

# The Effect of Colloidal Silica and Glaze Coatings on the Adhesion of Zirconia with Various Yttria Concentration

## Keywords

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## ABSTRACT

*Purpose:* This study evaluated the effect of coating traditional and translucent Y-TZP with an industrial nanometric colloidal silica or glaze before or after sintering on the adhesion of zirconia with various yttria concentration. *Materials and methods:* Specimens of Y-TZP with 3% and 5% yttria were subdivided into 5 groups (n=10), according to the coating applied and moment of application (before or after Y-TZP sintering): Control (no coating), Colloidal Silica/Sintering, Sintering/Colloidal Silica, Glaze/Sintering, Sintering/Glaze. Lithium disilicate (LD) was used as positive control. Except for Y-TZP controls, groups were conditioned with silane before cementation with a self-adhesive resin cement. After 24 hours, the shear bond strength and failure analysis were performed. Also, analysis of specimens' surface was accomplished with SEM-EDX. Kruskal-Wallis and Dunn tests were applied to analyze differences between groups ( $p < 0.05$ ). *Results:* Overall, the worst and best values of shear bond strength test were control and glaze after sintering groups. Different morphological and chemical aspects were observed in SEM-EDX analysis. *Conclusions:* Coating Y-TZP with colloidal silica showed unsatisfactory results. In 3Y-TZP, the surface treatment associated with the best adhesion values was the application of glaze after zirconia sintering. However, in 5Y-TZP, glaze application can be performed before or after the zirconia sintering to optimize clinical steps.

## INTRODUCTION

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) is progressively used in dental practice mainly because of a higher fracture resistance compared to other ceramics.<sup>1</sup> Excessive loads on the surface of Y-TZP lead to a tension-induced toughness mechanism opposed to the propagation of cracks.<sup>2</sup> This process results from the phase transformation of the Y-TZP particles from tetragonal to monoclinic phase, which leads to an increase in volume (3%-5%) at the crack origin.<sup>3</sup>

The Y-TZP with 3 mol% of yttria (3Y-TZP) is currently considered the strongest and most durable ceramic used in dentistry.<sup>4</sup> However, it is associated with greater opacity and, therefore, inferior aesthetics.<sup>5</sup> Technological advances allowed the achievement of a more natural appearance of monolithic zirconia.<sup>1</sup> The increase in yttria volume to 5 mol% of yttria (5Y-TZP) yielded the amplification of the cubic phase for greater translucency and aesthetics appearance.<sup>6</sup>

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The effective bonding between dental ceramics and resin cements is achieved by chemical bond and micromechanical association, which is a broadly established process for glass-ceramic restorations with a high silica composition.<sup>7,8</sup> In contrast, the zirconia is a polycrystalline material with no glass phase.<sup>2,9</sup> Therefore, the Y-TZP presents chemical inertia regardless of the variation in the volume of yttria, not being susceptible to the conventional adhesive cementation process.<sup>2,9</sup> This represents a point of weakness in the adhesion and clinical performance of this class of restorative material.<sup>6,10</sup>

Several techniques for covering the surface of the Y-TZP have been evaluated with the aim to increase the bonding to resin cements.<sup>6,7</sup> One of the coating techniques that shows promising results involves the application of a thin layer of vitreous porcelain on the surface of the Y-TZP – a process also known as vitrification, low-melting glaze, glaze-on, or ceramic coating.<sup>2,4,9,11</sup> The application of glaze is recommended by the manufacturer in Y-TZP sintered specimens, followed by ~900°C.<sup>2</sup> Because of the high content of silica or amorphous matrix of silica and pigments (metal oxides) in the glaze coat, the zirconia surface becomes vitrified and susceptible to acid etching and silanization.<sup>2,4,9,11,12</sup>

The aim of this study was to evaluate the coating of traditional and translucent Y-TZP with nanometric colloidal silica and glaze before or after the sintering of ceramics. The null

hypotheses were: (1) There is no difference in adhesion between Y-TZP and cement when an industrial nanometric silica in colloidal suspension or glaze coating is applied. (2) There is no difference in morphology and performance of the coating if it is applied before or after Y-TZP sintering.

## MATERIALS AND METHODS

### EXPERIMENTAL DESIGN AND GROUPS

Zirconia compositions of 3% and 5% yttria (ProtMat Advanced Materials, Juiz de Fora, MG, Brazil) were selected and divided into subgroups according to the different surface treatments received (*Table 1*). A control group (no coating treatment) and two different experimental groups were coated either with colloidal silica (Begosol HE; Bego – Wilcos, Petrópolis, RJ, Brazil) or with Glaze (Glaze - Vita Akzent Plus; Vita, Bad Säckingen, Germany) (*Table 2*). The coating were carried out before or after sintering. In addition, a lithium disilicate (LD) group was used for comparison. The adhesion of the Y-TZP specimens to the self-adhesive resin cement RelyX U200 Automix (3M ESPE, Sumaré, SP, Brazil) was evaluated regarding shear bond strength performance (n = 10 per group) with fracture pattern analysis.

**Table 1. Composition of the materials used.**

Material (Manufacturer)	Composition (WT%)
3 mol% Y-TZP (3Y-TZP; ProtMat Advanced Materials)	94.72% Zr <sub>2</sub> O, 5.2% de Y <sub>2</sub> O <sub>3</sub> , 0.25% de Al <sub>2</sub> O <sub>3</sub>
5 mol% Y-TZP (5Y-TZP; ProtMat Advanced Materials)	90.62% Zr <sub>2</sub> O, 9.3% de Y <sub>2</sub> O <sub>3</sub> , 0.05% de Al <sub>2</sub> O <sub>3</sub>
Lithium Disilicate (ProtMat Advanced Materials)	SiO <sub>2</sub> (59-73%), LiO <sub>2</sub> (13-15%), K <sub>2</sub> O (3-5%), other oxides (7-25%) *industrial secret
Begosol HE (Bego – Wilcos)	Mixture with nanometric silica in aqueous solution - Chemically prepared silicon dioxide (50-70%). *industrial secret
Glaze – Vita Akzent Plus (Vita)	Powder: Amorphous glass (ceramic with a greater glassy than crystalline composition). Liquid: glycol solution. *industrial secret
Porcelain Etch (Ultradent)	9% hydrofluoric acid.
RelyX Ceramic Primer (3M ESPE)	Pre-hydrolyzed, single-phase silane solution.
RelyX U200 Automix A2 (3M ESPE)	Base paste: Methacrylate monomers containing phosphoric acid groups, methacrylate monomers, silanized fillers, initiator components, stabilizers, rheological additives. Catalyst Paste: Methacrylate monomers, alkaline (basic) fillers, silanized fillers, initiating components, stabilizers, rheological additives, pigments.

\* Y-TZP: Yttria-stabilized tetragonal zirconia polycrystal. WT%: weight percentage. Zr<sub>2</sub>O: Zirconia oxide. Y<sub>2</sub>O<sub>3</sub>: Yttrium oxide. Al<sub>2</sub>O<sub>3</sub>: Aluminum oxide. SiO<sub>2</sub>: silicon dioxide (silica). LiO<sub>2</sub>: lithium superoxide. K<sub>2</sub>O: potassium oxide.

