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## Effect of cleaning protocol on silica deposition and silica-mediated bonding to Y-TZP

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### ABSTRACT

**Objectives.** To evaluate the effect of cleaning methods on the deposition of silica on yttria-stabilized zirconium dioxide (Y-TZP) surface and on the silane-silica mediated bond strength between Y-TZP and resin cement.

**Methods.** Y-TZP slabs were air-abraded with 30 μm silica-coated alumina particles and distributed in three groups: no cleaning, cleaning with a stream of oil-free air/water spray for 5 s and cleaning with an ultrasonic bath in water for 10 min. The distribution of Si on the Y-TZP surfaces was recorded using energy dispersive spectroscopy (EDS). After the treatment was applied, Y-TZP slabs (n = 20) received a primer application and resin cement cylinders were built on the surface. After storage (24 h) in water storage or 3 months plus thermo-cycling; n = 10), microshear bond strength test (μSBS) was performed. X-ray Photoelectron Spectroscopy (XPS) characterized the chemical bonds between the silica layer and the silane-containing primer. Data were analyzed using ANOVA and Tukey test, as well as Weibull analysis (α = 0.05).

**Results.** Cleaning method had a significant effect on the amount of Si deposited on zirconia surface (p < 0.001) and, consequently, on bond strength (p < 0.001). Storage/aging also had a significant effect on bond strength (p < 0.001). Low values of Weibull moduli for bond strength were observed for all groups after aging. XPS showed silane-silica chemical interaction for all groups.

**Significance.** The silica deposited by tribochemical coating to Y-TZP was removed by the cleaning methods evaluated, compromising bond strength. Stability of the bonding is also a concern when no cleaning method is applied.

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## 1. Introduction

The increasing demand for all-ceramic restorations has prompted the development of ceramic materials with optimized esthetic and mechanical properties [1,2]. In this context, yttria-stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP) is a promising material because of its high mechanical properties, chemical stability, biocompatibility, and esthetic whitish color. Y-TZP offers a large variety of clinical applications such as frameworks or monolithic restorations for fixed dental prostheses (FDP) and single crowns, implants, inlays, onlays and bridges [3,4]. However, achieving a suitable resin-zirconia bonding between Y-TZP and the underlying tooth structure is challenging because of the chemical composition, high density and lack of porosity of Y-TZP. Two systematic reviews showed that loss of retention is significantly higher for densely sintered zirconia, compared with all others types of ceramics and metal-ceramics, for both single and multiple crowns [5,6]. Y-TZP consists of 0.2–0.5  $\mu\text{m}$  diameter equiaxed grains of  $\text{ZrO}_2$  embedded in 1.75–3.5 mol% (3.5–8.7 wt%) of  $\text{Y}_2\text{O}_3$  [7]. As a result, this ceramic cannot be bonded using hydrofluoric acid etching and silanization, thus requiring alternative techniques to obtain a strong and stable resin bond to zirconia [8,9].

Tribochemical silica-coating has been advocated as a reliable technique to improve the bond strength between Y-TZP and the underlying tooth structure [10–14]. This technique involves blasting the Y-TZP surface with 30  $\mu\text{m}$  silica-embedded alumina particles. During the blasting, high temperatures are produced by the energy of impact (triboplasma), resulting in a silica-rich surface able to be tribochemically anchored. Tribochemistry means the creation of a chemical reaction between substrate and deposited layer by the use of mechanical energy [15–17]. A chemical bonding is promoted by silanization of the silica-deposited zirconia surface, when a covalent bond is formed between the alkoxy groups of the silanol unit  $(\text{RO})_3\text{Si}$  group and the reactive silica layer.

Several studies have demonstrated higher initial bond strength between zirconia and resin cement after tribochemical coating in comparison to alumina blasting [18,19]. This may be due to the micro-interlocking promoted in addition to the silane-silica chemical adhesion [9,19]. In contrast, the long-term effectiveness of the tribochemical silica coating is questionable due to significant decreases in the silane-silica mediated bond strength to zirconia after aging [9,19–22]. The decrease in bond strength has been argued to be related to the instability of silanized surfaces in contact with moisture [9,19]. There is also a clear lack of clinical studies presenting any positive effect of silica-mediated bonding on the stability of zirconia-based restorations [22].

Another possible reason for the discrepancy of the bond strength results reported in the literature is the lack of a procedural guideline. The cleaning of the inner surface of blasted zirconia restorations is generally recommended to remove dust and any residual blasting agent [23–25]. Clinicians conventionally employ an oil-free air stream or air/water spray for the removal of loose particles, as recommended by some manufacturers [26,27]. However, the effect of the cleaning

**Table 1 – Experimental groups and cleaning methods used.**

Group (label)	Cleaning method
NC	(1) 30 $\mu\text{m}$ silica-coated alumina particles were blasted on the surface.
AW	(1) 30 $\mu\text{m}$ silica-coated alumina particles were blasted on the surface; (2) Surface was cleaned with as oil-free air/water spray for 5 s at a 10 mm distance
UB	(1) 30 $\mu\text{m}$ silica-coated alumina particles were blasted on the surface; (2) Surface was cleaned by placing each sample in distilled water in a ultrasonic bath for 10 minutes followed by a stream of oil-free air spray for 10 seconds at a 10 mm distance.

method on the bonding durability after tribochemical silica coating is not known. The use of ultrasonic cleaning, for example, another method conventionally used in prosthetic and research laboratories, has been demonstrated to significantly compromise the shear bond strength between zirconia and resin cement [19].

