A Comparative Evaluation of the Effects of Surface Modification Techniques on Zirconia Substrates and their Effect on Adherence to Dual Cure Resin Cement: An In-Vitro Study

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Abstract: ***Background**: Zirconia-based ceramics have gained prominence in restorative dentistry due to their superior mechanical properties and biocompatibility. However, achieving reliable adhesion between zirconia and resin cements remains challenging due to zirconia's chemically inert surface. **Objective**: To comparatively evaluate the effects of various surface modification techniques on monolithic zirconia substrates and examine their influence on bond strength with dual-cure resin cement. **Methods**: One hundred Y-TZP ceramic specimens (15×10×3 mm) were randomly divided into five groups (n=20): Group A (control, no treatment), Group B (50 µm alumina air abrasion + 9% HF etching + MDP primer), Group C (glass bead air abrasion + 9% HF etching + MDP primer), Group D (4% acetic acid etching), and Group E (glass infiltration). Surface roughness was measured using profilometry, and tensile bond strength was evaluated using a universal testing machine. Surface morphology was analyzed using scanning electron microscopy (SEM). **Results**: Group C demonstrated the highest tensile bond strength (7.12 ± 0.69 MPa), followed by Group B (4.75 ± 0.53 MPa) and Group E (3.59 ± 1.16 MPa). Surface roughness was significantly higher in Groups B (4.95 ± 0.65 µm), C (4.61 ± 0.16 µm), and E (4.58 ± 0.67 µm) compared to controls. Group D showed minimal improvement over the control group. **Conclusion**: Glass bead air abrasion combined with HF etching and MDP primer application provided the most effective surface treatment for enhancing zirconia-resin bonding. The combination of mechanical and chemical surface modifications proved superior to individual treatments.***

Keywords: Zirconia, surface modification, resin cement, bond strength, air abrasion, glass infiltration

1. Introduction

The evolution of dental ceramics has led to the widespread adoption of zirconia-based restorations in contemporary prosthodontics. Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) offer exceptional mechanical properties, including high fracture toughness (6-10 MPa·m^1/2) and flexural strength (900-1200 MPa), making them ideal for high-stress applications (Piconi & Maccauro, 1999). Despite these advantages, the clinical success of zirconia restorations significantly depends on achieving reliable adhesion to resin-based luting agents.

Unlike silica-based ceramics, zirconia presents a chemically inert, non-etchable surface that lacks silica content, rendering traditional bonding protocols ineffective (Blatz et al., 2003). The absence of a glassy phase prevents conventional hydrofluoric acid etching and silane coupling agent application, necessitating alternative surface modification strategies (Kern & Thompson, 1995).

Various surface treatment methods have been proposed to enhance zirconia-resin adhesion, including mechanical approaches such as air abrasion with alumina particles, tribochemical silica coating, and laser treatment (Özcan et al., 2008). Chemical modifications involving the application of primers containing functional monomers, particularly 10-methacryloyloxydecyl dihydrogen phosphate (MDP), have shown promising results in forming chemical bonds with zirconia surfaces (Matinlinna et al., 2006).

Recent innovations include glass infiltration techniques that modify zirconia's surface chemistry while potentially preserving its mechanical integrity (Zhang et al., 2012). However, comprehensive comparative studies evaluating multiple surface modification approaches are limited. This study aims to systematically compare different surface treatments and their effects on zirconia-resin cement adhesion, providing evidence-based recommendations for clinical practice.

2. Materials and Methods

Specimen Preparation

Pre-sintered Y-TZP blocks (Lava™, 3M ESPE™, St. Paul, Minnesota, USA) containing 97% zirconium dioxide and 3% yttria were used. Specimens were fabricated using CAD/CAM technology to standardized dimensions of 15 mm × 10 mm × 3 mm, following ASTM guidelines. All specimens underwent sintering at 1450°C using a sintering furnace (inLab Profire™, Dentsply Sirona™, Germany) according to manufacturer specifications.

Sample Size Calculation

Sample size determination was based on power analysis using the formula: $n = 2\,[(Z\alpha/2 + Z\beta)^2 \sigma^2]/\Delta^2$
Where $Z\alpha/2 = 1.96$ (95% confidence), $Z\beta = 0.8416$ (80% power), and $\Delta = 2.0$ units minimum detectable difference.
The calculated sample size was 16 per group, increased to 20 for enhanced statistical power, resulting in 100 total specimens.