**Table 2.** Distribution of the groups evaluated.

Composition	Groups	Surface Characteristics	
Lithium Disilicate (n=10)	LD	Positive Control	(n=10)
	G1	3Y-TZP – 3% Control	(n=10)
3 mol% Y-TZP (n=50)	G2	3Y-TZP + Colloidal Silica/Sintering	(n=10)
	G3	3Y-TZP + Sintering/Colloidal Silica	(n=10)
	G4	3Y-TZP + Glaze/Sintering	(n=10)
	G5	3Y-TZP + Sintering/Glaze	(n=10)
	G6	5Y-TZP – 5% Control	(n=10)
5 mol% Y-TZP (n=50)	G7	5Y-TZP + Colloidal Silica/Sintering	(n=10)
	G8	5Y-TZP + Sintering/Colloidal Silica	(n=10)
	G9	5Y-TZP + Glaze/Sintering	(n=10)
	G10	5Y-TZP + Sintering/Glaze	(n=10)

\*Y-TZP: Yttria-stabilized tetragonal zirconia polycrystal.

## SAMPLE SIZE CALCULATION

The effect size for this study (2.57) was based on a previous study.<sup>13</sup> The analysis was performed by the software G \* Power 3.1 (Henrick Heine-Universität) with  $\alpha = 0.05$  and a power of 0.95. Four per group was considered the ideal sample size to observe a significant difference between groups. In addition, 6 samples were added to each group ( $n = 10$ ) to increase reliability, in line with previous studies that employed the same number of samples per group.<sup>2,4,9</sup>

## PRODUCTION OF Y-TZP SPECIMENS

The ceramic specimens were produced with a 10 x 10 mm squared format using a dental micromotor in 5 mm thick pre-sintered blocks (ProtMat Advanced Materials). The Y-TZP surface received different surface treatments according to the allocated group, with sintering being performed at different times (Table 3):

- Control: No coating treatment was performed;
- Colloidal Silica / Sintering: Colloidal Silica was applied 3 times using a brush before sintering at 1530°C;
- Sintering / Colloidal Silica: After sintering the ceramic at 1530°C, the colloidal silica was applied 3 times using a brush followed by a new sintering at 1000°C;
- Glaze / Sintering: Glaze applied once with a brush before sintering at 1530°C;
- Sintering / Glaze: After sintering the ceramic at 1530°C, the glaze was applied once with a brush followed by sintering at 900°C.

## CEMENTATION AND SHEAR BOND STRENGTH TEST

A silicone mold (Express XT Regular Body – VPS Impression Material, Medium-Bodied Consistency; 3M ESPE) with a hole was prepared by a Tygon tube precisely cut (ODEME Dental Research, Luzerna, SC, Brazil).<sup>14</sup> The silicone mold was prepared using a manual pistol-type dispenser (3M Scotch-Weld Epx Plus Applicator; 3M ESPE). After setting, the silicone mold was cut with a No. 11 scalpel blade to achieve 2 mm thick and sanded for planification of the surface.

With the exception of the Y-TZP control group, the specimens received the following protocol prior to cementation (Figure 1): 9% hydrofluoric acid gel, actively used with applicator tips for 20 seconds (Porcelain Etch; Ultradent, Indaiatuba, SP, Brazil), followed by irrigation with 5mL of distilled water, air jet for 3s, application of silane primer (RelyX Ceramic Primer, 3M ESPE, Sumaré, São Paulo, Brazil) for 60s and air jet for 3s.

RelyX U200 Automix cement (3M ESPE) was applied into the hole produced using the endodontic applicator tip of the system (Outer diameter = 0.8 mm; 3M ESPE). Next, the cement was light-cured with a Radii-cal LED light curing light (SDI, Bayswater, Australia) for 40s at 1200 mW/cm.<sup>2</sup> The integrity of the cement at the interface was confirmed by stereomicroscopy analysis (CARL ZEISS, Suzhou, China) at 10x magnification.<sup>15</sup> If an irregular cement interface was detected, the cylinder was eliminated and immediately prepared in another intact region on the Y-TZP surface (Figure 2).

Specimens were stored (SL 101; SOLAB, Piracicaba, SP, Brazil) immersed in distilled water for 24 hours at 37°C.<sup>16</sup> After storage, specimens that showed adhesion failure of the resin

**Table 3. Sintering cycles performed.**

STAGE 1 - Zirconia furnace: NBD 1700°C								
Ceramics	Preheat temp. (°C)	Preheat time (min)	Heating rate (°C/min)	Plateau temp. (°C)	Maintenance time (min)	Vacuum start (°C)	Vacuum termination (°C)	Cooling
Lithium Disilicate	-	-	-	-	-	-	-	-
Y-TZP - Control	-	-	5	1530	120	-	-	Natural
Y-TZP - Colloidal Silica/Sintering	-	-	5	1530	120	-	-	Natural
Y-TZP - Glaze/Sintering	-	-	5	1530	120	-	-	Natural
Y-TZP - Sintering/Colloidal Silica	-	-	5	1530	120	-	-	Natural
Y-TZP - Sintering/Glaze	-	-	5	1530	120	-	-	Natural
STAGE 2 - Ceramic oven: EDG Volcano								
Ceramics	Preheat temp. (°C)	Preheat time (min)	Heating rate (°C/min)	Plateau temp. (°C)	Maintenance time (min)	Vacuum start (°C)	Vacuum termination (°C)	Cooling
Lithium Disilicate	400	6	60	840	10	550	840	Slow
Y-TZP - Control	-	-	-	-	-	-	-	-
Y-TZP - Colloidal Silica/Sintering	-	-	-	-	-	-	-	-
Y-TZP - Glaze/Sintering	-	-	-	-	-	-	-	-
Y-TZP - Sintering/Colloidal Silica	500	6	50	1000	10	-	-	Natural
Y-TZP - Sintering/Glaze	500	6	80	900	1	-	-	Natural

\*Y-TZP: Yttria-stabilized tetragonal zirconia polycrystal. Temp. = temperature.

cement were excluded from this study and a new area of the ceramic was used for new cementation and analysis. Then, the cement diameter of specimens included was measured with a digital caliper with accuracy 0.001 (United Precision Machine; Shenzhen, China) and the shear bond strength test was performed in a universal testing machine (Microtensile OM150; ODEME). For this, a load of 50N was applied at 0.5 mm/min until cement displacement.<sup>17,18</sup> Bond strength values were expressed in MPa, according to the following formula:<sup>13</sup> Shear bond strength (MPa) = Maximum force (N) / Bonding area (mm<sup>2</sup>). The bonding area of the cements was defined by the circle area method:<sup>19</sup> Adhesion area (mm<sup>2</sup>) =  $\pi r^2$ , where  $\pi$  = constant 3.14,  $r$  = radius of the cement cylinders calculated from of the diameter measured with the digital caliper (mm).

