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## *In-situ* nano-silica deposition and air-abrasion with Bioglass 45S5 or aluminium oxide: Effects on methacrylate bonding to yttria-tetragonal zirconia polycrystal



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### ABSTRACT

This study aimed at assessing the bonding performance after water storage (24 h/6-month) of a methacrylate-based cement applied onto Yttria-Tetragonal Zirconia Polycrystal (Y-TZP) pre-treated using an innovative *in-situ* silica nanoparticle deposition method and/or air-abrasion with Bioglass 45S5 (BAG) or aluminium oxide (AlO).

Pre-sintered blocks of Y-TZP were coated with nano-silica using an experimental *in-situ* deposition method or used as received (control/silica-free). Air-abrasion was performed with AlO or BAG particles both on silica-coated and control Y-TZP specimens. All the specimens were then analysed using SEM-EDX. Further specimens were treated as described above, bonded using a dual-cure resin cement system and submitted to shear bond strength test after water storage (24 h and 6 months). Fracture analysis was subsequently performed using a stereo-microscope.

Uniform nano-silica deposition was achieved in the Y-TZP specimens after *in-situ* silica deposition treatment. However, AlO air-abrasion removed the nano-silica and roughened the Y-TZP surfaces. Conversely, BAG air-abrasion caused partial removal of the nano-silica layer and created only little retention in the control/silica-free Y-TZP specimens. The highest bond strength both at 24 h and 6-month water storage was attained with the silica-coated specimens air-abraded with BAG and with those which received no air-abrasion. AlO air-abrasion increased the bond strength (24 h) in the Y-TZP specimens compared to the control/silica-free specimens which received no air-abrasion or BAG air-abrasion.

The *in-situ* nano-silica coating method employed in this study may be a suitable, simplified and low-cost approach to provide reliable bond strength to Y-TZP ceramics. No air-abrasion is required after *in-situ* nano-silica deposition. However, AlO air-abrasion can create micro-retentions on the surface of silica-free Y-TZP ceramics and increases the immediate bond strength of methacrylate-based resin cements.

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### 1. Introduction

Yttria-Tetragonal Zirconia Polycrystal (Y-TZP) presents distinctive mechanical characteristics due to the presence of Y<sub>2</sub>O<sub>3</sub> (3.5 to 6 wt%), which stabilises its chemical structure into a tetragonal

phase [1,2]. Y-TZP differs from other high strength dental ceramics because of its stress-induced transformation toughening that allows microstructural changes and improving the fracture toughness; Y-TZP is a higher-strength ceramic, approximately six times more resilient than feldspathic porcelains.

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The application of Y-TZP ceramics is increasing both in bio-medicals (e.g. Orthopaedic surgery) as well as dental biomaterials fields for restorative dentistry and implantology. Although Y-TZP is characterised by a relatively opaque appearance, it can be milled in fine details and used in clinical situations of high mechanical stress to provide long-term durability, as well as exceptional aesthetic properties [3,4]. Furthermore, the advent of Computer-Aided Design and Computer-Aided Manufacturing (CAD/CAM) technology has simplified the laboratory procedures and reduced occurrence of failures when processing Y-TZP for dental prostheses; clinical studies have reported good results for some specific indirect restorations such as inlays, onlays and metal-free crowns [4,5].

The clinical success of Y-TZP as well as other ceramic materials mainly depends on an appropriate cementation procedure. Several methods have been advocated to improve adhesion between resin cements and Y-TZP [6–9]. For instance, surface treatment of Y-TZP using air-abrasion in combination with (Al<sub>2</sub>O<sub>3</sub>)-aluminium oxide (AIO) (particle size 50–100 µm) creates micro-retentions, which can increase the bond strength of methacrylate-based cements to Y-TZP [7–9].

Bioglass 45S5 (BAG) is a bioactive calcium/sodium phosphate-phylllosilicate used in dentistry as an alumina substitute in air-abrasion systems, and provides alternatives to traditional hand-pieces in removing dental hard tissues (e.g. enamel, dentine, and cementum) [10–12]. Unfortunately, there is no available information regarding bonding of methacrylate to Y-TZP after air-abrasion performed using such a silica-rich BAG. Hence, this needs to be further investigated as BAG is a less aggressive powder compared to AIO, which could be used for pre-treatment of thin margins of Y-TZP restorations such as ultra-conservative veneers, thereby reducing risk of failure during chair-side air-procedures. Moreover, air-abrasion treatment performed with silica-rich BAG may favour the embedment of silica residual onto Y-TZP surfaces and enhancing bonding ability of organo-silanes and methacrylate-based resin cements.

Despite some improvements, the adhesion of methacrylate-based cements to Y-TZP remains unreliable in terms of durability and longevity; this is a further aspect that needs further investigation in order to solve bonding drawbacks in zirconia ceramics [13–15]. Indeed, significant shortcomings of Y-TZP may be attributed to a lack of adhesion to methacrylate-based resin cements due to two main factors; (i) the homogeneous and inert single-phase structure of Y-TZP is highly dense to create selective micro-retentions [3]; (ii) absence of silica (glass-phase) in Y-TZP structure which hinders the establishment of chemical bonds mediated by organo-silanes [13,14].

Innovative methods such as vapour deposition of SiCl<sub>4</sub> and SiO<sub>2</sub> by plasma treatment have also been advocated to increase bonding performance of methacrylate-based resin cements to Y-TZP via establishment of a chemical bond when using organo-silanes. However, these approaches result both costly and complex in terms of equipment and/or particular technical expertise [9,16,17].