Experimental Groups

Specimens were randomly allocated into five groups (n=20 each):

- **Group A (Control):** No surface treatment
- **Group B:** 50 µm alumina air abrasion + 9% HF etching + MDP primer
- **Group C:** Glass bead air abrasion + 9% HF etching + MDP primer
- **Group D:** 4% acetic acid etching only
- **Group E:** Glass infiltration + furnace treatment

Surface Treatment Protocols

- **Air Abrasion (Groups B and C):** Performed using a sandblasting unit (Basic Classic™, Renfert™, Germany) at 2.5 bar pressure for 15 seconds at 10 mm distance. Group B used 50 µm alumina particles, while Group C used glass beads <50 µm. Post-treatment ultrasonic cleaning was performed for 5 minutes.
- **Chemical Etching:** 9% hydrofluoric acid gel (i-HYDRO™, UAB Medicinos linija, Lithuania) was applied for 90 seconds in Groups B and C, followed by thorough rinsing and drying. Group D specimens were immersed in 4% acetic acid solution for 10 minutes.
- **Primer Application:** MDP-containing ceramic primer (Clearfil™, Kuraray™, Japan) was applied to Groups B and C specimens and air-dried for 60 seconds.
- **Glass Infiltration (Group E):** Custom glass powder (SiO_2 55%, Na_2O 3%, ZnO 8%, B_2O_3 3%, TiO_2 2%, BaO 5.5%, K_2O 23.5%) was prepared and applied as a slurry coating. Specimens underwent furnace treatment at 900°C for 10 minutes.

Surface Characterization

Surface roughness (Ra) was measured using a profilometer (Kawasaki™, Mitutoyo™, Japan) with the tip perpendicular to the surface. Three measurements per specimen were averaged. Surface morphology was examined using scanning electron microscopy (FEI Quanta 200™, Netherlands) at 100×, 500×, and 1000× magnifications.

Bond Strength Testing

Specimens were embedded in acrylic resin blocks using custom stainless-steel molds (1.5×1.5×1.5 cm). Composite bars (Ivoclar Vivadent™, Liechtenstein) of matching dimensions were fabricated and similarly embedded. Bonding was performed using dual-cure resin cement (Panavia F 2.0™, Kuraray™, Japan) with a custom alignment jig under 1000g constant load.

Tensile bond strength was evaluated using a universal testing machine (Instron®, USA) at 2 mm/min crosshead speed. Bond strength was calculated in MPa based on the bonded surface area.

Failure Mode Analysis

Debonded specimens were examined under stereomicroscopy (Stemi 2000-C™, Carl Zeiss™, Germany) at 40× magnification. Failures were classified as:

- Adhesive: Separation at zirconia-resin interface
- Cohesive: Separation within the composite or resin
- Mixed: Combined adhesive and cohesive failure

Statistical Analysis

Data were analyzed using SPSS version 26.0. One-way ANOVA was used for intergroup comparisons, followed by Tukey's post hoc test for pairwise comparisons. Chi-square test analyzed failure mode distributions. Statistical significance was set at $p<0.05$.

3. Results

Surface Roughness Analysis

Surface roughness measurements revealed significant differences among treatment groups ($p<0.001$). Group B exhibited the highest mean surface roughness (4.95 ± 0.65 µm), followed by Group C (4.61 ± 0.16 µm) and Group E (4.58 ± 0.67 µm). These values were significantly higher than the control Group A (0.56 ± 0.10 µm) and Group D (0.63 ± 0.80 µm) (Table 1, Figure 1).