Therefore, the objectives of this study were: to evaluate the effect of cleaning methods on silica distribution on Y-TZP surface after tribochemical silica coating; to evaluate the effect of different cleaning methods and aging on the silane-silica mediated bond strength between Y-TZP and resin cement. The chemical interaction between the silica coverage of the blasted-zirconia and a silane primer was also characterized through X-ray photoelectron spectroscopy (XPS) after the different cleaning methods. The following null hypotheses were tested: (1) cleaning procedure has no effect on element distribution (silica - Si) on the silica-coated Y-TZP surface; (2) cleaning procedure and aging have no effect on bond strength between Y-TZP and resin cement.

## 2. Materials and methods

Yttria-stabilized zirconium dioxide (Y-TZP - Lava Plus, 3M-ESPE) slabs measuring 10 mm  $\times$  6 mm  $\times$  2 mm were milled from CAD/CAM blocks on an E4D Dentist System (D4D technologies, LLC, Richardson, TX, USA) using a custom-mill file. The fully-sintered zirconia slabs were ultrasonically cleaned in acetone for 10 min, followed by thorough drying with compressed air. One surface of each specimen was air-abraded with 30  $\mu\text{m}$  silica-coated alumina particles (CoJet Sand<sup>TM</sup>, 3M-ESPE, Seefeld, Germany). Then, the slabs were randomly distributed in three groups according to the following methods: no cleaning (NC — control), cleaning with a stream of oil-free air/water spray for 5 s (AW) and cleaning with an ultrasonic bath in water for 10 min (UB). Details of the treatments applied are provided in Table 1.

### 2.1. Energy dispersive X-Ray spectroscopy analysis

Samples from each cleaning method (NC, AW, and UB; n=5) were sputter-coated with carbon (Desk II, Denton, Vacuum, Moorestown, NJ, USA) and the entire surface, displayed at 500 X magnification, was analyzed using Energy Dispersive

**Table 2 – Manufacturer, batch number and composition of materials used.**

Material	Manufacture/Batch number	Composition
RelyX ceramic primer	3M ESPE-Saint Paul, Minnesota, USA/N843209	3-trimethoxysilylpropyl methacrylate (MPS), Ethanol, Water
RelyX ultimate	3M ESPE-Saint Paul, Minnesota, USA/N651485	Base paste: methacrylate monomers, radiopaque silanated fillers, initiator, stabilizer, rheological additives Catalyst paste: methacrylate monomers, radiopaque alkaline (basic) fillers, initiator, stabilizer, pigments, rheological additives, a fluorescence dye, dark cure activator.

X-ray Spectroscopy (EDS — Vantage Digital Microanalysis, Noran equipments, Middleton, WI, USA) in conjunction with a scanning electron microscope (SEM-JSM 5600 LV; JEOL, Tokyo, Japan). Then, “Si/Zr” ratio was calculated for each specimen for the average semi-quantification of element distribution for each experimental group. The semi-quantification of Si (%) was calibrated using a 0% Si standard.

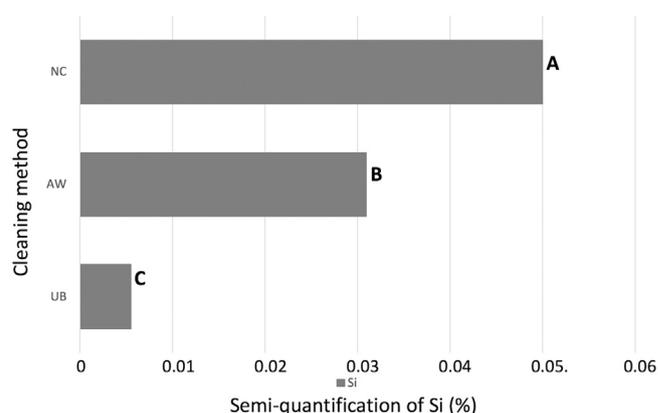
The powder used for the tribochemical coating (CoJet Sand™, 3M-ESPE, Seefeld, Germany) was also characterized by EDS (X-Max, Oxford Instruments, United Kingdom) and SEM (JSM-6610LV, JEOL, Tokyo, Japan) to verify composition and size/shape of the particles. For this purpose, an adhesive carbon tape-covered stub was placed in contact with the powder to collect some particles. The particles were sputter-coated with gold, and EDS was performed.

## 2.2. Microshear testing

For the bonding procedures, Y-TZP slabs tribochemically silica coated and cleaned according to the experimental group (NC, AW or UB; n = 20) were used. A ceramic primer (RelyX Ceramic Primer, 3M ESPE-Saint Paul, Minnesota) was applied on the zirconia surface in one coat with microbrush, left undisturbed for 60 s and gently air-dried for 5 s.

The microshear specimens were built on the Y-TZP surface by positioning and stabilizing a silicone mold (Express™ Impression Material, 3M ESPE-Saint Paul, Minnesota, USA; 1 ± 0.1 mm diameter × 1 ± 0.1 mm height) on the surface, and filling it with resin-based cement (RelyX Unicem, 3M ESPE-Saint Paul, Minnesota). The resin cement was light-cured using a polywave light emitting diode curing unit (Bluephase, Ivoclar Vivadent; Schaan, Liechtenstein) with a mean irradiance of 1100 mW/cm<sup>2</sup> for 40 s from the top of the silicon mold. Two resin cement cylinders were built on each zirconia slab and the silicone molds were removed after 5 min. The 20 slabs from each group were randomly distributed into two aging condition: 24-hs or 3 months plus thermocycling (5°–55 °C/3 m + TC) for 10,000 cycles (MSCT-1, Sao Carlos, SP, Brazil). The specimens were stored in 100% relative humidity at 37 °C. Table 2 shows the composition of the materials used in this study.

After the storage period, the specimens were placed in an universal testing machine (model 4411; Instron, Canton, MA, USA). A shear load was applied at the interface between the resin cement cylinder and the zirconia surface with a thin wire (0.20 mm diameter) at a crosshead speed of 0.5 mm/min until failure occurred. The microshear bond strength ( $\mu$ SBS) value for each resin cement cylinder was calculated based on the load at fracture and the adhesive interface dimensions.