Conversely, an innovative and affordable approach to attain reliable *in-situ* nano-silica deposition on surfaces of Y-TZP has been recently advocated to increase the bonding ability of resin cements to Y-TZP [13]. Furthermore, there is still little information about this novel approach, therefore further studies are required to confirm its ability in improving short- and long-term bonding performance of methacrylate-based cements.

The purpose of this study was to assess *in vitro* the short- (24 h) and long-term (6 months) bonding performance after water storage of a methacrylate-based cement applied onto Y-TZP ceramic pre-treated using an innovative simplified method to achieve *in-situ* nano-silica deposition through organic Silica (Si) and Zirconium (Zr) alkoxy R-Si(OR')<sub>3</sub> precursors. Moreover, the effect of BAG

or AIO air-abrasion on silica-coated or control/silica-free Y-TZP, as well as bonding performance of methacrylate-based cements was also investigated. The hypotheses tested were: (i) the bonding performance (at 24 h and 6 months of water storage) of a methacrylate-based cements applied onto Y-TZP air-abraded with BAG can be compared to that obtained with Y-TZP air-abraded using AIO; (ii) the innovative *in-situ* nano-silica deposition method tested in this study would improve bonding performance of a methacrylate-based resin cement to Y-TZP at 24 h and after 6 months of water storage both when used alone or in combination with subsequent air-abrasion performed with BAG or AIO.

## 2. Materials and methods

### 2.1. Specimen preparation and *in-situ* nano-silica deposition (SEM EDX)

An experimental primer was prepared using Tetra-Ethyl Orthosilicate (TEOS; 2.5 wt%) and Zirconium Tert-Butoxide (ZTB 2.5 wt%) diluted in hexane (95 wt%). The use of zirconia precursors mixed with silica precursors was tested in order to increase surface coating compatibility with zirconia substrate.

Pre-sintered specimens (40 × 19 × 19 mm<sup>3</sup>) of Y-TZP (ZirconCAD; Angelus, Londrina, PR, Brazil) were cut into eighteen smaller blocks measuring 10 × 9 × 9 mm<sup>3</sup>. Nine Y-TZP blocks were left untreated and used as received (Control), while the other nine blocks (Si/Zn-EXP) were completely immersed in an experimental Si/Zn primer for 5 min at 37 °C in order to attain an optimal infiltration of organic precursors into the Y-TZP surface. Subsequently, excess primer was removed by means of gentle air drying (2 s) and Y-TZP infiltrated specimens were treated in a computer-controlled furnace (FEZ-1600/4; INTI, São Carlos, SP, Brazil) using the protocol recommended by manufacturer: heating rate 100 °C/h up to 1350 °C constantly maintained for 2 h [13].

In order to evaluate the ultra-structure of Si/Zn-infiltrated specimens, two further specimens were prepared for each group (control and Si/Zn-EXP) and sputter-coated with carbon 10 s without affecting surface morphology of specimens and compositional analysis [13]. These specimens were analysed using a scanning electron microscope (SEM, SSX-550; Shimadzu, Tokyo, Japan) equipped with X-Ray Energy Dispersive Spectroscopy (EDX) for elemental analysis.

### 2.2. Air-abrasion, bond strength test and failure analysis

Both surfaces of each Y-TZP specimen in control group ( $n=18$  surfaces) were divided into three sub-groups and left untreated (UN-CRT;  $n=6$ ) or air-abraded (UN-AIO;  $n=6$ ) using a 50 µm aluminium oxide (AIO, VELOPEX International, London, UK) or (UN-BAG  $n=6$ ) Bioglass 45S5 (Sylc, VELOPEX International). The surfaces of Y-TZP specimens in Si/Zr-EXP group ( $n=18$  surfaces) were also divided into three sub-group and left untreated (Si/Zr-CRT;  $n=6$ ) or air-abraded (Si/Zr-AIO;  $n=6$ ) using aluminium oxide (AIO, VELOPEX International) or (Si/Zr-BAG;  $n=6$ ) Bioglass 45S5 (Sylc, VELOPEX International). The two surfaces of a further specimen per sub-group were prepared as described above, sputter-coated and analysed using a SEM-EDX (SSX-550, Shimadzu).

Standardised moulds with 1 mm thickness and 2 mm diameter were fabricated using a polyvinylsiloxane impression material (Aquasil Ultra XLV, Dentsply Caulk, Milford, USA). These were positioned on Y-TZP blocks and air-abrasion procedures were performed in a static way (no-movements) using Aquacut Quattro (VELOPEX International, London, UK) working with a pressure of 7 bar at a standardised distance of 1 mm from the specimens' surface.

Subsequently, the Y-TZP specimens in all groups were thoroughly rinsed for 10 s with H<sub>2</sub>O, immediately dried and coated with a primer/silane (Monobond Plus, Ivoclar Vivadent, Schaan, Liechtenstein) and solvent evaporation was permitted following the instructions of the manufacturer. Polyvinylsiloxane moulds (thickness 0.5 mm, diameter 1.5 mm) were placed onto the surface of zirconia blocks and filled with dual-cure resin cement (Variolink II). The composition of the resin cement and primer/silane used in this study are showed in Table 1. A polyester strip and glass slide were placed onto the filled moulds, and the cement was light-cured in direct contact with glass slide for 60 s using a light-emitting diode curing unit (Radii-Cal; SDI, Bayswater, Australia) with 1200 mW/cm<sup>2</sup> irradiance. Six resin cement cylinders (RCs) were built up on both specimens' surfaces with a total number of thirty-six RCs per sub-group. Specimens of each sub-group were stored in distilled water at 37 °C for 24 h ( $n=18$ ) or for 6 months ( $n=18$ ); water was replaced every two weeks.

