Improving the bonding stability between resin cements and zirconia-based ceramic using different surface treatments

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**Abstract:**

**Purpose:** To evaluate the effects of airborne-particle abrasion with alumina particles or silica-modified alumina particles on the bond strength between zirconia and conventional MDP-based (Ph; Panavia F 2.0, Kuraray) or self-adhesive (SA; RelyX U200, 3M ESPE) resin cements. **Materials and Methods:** Five surface treatments were evaluated: C = no surface treatment; AB = airborne-particle abrasion with alumina particles (BIO-ART Dental Supplies and Equipment); ABP = AB combined with MDP-based primer (Alloy Primer, Kuraray); SS
= airborne-particle abrasion with silica-modified alumina particles (CoJet, 3M ESPE) combined with silane (RelyX Ceramic Primer, 3M ESPE); and SSP = SS combined with MDP-based primer. The surface roughness (Ra) of the airborne particle–abraded samples (n = 5) was measured by a contact profilometer (Mitutoyo Surftest SJ-401, Mitutoyo). Cylinders of the resin cements tested were bonded to the surface-treated zirconia. The microshear test was performed by the application of a load with a wire loop parallel to the adhesive interface until debonding of the resin cement cylinders. The microshear bond strength ($\mu$SBS) of the samples was measured before and after being subjected to thermocycling (TC; 5°C to 55°C, 60 seconds dwell time for 3,000 cycles; MSCT, Marcelo Nucci). One-way (Ra) and two-way ($\mu$SBS) analysis of variance followed by Tukey post hoc test ($\alpha = .05$) were used. Results: The SS (Ph: 12.6 MPa; Ph-TC: 6.37 MPa; SA: 11.8 MPa; SA-TC: 9.37) and SSP (Ph: 10.4 MPa; Ph-TC: 5.82 MPa; SA: 10.4 MPa; SA-TC: 10.0) surface treatments produced the highest surface roughness values ($P < .001$). The SS samples achieved the highest immediate bond strength for both resin cements. However, after TC, SA resin cement associated with any surface treatment produced the highest bond strength values. Conclusion: The self-adhesive resin cement promoted higher and more stable bond strength values when associated with a surface roughening method. Int J Prosthodont 2021. doi: 10.11607/ijp.6797

Introduction:
Zirconia-based ceramics exhibit both high mechanical strength and toughness, and such material is considered suitable for the replacement of metal frameworks in prosthetic restorations [1]. However, literature indicates that the incidence of retention loss of single crowns or multi-unit fixed dental prostheses (FDP) based on a zirconia framework could be higher than that of all other types of restorations evaluated [2,3]. The chemical inertness (i.e.
polycrystalline ceramic with absent of glassy phase) and suboptimal fitting of zirconia-based restorations may be the reason for the problems related to loss of retention [2].

Improved adhesive bonding to zirconia-based restorations would decrease the occurrence of clinical retention loss, which is important for achieving long-lasting clinical use [4]. Besides that, the adhesive cementation [5] and the surface treatment at the cementation surface [6] could enhance the maximum load to failure and fatigue resistance of zirconia crowns.

Airborne-particle abrasion with alumina or silica modified alumina particles (silicatization) are currently the gold-standard pretreatment methods for zirconia surfaces [7]. Despite reported disadvantages, as the decrease in fatigue strength [8], the air abrasion of a zirconia surface with small particles (30–50 µm) does not alter the inherent properties of the material, even after aging processes [9,10]. Air abrasion roughens the cementation surface [11], enhancing the bonding area and surface energy of the material; and both of these outcomes are desirable for optimal adhesion. When combined with chemical agents, both of the aforementioned methods have shown advantages over other surface treatments, such as Er:YAG laser irradiation [12], nanofilms [13], and chemical agents used in a single form [14].

