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# Different Strategies to Bond Bis-GMA-based Resin Cement to Zirconia

Guilherme Carpena Lopes<sup>a</sup> / Ana Maria Spohr<sup>b</sup> / Grace M. De Souza<sup>c</sup>

**Purpose:** To evaluate the effect of different bonding strategies on short- and long-term bis-GMA-based resin cement bond strengths to zirconia.

**Materials and Methods:** One hundred twenty samples of fully-sintered zirconia (Prettau Zirconia) were sandblasted and randomly distributed into 5 groups (n = 24): UA: Scotchbond Universal Adhesive; SZP: Signum Zirconia Bond I + II; ZPP: Z-Prime Plus; EXP: MZ experimental primer; CO: no primer application (control). After performing these surface treatments, translucent tubes (0.8 mm diameter and 1.0 mm height) were placed on the zirconia specimens, and bis-GMA-based cement (Duo-Link) was injected into them and light cured. Specimens were tested for microshear bond strength either 24 h or 6 months (m) after water storage (37°C) and surfaces were characterized by SEM and EDX. Two-way ANOVA and Tukey's post-hoc test (p < 0.05) were used to evaluate bond strength results.

**Results:** The mean bond strengths (MPa ± SD) were: UA=14.6 ± 4.7<sup>a</sup> (24 h); 16.0 ± 4.8<sup>a</sup> (6 m); SZP = 14.0 ± 5.4<sup>ab</sup> (24 h); 11.9 ± 2.6<sup>ab</sup> (6 m); ZPP=8.0 ± 1.8<sup>b</sup> (24 h); 8.6 ± 3.3<sup>b</sup> (6 m); EXP = 1.2 ± 0.5<sup>c</sup> (24 h); 0.6 ± 0.7<sup>c</sup> (6 m); CO=1.0 ± 1.2<sup>c</sup> (24 h); 1.3 ± 1.2<sup>c</sup> (6 m). Bonding strategy significantly influenced bond strength (p = 0.0001), but storage time did not (p = 0.841). Groups UA and SZP showed a homogeneous layer covering the zirconia surface. In these groups, EDX demonstrated the presence of phosphorus. Group ZPP resulted in a nonhomogeneous layer, exposing the zirconia substrate underneath. EXP application resulted in an undetectable layer.

**Conclusion:** Water storage did not affect resin cement bond strengths to zirconia irrespective of the surface treatment. Bis-GMA-based resin cement bond strengths to zirconia are affected by specific bonding strategies.

**Keywords:** dental ceramic, zirconia primers, microshear bond strength, energy dispersive x-ray spectroscopy, resin cement, multimode adhesive.

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The recent evolution of ceramic systems has reduced the need for metal infrastructures in most clinical scenarios. The high flexural and compressive strength of high crystalline-content ceramics such as alumina (Al<sub>2</sub>O<sub>3</sub>) and zirconia

(3 mol% yttria-tetragonal zirconia polycrystal, 3Y-TZP) makes it possible to use metal-free restorations in areas with heavy occlusal loads.<sup>23,24</sup> However, the clinical success of an indirect restoration depends greatly on the quality and stability of the bond between the abutment tooth/material and the ceramic material.<sup>10,18</sup> The factor determining the appropriate surface treatment is the structural composition of the ceramic.<sup>3</sup> When luting to zirconia, many adhesive strategies have been proposed to overcome the weakness and instability of the bond at the interface between zirconia and resin-based cement. This is due to the fact that alumina- and zirconia-based ceramics are resistant to hydrofluoric acid etching of the surface.<sup>10</sup> This the most frequently applied acid and is intended to remove the silica-rich glass matrix,<sup>32</sup> but this phase is absent in high-crystalline content ceramics such as those based on alumina and zirconia. Therefore, the use of different strategies alone or in combination has been proposed. One possibility

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is mechanical alteration of the ceramic surface, eg, to increase the material's roughness, which can facilitate micro-mechanical interlocking with the luting system penetrating into the ceramic's microirregularities.<sup>34</sup> The quality of the adhesive interface may also rely on a chemical interaction between restorative materials and resin-based cements, which may be improved by the application of bond-promoting agents with specific functional monomers.<sup>8,11,31</sup>