The specimens were submitted to shear bond testing using a stainless steel wire (diameter 0.2 mm) looped around each cement

**Table 1**  
Compositions of the resin cement and silane/primer used in this study.

| Products (type)               | Composition  | Products of number |
|-------------------------------|--|--------------------|
| Variolink II (resin cement)   | Bis-GMA, TEGDMA, UDMA, inorganic fillers, ytterbium trifluoride, initiators, stabilizers, pigments, benzoyl peroxide | High: J24363       |
| Monobond plus (silane/primer) | 3-MPS, 10-MDP, sulphide methacrylate, ethanol  | M24811             |

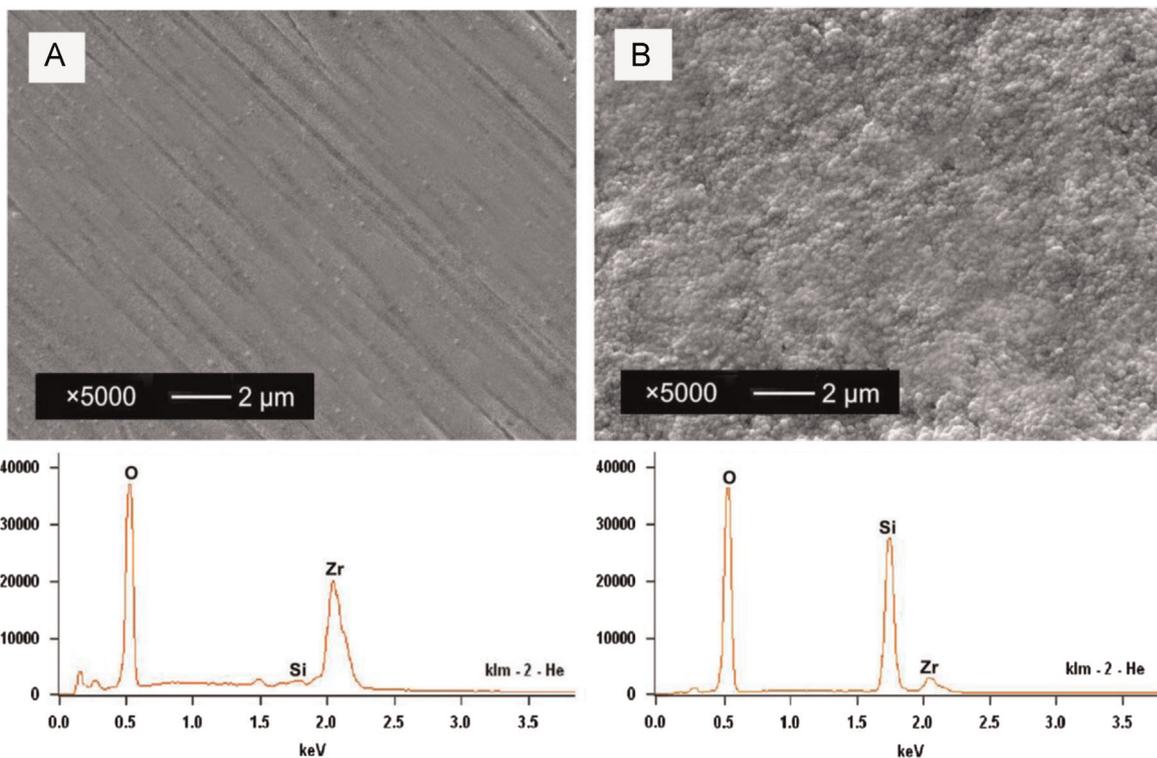
**Abbreviations:** 3-MPS: 3-Methacryloxypropyltrimethoxysilane; 10MDP: 10-methacryloxydecyldihydrogenphosphate; TEGDMA: Triethylene glycol dimethacrylate; Bis-GMA, bisphenol A diglycidyl ether methacrylate; UDMA, urethane dimethacrylate; HEMA: 2-hydroxyethyl methacrylate.

cylinder, aligned with bonding interface [13]. The shear test performed on a universal testing machine (Bisco Inc., Schaumburg, USA) at a crosshead speed of 1 mm/min until failure. The fractured specimens were observed using a magnification  $\times 20$ –60 stereo microscope. Failures were classified as following: mixed (remnants of cement left on ceramic); adhesive (interfacial debonding); cohesive (fracture within the cement). The bond strength values (Newtons) were converted into MPa and considered as statistical units. Statistical analysis was performed using two-way ANOVA (surface treatment and storage time). All pairwise multiple comparison procedures were performed by the Student-Newman-Keuls' method. The power analysis showed 99.8% with  $\alpha$  set at 0.05.

### 3. Results

The SEM–EDX analysis showed no remarkable presence of silica on Y-TZP specimens surface (Fig. 1A); while, a uniform and consistent silica deposition was attained on surface of Y-TZP specimens after *in-situ* nano-silica deposition (Fig. 1B).