Furthermore, air abrasion must be followed by the application of chemical bonding agents containing silane (silanization) and/or phosphate monomers [7,15]. Silane is a bifunctional molecule that bonds to both the silica present in the restorative material and the organic matrix of the resin cement [16]. Phosphate monomers, such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP), have an affinity for bonding to metallic oxides (e.g., ZrO₂ and Al₂O₃) [17].

Several procedures have been suggested for the surface treatment of zirconia, but the increase in the number of clinical procedures increases the possibility of any mistake during the cementation process. The use of self-adhesive resin cements reduces the clinical steps...
Self-adhesive resin cements present low pH and hydrophilicity when are just prepared, and that promotes etching and wettability of the substrate surface [19]. During the reaction, the acidity is neutralized by the reaction with tooth apatite [20] and/or metal oxides [19]. The cement also becomes more hydrophobic, preventing degradation by water [21]. They present good results when mechanical retention is associated [22], and yet, lack of adhesion in non-retentive configuration such as, in the test of microtensile bond strength [23]. Furthermore, additional surface treatment is recommended for bonding to enamel [24] and indirect restorations [15].

Thus, the aim of this study was to evaluate the effects of air abrasion with alumina particles or silica-modified alumina particles on the micro-shear bond strength between zirconia and conventional MDP-containing or self-adhesive resin cements. The tested hypothesis is that applying a combination of silicatization and silane application on zirconia surface enhances the bond strength to resin cements.

**Materials and Methods:**

**Sample preparation:**

Blocks of pre-sintered zirconia (LAVA, 3M ESPE Dental Products, St. Paul, MN, USA) were sectioned using a high-precision saw (IsoMet 1000 Precision Saw, Buehler Ltd., Lake Bluff, IL, USA) with a diamond blade (4-inch wafering blade, M412H, MetLab Corp., Niagara Falls, NY, USA). After cutting the ceramic plates (6 x 8 x 3 mm) were sintered and embedded into epoxy resin (Valglass, São José dos Campos, SP, Brazil) with one surface of the ceramic plate exposed for bonding. The zirconia plate surfaces were ground with 100-, 300-, 600- and 1200-grit silicon carbide abrasive paper (Aropol, Arotec Ind. e Com., São Paulo, Brazil) under water cooling and then ultrasonically cleaned in distilled water for 5 minutes. Assemblies were randomly distributed into 5 groups, according to surface treatment applied to the exposed surface of zirconia plate:
1. Control group (C) – No surface treatment. The samples were ultrasonically cleaned and air-dried.

2. Air abrasion group (AB) – the zirconia surface was held perpendicular to air-abrasion unit, at a distance of 10 mm, during 15 s/cm² and subjected to air abrasion with 50-µm alumina particles (Al₂O₃; Bio-Art Equip. Odont. Ltd., São Carlos, SP, Brazil) under 0.28 MPa air pressure. The treated surface was then ultrasonically cleaned in distilled water for 3 min and air-dried.

3. Air abrasion and primer group (ABP) – The air abrasion was performed according to the method described for the AB samples, followed by the application of an MDP primer (Alloy Primer, Kuraray Medical Co., Osaka, Japan) to the ceramic surface - 5 min waiting time.

4. Silica coating group (SS) – The air abrasion was performed according to the method described for the AB samples, but with 30-µm silica particles (silicatization, CoJet, 3M ESPE Dental Products, St. Paul, MN, USA) were used instead of the alumina particles, followed by the application of a silane-based coupling agent (silanization, RelyX Ceramic Primer, 3M ESPE Dental Products, St. Paul, MN, USA) to the ceramic surface - 5 min waiting time.

5. Silica coating and primer group (SSP) – The samples were prepared according to the protocol described for the SS samples. Additionally, an MDP primer was applied on the silanized ceramic surface and allowed to dry for 5 min.

**Surface roughness test:**

The surface roughness of air abraded surfaces (n = 5) was measured by a contact profilometer (Mitutoyo Surftest SJ-401, Mitutoyo Corporation, Japan). The reading was
performed three times in parallel lines for each surface. The mean roughness (Ra) was used to represent the characteristic roughness of the surfaces.