## FAILURE CLASSIFICATION

The cement/zirconia interface of all specimens was evaluated under a stereomicroscope (20x) after shear bond strength test to classify the failure pattern into 3 types: Adhesive (failure at the cement/zirconia interface), cohesive (when failure occurs in the cement) or mixed (combination between adhesive and cohesive).<sup>15,18</sup>

## MICROSCOPY ANALYSIS

Two extra specimens of each group not submitted to the shear bond strength test were coated with 20 nm of gold and evaluated with Scanning Electron Microscopy (SEM; Nova

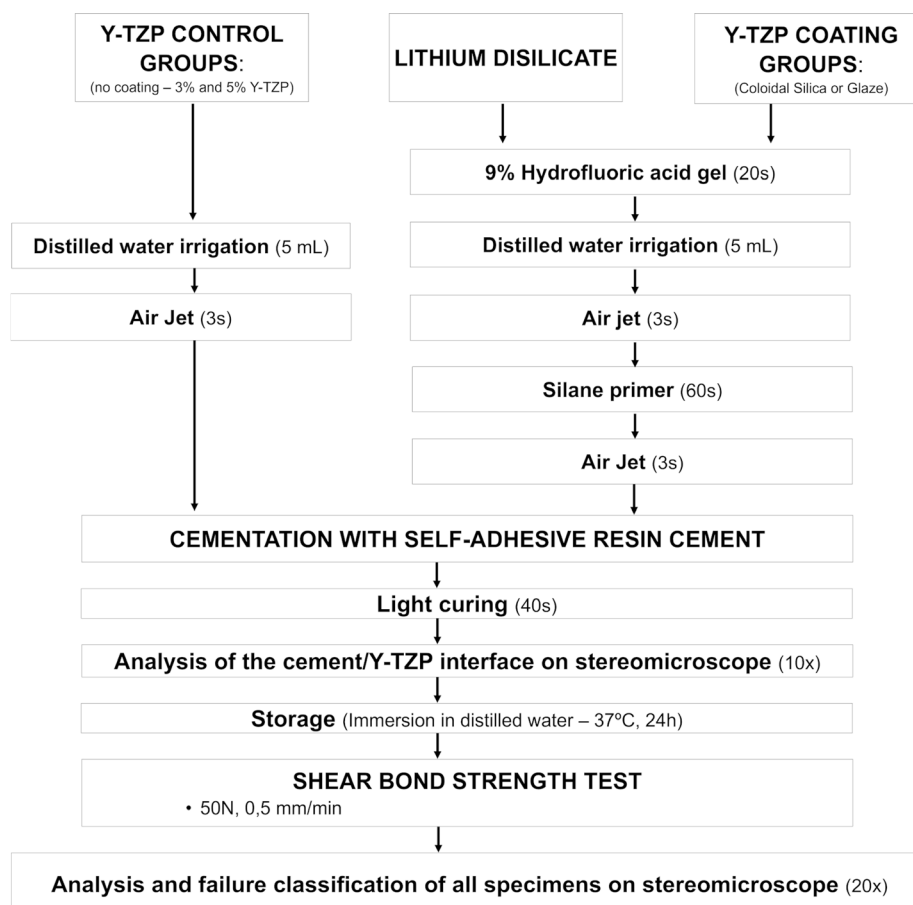


Figure 1: Flowchart of the protocol used for cementation and shear bond strength testing.

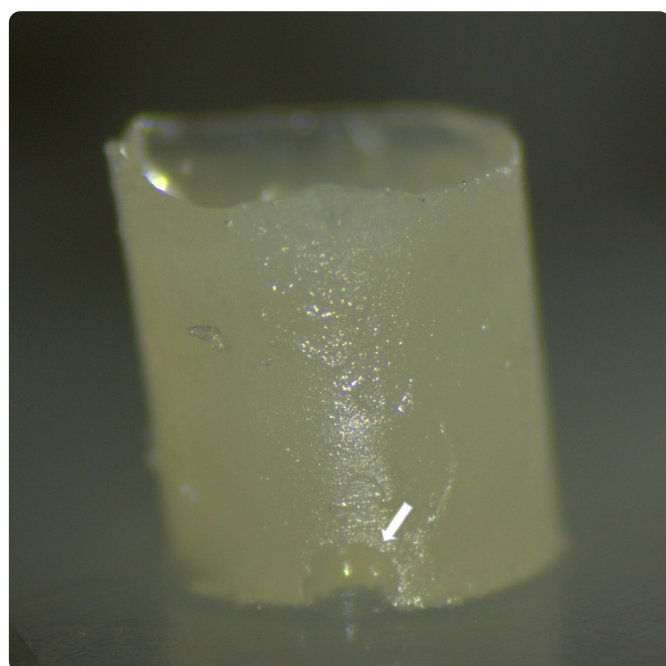


Figure 2: Interface discontinuity (see arrow) on specimen eliminated after the analysis of the cement/specimen interface.

NanoLab™ DualBeam FIB). For Energy-Dispersive X-ray Spectroscopy (EDX; Helios NanoLab, DualBeam FIB) samples were coated with 20 nm of C. For evaluating the effect of conditioning samples with 9% hydrofluoric acid, only half of the specimens was attached followed by irrigation with distilled water, whereas the other half was only irrigated with distilled water.

SEM images were collected at 2 kV. Magnifications as high as 32x and 150x are firstly used for looking the appearance of the samples. Then, images at 150x, 3000x and 15000x of the most representative areas of all specimens were prepared in the conditioned and non-conditioned regions. EDX was performed at 10 kV in the selected image of size 1.38 x 0.92 mm<sup>2</sup>. Some of the samples were also imaged uncoated by Orion NanoFab Helium Ion Microscope (HIM). The image were acquired at 30 KV and sample current ~1 nA. The sample charging is compensated by a flood gun beam (voltage and intensity optimized for each sample).

## STATISTICAL ANALYSIS

Initially, the Shapiro-Wilk test was used to assess data distribution. As it did not show a normal distribution, the Kruskal-Wallis and Dunn tests were applied to analyze the differences between the groups and between the zirconia compositions. The significance level was set at 5%.