The shear bond test results (MPa mean  $\pm$  SD) are shown in Table 2. The factors 'surface treatment' and 'storage time' were both statistically significant ( $p < 0.001$ ), as well as interaction between the two factors ( $p = 0.031$ ). The zirconia (Y-TZP) specimens treated with the *in-situ* nano-silica deposition method exhibited at 24 h significantly ( $p < 0.05$ ) higher bond strength (37.1 MPa) compared to those attained with the specimens in Y-TZP control group (non-treated) (14.5 MPa). The *in-situ* nano-silica coated specimens debonded prevalently in cohesive (75%) and only 25% of the total number of specimens failed in mixed mode; whereas those in control Y-TZP group failed mainly in adhesive mode (80%). The zirconia specimens treated with the *in-situ* nano-silica deposition method (34.2 MPa) and the same



**Fig. 1.** SEM–EDX analysis for the *in-situ* nano-silica deposition using the Si/Zn experimental primer. A: SEM–EDX micrograph of the untreated Y-TZP surface (Control) showing a surface with no presence of nano-silica deposition (Control). The EDX analysis confirms the absence of silica on the Y-TZP surface. B: SEM–EDX micrograph of Y-TZP treated by the silica-coating method using the Si/Zn experimental primer showing a surface entirely covered by silica nanoparticle clusters. The EDX analysis confirms the presence of silica on the Y-TZP surface (Si/Zn EXP).

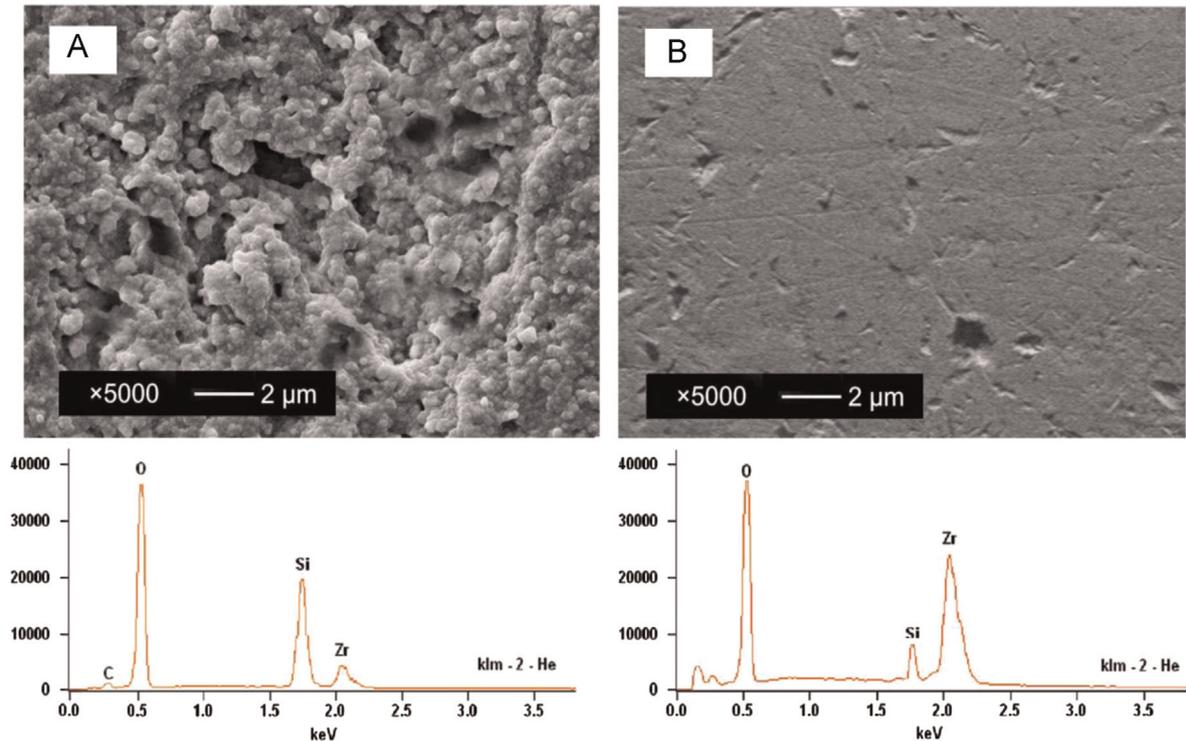
**Table 2**Micro-Shear bond strength results (Mean  $\pm$  SD and failure mode) and statistical analysis.

|                                 | Si/Zr-EXP                              |   | Control                                |  |
|---------------------------------|--|---|--|--|
|                                 | 24 h                                   | 6 months                                | 24 h                                   | 6 months                               |
| <b>NO treatment (untreated)</b> | 37.1 $\pm$ 3.5 <sup>a1</sup> [75/25/0] | 34.2 $\pm$ 4.1 <sup>a1</sup> [40/55/5]  | 14.5 $\pm$ 2.2 <sup>a3</sup> [5/15/80] | 4.5 $\pm$ 3.2 <sup>a4</sup> [0/10/90]  |
| <b>Aluminium oxide (AIO)</b>    | 29.1 $\pm$ 5.6 <sup>b1</sup> [60/35/5] | 25.3 $\pm$ 5.2 <sup>a2</sup> [10/35/55] | 21.4 $\pm$ 4.1 <sup>b3</sup> [0/55/45] | 15.1 $\pm$ 5.1 <sup>b4</sup> [0/25/75] |
| <b>Bioglass (BAG)</b>           | 35.9 $\pm$ 4.3 <sup>a1</sup> [70/30/0] | 31.5 $\pm$ 6.1 <sup>a1</sup> [55/35/10] | 12.4 $\pm$ 3.1 <sup>a2</sup> [0/15/85] | 3.8 $\pm$ 3.1 <sup>a2</sup> [0/5/95]   |

Same letters in column indicate no significant difference induced by each treatment (AIO; BAG; Untreated) on the same surface (Si/Zr-EXP or Control) at 24 h or 6 months of aging.

Same numbers in row indicate no significant difference induced by aging periods (24 h or 6 months) for the specimens in Si/Zr-EXP and Control groups after air-abrasion treatments (AIO or BAG) or no treatment (untreated).