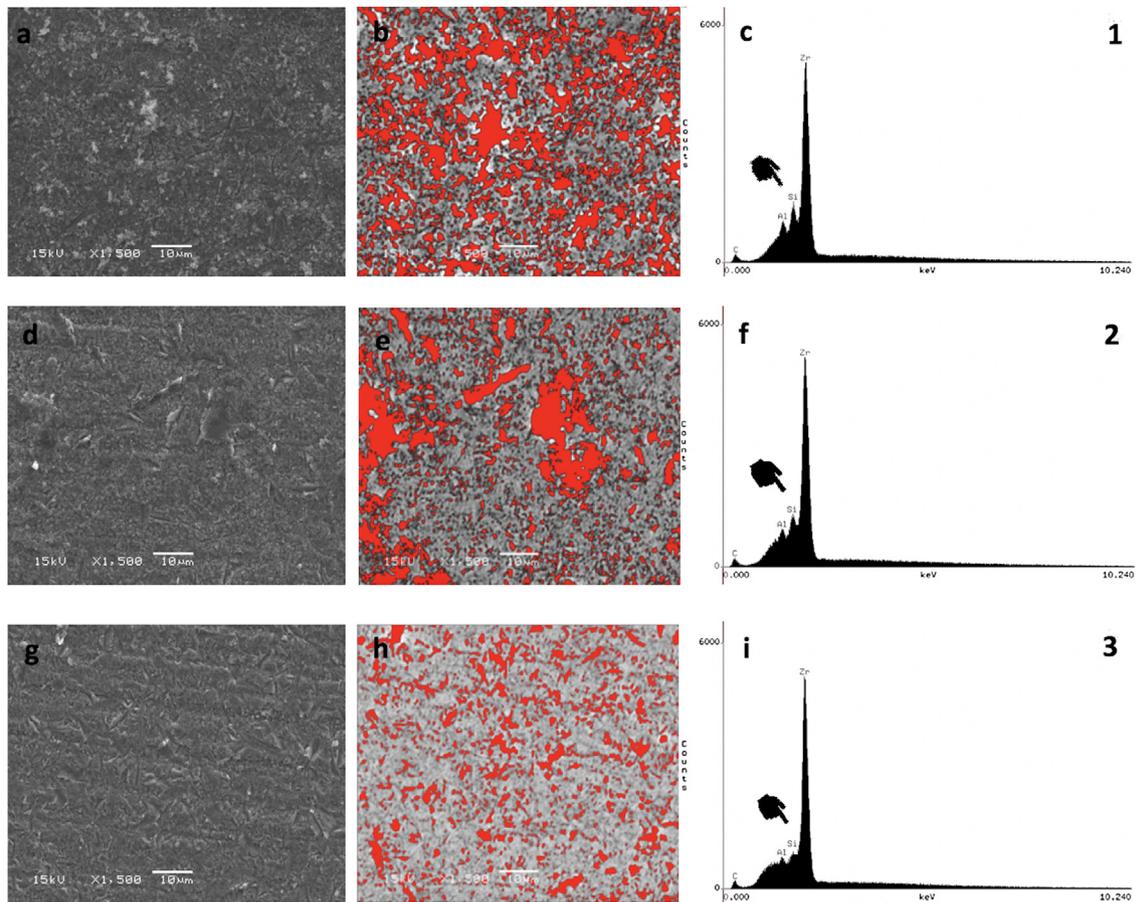
**Fig. 1 – Graph representing the semi-quantification of Si (%) on the tribochemically-treated Y-TZP surface after cleaning with different methods (UB = ultrasonic bath; AW = air/water spray; NC = no cleaning). Dissimilar uppercase show significant differences for Si amount between cleaning methods ( $p < 0.05$ ).**

## 2.3. X-ray photoelectron spectroscopy (XPS) analysis

In order to characterize the chemical bonds between the silane primer and the silica-coated zirconia, two regions on the silicized/silanized Y-TZP surface after each cleaning procedure were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha, Thermo Fisher Scientific, East Grinstead, England). The experimental conditions were as follows: monochromatic Al-K $\alpha$  radiation source (1486.6 eV), X-ray beam diameter (400  $\mu$ m). High-resolution spectra were acquired using a pass energy of 50 eV and a step size of 0.01 eV. Survey spectra were collected with a pass energy of 200 eV and a step size of 1 eV. The power range was 0–1300 eV.

## 2.4. Statistical analysis

Data normality was assessed using the Shapiro–Wilk test. The effect of cleaning protocol on Si distribution was analyzed using one-way Analysis of Variance (ANOVA) and post hoc Tukey test (SPSS 20, SPSS Inc., Chicago, IL, USA). The effect of cleaning protocol, aging method and the interaction between them on  $\mu$ SBS values was analyzed using two-way ANOVA and post hoc Tukey test (SPSS 20, SPSS Inc., Chicago, IL, USA). An average bond strength value was calculated for each sample (n = 10) based on the two resin cement micro-shear cylinders built on each sample’s surface. The overall statistical significance was pre-set at 5%. Additionally, the reliability of the



**Fig. 2** – Representative SEM images and EDS analysis of tribochemically-coated Y-TZP after different cleaning methods: (a) Secondary and (b) atomic number contrast backscattered electron images showing a uniform silica coverage (c) observed on control (NC) sample (finger point); (d) Secondary and (e) atomic number contrast backscattered electron images of Y-TZP surface after AW cleaning, showing a lower amount of silica (f) on the ceramic surface (finger point); (g) Secondary and (h) atomic number contrast backscattered electron images of Y-TZP surface after UB cleaning, revealing a scatter amount (i) of silica (finger point).

bond strength after each cleaning treatment was analyzed by Weibull analysis. The Weibull moduli (shape parameter) (slope of the line relating applied stress and the probability of specimen failure,  $m$ ) were calculated, applying maximum likelihood estimation. The 95% upper and lower confidence intervals were calculated using the likelihood ratio (MINITAB 17.0, State College, Pennsylvania, USA). Differences between the paired values for  $m$  were considered significant when the 95% confidence intervals did not overlap.