**Microshear bond strength test (μSBS):**

Samples from each surface treatment were divided according to the cement used: conventional dual-cure MDP-containing resin cement (Ph – composition according to manufacturer: 10-MDP, 5-NMSA, silica, dimethacrylates, barium glass, sodium fluoride, dimethacrylates, BPO; Panavia F 2.0, Kuraray Medical Inc., Osaka, Japan); or self-adhesive dual-cure resin cement (SA – composition according to manufacturer: silane treated glass powder, esters, dimethacrylate and phosphorus oxide, triethylene glycol dimethacrylate, silane treated silica, sodium persulfate, substituted dimethacrylate, sodium p-toluenesulfonate and calcium hydroxide; RelyX U200, 3M ESPE Dental Products, St. Paul, MN, USA).

Five cylindrical and transparent matrices (diameter = 0.7 mm, height = 1.0 mm; Tygon Tubing, TYG-030, Saint-Gobain Performance Plastic, Miami Lakes, FL, USA) were positioned on each surface-treated zirconia block. The cements were handled according to the instructions provided by the manufacturer and inserted into matrices. The cements were light-cured for 40 seconds (λ = 450–470 nm, Demi Plus, Kerr Sybron Dental Specialties, Orange, CA, USA).

Half of the samples from each cementation protocol (surface treatment + resin cement) (n=5) were tested after storage in 100% humidity for 24 hours at 37 °C; and the other half were subjected to thermocycling (TC; MSCT, Marcelo Nucci ME, São Carlos, SP, Brazil) at 5 ± 1 °C, 37 ± 1 °C, and 55 ± 1 °C, 60 s dwell time, 3,000 cycles.

The μSBS test was performed with a universal testing machine (DL2000, EMIC, São José dos Pinhais, PR, Brazil) using a wire loop (diameter = 0.2 mm). A tensile load was applied at a crosshead speed of 0.5 mm/min until failure of the samples. The maximum applied load (L, N) was recorded. The μSBS (MPa) was calculated with the equation μSBS =
L/A, where A is the interfacial area (mm²). The μSBS from each sample was the mean value obtained by the test of the five resin cement cylinders.

Failure modes were evaluated using an optical microscope with 80× magnification. Failures were classified as adhesive (failure occurring across the zirconia-resin cement interface); mixed (cohesive failure of the resin cement associated to adhesive failure at zirconia-cement interface); or cohesive (cohesive failure of resin cement).

The data obtained from the surface roughness measurements were subjected to one-way analysis of variance (ANOVA) followed by Tukey’s post-hoc test (α = 0.05). The μSBS values were subjected to two-way ANOVA (cementation strategy × TC) followed by Tukey’s post-hoc test (α = 0.05).

Results:

Surface roughness:

Figure 1 shows that both air abrasion methods used in this study increased the surface roughness of the zirconia plates compared to untreated surfaces – control group (P < 0.001). The air abrasion with 30-μm silica particles produced the highest roughness values.

Micro shear bond strength (μSBS):

For μSBS values, the thermocycling (TC) decreased the μSBS values for all cementation strategies except the SSP-SA and AB-SA groups (Table 1). Without the TC treatment, the SS surface treatments achieved the highest μSBS values (Table 1) despite the resin cement used, but after TC, SA resin cement promoted the highest values, despite surface treatment (P < 0.001).

The failure modes observed when the Ph resin cement used were predominantly adhesive for the TC-treated samples and mixed for the non-TC-treated samples (Table 2). On the other hand, the failure modes observed when the SA resin cement used were
predominantly adhesive for the C/TC and AB/TC samples and mixed for the remaining sample groups.

Discussion:

The results of the present research showed that a combination of mechanical and chemical treatments enhanced the µSBS, confirming the proposed hypothesis. Ageing performed by thermocycling, lead to a decrease in µSBS values in all tested cementation strategies, except for the self-adhesive resin cement combined to zirconia surface treatment (SSP-SA and AB-SA groups). Without TC, the silicatization + silanization groups achieved the highest µSBS values, despite the use of different resin cements (SS-SA and SS-Ph groups). The roughest surface was produced by silicatization (SS and SSP groups).