Numbers in parenthesis indicate the percentage of debonding failures obtained in each experimental group [cohesive/mixed/adhesive].

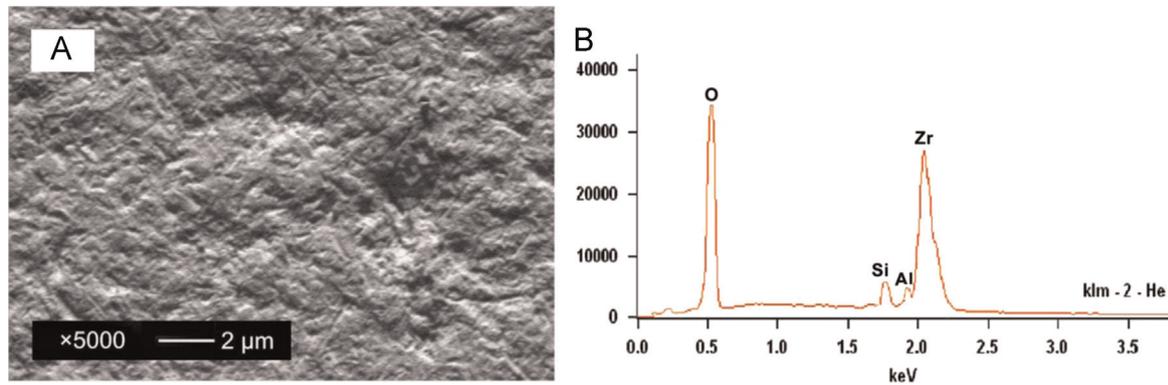


**Fig. 2.** SEM–EDX analysis for the specimens treated with BAG air-abrasion. A: SEM–EDX micrograph of Y-TZP treated by the silica-coating method and air-abraded using Bioglass 45S5 (BAG) showing a surface still covered by silica nanoparticle clusters. The EDX analysis confirms an important remaining presence of silica on the surface. B: SEM–EDX micrograph of the Y-TZP surface air-abraded using Bioglass 45S5 (BAG) showing a surface relatively flat with only few irregularities created by the air-abrasion treatment. The EDX analysis confirms the presence of a very low and almost absent silica on the Y-TZP surface.

specimens air-abraded with BAG (31.5 MPa) exhibited highest bond strength ( $p < 0.05$ ) after prolonged 6-month storage in water; no significant statistical differences were observed between these two groups ( $p > 0.05$ ), and in both cases a mixed and cohesive mode of failure was prevalently observed (Table 2). The Y-TZP specimens treated with the *in-situ* nano-silica deposition method and subsequently air-abraded with BAG showed a rough surface still characterised by abundant presence of silica when analysed using SEM–EDX (Fig. 2A). On the contrary, the Y-TZP specimens treated with BAG air-abrasion only showed irrelevant superficial rough and very slight presence of silica on the surface (Fig. 2A). These latter specimens showed the lowest bond strength ( $p < 0.05$ ) both after 24 h (12.4 MPa) and after 6-month storage in water (3.8 MPa), showing a failure mode prevalently adhesive. These results were comparable ( $p > 0.05$ ) to those in Y-TZP control group, which received no treatment both at 24 h (14.5 MPa) and after 6-month storage in water (4.5 MPa).

The Y-TZP specimens air-abraded with AIO exhibited, at 24 h, significantly ( $p < 0.05$ ) higher bond strength (21.4 MPa) compared to those in the Y-TZP control group (non-treated) (14.5 MPa). The

specimens air-abraded with AIO debonded prevalently in mixed (55%) and adhesive (45%) mode. The zirconia (Y-TZP) specimens treated with the *in-situ* nano-silica deposition method and then air-abraded with AIO exhibited at 24 h, significantly ( $p < 0.05$ ) higher bond strength (29.1 MPa) compared to the Y-TZP specimens air-abraded with AIO. The specimens treated with *in-situ* nano-silica deposition method and then air-abraded with AIO, debonded prevalently in cohesive (60%) and mixed (55%). The SEM–EDX analysis showed that air-abrasion executed using AIO could create important roughness both on the surface of control Y-TZP specimens (no *in-situ* nano-silica coating) as well as the surface of the specimens coated with nano-silica (*in-situ* deposition method) (Fig. 3A). However, AIO air-abrasion treatment, removed most of nano-silica from specimens treated with *in-situ* deposition method and only little presence of Si and Al were detected during SEM–EDX analysis (Fig. 3B). Nevertheless, the bond strength of the latter specimens (25.3 MPa) resulted significantly higher ( $p < 0.05$ ) than the control Y-TZP specimens air-abraded with AIO (15.1 MPa) after 6 months of water storage; both groups mainly failed in adhesive



**Fig. 3.** SEM-EDX analysis for the specimens treated with AIO air-abrasion. A: SEM-EDX micrograph of Y-TZP air-abraded using bioglass AIO (BAG) showing a rough surface characterised by several irregularities. B: EDX spectra of Y-TZP treated by the silica-coating method and air-abraded using AIO showing the presence of a very little or almost absent silica and aluminium elements remaining on the surface.

mode during bond strength (Table 2). Optical images for the failure analysis are illustrated in Figs. 4 and 5.