### 3. Results

#### 3.1. Energy dispersive X-Ray spectroscopy analysis (EDS)

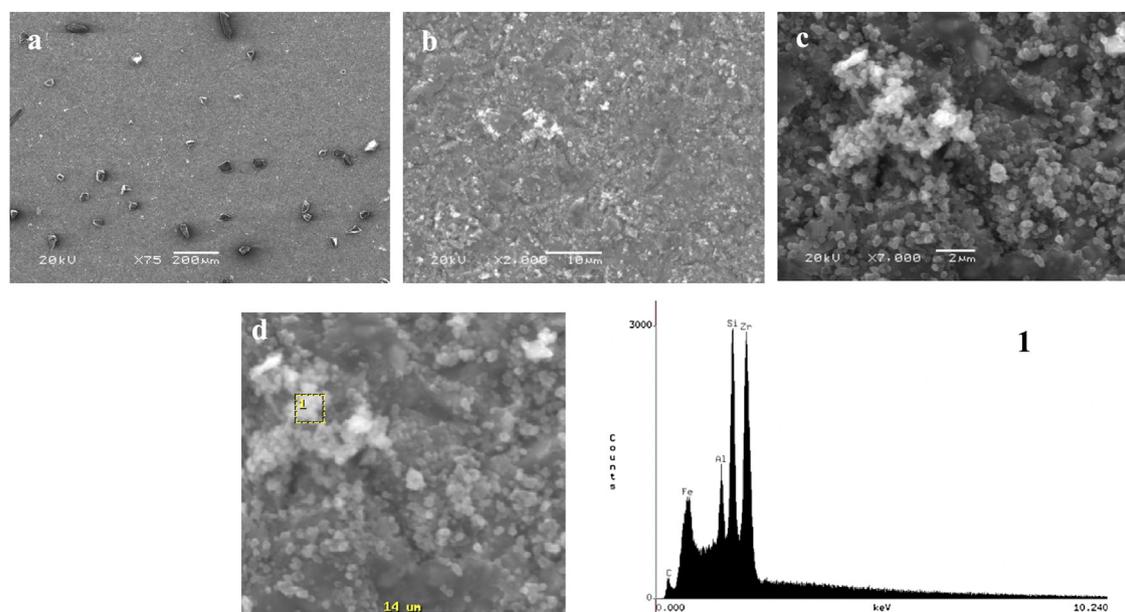
Fig. 1 shows the semi-quantification of silicon (Si) (%) by EDS analysis. Cleaning method significantly affected the amount of Si on the tribochemically coated zirconia surface ( $p < 0.001$ ). The lowest amount of Si (%) was observed when the zirconia surface was cleaned by an ultrasonic bath in distilled water for 10 min.

In accordance with the EDS analysis, SEM images indicated higher amounts of Si in the control Y-TZP surface as opposed to surfaces cleaned either with air/water or ultrasonic bath (Fig. 2). After air/water spray and ultrasonic bath cleaning, it is possible to observe the presence of exposed grooves irregularly distributed throughout the surface.

Fig. 3 shows SEM images of control Y-TZP under different magnifications. A uniform silica coverage in the micrometer range can be observed when no cleaning was applied (Fig. 3a and b). Under higher magnification ( $\times 7000$ ) sub-micron particles seem to be deposited on the surface mixed with some alumina content (Fig. 3c), which is confirmed by EDS analysis (Fig. 3d). SEM characterization of the powder used (Cojet™ sand) revealed a combination of spherical Si particles in the micrometer range (around  $30 \mu\text{m}$ ) and alumina particles covered with a sand of Si in the sub-micron range (Fig. 4).

#### 3.2. Microshear bond strength testing

“Cleaning method” ( $p < 0.001$ ) and “aging” ( $p < 0.001$ ) were significant for bond strength values. However, the interaction between these factors was not significant ( $p = 0.233$ ). The



**Fig. 3 – SEM micrographs of the no cleaning (control) Y-TZP surface: (a) showing the distribution of CoJet™ particles on the ceramic surface; (b) uniform coverage of the surface with a smear of silica; and (c) Higher magnifications of showing silica and alumina deposition — yellow square was analyzed by EDS; (d) EDS analysis of the Y-TZP surface with no cleaning showing high concentration of silica and alumina throughout the surface (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).**

results of  $\mu$ SBS values are shown in Fig. 5. The lowest  $\mu$ SBS values were presented by specimens cleaned with air/water spray, which was significantly lower than the control group (no cleaning), but similar to the ultrasonic bath group at both storage times.

Regarding the Weibull moduli ( $m$ ), for NC and AW groups, a decrease in  $m$  values was observed after 3 months- storage in water and 10,000 thermocycles (Table 3 and Fig. 6). No change in the Weibull parameter was noted for UB samples.

### 3.3. X-ray photoelectron spectroscopy (XPS) analysis

Fig. 7 shows the survey XPS spectra of the zirconia surfaces cleaned with different methods: no cleaning (NC) (7a), air/water spray (7b) and ultrasonic bath (7c) followed by silane application. Furthermore, the detailed XPS spectra of Si 2p are demonstrated.