Airborne particle abrasion of the ceramic's intaglio surface with aluminum oxide ( $\text{Al}_2\text{O}_3$ ) particles increases the surface area available for adhesion by creating superficial microretentions.<sup>3</sup> This improvement of the contact surface allows a better flow of the luting system or adhesive resin, enhancing the interfacial strength between the two substrates.<sup>31,33</sup> This also occurs due to the smaller contact angle between sandblasted ceramics and primer as opposed to non-sandblasted ceramics.<sup>21</sup> Although it has been demonstrated that airborne particle abrasion of high-crystalline-content ceramics significantly reduces their fatigue strength due to the generation of large surface flaws,<sup>35</sup> researchers later found that the size of the particle employed plays a critical role in controlling the surface damage and improving the material's fatigue behavior.<sup>26</sup> The silicization of the zirconia surface by means of sandblasting with silica-coated particles (tribochemical silica coating) followed by silane application is another approach to potentially developing a strong bond to zirconia,<sup>7,31</sup> but the mechanism of attachment between the silica and the underlying zirconia as well as its predictability is still under debate.<sup>6,33</sup>

The chemical interaction between zirconia and specific functional monomers is another extensively investigated possibility. The final goal is to promote a strong, stable bond between the primer and metallic oxides.<sup>21,22,31,33</sup> MDP (10-methacryloxydecyl dihydrogen phosphate) is a phosphate monomer with affinity to base metals, and previous studies have demonstrated its efficacy in bonding to zirconia substrate,<sup>1,7,8</sup> indicating that appropriate chemical treatment is a stronger contributing factor to high bond strength than is mechanical alteration of the zirconia surface.<sup>16</sup> This is probably due to the formation of phosphate salts in the zirconia surface.<sup>22</sup> However, the interaction of MDP with other monomers in the primer, adhesive, or cement may compromise its effectiveness in bonding to zirconia hydroxyl groups.<sup>29,31,33</sup> The role of MDP in either the primer or the adhesive in bonding to zirconia also needs to be studied further.<sup>8,17</sup>

In an attempt to improve bonding, many studies also consider the use of phosphate-based cements or self-adhesive cements associated or not with primers to improve zirconia bonding.<sup>7,8,33</sup> However, to properly evaluate the effect of different bonding strategies on the bond strength between zirconia and resin cement, the application of a bis-GMA-based cement would allow a more realistic interpretation of the results, since it has already been shown that bis-GMA-based cements do not adhere to zirconia surfaces.<sup>7,8,21</sup> Furthermore, if a strong, stable bond between zirconia and bis-GMA-based cement could be established

by means of any of the bonding strategies proposed in this study, the clinician would have a broader range of materials available to work with, including different shades, viscosities, and curing modes. Therefore, the aim of this study was to evaluate the effect of materials for zirconia bonding on the dual-curing bis-GMA-based resin-cement bond strengths to zirconia. The null hypotheses are that the application of zirconia bonding agents does not affect resin cement bond strengths to zirconia and that the resin cement bond strengths to zirconia are not affected by long-term water storage.

## MATERIALS AND METHODS

Table 1 shows information regarding the materials used in the present study, their corresponding batch numbers and composition.

### Specimen Preparation

One hundred twenty cylinders of zirconia (3 mm diameter, 5 mm thick) were produced from presintered blocks of zirconia (Prettau Zirconia, Zirkonzahn; Gais, Italy). After being fully sintered following manufacturer's instructions, specimens were embedded in autopolymerizing acrylic resin (Jet; São Paulo, SP, Brazil) encircled by plastic rings, roughened using up to 600-grit silicon carbide papers (Buehler; Lake Bluff, IL, USA) for 5 min, and ultrasonically cleaned (Ultrasonic Cleaner 1440 D, Vita Zahnfabrik; Bad Säckingen, Germany) in distilled water.