## RESULTS

### SHEAR BOND STRENGTH TEST

The shear bond strength results are shown in Table 4. In the 3Y-TZP groups, the lowest median values were obtained as 0.53 MPa for the control sample. Coating the sample with colloidal silica, was not so effective for increasing this value and values of 0.67 MPa and 0.83 MPa was obtained for application

**Table 4. Median (min-max) of the shear strength values of the evaluated groups, expressed in MPa.**

	3Y-TZP	5Y-TZP	K-W (p value)
Control	0.53 (0.31 – 0.8) <sup>a C</sup>	0.38 (0 – 0.53) <sup>a C</sup>	0.130
Colloidal Silica / Sintering	0.83 (0.33 – 1.49) <sup>ab BC</sup>	0.95 (0.54 – 1.2) <sup>a B</sup>	0.040
Sintering / Colloidal Silica	0.67 (0.45 – 2.33) <sup>a BC</sup>	0.96 (0.7 – 1.68) <sup>a B</sup>	0.370
Glaze / Sintering	0.89 (0.57 – 1.35) <sup>b B</sup>	1.48 (0.72 – 2.58) <sup>a A</sup>	0.010
Sintering / Glaze	1.87 (1.21 – 3.49) <sup>a A</sup>	2.51 (1.77 – 3.74) <sup>a A</sup>	0.180
Lithium Disilicate	2.65 (1.49 – 2.97) <sup>A</sup>	2.65 (1.49 – 2.97) <sup>A</sup>	-
K-W (p value)	0.001	0.001	-

\*Different lowercase letters represent significant differences in the line by the Kruskal-Wallis and Dunn tests ( $p < 0.05$ ). Different capital letters represent significant differences in the column by the Kruskal-Wallis and Dunn tests ( $p < 0.05$ ).

before and after sintering, respectively. Likewise, these values increased significantly with the application of glaze in relation to the control ( $p < 0.001$ ). The best result was obtained when glaze coating was applied after sintering (1.87 MPa;  $p < 0.001$ ), which was lower to lithium disilicate (2.65 MPa;  $p > 0.05$ ). In the 5Y-TZP groups, the sintering moment according to coating application did not influence the results ( $p > 0.05$ ). Both colloidal silica and glaze increased the bond strength compared to the control (0.38 MPa;  $p < 0.001$ ). However, the best results were from the glaze coating (1.48 MPa and 2.51 MPa;  $p < 0.001$ ), which were similar to the lithium disilicate (2.65 MPa;  $p > 0.05$ ). Regarding the different compositions of Y-TZP, there were no significant differences in adhesion between 3Y-TZP and 5Y-TZP in the control groups, colloidal silica groups and sintering/glaze ( $p > 0.5$ ). However, when glaze was applied before sintering, 5Y-TZP (1.48 MPa) showed higher values than 3Y-TZP (0.89 MPa;  $p < 0.05$ ).

## FAILURE ANALYSIS

The cement failure classifications corresponded to the shear bond strength results, with the worst values associated with adhesive failure and the best with mixed failure (Table 5 and Figure 3). The lithium disilicate group demonstrated an adhesive/mixed proportion of failures of 20%/80%, showing no statistical difference with glaze/sintering group (5Y-TZP: 30%/70%) and with groups coated with colloidal silica (3Y-TZP: 70%/30%; 5Y-TZP: 60%/40%) or glaze (3Y-TZP: 10%/90%; 5Y-TZP: 20%/80%) after sintering for all Y-TZP compositions ( $p > 0.05$ ). The worst results observed were the control (100%/0;  $p < 0.001$ ) and colloidal silica/sintering (3Y-TZP: 90%/10%; 5Y-TZP: 80%/20%;  $p < 0.05$ ).

## MICROSCOPY ANALYSIS

SEM analysis of the control specimen (3Y-TZP and 5Y-TZP) shows grainy surface with grain area increasing from  $\sim 0.5$ - $1.8 \text{ mm}^2$  to  $\sim 6 \text{ mm}^2$  with raising Y mol concentration from 3% to

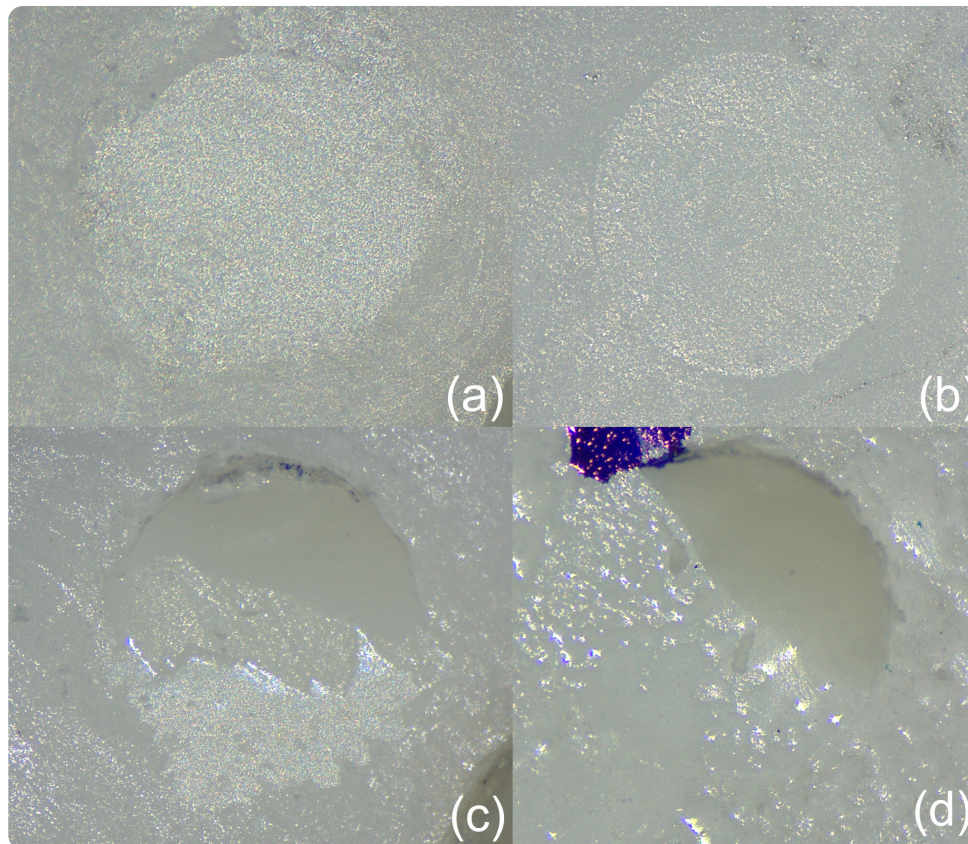
5% mol in TZP, and therefore reflecting the modification in the structural conformation (Figure 4 1a to 2b). Unlike, Y-TZP controls, the lithium disilicate shows a rather smooth surface without grains, which is modified in a rather rough surface by the acid treatment (Figure 4 3a to 3Ac). Figure 5 and 6 display the modification of the surface morphology of 3Y-TZP and 5Y-TZP, respectively, upon coating (silica and glaze) before or after sintering and with or without an acid treatment. Similar aspects were observed between the coating treatments in 3Y-TZP and 5Y-TZP compositions. The coated Y-TZP specimen with both silica and glaze and post-sintered present grainy surface alternated with continuous film (Figure 5-6.1a-3a), whereas a continuous smooth surface (Figure 5-6.2a-4a) is characteristic of Y-TZP pre-sintered before the film deposition. On the one end, the groups that were submitted to coating before Y-TZP sintering and conditioned by acid present extended regions with grainy surface with respect to smooth region. Also, the grains are more round shaped after acid treatment, mainly when sintering is made after silica coating. When sintering is made previously to the coating a smoother surface, covered with silica can be observed. For Glaze, this difference is more clear.