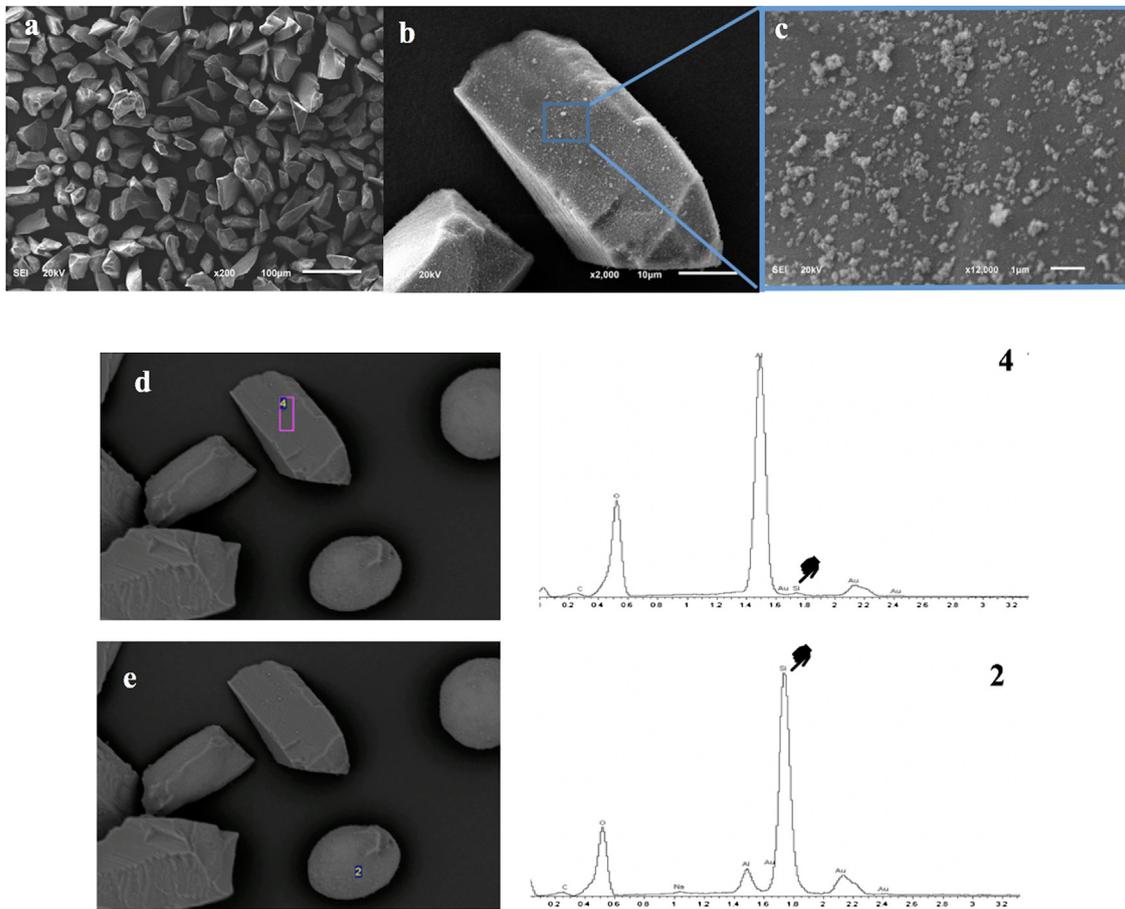
The survey XPS spectra show that the elemental composition of the Y-TZP surface changed after silicization followed by different cleaning methods and silanization process (Fig. 7). In the survey XPS spectra, the Si 2p peaks detected on the zirconia surface were split into three peaks:  $101.8 \pm 0.1$  eV,  $102.2 \pm 0.2$  eV and  $103.4 \pm 0.6$  eV. The presence and relative area of these peaks were dependent on the cleaning method applied and the region analyzed on the surface. Table 4 demonstrates Si 2p peak at  $102.2 \pm 0.2$  eV and  $103.4 \pm 0.6$  eV in region 1 for the no cleaning and air/water spray group. For the UB cleaned samples, two peaks were identified:  $101.8 \pm 0.1$  eV,  $102.2 \pm 0.2$  eV. On the other hand, for region 2, the no cleaning and air/water spray group presented only one peak with

binding energy of  $102.2 \pm 0.2$  eV and  $103.4 \pm 0.6$  eV, respectively.

## 4. Discussion

The cleaning of alumina-blasted zirconia-based restorations is recommended to improve bond strength and durability of the bonding, since loose alumina particles may interfere with the bonding between zirconia and resin-bonding treatment [9,24,25]. However, the effectiveness of the tribochemical grit blasting after cleaning has been questioned because the coating particles are weakly deposited on the zirconia surface [19,25] and may be easily removed. In the current study, two types of cleaning methods were evaluated: air/water spray for 5 s and ultrasonic bath in distilled water for 10 min. According to the results of this study, cleaning with either ultrasonic bath or air/water spray resulted in a significant decrease on Si deposition in comparison to the no-cleaning (control) samples (Fig. 1). Therefore, the first null hypothesis of this study was rejected. Fig. 2 provides further evidence of the distribution of Si on Y-TZP surface after the various cleaning methods.

