DENTAL MATERIALS 35 (2019) 1557–1567

Available online at www.sciencedirect.com

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journal homepage: www.intl.elsevierhealth.com/journals/dema

Effect of silane and MDP-based primers on physico-chemical properties of zirconia and its bond strength to resin cement

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ARTICLE INFO

Article history:
Received 4 January 2019
Received in revised form
17 May 2019
Accepted 16 July 2019

Keywords:
Y-TZP
Adhesion
Phosphate ester
Air abrasion

ABSTRACT

Objective. To evaluate the effect of surface treatments on yttria-tetragonal zirconia polycrystal (Y-TZP) characteristics and on resin-mediated zirconia bond.

Methods. Y-TZP slabs were grit blasted with 45 μm alumina or with 30 μm silica-coated alumina particles. The chemical treatments were: no-chemical treatment (NC), silane-containing primer (SP), MDP (10-Methacryloyloxydecyl dihydrogen phosphate) and silane-containing primer (MPS), MDP-containing primer (MP) and MDP and silane-containing adhesive (MPA). Contact angle as a function of surface roughness (θ_m) and surface roughness parameter (Sdr) were measured using Fringe Projection Phase Shifting (FPPS). Surface free energy (γ_s^{TOT}) was calculated with a goniometer. Chemical interaction between primers/adhesive and zirconia was analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Resin cement microshear bond strength (μSBS) was analyzed at either 24-h or 8-months water storage (37 °C). θ_m values, Sdr values, γ_s^{TOT} and μSBS values were analyzed using Analysis of variance (ANOVA) and post hoc Tukey test ($\alpha = 0.05$).

Results. Chemical treatment had an effect ($p < 0.001$) on all surface parameters analyzed: θ_m, γ_s^{TOT} and Sdr. MP-treated group showed higher incidence of P–O–Zr bonds than the other groups, indicating more chemical linkages. Grit blasting ($p < 0.001$) and the interaction chemical treatment*storage ($p < 0.001$) did not affect μSBS; all silane-containing primers showed significant drop in μSBS after aging.

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https://doi.org/10.1016/j.dental.2019.07.008

Significance. MDP and/or silane-based solutions affect the physicochemical properties of blasted-zirconia. An MDP-based primer is fundamental to achieve a stable resin-zirconia bonding, but the chemical reactivity of MDP is impaired when this molecule is present in a multicomponent system.

1. Introduction

In clinical dentistry, the use of all-ceramic restorations has increased in an early basis since they provide excellent esthetic and high mechanical performance. Moreover, the introduction of CAD-CAM technologies has contributed to simplifying the manufacturing of dental prosthesis, further contributing to the use of ceramic restorative materials [1–3]. Clinical success of all-ceramic restorations is widely dependent on establishing a strong and stable bond between these materials and dental hard tissues. All-ceramic restorations can be luted either by conventional or resin-based adhesive protocols, but the adhesive cementation is desired to achieve a strong and stable interface between ceramic restorations and tooth structure [4,5]. The luting protocol for silica-based ceramic surfaces is well defined and involves etching the ceramic with hydrofluoric acid followed by silanization for establishment of a chemical bond. Yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP), however, still has a protocol with controversial guidelines [6]. This fact is due to the microstructural characteristic and chemical and biological inertness of Y-TZP, which are natural challenges for a resin-mediated bonding [6]. Some clinical studies have reported the loss of retention of zirconia crowns due to the difficulty to establish a reliable bonding between zirconia substrate and resin cement [7,8], showing the need for the establishment of a protocol that will result in a more predictable bonding between zirconia-based restorations and toot substrate.

Different grit blasting protocols and chemical surface treatments have been proposed to modify the surface properties of Y-TZP and enhance bond strength to the underlying structure. Three independent meta-analyses of bonding to zirconia concluded that the combination of grit blasting and chemical pre-treatments increased the bond strength between zirconia and resin-based cements [9–11]. The most commonly used mechanical method involves blasting the surface with alumina oxide particles to increase surface area and produce micromechanical retention [12,13]. Tribochemical silica coating has also been considered a reliable alternative to blasting with alumina particles [9,11], and a more stable resin-zirconia bonding can be achieved. This may be because the tribochemical coating combines micromechanical interlocking with a surface coating through the deposition of a silica layer, which can react with silane-containing bonding agents. As a result, an increase in the effectiveness of the adhesive cementation may be seen by the copolymerization between silane and resin cement [14,15]. Nevertheless, it remains unclear whether the silica is chemically bonded to zirconia or weakly attached to it [13,14].