The EDX analysis indicates the surface composition and roughly its elemental quantification. The support Y-TZP should present only O, Zr, and trace of Y varying from 3 to 5%. Other elements appearing in the EDX spectra reflect the composition of the coating and indirectly its thickness. The EDX analysis showed that the groups coated with glaze after Y-TZP sintering presented the highest levels of silicon element (Table 6). The application of a coating treatment before the zirconia sintering reduced the Si content, and therefore the layer thickness. Also, the acid conditioning affected considerably specimens with Colloidal Silica coating in terms of Si composition and apparently did not affect the chemical surface composition of Glaze specimens, within EDX sensitivity.

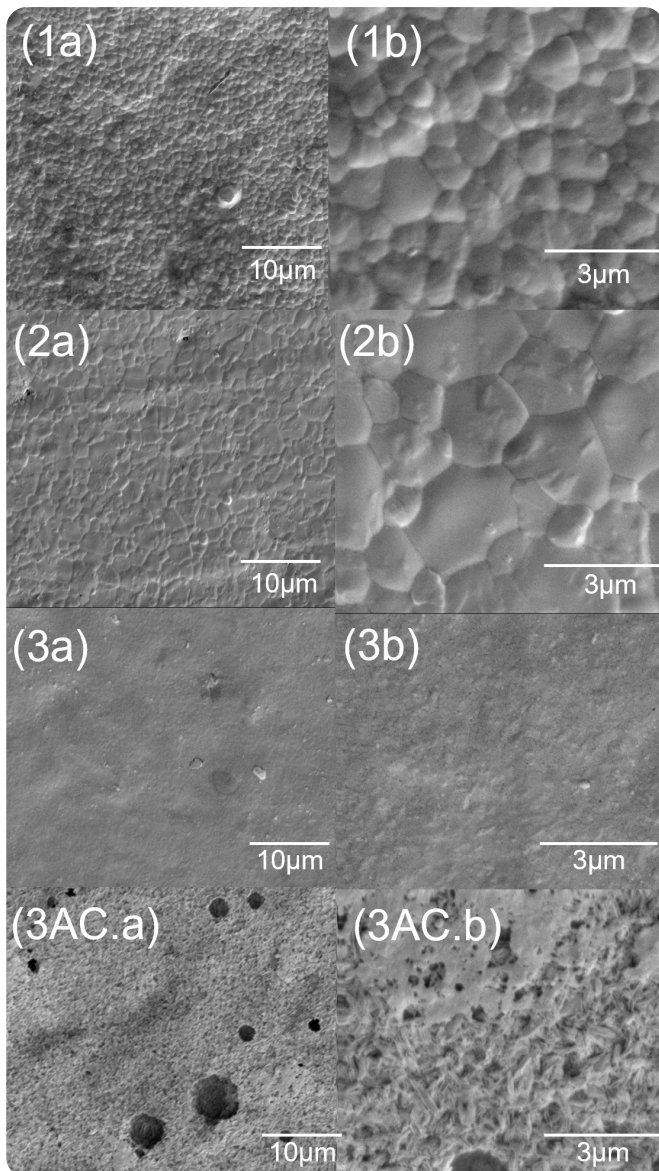
**Table 5.** Failure classifications demonstrated by the groups.

3Y-TZP						
Groups/ Failure Mode	Lithium Disilicate	Control	Colloidal Silica / Sintering	Sintering / Colloidal Silica	Glaze / Sintering	Sintering / Glaze
Adhesive	20% (2)	100% (10)	90% (9)	70% (7)	90% (9)	10% (1)
Mixed	80% (8)	0% (0)	10% (1)	30% (3)	10% (1)	90% (9)
p-value of Fisher's exact test vs LD	-	0.001	0.005	0.070	0.005	1.000
5Y-TZP						
Groups/ Failure Mode	Lithium Disilicate	Control	Colloidal Silica / Sintering	Sintering / Colloidal Silica	Glaze / Sintering	Sintering / Glaze
Adhesive	20% (2)	100% (10)	80% (8)	60% (6)	30% (3)	20% (2)
Mixed	80% (8)	0% (0)	20% (2)	40% (4)	70% (7)	80% (8)
p-value of Fisher's exact test vs LD	-	0.001	0.023	0.170	1.000	1.000

\* LD = Lithium Disilicate.



**Figure 3:** Illustrative images of failure classifications observed. (a) and (b) Adhesive failure. (c) and (d) Mixed failure.



**Figure 4:** Micrographs of control groups of 3Y-TZP (1), 5Y-TZP (2), Lithium Disilicate (3) at 3000x (a) and 15000x (b) the control group (3) and control group after acid conditioning (AC).

To corroborate the EDX and SEM results concerning film behavior under post-sintering and acid conditioning, samples Y3-TZP and Y5-TZP coated with glaze film (G4 and G9) were investigated by HIM microscope. Figure 7 displays HIM images. The samples were characterized by alternating regions with smooth and grainy morphology attributed to the film and substrate, respectively. The glaze film once treated with acid is kept only in the void areas; the effect is more pronounced in the case of Y3-TZP substrate. The finding may suggest a role of the grain size in the film behavior.

## DISCUSSION

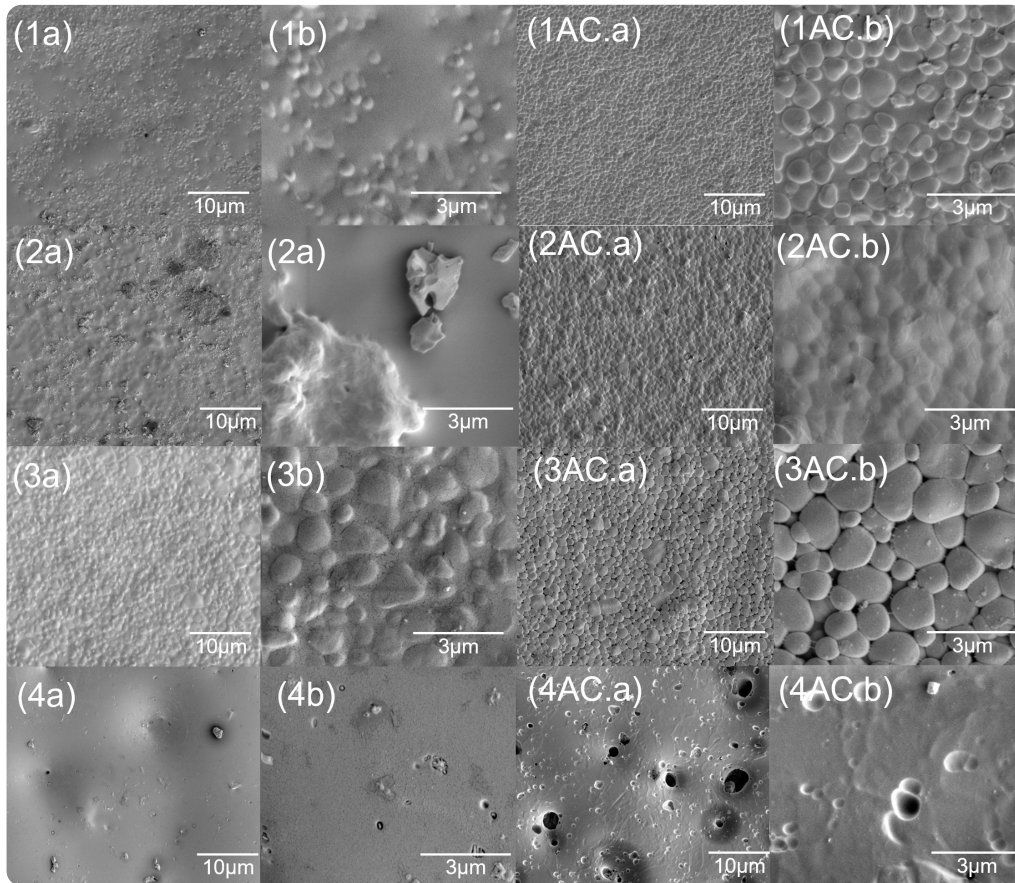
In the present study, the surface modification of Y-TZP by silica incorporation was carried out with the aim to favor the adhesive cementation procedure. However, both null hypotheses tested were rejected because significant differences were found between coating treatments and moments of coating application.