The silica deposited on the zirconia surface was further characterized by SEM micrographs (Fig. 3). In the lower magnification ( $450\times$ ) (Fig. 3a), silica-coated alumina microparticles in the range of  $35 \mu\text{m}$  to  $100 \mu\text{m}$  can be identified in the form of a “dust” on the Y-TZP surface. Silica-alumina particles in the submicron range ( $0.2\text{--}1 \mu\text{m}$ ) are also observed under higher magnifications ( $2000\times$  and  $7000\times$ , Fig. 3b and 3c respectively). These findings can be confirmed by SEM and EDS analysis of the CoJet™ powder (Fig. 4). Fig. 4. (a, b and c) revealed a

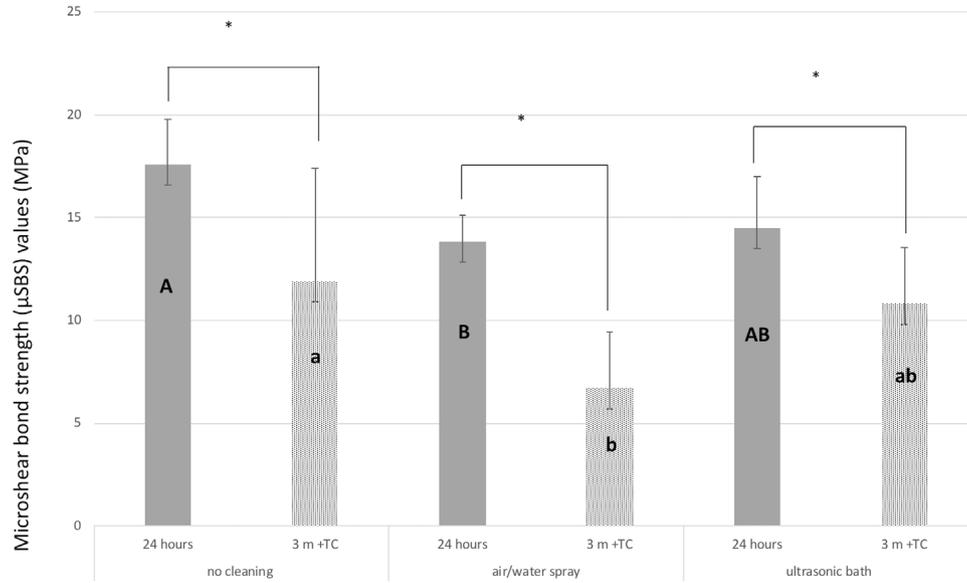


**Fig. 4 – (a and b) SEM micrographs of 30  $\mu\text{m}$  silica-coated alumina-particles. (c) is a higher magnification of “b” ( $\times 12,000$ ) showing deposition of a sand in the sub-micron range adhered to the surface of alumina particles. EDS analysis of the powder shows a mixture of (d) alumina particles with low concentration of silica nanoparticles deposited on them (finger point) and (e) pure silica spherical particles (finger point).**

mixture of two shapes of particles, whereby spherical particles of Si ( $\sim 30 \mu\text{m}$ ) are mixed with irregular-shaped particles of alumina ( $\sim 50 \mu\text{m}$ ) with a thin coating of silica deposited on them (silica-coated alumina) (Fig. 4.d and e). It is hypothesized that, during the AW cleaning process, the majority of the weakly deposited larger particles (in the micrometer range) were removed from the zirconia surface. The submicron particles, which remained on the zirconia surface, were possibly being held by the undercuts produced on the zirconia surface by the abrasion of the alumina particles under pressure. However, ultrasonic bath triggered the release of the larger particles and some sub-micron particles, significantly reducing the amount of silica left on the surface after UB cleaning in comparison to AW spray (Fig. 2i). Other studies have reported that ultrasonic cleaning after tribochemical grit blasting eliminates most of the alumina and silica particles on the zirconia surface [19,24].

The bonding between Y-TZP and resin-based cement after silica coating and silanization is expected to be a two-fold mechanism: micromechanical interlocking and chemical adhesion. Further to the surface roughening effect, the substrate wettability is enhanced by increasing its surface energy.

Surface roughening is confirmed by Fig. 2g, which shows an ultrasonically cleaned surface with shallow and elongated fissures. The chemical bond with the silica deposited on the zirconia surface is then obtained by a siloxane (Si–O–Si) linkage formed between the silanols (Si–OH — formed after an acid-catalyzed hydrolysis of silane) from the silane coupling agent and hydroxyl groups (–OH) present on the silica-coated zirconia [15,28]. This chemical interaction was investigated in the present study by XPS. Analyzing the Si 2p binding energy, it is possible to distinguish between the Si present in the SiO<sub>2</sub> substrate and the Si in the silane agent (3-methacryloxy-propyltrimethoxysilane -MPS). The Si in the SiO<sub>2</sub> substrate (silica-coating) has a binding environment corresponding to  $103.4 \pm 0.6 \text{ eV}$  [29]. This peak was not observed in the UB groups due to the lower amount of silica sub-micron particles covering the surface after UB cleaning. However, a peak at  $101.8 \pm 0.1 \text{ eV}$  was detected for that group. It is possible that this peak characterizes the formation of silicate in the undercuts produced by the air abrasion process (Fig. 7) [30]. As seen in Fig. 7, which shows the survey spectra for the silicized/silanized Y-TZP surface after different cleaning methods, all groups showed a peak located at the binding



**Fig. 5** – Mean and standard deviation of  $\mu$ SBS values for cleaning method tested after 24-h and 3 months water storage plus thermocycling. Dissimilar uppercase show significant differences between cleaning methods after 24 h ( $p < 0.05$ ). Dissimilar lowercase letters show significant differences between cleaning methods after 3 months storage plus thermocycling ( $p < 0.05$ ). Asterisks indicate significant difference for microshear bond strength between both storage times ( $p < 0.05$ ).

**Table 3** – Weibull moduli ( $m$ ) values, among the experimental groups comparing different cleaning methods and storage time.