#### 4. Discussion

The introduction of adhesive systems and resin cements has allowed practitioners to increase retention of conventionally indirect ceramic restorations to hard dental tissues (e.g. enamel and dentine) and achieve optimal aesthetic results. However, the bonding of such restorations when placed in oral environments is still one of the most important factors in durability terms [7,18,19]. Evidently, this can be attributed to bonding established between different structures such as ceramic surface, cement and dentine/enamel. The bonding between traditional glass-containing ceramics and dental tissues is essentially based on micro-mechanical and/or chemical-adhesive methods. The establishment of a mechanical bonding requires micro-interlocking between the resin cement and the rough surface of silica-based ceramics. However, this bonding can be influenced by various factors such as: wettability, roughness and nature of ceramics, as well as surface contamination [20–22].

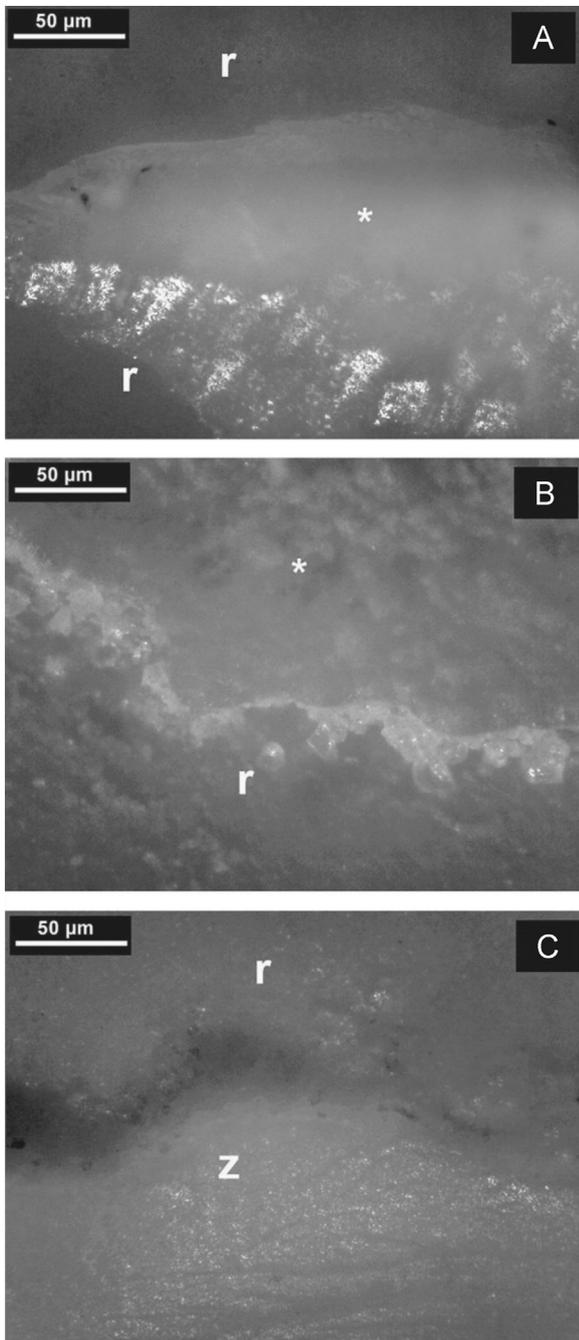
The use of zirconia ceramics (Y-TZP) has become a popular choice for indirect restorations. Some mechanical properties of Y-TZP such as toughness and hardness result much higher than other dental silica-based ceramic, which are generally employed in prosthodontics. Y-TZP ceramics can be used as an alternative to metal-ceramics restorations for posterior and anterior restorations; their performance has been demonstrated in laboratory and clinical studies [23–25]. However, main concerns remain related to adhesion of methacrylate-based resin cements employed for luting purposes; the bonding of methacrylate to zirconia results much more difficult to achieve if compared to silica-based ceramic materials due to structural integrity and chemical inertia of Y-TZP [26,27]. Furthermore, silica absence in microstructure of Y-TZP undermines silanes in developing chemical bonds [21,22].

The results of this study showed that the methacrylate-based resin cement (Variolink II, Ivoclar) used in this study was able to create a “weak” bonding to Y-TZP; the bond strength attained after 24 h of water storage was 14.5 MPa with a failure mode prevalently adhesive (Table 2). Moreover, a significant drop of bond strength was attained in these specimens after prolonged water storage (6 months) up to 4.5 MPa. The initial bond strength has been probably achieved due to the unique chemical composition of the primer used in this study (Monobond Plus); this contains an organo-silane (3-Methacryloxypropyltrimethoxysilane; < 3 wt%) and a functional monomer (12-Methacryloyldodecylphosphate; < 3 wt%) diluted in an ethanol solution (> 50 wt%). Indeed, it has

been advocated that ceramic primers containing functional monomers such as methacryloyldodecylphosphate can improve methacrylate bonding to Y-TZP [6]. A further factor which may have promoted such a bonding between methacrylate-based resin cement and Y-TZP may be attributed to the 3-methacryloxypropyltrimethoxysilane, which may improve the wettability of resin cements on dental substrate [32]. On the other hand, the drop in bond strength observed after prolonged 6-month water storage may be attributed to hydrolytic degradation of the functional monomer and/or silane as well as a result of plasticisation of polymeric network within the resin cement [30,33].