In comparison with lithium disilicate, the application of nanometric silica in colloidal suspension showed unsatisfactory adhesion and intermediates results in 3Y-TZP and 5Y-TZP, respectively. The proposal of using colloidal silica for Y-TZP coating was based on the hypothesis that a modification of the surface chemistry would occur and favor the adhesion. The high temperature achieved during sintering cycles increase the kinetics of the zirconia particles;<sup>20</sup> this was expected to increase atomic diffusion with no significant volatilization of the silica due to the high melting point of this component.<sup>21</sup> After the Y-TZP sintering, a reduction in surface energy and in the population of pores and defects through the surface occur, but atomic diffusion of colloidal silica still could occur through the solid at high temperature during coating sintering.<sup>20</sup> Therefore, in contrast to glaze, colloidal silica acts in atomic levels and does not form a coating layer.<sup>9</sup> The superior result of glaze coating can be attributed to a micromechanical action of the glass-ceramic layer formed, which was incompletely formed by the colloidal silica.<sup>9,20</sup>

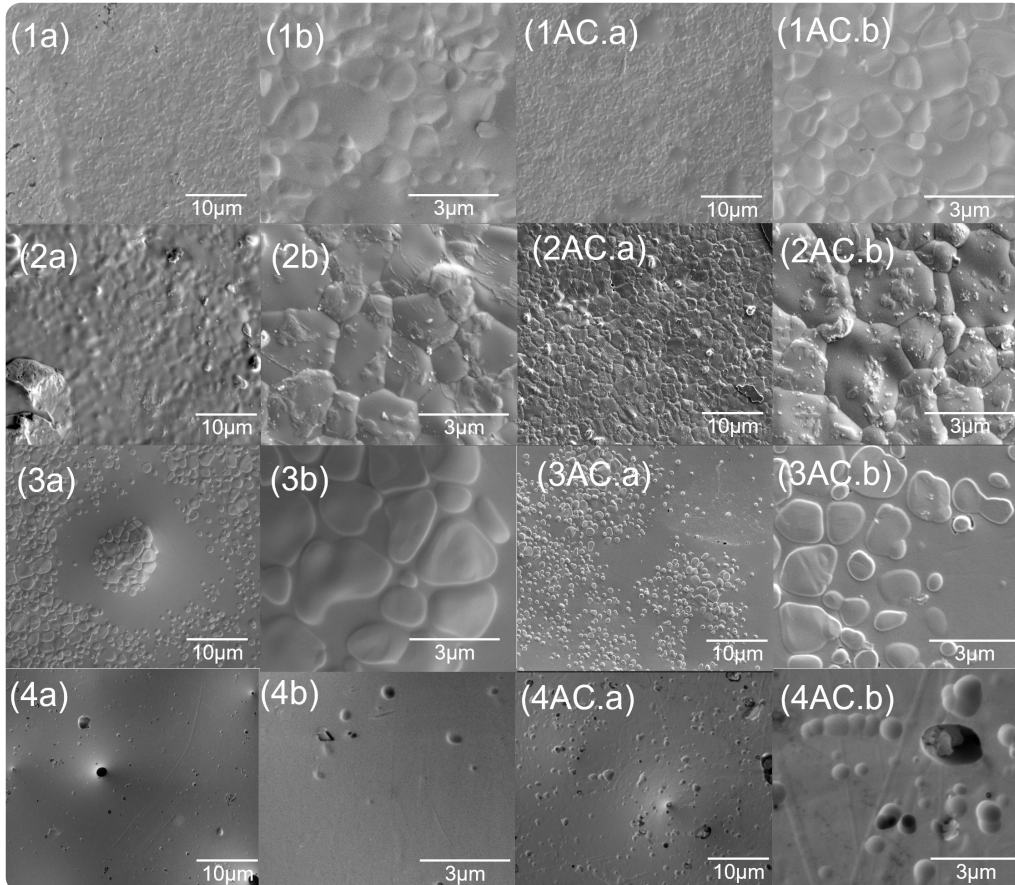
The application of a low melting glaze in Y-TZP surface aims to produce a glass-ceramic layer with micrometric thicknesses (29.1–140 µm), which allows conventional adhesive cementation of zirconia.<sup>9,12</sup> As the glaze has a low melting point compared to zirconia, its application is recommended by manufacturers after Y-TZP sintering (~1500°C) and followed by a new sintering of the ceramics at ~900°C.<sup>2</sup> In this study, the application of glaze after 3Y-TZP sintering allowed excellent results with adhesion values similar to a glass-ceramic restoration. Previous studies also observed favorable adhesion with glaze coating after Y-TZP sintering<sup>4,9,11,12</sup> with comparable results to lithium disilicate.<sup>2,22</sup> However, considerable variations in cementation methodology (e.g., cementation of resin blocks to Y-TZP or bonding Tygon tubes to Y-TZP surfaces for cementation) between studies should be highlighted.<sup>2,23</sup> In the present study, in 5Y-TZP, the application of glaze underscored excellent values similar to lithium disilicate irrespective of the sintering moment.

Regarding the results between the controls of the different Y-TZP compositions, similar results were demonstrated ( $p > 0.05$ ). Under similar cementation conditions, the translucent Y-TZPs perform similarly to the traditional 3Y-TZP in terms of adhesion.<sup>6,24–26</sup> This finding agrees with the previous literature.<sup>6,24–26</sup>

Moreover, there was no significant difference in the bonding strength comparing 3Y-TZP and 5Y-TZP when the coating was performed after the zirconia sintering. This can be attributed to the low adhesion between this layer and the ceramics. However, when glaze coating was applied to the ceramics before sintering, 5Y-TZP shear result was significantly higher than 3Y-TZP, indicating that the glaze film was preserved and presented good adhesion to both the ceramics and the cement. Furthermore, the application of glaze can be performed before sintering for optimization of clinical steps in 5Y-TZP. The explanation for this difference in Y-TZP compositions may



**Figure 5:** Micrographs of 3Y-TZP groups at 3000x (a) and 15000x (b) in regions submitted or not to acid conditioning (AC.). Colloidal Silica / Sintering (1), Sintering / Colloidal Silica (2), Glaze / Sintering (3), Sintering / Glaze (4).