All specimens were airborne particle abraded (Precision 3, Essence Dental VH; Araraquara, SP, Brazil) using 50- $\mu\text{m}$   $\text{Al}_2\text{O}_3$  particles at an air pressure of 2.8 bar for 60 s at a distance of 10 mm. After cleaning the specimens ultrasonically with distilled water for 10 min, they were randomly divided into 5 groups, each containing 24 specimens, according to the following surface treatment methods:

- UA: A multimode adhesive system (Scotchbond Universal Adhesive, 3M ESPE; St Paul, MN, USA) was applied with a microbrush, dried with oil-free air for 10 s and light cured for 10 s with an LED light-curing unit (Translux Power Blue, Heraeus Kulzer; Hanau, Germany) at an output of 650 mW/cm<sup>2</sup>.
- SZP: A zirconia primer (Signum Zirconia Bond I + II, Heraeus Kulzer) was applied with a microbrush (Signum Zirconia Bond part I) and then dried with oil-free air. Two coats of Signum Zirconia Bond part II (Heraeus Kulzer) were applied with a microbrush and light cured for 40 s with the same light-curing unit and power.
- ZPP: A zirconia primer (Z-Prime Plus, Bisco; Schaumburg, IL, USA) was applied in two consecutive coats with a microbrush and then dried with oil-free air for 5 s.
- EXP: An experimental zirconia primer (MZ Primer, Angelus; Londrina, Brazil) was applied with a microbrush, left undisturbed on the surface for 40 s, dried with oil-free air for 5 s and light cured for 40 s with the same light-curing unit and power.
- CO: Control, no surface treatment was applied.

**Table 1** Materials name, composition, batch numbers and manufacturers

Material	Composition	Batch number	Manufacturer
Prettau Zirconia	Yttrium partially stabilized with tetragonal polycrystalline structure (Y-TZP)	ZRAD8001	Zirkonzahn; Gaís, Italy
UA Scotchbond Universal Adhesive	Ethanol 10–15 wt%, 10-MDP, HEMA	466384	3M ESPE; St Paul, MN, USA
SZP Signum Zirconia Bond I + II	Part I: acetone, 10-MDP, acetic acid Part II: methyl methacrylate, diphenyl(2,4,6- trimethylbenzoyl)phosphinoxide	010128	Heraeus Kulzer; Hanau, Germany
ZPP Z-Prime Plus	10-MDP, carboxylic acid resin monomer, bis-GMA, HEMA, other resin monomers	1000010258	Bisco; Schaumburg, IL, USA
EXP MZ Primer	PMDM, HEMA-p, methacrylate acid, benzoyl peroxide, acetone	23927	Angelus; Londrina, Brazil
Duo-Link Dual-Syringe	Bis-GMA, triethyleneglycol dimethacrylate, urethane dimethacrylate, glass filler	1200008154	Bisco
Composition information provided by the manufacturers. Abbreviations: 3-MPS: 3-methacryloxypropyltrimethoxysilane; bis-GMA: bisphenol A diglycidyl methacrylate; DMA: aliphatic dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate; TEG-DMA: triethylene glycol dimethacrylate.			

The surface area to be treated was previously delimited by placing adhesive tape with a 1-mm-diameter perforation on the center of each zirconia surface. After surface treatment, translucent Tygon tubes (Tygon Medical Tubing, Saint-Gobain; Akron, OH, USA) with an internal diameter of 0.8 mm and a height of 1.0 mm were used as matrices. Each tube was positioned on the tape ensuring that its lumen coincided with the circular ceramic area delimited by the tape perforation. One trained operator using magnifying loupes positioned the matrices on the zirconia surfaces, then carefully inserted bis-GMA-based dual-curing resin cement (Duo-Link Dual-Syringe, Bisco) into each matrix. A mylar strip was placed on the filled tube and gently pressed. Resin cement was light cured for 40 s (Translux Power Blue) with an output of 650 mW/cm<sup>2</sup>. The light intensity was checked daily using a radiometer (L.E.D. Radiometer, SDS Kerr; Danbury, CT, USA). After 24 h of storage in distilled water at 37°C, matrices and tapes were carefully removed using a sharp blade to expose the resin cement cylinders. Each specimen was checked for the presence of defects (bubbles, overflow of the cement beyond the limits of the bonding area, and mismatch between the cylinders and their respective delimited areas) with magnifying loupes (Optivisor, Donegan Optical Company; Lexena, KS, USA). Those with defects or mismatch were discarded.

### Microshear Bond Strength

Specimens were tested for microshear bond strength ( $\mu$ SBS) either after 24 h or 6 months of distilled water storage at 37°C. For the aged specimens, distilled water was replaced every 15 days.