The deposition of silica on the surface of crystalline ceramics and the chemical action of the bifunctional silane molecules are responsible for the improved µSBS of resin cements to acid-resistant ceramics [7,15,25]. The SS surface treatment also produced relatively stable µSBS values after the samples were subjected to TC [26]. The sandblasting of zirconia with alumina particles (AB) is considered less stable than the tribochemical sandblasting of zirconia with silica [25].

In general, the µSBS values of mechanically pretreated zirconia surfaces are higher and more consistent than that of chemically-only treated surfaces [25,27]. In the present study, the control group subjected to TC exhibited the lowest µSBS values, indicating that surface roughening is necessary to achieve a more reliable resin/ceramic bonding [28].

The acidity conferred by the multifunctional phosphoric-acid-modified methacrylates that are present in the self-adhesive resin cement formulation appears to enhance the µSBS, even when used on the untreated surfaces of zirconia ceramics [29]. This resin cement also has a high density and low degree of shrinkage because of the inherent viscoelastic properties, which improves the intimate contact between the resin cement and the treated surfaces [30].
The reaction of the self-adhesive resin cement also enhances the hydrophobicity of the material, preventing the decrease in µSBS values after TC [21], as shown in Table 1. The association of primers containing silane and MDP-monomers in one solution, as the universal primers and adhesive, shows good adhesion results in literature [14]. But in the present study, the association of both primers was only beneficial when associated to SS and Ph resin cement (SSP/Ph > SS/Ph).

The effect of the ageing method applied in the present study may be observed by the changing in failure mode of Ph resin cements from predominantly mixed in the non-TC groups, to adhesive failure in TC groups. The change in failure mode was combined with the decrease of µSBS values, showing the low stability at Ph resin cement-zirconia interface [25]. Adhesive failures are usually associated with low bond strength values [31]. The SA cement produced µSBS values higher than the Ph cement, where its predominant failure mode was mixed.

The µSBS tests performed in this study exhibit some limitations, such as an irregular stress distribution, the formation of tensile and compressive stresses at the interface, and a high spread (high standard deviation) in the results [32]. During the micro-shear tests, tensile stress is induced at the lower half of the interface (near the application of the load) inside the zirconia block, while compressive stress is induced at the upper half of the interface inside the resin cement [32], which is where the cohesive failure of the cement occurs. However, it is the most commonly applied testing method for accessing the interface between zirconia and cementation agents because only a few methods are required to prepare suitable samples. Zirconia is a high-strength material, and the more elaborate methods of sample preparation, such as cutting for micro-tensile bond strength test, weaken the adhesive interface, which may lead to a high number of premature failures [26].
The results of this study indicate that the SA resin cement behaves in a more positive way after ageing. Literature stands out that the long-term clinical success of zirconia-based restorations depends on the cement properties, pretreatment of the surfaces to be bonded, and bond strength between the cement and the ceramic [33].

**Conclusions:**

When associated to sandblasting, even with silica modified or single alumina particles, the self-adhesive resin cement promotes higher and more stable bond strength values compared to a conventional MDP-containing resin cement.

**References:**

2. Pjetursson BE, Sailer I, Makarov NA, Zwahlen M, Thoma DS. All-ceramic or metal-ceramic tooth-supported fixed dental prostheses (FDPs)? A systematic review of the survival and complication rates. Part II: Multiple-unit FDPs. Dent Mater 2015;31:624–639.


Figure 1: Mean surface roughness values (Ra) and the corresponding standard deviations after performing the five surface treatments.

C = control; AB = air abrasion; ABP = air abrasion and primer; SS = silica coating and silane; and SSP = silica coating, silane and primer.
Table 1: Mean bond strength (BS) values, the corresponding standard deviations and statistical significance between the different cementation strategies with and without thermocycling.