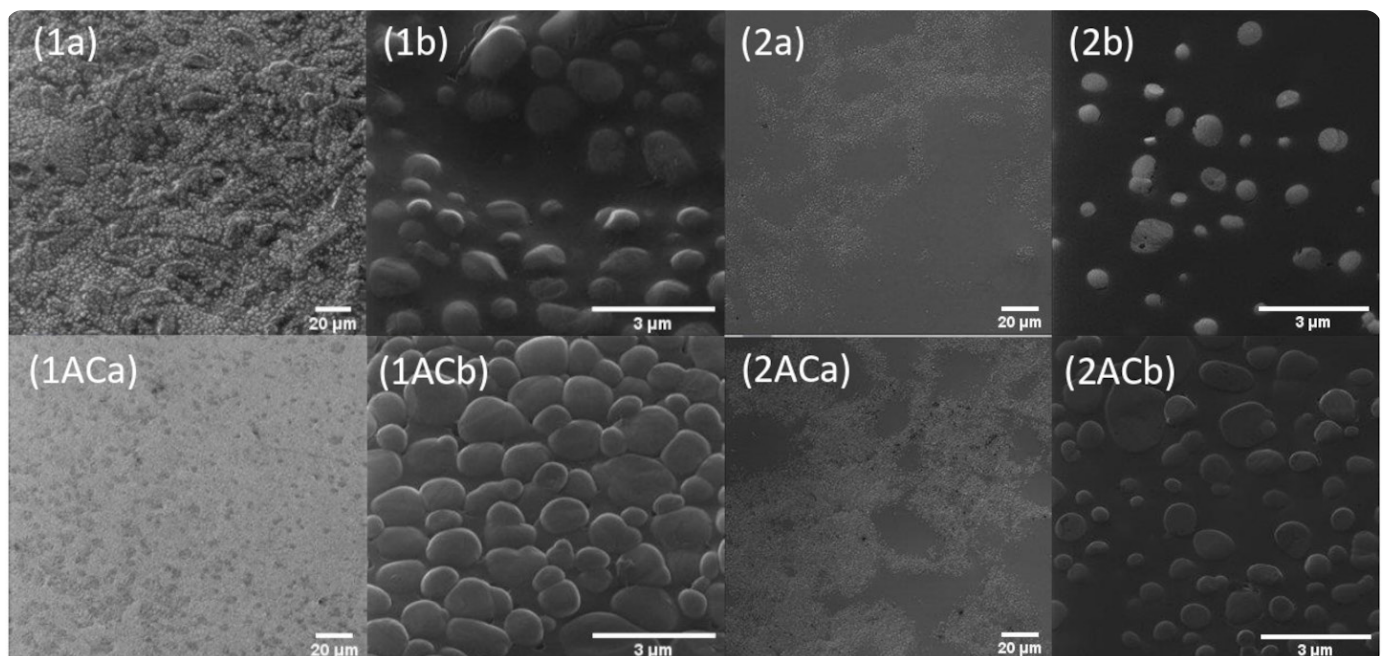


**Figure 6:** Micrographs of 5Y-TZP groups at 3000x (a) and 15000x (b) in regions submitted or not to acid conditioning (AC.). Colloidal Silica / Sintering (1), Sintering / Colloidal Silica (2), Glaze / Sintering (3), Sintering / Glaze (4).

**Table 6.** Quantitative results [Mean of Weight (%)] of elements obtained by groups in Energy-Dispersive X-ray Spectroscopy (EDX):

	Not Conditioned										Acid Conditioned								
	O	Y	Na	Al	Si	K	Ca	Cl	Zr		O	Y	Na	Al	Si	K	Ca	Cl	Zr
3Y-TZP	G1	31	6	-	-	-	-	-	-	63					X				
	G2	46	-	3	-	5	-	-	-	46	40	-	-	-	1	-	-	-	60
	G3	42	-	3	-	10	-	-	-	45	37	-	-	-	5	-	-	-	57
	G4	41	-	-	-	6	-	-	-	52	41	-	-	-	4	-	-	-	55
	G5	55	-	5	3	33	-	-	-	4	48	-	5	3	34	-	-	-	9
5Y-TZP	G6	41	10	-	-	-	-	-	-	49					X				
	G7	53	-	-	-	5	-	-	-	41	54	-	-	-	5	-	-	-	40
	G8	41	-	-	-	14	-	-	-	44	32	-	-	-	3	-	-	-	65
	G9	53	-	2	-	22	-	-	-	20	46	-	-	3	22	-	-	-	26
	G10	52	-	5	3	33	3	3	-	-	51	-	4	3	31	3	3	-	3
LD	56	-	-	2	34	3	-	-	4	57	-	-	2	35	3	-	-	3	

\* LD: Lithium disilicate. -: element detection below 1%. X: The zirconia control groups were not submitted to acid conditioning with 9% hydrofluoric acid gel.



**Figure 7:** Micrographs of HIM microscope of 3Y-TZP (1) and 5Y-TZP (2) specimen in regions submitted or not to acid conditioning (AC) for Glaze / Sintering.

lie in the grain structure present in its pre-sintered state, or in the difference in the diffusion coefficient resulting from the compositional differences. The pattern in 5Y-TZP may have al-

lowed a deeper absorption of glaze components in the grain boundaries presented in the pre-sintered ceramic compared to the 3Y-TZP ceramics.

The groups with low values on shear bond strength analysis – which were overall represented by controls, colloidal silica and coating before Y-TZP sintering – resulted in a higher majority of specimens with adhesive failures and reduced number of specimens with mixed failure after test. This indicates that adhesion to Y-TZP surface was the main cause of failure. In contrast, the groups Lithium Disilicate, “Sintering / Glaze” and “Glaze / Sintering” of 5Y-TZP, which showed the highest values on shear strength analysis, were mainly associated with mixed failure. In a mixed type of failure, adhesive and cohesive failure take place simultaneously, thus showing that the adhesion to the ceramics was higher than the structural strength of resin cement in some regions.<sup>15,18</sup>

The present study adds new information regarding bonding to vitrified surface of Y-TZP of different compositions, but it still presents some limitations that should be indicated. As in all *in vitro* methodologies, it is not possible to simulate all clinical oral conditions such as the presence of saliva humidity and technical issues. Also, human teeth were not used to simulate the impact on dentin surface. Therefore, results should be interpreted with caution considering that testing was performed in controlled environment. Moreover, although efforts were made for microscopy analyses – by the adequate preparation of specimens and by the previous observation of the entire area of specimens to select representative regions –, a misinterpretation of results is possible.