The plastic rings containing the bonded specimens were attached to a shear-testing jig. A stainless steel orthodontic

wire (0.2 mm diameter) was looped around the base of each resin cement cylinder, in contact with half of its circumference, keeping the setup aligned to ensure the correct orientation of the shear forces. The resin cement/zirconia interface was then tested using shear mode in a universal testing machine (Instron 4444, Instron; Canton, MA, USA) at a crosshead speed of 0.5 mm/min until failure. The  $\mu$ SBS values were calculated in MPa by dividing the load at failure by the surface area (mm<sup>2</sup>) of each specimen. The results were statistically analyzed with two-way ANOVA and Tukey's post-hoc test ( $p < 0.05$ ).

### Failure Mode

The failure mode of debonded specimens was determined using digital close-up photographs (Nikon D70, Japan) taken with a macro lens (Nikkor Medical 120 mm; Tokyo, Japan). The digital photographs were evaluated on a 27-inch LCD panel display and classified as adhesive (A), mixed (M), cohesive in resin cement (CR), or cohesive in zirconia (CZ).

### SEM and Energy Dispersive X-ray (EDX) Analysis

Ten additional zirconia specimens ( $n = 2$ ) were prepared for surface analysis of the 4 treated groups and the untreated zirconia surface (control). For that purpose, specimens were ultrasonically cleaned in distilled water, air dried for 10 s, surface treated according to the respective experimental group as previously described. They were then mounted on aluminum stubs with adhesive carbon tape (Ted Pella; Redding, CA, USA), sputter coated with gold-palladium for 90 s, and observed using SEM (JEOL, Model 6610LV; Tokyo, Japan) and an energy dispersive x-ray device (EDX, Silicon Drift Detector with INCA data acquisition software, Oxford Instruments; High Wycombe, UK).

**Table 2 Mean resin cement microshear bond strengths to zirconia (in MPa) and standard deviation (SD) for each surface treatment**

Group	Storage time	Mean bond strength (SD) in MPa	% of failure mode
UA	24 h	14.6 (± 4.9) <sup>a</sup>	M: 92; C: 8
	6 m	16.0 (± 4.8) <sup>a</sup>	M: 100
SZP	24 h	14.0 (± 5.4) <sup>ab</sup>	M: 84; C: 16
	6 m	11.9 (± 2.6) <sup>ab</sup>	M: 92; C: 8
ZPP	24 h	8.0 (± 1.8) <sup>b</sup>	A: 8; M: 92
	6 m	8.6 (± 3.3) <sup>b</sup>	A: 16; M: 84
EXP	24 h	0.6 (± 0.7) <sup>c</sup>	A: 100
	6 m	1.2 (± 0.5) <sup>c</sup>	A: 100
CO	24 h	1.3 (± 1.2) <sup>c</sup>	A: 100
	6 m	1.0 (± 1.2) <sup>c</sup>	A: 100

Different letters indicate significant differences among experimental groups ( $p = 0.0001$ ). There was no significant difference in bond strength by storage time ( $p = 0.841$ ). A: adhesive failure between zirconia and resin cement; M: mixed failure (cohesive in resin cement, adhesive between primer/adhesive and resin cement and/or adhesive failure on the zirconia/surface treatment interface); C: cohesive failure in the resin cement.

## RESULTS

### Microshear Bond Strength

Two-way ANOVA indicated a significant effect of surface treatment ( $p = 0.0001$ ) and no effect of storage time ( $p = 0.841$ ) on resin-cement bond strengths to zirconia (Table 2). The mean  $\mu$ SBS, standard deviation, and Tukey's post-hoc test results are also summarized in Table 2. After 24 h, the mean  $\mu$ SBS ranged from  $1.0 \pm 1.2$  (CO) to  $14.6 \pm 4.7$  (UA). After 6 months, mean bond strength ranged from  $0.6 \pm 0.7$  (EXP) to  $16.0 \pm 4.8$  (UA). UA-treated surfaces presented the highest  $\mu$ SBS, which were similar to SZP-treated surfaces. Groups UA and SZP had the highest  $\mu$ SBS. ZPP-treated specimens presented intermediate values, which were significantly lower than UA-treated specimens and significantly higher than the controls. There was no difference between EXP-treated and control groups, which presented the lowest bond strength values.