Table 1: Surface Roughness Measurements (µm)

Group	Treatment	Mean ± SD	Range
A	Control	0.56 ± 0.10	0.42-0.71
B	Alumina + HF + Primer	4.95 ± 0.65	4.15-6.20
C	Glass Bead + HF + Primer	4.61 ± 0.16	4.35-4.85
D	Acetic Acid	0.63 ± 0.80	0.08-2.15
E	Glass Infiltration	4.58 ± 0.67	3.65-5.85

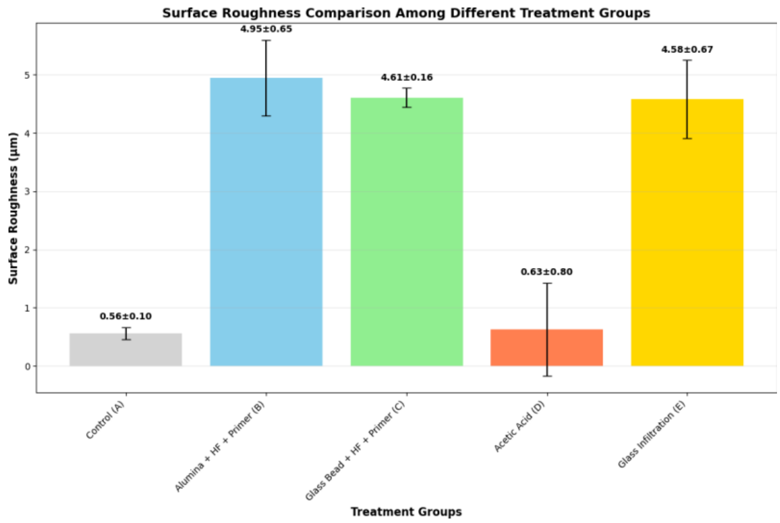

Figure 1: Surface Roughness Comparison Among Different Treatment Groups

Tensile Bond Strength Results

Tensile bond strength testing demonstrated significant variations among groups ($p<0.001$). Group C achieved the highest bond strength (7.12 ± 0.69 MPa), significantly exceeding all other groups. Group B showed substantial improvement (4.75 ± 0.53 MPa) over controls, while Group E demonstrated moderate enhancement (3.59 ± 1.16 MPa). Group D (2.03 ± 0.58 MPa) showed no significant improvement over the control Group A (2.07 ± 0.66 MPa) (Table 2, Figure 2).

Table 2: Tensile Bond Strength Results (MPa)

Group	Treatment	Mean ± SD	Range
A	Control	2.07 ± 0.66	1.15-3.25
B	Alumina + HF + Primer	4.75 ± 0.53	3.95-5.85
C	Glass Bead + HF + Primer	7.12 ± 0.69	6.15-8.45
D	Acetic Acid	2.03 ± 0.58	1.25-3.15
E	Glass Infiltration	3.59 ± 1.16	2.05-5.95