## CONCLUSIONS

Based on the findings of this study, the coating of Y-TZP with industrial nanometric silica in colloidal suspension present unsatisfactory results. In 3Y-TZP, the surface treatment associated with the best adhesion values was the application of glaze after zirconia sintering. However, in 5Y-TZP, glaze coating showed the best results irrespective of the sintering moment. Therefore, in 5Y-TZP, glaze application can be performed before or after zirconia sintering to optimize clinical steps.

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## REFERENCES

- Aljomard, Y.R.M., Altunok, E.Ç. and Kara, H.B. Enamel wear against monolithic zirconia restorations: A meta-analysis and systematic review of *in vitro* studies. *J. Esthet. Restor. Dent.* 2021; **34**:473-489.
- Maroun, E.V., Guimarães, J.G.A., de Miranda, W.G., Netto, L.R.C., Elias, A.B. and da Silva, E.M. Bond strength stability of self-adhesive resin cement to etched vitrified yttria-stabilized tetragonal zirconia polycrystal ceramic after thermomechanical cycling. *Oper. Dent.* 2019; **44**:545-555.
- Miragaya, L.M., Guimarães, R.B., Souza R.O.A., Botelho, G., Guimarães J.G.A. and da Silva, E.M. Effect of intra-oral aging on t→m phase transformation, microstructure, and mechanical properties of Y-TZP dental ceramics. *J. Mech. Behav. Biomed. Mater.* 2017; **72**:14-21.
- Van Vuuren, W.A.J., Wong, P., Al-Amleh, B., Lyons, K.M., Li, K.C. and Waddell, J.N. Effect of a glaze layer on adhesion energy between resin cements to zirconia ceramic. *Int. J. Adhes.* 2018; **84**: 451-456.
- Della Bona, A. and Kelly, J.R. The Clinical Success Of All-Ceramic Restorations. *J. Am. Dent. Assoc.* 2008; **139**:S8-13.
- Chen, B., Yan, Y., Xie, H., Meng, H., Zhang, H. and Chen, C. Effects of Tribochemical Silica Coating and Alumina-Particle Air Abrasion on 3Y-TZP and 5Y-TZP: Evaluation of surface hardness, roughness, bonding, and phase transformation. *J. Adhes. Dent.* 2020; **22**:373-382.
- Shelar, P., Butler, S. and Abdolvand, H. On the behaviour of zirconia-based dental materials: A review. *J. Mech. Behav. Biomed. Mater.* 2021; **124**:104861.
- Sheth, J., Jensen, M. and Tolliver, D. Effect of surface treatment on etched porcelain bond strength to enamel. *Dent. Mat.* 1988; **4**:328-337.
- Everson, P., Addison, O., Palin, W.M. and Burke, F. Improved bonding of zirconia substructures to resin using a “glaze-on” technique. *J Dent.* 2012; **40**:347-351.
- Murakami, T., Takemoto, S., Nishiyama, N. and Aida, M. Zirconia surface modification by a novel zirconia bonding system and its adhesion mechanism. *Dent Mater.* 2017; **33**:1371-1380.
- Wandscher, V.F., Prochnow, C., Rippe, M.P., Dorneles, L.S., Callegari, G.L., Baldissara, P., et al. Retentive strength of Y-TZP crowns: comparison of different silica coating methods on the intaglio surfaces. *Oper. Dent.* 2017; **42**:E121-133.
- Ntala, P., Chen, X., Niggli, J. and Cattell, M. Development and testing of multi-phase glazes for adhesive bonding to zirconia substrates. *J Dent.* 2010; **38**:773-781.
- Moezzizadeh, M., Nojehdian, H. and Haghi, H.V. Effect of bioglass and silica coating of zirconia substrate on its bond strength to resin cement. *Dent. Mater. J.* 2017; **36**:54-62.
- Rigolin, F.J., Negreiros, W.M., Giannini, M. and Barbosa, C.M.R. Effects of sandblasting and hydrofluoric acid etching on surface topography, flexural strength, modulus and bond strength of composite cement to ceramics. *J. Adhes. Dent.* 2021; **23**:113-119.
- da Silva, E.M., Miragaya, L., Sabrosa, C.E. and Maia, L.C. Stability of the bond between two resin cements and an yttria-stabilized zirconia ceramic after six months of aging in water. *J. Prosthet. Dent.* 2014; **112**:568-575.
- Park, C., Yoo, S.H., Park, S.W., Yun, K.D., Ji, M.K., Shin, J.H., et al. The effect of plasma on shear bond strength between resin cement and colored zirconia. *J. Adv. Prosthodont.* 2017; **9**:118-123.
- Lima, T.F.R., Ascendino, J.F., Cavalcante, I.D.O., D’Assunção, F.L.C., Salazar-Silva, J.R., da Silva, E.J.N.L., et al. Influence of chlorhexidine and zinc oxide in calcium hydroxide pastes on pH changes in external root surface. *Braz. Oral. Res.* 2019; **33**:e005.
- Omidi, B.R., Yeganeh, P.K., Oveisi, S., Farahmandpour, N. and Nouri, F. Comparison of micro-shear bond strength of resin cement to zirconia with different surface treatments using universal adhesive and zirconia primer. *J. Lasers. Med. Sci.* 2018; **9**:200-206.

19. Butler, S., Linke, B. and Torrealba, Y. Effect of MDP-based primers on the luting agent bond to Y-TZP ceramic and to dentin. *Biomed. Res. Int.* 2018; **2018**:2438145.
20. German, R.M. *Sintering: From empirical observations to scientific principles*, 1st edn. Pittsburgh: Elsevier Inc. 2014; 1-536.
21. Allendorf, M.D. and Spear, K.E. Thermodynamic Analysis of Silica Refractory Corrosion in Glass-Melting Furnaces. *J. Electrochem. Soc.* 2001; **148**:B59.
22. Woo, E.S., Goldstein, G., Choi, M. and Bromage, T.G. *In vitro* shear bond strength of 2 resin cements to zirconia and lithium disilicate: An *in vitro* study. *J. Prosthet. Dent.* 2021; **125**:529-534.
23. Go, E.J., Shin, Y. and Park, J.W. Evaluation of the Microshear Bond Strength of MDP-containing and Non-MDP-containing Self-adhesive Resin Cement on Zirconia Restoration. *Oper. Dent.* 2019; **44**:379-385.
24. Kwon, S.J., Lawson, N.C., McLaren, E.E., Nejat, A.H. and Burgess, J.O. Comparison of the mechanical properties of translucent zirconia and lithium disilicate. *J. Prosthet. Dent.* 2018; **120**:132-137.
25. Russo, D.S., Cinelli, F., Sarti, C. and Giachetti, L. Adhesion to Zirconia: A Systematic Review of Current Conditioning Methods and Bonding Materials. *Dent. J. (Basel)*. 2019; **7**:74.
26. Serichetaphongse, P., Chitsutheesiri, S. and Chengprapakorn, W. Comparison of the shear bond strength of composite resins with zirconia and titanium using different resin cements. *J. Prosthodont. Res.* 2022; **66**:109-116.