### Failure Mode

The incidence of each failure mode is shown in Table 2. Adhesive failure between zirconia and resin cement was frequently observed for the EXP and CO groups on specimens tested both after 24 h and 6 months of storage. However, a closer look at the EXP specimens showed that the failure was actually adhesive between the primer and the resin cement, since a thin layer of primer could be identified on the zirconia surface.

Mixed failure showing cohesive failure in the resin cement as well as adhesive failure between zirconia and resin cement which exposed the zirconia surface was frequently observed in groups UA, SZP, and ZPP after both 24 h and 6 months of water storage.

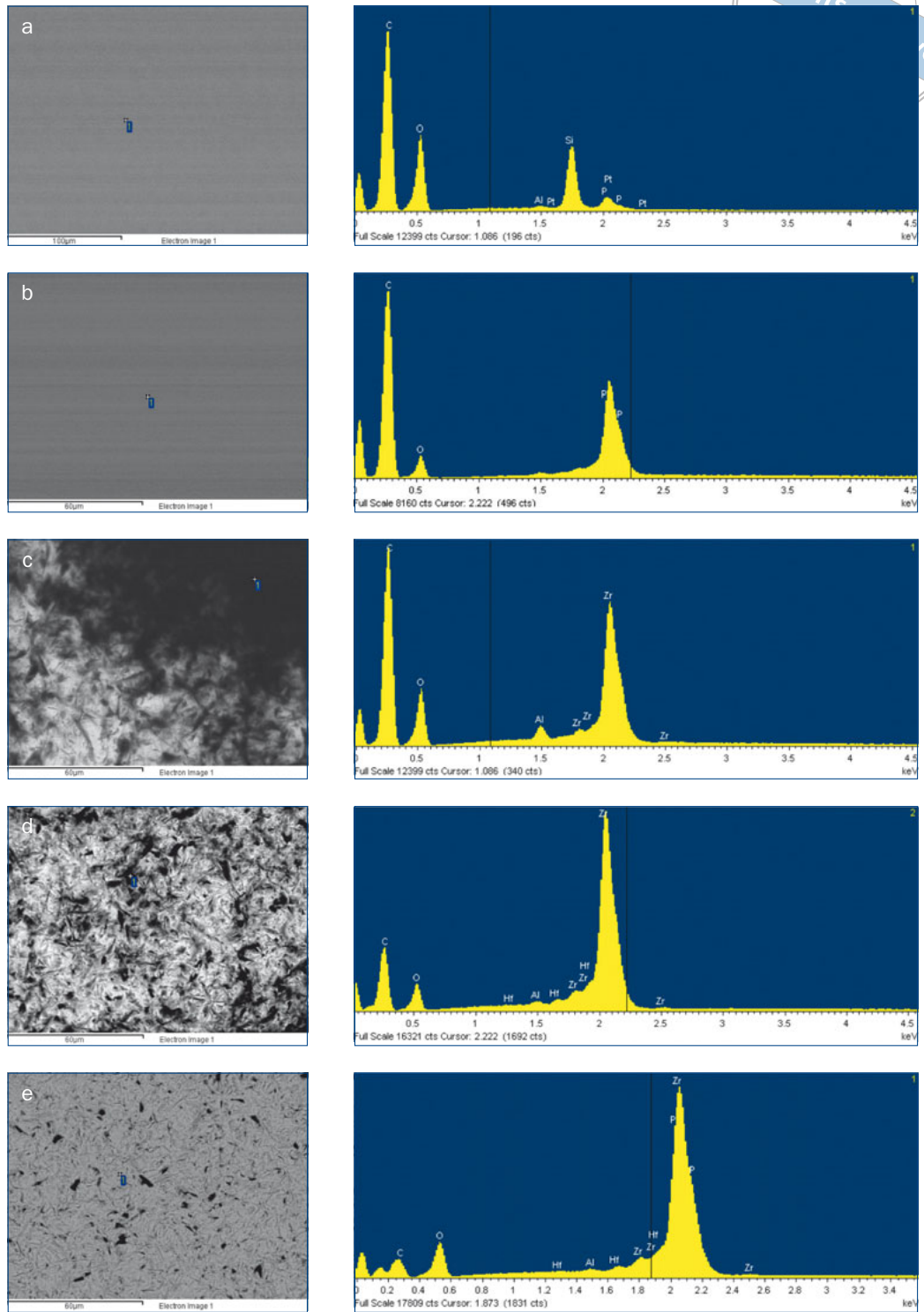
### SEM and Energy Dispersive X-ray (EDX) Analysis