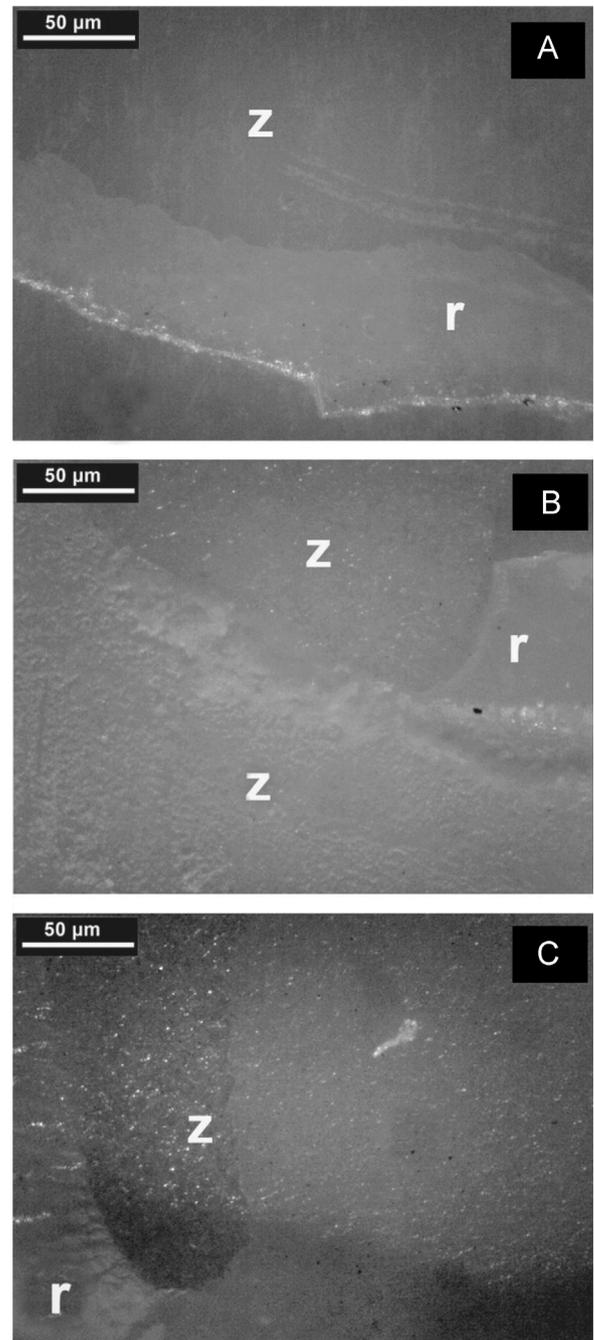
In order to obtain a suitable bonding to Y-TZP ceramics, it is important to remove any contaminants surfaces of the Y-TZP [20,21]. Surface abrasion or roughening through grinding, airborne-particle and rotary diamond burs can create micro-mechanical retentions and establish a suitable adhesion between ceramics and luting cements. There is a general consensus that airborne-particle abrasion (air-abrasion) with aluminium oxide (AIO; 50–110 μm) is effective in roughening and cleaning the bonding surface of Y-TZP [20]. However, the effect of those treatments on bonding and mechanical properties of Y-TZP is controversial and both positive and negative results have been described in literature [28–31]. Furthermore, it has been reported that air-abrasion may create sharp crack tips and structural defects, making zirconia more susceptible to radial cracking during function, therefore it could be beneficial if the pressure during air-abrasion is reduced [31] or, for example in this study case, alternative air-abrasion powders such as Bioglass 45S5 is employed for such purposes.

Unfortunately, this study showed that silica-free Y-TZP air-abraded using BAG as well as those without air-abrasion pre-treatment debonded mainly in adhesive mode and only rarely in mixed mode (Fig. 5C); these specimens showed a bond strength significantly lower than that obtained when performing air-abrasion with AIO (Table 2). Moreover, SEM results showed that BAG was unable to produce any essential roughness on Y-TZP surface (Fig. 2B), when compared to that obtained after AIO air-abrasion (Fig. 3A). This latter could be a possible explanation for differences in bond strength between BAG-treated and AIO-treated Y-TZP specimens. However, it is important to consider that specific formulation of BAG created for air-abrasion procedures has a Young's modulus of 35 GPa and Vickers' hardness of 458 VHN, while alumina (AIO) presents 380 GPa and 2300 VHN respectively [10–12]. Hence, the mechanical properties of BAG 45S5 results are inappropriate for application on Y-TZP ceramics. An additional suitable explanation to justify these differences may be found on reactive nature of the BAG. Indeed, although BAG can fragmentise on Y-TZP surfaces, only scant presence of silica was available on Y-TZP



**Fig. 4.** Representative optical images for the failure analysis of nano-silica coated specimens. A: This image shows the surface of a nano-silica coated Y-TZP specimen after micro-shear bond test at 24 h of water storage. It is possible to note a mixed fracture with very little exposed zirconia (\*) and a great presence of resin (r). B: Image showing the surface of a nano-silica coated Y-TZP specimen subsequently air-abraded with AIO after micro-shear bond test at 6 months of water storage. In this case it can be seen a mixed debonding with both presence of resin (r) and exposed zirconia (\*). C: This image shows the surface of a nano-silica coated Y-TZP specimen subsequently air-abraded with air-abraded with BAG after micro-shear bond test at 6 months of water storage. Also in this case it can be observed a mixed debonding with both presence of resin (r) and exposed zirconia (z).

surface (EDX, Fig. 2B) for chemical bonding with silane and/or functional monomer of the primer used in this study. Nevertheless, due to the presence of 12-MDP, this primer is characterised by an acidic pH (2–3), which may have alternated the chemical-physical characteristics of Bioglass 45S5 (BAG) and converted it into di-calcium phosphate. Profeta et al. [34] showed that in acidic environment, BAG can dissolve and re-precipitate into



**Fig. 5.** Representative optical images for the failure analysis of air-abraded specimens after 6-month storage. A: This image shows the surface of a control Y-TZP specimen (no treatment) after micro-shear bond test which debonded in adhesive mode leaving a very little remaining presence of resin (r) on the zirconia surface (Z). B: Image showing the surface of Y-TZP air-abraded with BAG after micro-shear bond test which debonded in adhesive mode leaving a very little remaining presence of resin (r) on zirconia surface (Z). C: This image shows the surface of Y-TZP air-abraded with AIO after micro-shear bond test. Also in this case it was quite often observed a surface characterised by a very little remaining presence of resin (r) on zirconia surface (Z).

brushite. Consequently, the first hypothesis that bonding performance of methacrylate-based resin cements to Y-TZP air-abraded with BAG can be compared to that obtained with aluminium oxide (AIO) must be rejected as the latter results one of the few methods to increase roughness of Y-TZP ceramics for a reliable “short-term” bonding.