Cleaning method	Storage time	
	24 h $m$	3 m + TC $m$
No cleaning (NC)	10.29 (6.17–17.15)Aa	2.45 (1.51–3.98)Ab
Air/water spray (AW)	11.5 (7.41–18.04)Aa	2.83 (1.69–4.73)Ab
Ultrasonic bath (UB)	5.92 (3.79–9.24)Aa	4.25 (2.65–6.83)Aa

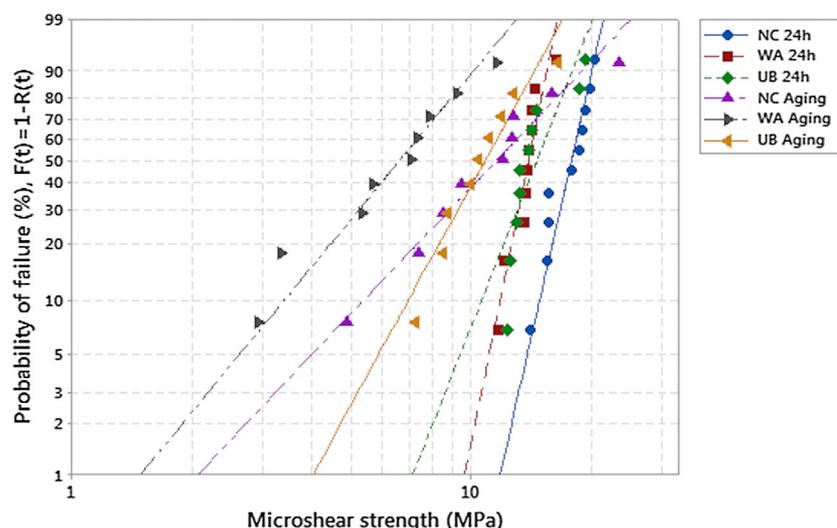
Dissimilar uppercase letters within the same column show significant differences between cleaning methods within the same storage time ( $p < 0.05$ ). Dissimilar lowercase letters within the same row show significant differences between storage time within the same cleaning method ( $p < 0.05$ ).

**Table 4** – Report of XPS analysis: ratio of peak areas for Si 2p present in each cleaning method group for region 1 and 2.

Cleaning method	Region 1			Region 2		
	101.8 ± 0.1 eV	102 ± 0.2 eV	103.4 ± 0.6 eV	101.8 ± 0.1 eV	102 ± 0.2 eV	103.4 ± 0.6 eV
No cleaning	–	98.24	1.76	–	100	–
Air/water spray	–	87.89	12.11	–	–	100
Ultrasound	47.25	52.75	–	14.7	85.3	–

energy of  $102.1 \pm 0.2$  eV. This peak corresponds to the MPS bonded to the silica particles (Si–O–Si) [29]. The percentages of the Si–O–Si component peak varied according to the region analyzed for each cleaning procedure (Table 4). Therefore, it seems that the bonding generated by the silica coating and the silane layer is not homogeneous throughout the surface. This fact was mainly evidenced by the AW group, which showed 87.89% of  $102.1 \pm 0.2$  eV peak for region 1 while this peak was not even detected in region 2.

The effect of the cleaning method on the silica-mediated bond strength between Y-TZP and resin-based cement was evaluated by micro-shear testing. The bond strength values recorded for the unaged samples were in the range of 15 MPa and in the range of 10 MPa for the aged samples. These values are in agreement with other studies using micro-shear testing for the analysis of bond strength between zirconia and various materials [21,31,32]. The results of this study showed that both, cleaning method and aging, had a significant effect



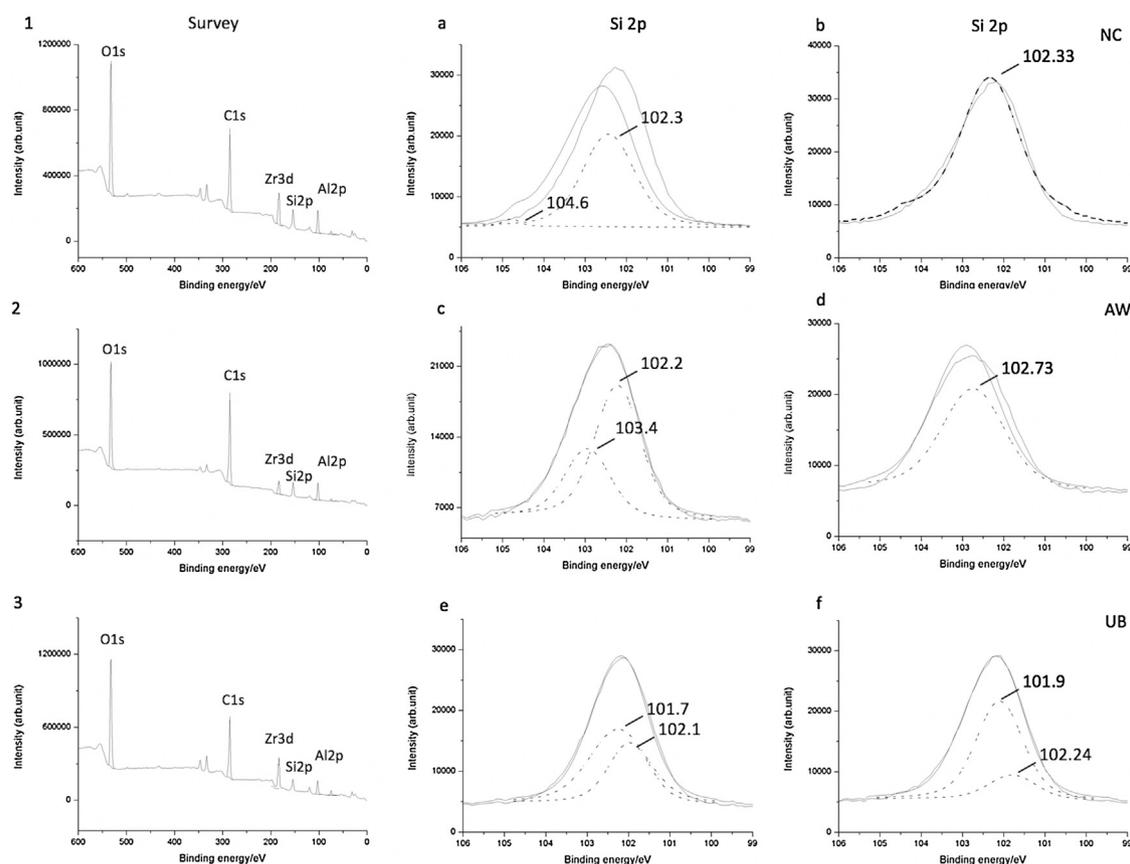
**Fig. 6 – Weibull distribution plots of microshear bond strength data for different cleaning methods. UB- ultrasonic bath; AW- air/water spray; NC- no cleaning.**