UA and SZP specimens exhibited a homogeneous layer covering the zirconia surface (Figs 1a and 1b). EDX indicated the presence of phosphorus and silica in UA-treated specimens (Fig 1a). SZP-treated specimens (Fig 1b) presented the highest concentration of phosphorus among all groups. ZPP-treated specimens showed non-homogeneous primer coverage, in which areas without primer with exposed, untreated zirconia were evident (Fig 1c) and no phosphorus was detected. EXP-treated specimens exhibited a very thin primer layer, undetectable in many areas evaluated (Fig 1d), clearly exposing the sandblasted zirconia underneath. The concentration of phosphorus was insignificant in the EXP specimens. Specimens from EXP and CO groups analyzed in backscatter mode showed darker areas in which EDX revealed high concentrations of aluminum, which was compatible with the aluminum oxide particles originating from the sandblasting procedure (Figs 1d and 1e). CO samples also exhibited high zirconia concentration.

## DISCUSSION

There are various methods currently available to investigate the bonding between two different substrates. This study evaluated the bond strength between zirconia and resin cement by means of the microshear bond strength test with a stainless-steel wire loop. The smaller adhesive interface of the  $\mu$ SBS samples as opposed to shear bond strength samples allows better inspection of the adhesive interface, therefore limiting the occurrence of bubbles and other defects. When the two methods were compared, the  $\mu$ SBS test showed significantly higher bond strength.<sup>16</sup> This was previously explained by Sano et al,<sup>25</sup> who observed that the bond strength is inversely related to the tested surface area due to the lower incidence of flaws in the adhesive interface. Overall, higher bond strength values associated with relatively small standard deviations culminate in a method that is more sensitive and reliable than the conventional shear strength test.<sup>16</sup> The microshear load application with a wire loop allows more precise results than the knife-edge chisel, due to the better distribution of stresses around the loop.<sup>9</sup> However, failure initiation seems to be related to the high concentration of tensile stresses at the adhesive interface as opposed to the shear stresses.<sup>4</sup> Another alternative to examine the efficacy of the bond between different substrates is the tensile test, especially the microtensile, which allows the analysis of a very small interface, therefore with less chance of defects, under tensile stress. Microtensile methodology has been advocated as a reliable alternative due to the larger number of samples tested per group.<sup>8</sup> How-





**Fig 1** Photomicrograph (left) and chemical analysis using EDX (right) of zirconia surfaces after various treatments. a. UA: multimode adhesive (Scotchbond Universal Adhesive), original magnification 500X. A homogeneous layer covering the zirconia surface is evident. b. SZP: zirconia primer (Signum Zirconia Primer I + II), original magnification 1000X. A homogeneous layer covering the zirconia surface is evident. c. ZPP: zirconia primer (Z-Prime Plus); original magnification 1000X. Light-gray areas lack primer and show exposed, untreated zirconia. d. EXP: experimental zirconia primer (MZ Primer), original magnification 1000X. Very thin to undetectable primer layer, exposed sandblasted zirconia underneath. Darker areas are aluminum oxide particles originating from the sandblasting procedure. e. CO: zirconia surface after sandblasting with no further surface treatment (control), original magnification 1000X. Darker areas are aluminum oxide particles originating from the sandblasting procedure. The small blue rectangles in the left-hand images indicate the area that is chemically represented in the graph on the right.

ever, the cutting procedure generates cracks and substantial damage to the materials and to the adhesive interface,<sup>12</sup> which is especially critical when dealing with brittle materials like zirconia.<sup>8</sup> The tensions generated at the adhesive interface may result in a high number of pre-test failures, which are sometimes disregarded by the researchers and sometimes considered as specimens with 0 MPa bond strength,<sup>13,21</sup> which may compromise the discriminative power of the test.<sup>17</sup> Tensile testing with alternative sample designs has been used as a way to overcome the limitations of dealing with brittle materials like zirconia, and the bond strength values reported are similar to previous studies using either microshear or microtensile bond strength evaluations.<sup>2</sup> In the present study, the use of the  $\mu$ SBS test did not result in pre-test or cohesive failures within the adherent materials, and the overall values obtained ranged from 0.6 to 16 MPa, which agrees with the values reported in the literature for zirconia bonding.<sup>5,17</sup>