(C = control; AB = air abrasion; ABP = air abrasion and primer; SS = silica coating and silane; SSP = silica coating, silane, and primer; and TC = thermocycling).

<table>
<thead>
<tr>
<th>Cementation Strategy</th>
<th>Without TC*</th>
<th>With TC*</th>
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<tbody>
<tr>
<td></td>
<td>Mean BS (MPa)</td>
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<tr>
<td>Phosphate-Based Resin Cement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>7.61 (2.0)</td>
<td>1.08 (1.1)</td>
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<tr>
<td>AB</td>
<td>10.1 (2.1)</td>
<td>2.77 (2.3)</td>
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<tr>
<td>ABP</td>
<td>9.56 (1.5)</td>
<td>3.28 (0.9)</td>
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<td>SS</td>
<td>12.6 (2.3)</td>
<td>6.37 (1.7)</td>
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<tr>
<td>SSP</td>
<td>10.4 (2.2)</td>
<td>5.82 (2.0)</td>
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<tr>
<td>Self-Adhesive Resin Cement</td>
<td></td>
<td></td>
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<tr>
<td>C</td>
<td>9.90 (2.2)</td>
<td>2.83 (2.2)</td>
</tr>
<tr>
<td>AB</td>
<td>10.3 (1.6)</td>
<td>9.66 (2.2)</td>
</tr>
<tr>
<td>ABP</td>
<td>6.15 (3.8)</td>
<td>10.4 (1.8)</td>
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<tr>
<td>SS</td>
<td>11.8 (1.8)</td>
<td>9.37 (1.8)</td>
</tr>
<tr>
<td>SSP</td>
<td>10.4 (1.6)</td>
<td>10.0 (3.0)</td>
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<td>Total</td>
<td><strong>10.3 (2.3)</strong></td>
<td><strong>5.73 (3.8)</strong></td>
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*Different uppercase letters indicate statistical difference in the same line. Different lowercase letters indicate statistical difference in the same column.
Table 2: Percentage of failure modes observed for each sample group tested.

(C = control; AB = air abrasion; ABP = air abrasion and primer; SS = silica coating and silane; SSP = silica coating, silane, and primer; and TC = thermocycling).

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<tr>
<th>Resin Cement</th>
<th>Sample Groups</th>
<th>Adhesive (%)</th>
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<tr>
<td></td>
<td>C</td>
<td>28</td>
<td>68*</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>C/TC</td>
<td>64.7*</td>
<td>35.3</td>
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<tr>
<td></td>
<td>AB</td>
<td>0</td>
<td>88*</td>
<td>12</td>
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<tr>
<td></td>
<td>AB/TC</td>
<td>54.54*</td>
<td>36.36</td>
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<td></td>
<td>ABP</td>
<td>0</td>
<td>56*</td>
<td>44</td>
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<tr>
<td></td>
<td>ABP/TC</td>
<td>64*</td>
<td>36</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>SS</td>
<td>0</td>
<td>68*</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>SS/TC</td>
<td>16</td>
<td>48*</td>
<td>36</td>
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<tr>
<td></td>
<td>SSP</td>
<td>0</td>
<td>64*</td>
<td>36</td>
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<tr>
<td></td>
<td>SSP/TC</td>
<td>52*</td>
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<td>20</td>
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<tr>
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<td>C</td>
<td>22</td>
<td>78*</td>
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<td></td>
<td>C/TC</td>
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<td>ABP/TC</td>
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<td>60*</td>
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<tr>
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<td>SS</td>
<td>8</td>
<td>92*</td>
<td>0</td>
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<td>SS/TC</td>
<td>44</td>
<td>56*</td>
<td>0</td>
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<td></td>
<td>SSP</td>
<td>32</td>
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<td></td>
<td>SSP/TC</td>
<td>33.33</td>
<td>66.66*</td>
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*main failure mode for the respective group