on bond strength. The mean bond strength values were significantly reduced for all groups after aging (3 months-water storage and 10,000 thermocycles). Hence, the results lead to the rejection of the study second null hypothesis. As observed in the EDS and XPS analysis, the silane-silica layer formed after tribochemical treatment is not homogeneous. Therefore, there are regions where it is possible to find the Si–O–Si bond, which is considered a hydrolytically stable chemical bond due to its high strength energy (111 Kcal/mol), and Si–O–Zr bond (ionic interaction), which is considered a weaker bond (less than 10 Kcal/mol) [33]. The regions characterized by the ionic interaction between silane and zirconia are susceptible to water degradation, compromising the bond strength. Furthermore, it is possible that silanol groups (Si–OH) remain on the zirconia surface, increasing the hydrophilicity of silane layer and predisposing the interface to hydrolytic degradation [15,34,35]. Fig. 3 (a, b and c) indicates the deposition of a “dust” of silica, weakly deposited on the surface of the control Y-TZP. It is possible that this layer also allowed for the infiltration of water, leading to a more significant degradation of the bonding for the control samples.

When comparing the effect of the cleaning methods, results indicated that the control samples presented significantly higher bond strength ( $14.9 \pm 4.9$  MPa) than the samples cleaned by air/water spray ( $10.45 \pm 4.1$  MPa), regardless of storage time. Ultrasonic cleaning resulted in intermediate values ( $12.7 \pm 3.3$  MPa). Surface mapping and EDS spectra (Fig. 2) indicate the presence of silica on the surface for all cleaning procedures. UB cleaning, for example, resulted in the lowest deposition of silica on the surface, but intermediate bond strength values. On the other hand, AW spray cleaning resulted in intermediate values of silica deposition, but the lowest bond strength values. In the UB group, the silica may be strongly attached to the zirconia-surface undercuts (silicate), as a result of effective tribochemistry. This effect is characterized by the chemical reaction between zirconia and nano-silica particles, which is created when silica-coated alu-

mina particles hit the Y-TZP ceramic surface, leading Zr–O–Zr bond breaking. As a consequence, a silicate melted layer is formed, which is an important factor for a stable bonding between luting resin and dental ceramic surface, since the silicate layer are less susceptible to degradation. This assumption is confirmed by the similarity of the Weibull moduli values (Table 3) for UB cleaning samples between two aging conditions. The silicate layer was observed in the binding energy of Si 2p only for UB group, indicating that the very thin silicate layer was covered by the rather thick layer of loosely deposited silica particles in the NC and AW groups [30]. For the AW cleaning samples, it is some water remained on the silica-covered surface after air-water cleaning, because of the short dry time used (5 s). Consequently, a decrease in the number of active surface hydroxyl groups (silanol vs absorbed water) per unit area of substrate may have occurred due to the interaction of silanols with OH groups of the water [34], following the significant decrease in the Weibull moduli. The inhibition of the chemical bond between the silica particles and the silane-containing primer was confirmed in the XPS analysis. Weibull survival analysis is an engineering-designed method for the analysis of reliability and failure prediction of components, often being referred to as “reliability engineering”. The Weibull moduli reveals how homogeneous a data set is distributed due to the total flaw population present in the material and consequently how reliable a given treatment is [36]. The low  $m$  values observed for all groups after aging in the current study suggest that the silica-mediated bonding between the zirconia and surface treatment investigated cannot be considered reliable over time regardless of the cleaning procedure employed (air/water spray or ultrasonic bath). These findings imply that clinicians may not find a consistent performance in the long-term when using tribochemical silica coating for enhanced bonding to zirconia restorations.

In the present study, the specimens were subjected only to short-term water degradation (3 months) and thermal stresses. The specimens evaluated were not exposed sub-



**Fig. 7 – Survey XPS spectra and detailed spectra of Si 2p of the “no cleaning” zirconia surface in region 1 (7.1a) and region 2 (7.1b), surface cleaned with air/water spray in region 1 (7.2c) and region 2 (7.2d) and ultrasonic bath in region 1 (7.3e) and region 2 (7.3f).**

jected to repeated mechanical fatigue or chemical challenges in saliva, as it occurs in a clinical scenario. Another limitation of this study is that the chemical stability of the silane bonding to silica-coated zirconia, which was analyzed using XPS, was only evaluated in the short-term (24 h). Therefore, it is recommended that future investigations consider testing the chemical stability of the silane-silica mediated bonding to zirconia under simulated oral conditions.

## 5. Conclusion

- 1 Cleaning the surface of tribochemically silica-coated Y-TZP with either air/water spray or ultrasonic bath reduces the amount of silica deposited on the surface and available for bonding.
- 2 Cleaning the surface of Y-TZP after tribochemical silica coating with air-water spray compromises the silica-mediated bonding to Y-TZP, both, immediately and after aging.
- 3 The chemical interaction between the silica coverage of the blasted-zirconia and a silane primer can be compromised by the cleaning methods tested.
- 4 Bond strength to the tribochemically-coated Y-TZP investigated in this study did not show a reliable performance over

time regardless of the cleaning method employed (air/water spray or ultrasonic bath).

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