N-Z (Figure 4C) groups exhibited the largest increases in surface roughness, and numerous undercuts formed on the surfaces of these groups. The observed high bond strength can be attributed to the mechanical interlocking between the resin cement and the surface of zirconia. On the other hand, in the N-P or N-C group, it could be seen that the undercut of the surface is almost invisible, which may affect the bond strength.

In this study, the effects of various commercial etching solutions on the bond strength of zirconia were investigated. After surface treatment of zirconia, a high bond strength was observed for the N-S and N-Z groups, indicating that sandblasting and strong-acid treatment are effective for increasing the surface roughness of zirconia. After thermocycling, the M group showed the least decrease in bond strength, showing stability in bond strength. However, the bond strength could not be accurately measured because the various forces that are applied in the oral cavity were not considered, and the number of specimens was small. Considering these factors in a follow-up study will help obtain more reliable experimental results.

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5. CONCLUSION

In this study, a shear bond strength test was conducted to evaluate whether various acid-etching methods for surface pretreatment of zirconia were more effective in enhancing bond strength with resin cement compared to conventional sandblasting. Within limitations in this study, the subsequent section presents a concise summary of the key conclusions derived from this experiment.

1. The results revealed that both acid-etching treated and sandblasted zirconia specimens exhibited a significant increase in bond strength compared to surface untreated zirconia.
2. The bond strength achieved after surface pretreatment with a commercial acid-etching solution was not significantly higher than that obtained through sandblasting alone prior to zirconia bonding.
3. After thermocycling, all groups showed a statistically significant decrease in bond strength, with Group M (smart-etching) demonstrating the least reduction, indicating greater long-term stability.
4. In Group Z (Zircos-E), no phase transformation of zirconia was detected in XRD analysis, which may explain its high adhesive strength.

This study provides insights that may contribute to the development of more effective zirconia surface pretreatment methods, enhancing both the durability and strength of zirconia-based dental restorations.

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Abstract in Korean

이중 중합 레진 시멘트와 3Y-TZP 지르코니아의 전단 결합 강도에 대한 표면 에칭 시스템의 영향 연구

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지르코니아 기반 치과 보철물의 장기적인 성공에 있어 지르코니아와 레진 시멘트 사이의 접착 강도는 중요한 요소 중에 하나이다. 이러한 지르코니아의 접착 강도를 높이기 위해 전통적으로는 샌드 블라스팅 같은 기술이 사용되어 표면처리를 하였으며, 이러한 물리적 처리 방식은 표면 거칠기를 증가 시키고 반응성을 높여 주어 지르코니아 표면처리 방법의 표준으로 여겨지고 있다. 그러나 최근에는 다양한 화학적 에칭 시스템이 개발되어 더 우수한 접착 강도를 제공할 수 있는 대안적인 방법을 제시하였다. 따라서 본 연구는 다양한 에칭 시스템을 사용한 지르코니아의 표면 처리와, 열순환(에이징) 여부에 따른 이중 중합 레진 시멘트와 지르코니아의 전단 결합 강도 차이를 비교 분석하는 것을 목표로 한다.

총 100개의 지르코니아 시편이 5개 그룹으로 나뉘었고, 각 그룹은 서로 다른 표면처리를 받았다. 그중 20개의 블록은 표면처리 되지 않았고, 20개의 블록은 샌드블라스팅 처리 하였으며, 나머지 60개의 블록은 3가지의 서로 다른 지르코니아 에칭 시스

템을 사용하여 표면 처리되었다: 지르코스-E(강산 에칭), 스마트 에칭(샌드블라스팅 후 산 에칭), 클라우드 에칭 시스템(고온 증기를 이용한 산 에칭). 그후 각 그룹은 이중 중합 레진 시멘트를 사용한 동일한 접착 절차를 거쳤으며, 이중 절반인 각각의 10개의 시편을 열 순환(에이징)시켰다. 이후 열 순환 전과 후의 레진 시멘트와 지르코니아 사이의 전단결합 강도를 평가하였다. 추가로 처리된 지르코니아의 표면을 X선 회절 분석, 표면 거칠기 측정 및 주사 전자 현미경을 사용하여 표면 분석을 수행하였다.

실험 결과, 샌드블라스팅이나 에칭 시스템을 이용하여 표면 처리한 그룹들은 표면 처리하지 않은 그룹에 비해 유의미한 접착강도의 증가를 보였다($p < 0.05$). 열 순환(에이징)을 거치지 않은 그룹 중에서는, 산 에칭 용액으로 처리된 시편들이 샌드블라스팅 처리된 시편들과 비교했을 때 접착 강도에서 유의미한 증가를 보이지 않았다($p > 0.05$). 그러나 열 순환 처리를 받은 그룹에서는 스마트 에칭 처리를 받은 시편들이 가장 높은 전단결합강도를 나타냈다. 다양한 지르코니아 에칭 시스템들로 표면 처리된 시편들은 단기적으로 샌드블라스팅 단독처리한 시편에 비해 접착 강도를 크게 향상시키지는 않았으나, 스마트 에칭 처리된 시편은 장기적으로 더 높은 안정성을 보였으며, 열순환(에이징) 후 접착 강도의 감소가 적었다($p < 0.05$).

핵심 되는 말: 산 부식, 세라믹 접착, 열 순환 처리, 전단 결합 강도, 접착, 지르코니아, 표면 처리