The results obtained from applying different bonding strategies to zirconia surfaces led to the rejection of the first null hypothesis (the application of zirconia bonding agents does not affect bis-GMA-based resin-cement bond strengths to zirconia), because the treatment of zirconia with an adhesive system or zirconia primer resulted in higher bond strengths than those presented by the control group, except when an experimental primer was applied. These findings indicate that it is clinically viable to use bis-GMA-based resin cement to bond zirconia to a given substrate – either tooth structure or a restorative material – as long as the correct treatment modality is employed. The highest bond strengths resulted after both storage times when an MDP-containing multimode adhesive system (UA) was applied to zirconia. High bond strengths after application of an MDP-containing adhesive as opposed to a non-MDP-containing adhesive have already been reported.<sup>17</sup> The application of a resin-based adhesive per se is expected to enhance bond strength by enhancing the flow of the resin cement,<sup>17</sup> but the presence of MDP plays a significant role in improving bond strength, due to the strong interaction of the hydroxyl groups in the phosphate moiety of MDP and the hydroxyl groups in the oxide layer of Y-TZP, which are then bonded by either Van der Waals forces or hydrogen bonds.<sup>8,17</sup> Indeed, when the role of MDP-based materials was compared, researchers demonstrated that the presence of MDP monomer in the adhesive, as opposed to being in either the cement or the primer, is the most significant factor for improving adhesion.<sup>8</sup>

Interestingly, the treatment of sandblasted zirconia with Signum Zirconia Bond I + II (SZP) resulted in bond strength values that were slightly lower but statistically similar to the previous application of an MDP-containing adhesive system (UA). This behavior is clarified by the results of the EDX analysis, which found evidence of a higher concentration of phosphorous in the SZP-treated surfaces, indicating a higher concentration of MDP in the zirconia primer (SZP group) than in the multimode adhesive (UA group), which may have positively affected bond strength. Superior bond strength between resin cement and sandblasted zirconia after surface

treatment with SZP compared to other zirconia primers has been previously reported,<sup>21</sup> indicating that the effectiveness of primers for zirconia bonding is material related.

The EDX analysis showed that specimens treated with Z-Primer Plus (ZPP) presented non-homogeneous surface coverage and barely detectable phosphorous peaks, explaining why ZPP-treated specimens showed significantly lower bond strength values when compared to the UA-treated specimens. Nevertheless, the bond strength of ZPP-treated specimens was significantly higher than that of both the CO and the EXP groups. However, considering a previously established threshold of 10 to 13 MPa to deliver optimum clinical service in terms of adhesion,<sup>19</sup> the results presented by the treatment with ZPP would not be sufficient to stabilize a zirconia-based indirect restoration. As previously mentioned, the chemical analysis of the surface indicated a low concentration of MDP in the primer. Furthermore, Z-Prime Plus contains both bis-GMA and HEMA (Table 1), with the intent to form a film that contains both hydrophobic and hydrophilic methacrylates. However, the presence of HEMA in adhesive films has been criticized due to the hydrolytic instability of this monomer.<sup>14</sup> Additionally, the reactivity of HEMA with the oxide layer is lower than that of acidic monomers such as MDP, and the HEMA-oxide layer interaction might result in the generation of compounds whose effect on the bond strength is not known.<sup>22,31</sup> Interestingly, in other studies, the prior application of Z-Prime Plus resulted in significantly higher, more stable bond strengths when zirconia was bonded to an MDP-containing resin cement as opposed to samples previously treated with MDP-free primers.<sup>1,33</sup> It is possible that an insufficient concentration of MDP in the primer is compensated by the MDP in the cement, improving the overall adhesive strength at the interface.