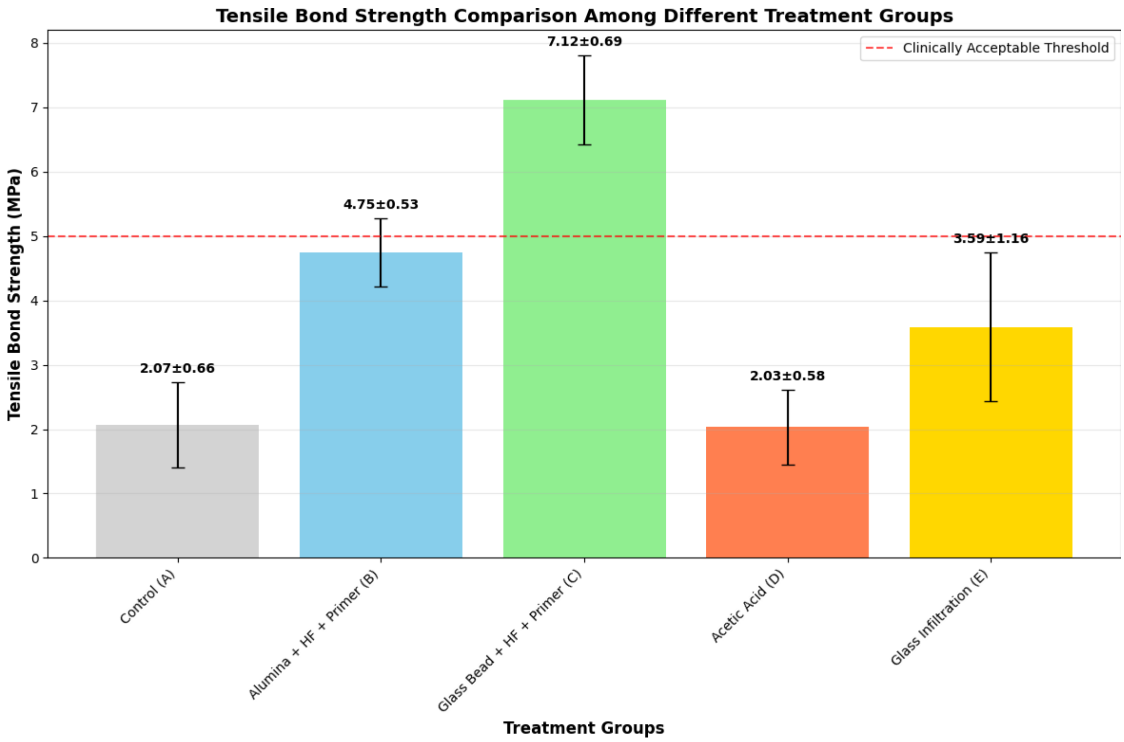

Figure 2: Tensile Bond Strength Comparison Among Different Treatment Groups

Statistical Comparisons

Tukey's post hoc analysis revealed significant differences between most group pairs (Table 3). Groups B, C, and E showed significantly higher surface roughness compared to Groups A and D ($p<0.001$). For tensile bond strength, Group C was significantly superior to all others ($p<0.001$), while Groups B and E significantly outperformed Groups A and D ($p<0.001$).

Table 3: Tukey Post Hoc Comparisons for Tensile Bond Strength

Comparison	Mean Difference (MPa)	95% CI	p-value
C vs A	5.05	4.36-5.74	<0.001***
C vs B	2.37	1.68-3.06	<0.001***
C vs D	5.09	4.40-5.78	<0.001***
C vs E	3.53	2.84-4.22	<0.001***
B vs A	2.68	1.99-3.37	<0.001***
B vs D	2.72	2.03-3.41	<0.001***
B vs E	1.16	0.47-1.85	0.010**

Scanning Electron Microscopy Analysis

SEM examination revealed distinct surface morphologies across treatment groups (Figure 3). Group A exhibited smooth, uniform surfaces with minimal irregularities. Group B showed pronounced micro-cracks and sharp surface discontinuities from alumina impact. Group C displayed characteristic crater-like formations with rounded profiles. Group D revealed minimal surface alterations with occasional shallow depressions. Group E demonstrated uniform spherical glass deposits ranging 30-70 μm in diameter without evidence of micro-cracking.

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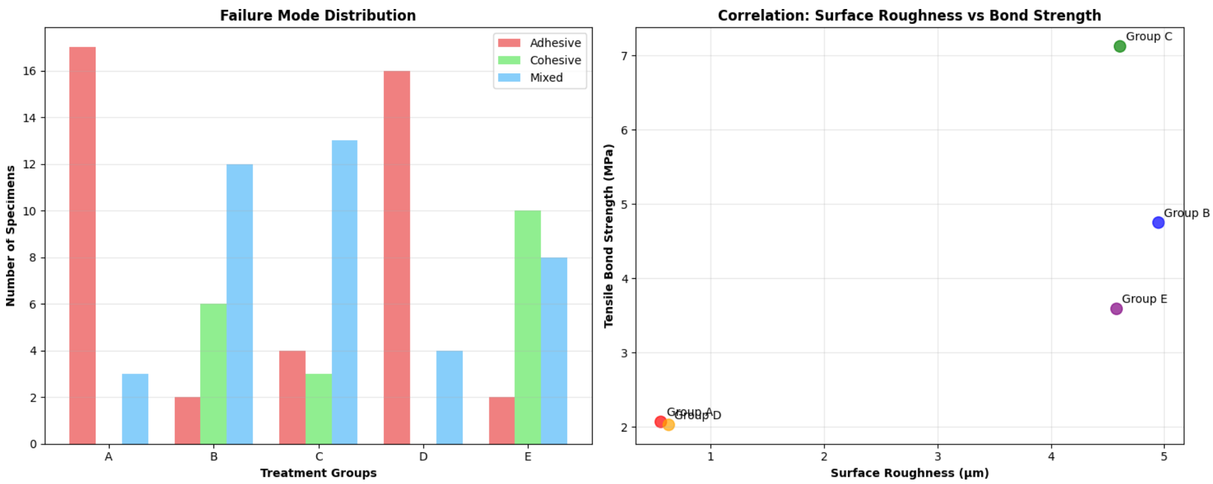

Figure 3: Correlation: Surface Roughness vs Bond Strength

Failure Mode Analysis

Failure mode distribution varied significantly among groups ($p<0.001$). Group A exhibited predominantly adhesive failures (85%), indicating weak interfacial bonding. Groups B and C showed increased mixed and cohesive failures, suggesting stronger interfacial adhesion. Group E demonstrated the highest proportion of cohesive failures (50%), indicating superior bond quality. Group D maintained predominantly adhesive failure patterns similar to controls.