Conversely, this study has confirmed that air-abrasion with AIO can increase bond strength of methacrylate-based cements to

Y-TZP compared to non-treated (control) specimens after 24 h of water storage (Table 2). Although after 6 months of water storage, the bond strength of specimens air-abraded with AIO (15.1 MPa) was still significantly higher than the control Y-TZP specimens (4.5 MPa), it significantly dropped compared to results attained after 24 h (21.4 MPa). These differences at 24 h can be attributed to micro-retentions created by air-abrasion procedures executed using AIO (Fig. 3A) which favoured bonding of methacrylate-based cement used in this study.

The explanation for reduction of bond strength for the specimens stored in water for 6 months may be the same as previously described for the control Y-TZP specimens; hydrolytic degradation and plasticisation of polymeric network within the resin cement may have occurred at the bonding interface [30,33].

In view of the results discussed so far, it is possible to state that further alternative treatments are required to achieve a long-term adhesion between methacrylate-based cements and Y-TZP ceramics.

In this aspect, the *in-situ* nano-silica deposition method tested in this study was able to increase the bond strength of methacrylate-based cement up to 37.1 MPa at 24 h of water storage and 75% of these specimens debonded prevalently in cohesive mode. However, most interesting results were observed after prolonged water storage where Y-TZP specimens treated coated with nano-silica showed no significant drop in bond strength (34.2 MPa). Comparable results ( $p > 0.05$ ) were observed when specimens coated with nano-silica were air-abraded with BAG; the specimens of both groups exhibited the highest bond strength ( $p < 0.05$ ) after prolonged storage in water and in both cases mixed and cohesive mode of failure was prevalently observed (Table 2). The experimental silica-coating method used in this study was able to uniformly coat the zirconia surface with silica nanoclusters (particle size between 140 nm and 300 nm; Fig. 1B), which promoted a significant increase in surface area of the ceramic available for bonding. The EDX profile of silica nanoparticle deposited on Y-TZP surfaces in this experimental method is comparable to the profile obtained in studies, where hexamethyldisilazane was deposited by plasma on polymeric substrates of polyethylene naphthalate or when using spray-drying technique [13,16,17]. The Y-TZP specimens treated with the *in-situ* nano-silica deposition method and subsequently air-abraded with BAG showed a rough surface still characterised by abundant presence of silica (Fig. 2A). This is probably the reason why these latter specimens performed similarly to those coated with nano-silica. This experimental silica-deposition method was able to encourage adhesion of methacrylates to zirconia. The improved bonding ability both at 24 h and after 6-month water storage may be explained by the deposition of silica on the surface, which allowed substantial surface area increase (improving micro-mechanical interlocking) and subsequent chemical coupling *via* silanisation. Silane coupling agents lower the surface tension of a substrate, increase wetting and surface energy and improve bonding effectiveness. Thus, a hydrophobic luting resin could adhere to hydrophilic surfaces of silica (glass, glass-ceramic). Additionally, due to the inorganic-organic silanes nature, this hybrid agent along with 12-MDP monomer may have been capable of forming strong covalent bonds to silica coated zirconia through formation of silanol groups and ionic bonds respectively [35,36]. Notably, this method to deposit nano-silica seems to address the problem of yielding adhesion to zirconia ceramics by using an easy and economical approach. In fact, this technique may be a feasible alternative to deposit silica onto zirconia in laboratory to improve the subsequent adhesion with methacrylate-based materials [13].

However, the second hypothesis that the use of organic Si/Zr precursors would enhance bonding performance of methacrylate-based resin cements to Y-TZP at 24 h and after 6 months of water

storage both when used alone or in combination with the air-abrasion performed using BAG or AIO must be partially accepted. That is, air-abrasion application with AIO on Y-TZP surface coated with nano-silica showed significant ( $p < 0.05$ ) lower bond strength results both after 24 h and prolonged water storage compared to the other two treatments just discussed (Table 2). The main reason for these differences observed between these groups is that air-abrasion with AIO results quite aggressive in removing nano-silica layer from the Y-TZP surfaces (Fig. 3). Thus, these specimens have the same condition as those discussed above where air-abrasion with AIO was performed on the control Y-TZP surfaces.

## 5. Conclusion

The present study confirms that *in-situ* nano-silica deposition method used in this study results as suitable simplified low-cost approach to provide reliable bond strength between methacrylate-based resin cements and zirconia ceramics. The proposed method could also be considered for bonding of other types of polymeric materials for varied applications of Y-TZP as biomaterials. However, no air-abrasion treatment is required to improve bond strength when using this innovative *in-situ* nano-silica deposition method. Conversely, only the use of air-abrasion with AIO can roughen the surface of Y-TZP and increase the initial (short-term) bonding of methacrylate-based resin cements, while the use of air-abrasion with BAG results inappropriate for application in Y-TZP.

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