The experimental primer evaluated in this study (EXP) resulted in bond strength values that were similar to those of the control group, and significantly lower than the values presented by all the other surface treatments applied. Due to the confidentiality of the chemistry used to develop this experimental primer, it is not possible to discuss the effect of any of the monomers present in the material's composition. However, EDX analysis of the EXP-treated specimens shows that the chemical elements detected on the zirconia surface are very similar to the elements detected in the control group. Although there is a higher carbon (C) peak, this is possibly due to the contamination of the surface. In addition, analysis of the failure mode revealed that failure occurred mostly between the resin cement and the primer, since a thin film of primer was observed on the zirconia surface. Therefore, it seems likely that the bond between the EXP-primer and zirconia was first compromised by the lack of chemical affinity between the primer and the resin cement. Additional information about the primer composition and further analysis of the interaction with other resin-based cements would help explain this effect.

The comparison between different groups demonstrated the lowest bond strength values in the control group, in which sandblasting but no further surface treatment was

performed. This result was expected due to the absence of a functional molecule in the resin cement that could promote bonding to zirconia.<sup>13</sup> Nonetheless, Kim et al<sup>16</sup> observed that the passive film of zirconia deposited onto the Y-TZP surface could potentially attach to any luting system containing polymers or monomers with polar functional groups. In fact, similar bond strengths were reported when MDP- and non-MDP-based resin cements were compared; the authors explained that, besides the composition of the resin cement, factors such as the viscosity of the material, its wettability, and other mechanical properties may play a significant role in bonding to Y-TZP.<sup>8,30</sup>

Two-way ANOVA indicated that storage time did not have an effect on bond strength between zirconia and resin cement. Therefore, the second null hypothesis, which stated that the resin cement bond strengths to zirconia are not affected by long-term water storage, failed to be rejected. It was expected that 6-month water storage would have a significant effect on the bonding due to the hydrolytic degradation of the adhesive interface, which has been previously reported for zirconia-bonded interfaces.<sup>7,8,11,28</sup> These results are not in agreement with the microshear bond strength findings of Da Silva et al,<sup>7</sup> who observed a significant degradation after 6-month storage in water. However, those specimens were not previously sandblasted, as opposed to the specimens of this study, which were airborne-particle abraded with 50- $\mu\text{m}$   $\text{Al}_2\text{O}_3$  prior to the bonding procedures. According to De Souza et al,<sup>8</sup> the adhesion obtained between MDP/non-MDP-based materials and zirconia is not stable and some micromechanical interlocking is desirable to improve the retention of the indirect restoration. Indeed, it has been demonstrated that sandblasting the zirconia surface reduces the surface contact angle between zirconia and primers, improving its wettability.<sup>21</sup> Therefore, it can be speculated that the improved surface wettability facilitated the flow and subsequent infiltration of the resin cement into the micromechanical retentions created by the sandblasting procedure, creating a more effective seal which hindered water infiltration. The importance of the sandblasting procedure was shown in recently published studies, where specimens with and without airborne-particle abrasion received the same chemical surface treatment, and those previously abraded performed significantly better in terms of bond strength.<sup>1,16,30</sup>

In spite of the similarity between short- and long-term water storage results in the present study, 6-month water storage may be considered severe conditions for the degradation of the bond, since significant differences in bond strength are frequently observed after this period of storage.<sup>7,8,11,28</sup> Many other methodologies have been employed to simulate the hydrolytic degradation of the adhesive interface, such as 5000<sup>33,34</sup> or 10,000 thermocycles,<sup>15-17</sup> water storage for 60 days,<sup>21</sup> 150 days + 37,500 thermocycles,<sup>30</sup> or 20,000 thermocycles + 40 days.<sup>31</sup> However, a recent review and meta-analysis concluded that both long-term water storage and thermocycling have a bond-degrading effect.<sup>20</sup> Under the limitations of an in vitro study, it is not possible to correlate the effect of 6-month water storage to the in vivo

aging of the adhesive interface in an indirect zirconia restoration. In vivo, the restoration has a much larger adhesive interface, and is exposed to different challenges such as mechanical loading and pH variation. Nonetheless, the severity of the aging protocol allows prediction of the hydrolytic stability of the adhesive interface, which is a crucial property for a material employed in the mouth.

## CONCLUSION

Bonding of a bis-GMA-based resin cement to zirconia may be improved by means of specific surface treatments. The effectiveness of primers for zirconia bonding is material related. Six-month water storage does not affect bis-GMA-based resin-cement bond strengths to zirconia.

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**Clinical relevance:** The composition of the primer or adhesive used in bonding bis-GMA-based resin cement to sandblasted Y-TZP is the key to clinically viable and stable adhesion.