4. Discussion

The present study systematically evaluated multiple surface modification approaches for enhancing zirconia-resin cement adhesion. The superior performance of Group C (glass bead air abrasion combined with HF etching and MDP primer) challenges the conventional preference for alumina air abrasion in zirconia surface treatment.

The higher bond strength achieved with glass bead treatment may be attributed to the creation of more favorable surface topography. Unlike the sharp micro-fractures produced by alumina particles, glass beads generate rounded crater-like depressions that may provide superior mechanical interlocking while minimizing stress concentration points (Hallmann et al., 2012). This morphological difference could explain the improved tensile bond strength and the higher proportion of cohesive failures observed in Group C.

The effectiveness of combining mechanical and chemical treatments was clearly demonstrated. Groups B and C, which incorporated both air abrasion and chemical conditioning, significantly outperformed Group D, which relied solely on chemical etching. This finding supports the established paradigm that zirconia bonding requires a multi-modal approach addressing both micromechanical retention and chemical adhesion (Kern & Barloi, 2009).

The moderate success of glass infiltration (Group E) presents an intriguing alternative approach. The formation of uniform spherical glass deposits observed in SEM analysis suggests successful surface modification without inducing structural damage. The 50% cohesive failure rate in this group indicates robust interfacial bonding, though the overall bond strength remained lower than mechanical treatments. This technique may be particularly valuable when preservation of zirconia's mechanical properties is paramount.

The poor performance of 4% acetic acid etching alone (Group D) confirms that mild chemical etchants are insufficient for modifying zirconia's highly crystalline, chemically inert surface. This finding has important clinical implications, as it suggests that practitioners should avoid relying on chemical etching as a sole surface treatment modality.

The correlation between surface roughness and bond strength observed in this study aligns with established principles of adhesive dentistry. However, the relationship is not purely linear, as evidenced by Group C's superior bond strength despite slightly lower roughness than Group B. This suggests that surface quality and morphology may be as important as absolute roughness values.

5. Clinical Implications

The findings of this study have several important clinical implications:

1) **Treatment Protocol Selection:** Glass bead air abrasion combined with HF etching and MDP primer application emerges as a superior alternative to conventional alumina treatment.
2) **Surface Preservation:** Glass infiltration offers a promising approach for situations requiring minimal surface disruption while maintaining adequate bond strength.
3) **Combined Approach:** The necessity of combining mechanical and chemical treatments is clearly demonstrated, supporting current clinical protocols.
4) **Quality Control:** The variability in bond strength emphasizes the importance of standardized surface treatment protocols in clinical practice.

6. Limitations

This study's in vitro design limits direct clinical applicability. Long-term aging studies incorporating thermal cycling and mechanical fatigue would provide valuable insights into bond durability. Additionally, evaluation of these treatments' effects on zirconia's intrinsic mechanical properties would be beneficial for comprehensive assessment.

7. Conclusion

This comprehensive evaluation of surface modification techniques reveals that glass bead air abrasion combined with hydrofluoric acid etching and MDP primer application provides the most effective enhancement of zirconia-resin cement adhesion. The superior bond strength (7.12 ± 0.69 MPa) and favorable failure mode distribution demonstrated by this treatment protocol suggest its potential as an improved alternative to conventional alumina air abrasion.

The study confirms that successful zirconia bonding requires a synergistic approach combining mechanical surface roughening with chemical conditioning. Glass infiltration emerges as a promising technique for situations requiring surface modification with minimal structural disruption. Conversely, chemical etching alone proves inadequate for clinical application.

These findings provide evidence-based guidance for clinicians seeking to optimize zirconia restoration longevity through improved bonding protocols. Future research should focus on long-term clinical evaluation of these surface treatments and their effects on restoration durability under oral environmental conditions.

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