In terms of chemical bonding, 10-metacryloyloxydecyl dihydrogen phosphate (10-MDP) has been extensively used as a coupling agent for Y-TZP bonding. This acid functional monomer has a chemical structure with long and hydrophobic spaced carbon chains, which can create a durable bonding with zirconium dioxide [16–18]. Several chemical analytic techniques have validated the chemical reaction between MDP and zirconia [3,19,20]. There is a variety of MDP-based primers available in the market, making it difficult for the clinicians to choose which one to use in a specific clinical situation [6]. These primers are often formulated by adding the MDP molecule to a solvent (acetone, ethanol, or water) [18]. In order to generate a single agent which can be effectively used for different ceramics, primer or adhesives containing 10-MDP, silane (γ-Methacryloxypropyltrimethoxysilane) molecules and other ingredients in a single bottle have been developed [3,21]. However, variations in the chemical formulation of different MDP-based primers or adhesives can affect the bonding efficacy of 10-MDP to Y-TZP [18], since different ingredients may mutually compete to contact the zirconia surface. For example, the effect of the MDP-functional group on the zirconia surface may be inhibited by the reaction of the phosphate-functional group with other compounds [14,20,22]. Although initial bond strength values may be high, there is no consensus about the durability of the bonding between zirconia and those products [3,15–17,21,23,24]. The synergistic or antagonistic bond-promoting effect from the combination of MDP and silane molecules [3,20] still requires clarification.

The objectives of this laboratory study are: to evaluate the surface properties (wettability, roughness and surface free energy) of Y-TZP after different grit blasting protocols and chemical pre-treatments; to evaluate the effect of grit blasting and chemical pre-treatments on the bond strength between resin cement and Y-TZP. The bonding between the different chemical treatments and the Y-TZP surface was analyzed by Time-of-Flight secondary ion mass spectrometry (ToF-SIMS). Two null hypotheses were tested: (1) Surface properties (wettability, roughness and surface free energy) are not affected by the different surface pre-treatments; (2) Bond strength between resin cement and Y-TZP is not affected by the surface pre-treatments evaluated.

2. Materials and methods

Y-TZP (Lava Plus, 3M-ESPE) slabs measuring 10 mm × 6 mm × 2 mm were milled from CAD/CAM blocks on an E4D Dentist System (D4D technologies, LLC, Richardson, TX, USA) using a custom-mill file. After being fully sintered according to manufacturer's instructions, the slabs were

Table 1 – Overview of different materials employed.

Material	Manufacturer/Batch number	Composition	Chemical treatment/protocol
RelyX Ceramic Primer (SP)	3M ESPE-Saint Paul, Minnesota, USA/N843209	3-trimethoxysilylpropyl methacrylate (MPS), Ethanol, Water	Rely X Ceramic Primer applied in one coat with microbrush, left undisturbed for 60 s and gently air-dried for 5 s.
Clearfil Ceramic Primer (MPS)	Kuraray Dental-Kurashiki, Okayama, Japan/7N0017	MPS, 10-Methacryloyloxydecyl dihydrogen phosphate (MDP), Etanol	Clearfil Ceramic Primer applied in one coat with microbrush, left undisturbed for 10 s and gently air-dried for 5 s.
Alloy Primer (MP)	Kuraray Dental-Kurashiki, Okayama, Japan/A50077	MDP, 6-(4-Vinylbenzyl-*n*-propyl) amino-1, 3, 5-triazine-2, 4-dithione (VBATDT), Acetona	Alloy Primer applied in one coat with microbrush, left undisturbed for 10 s and gently air-dried for 5 s.
Clearfil Universal Bond (MPA)	Kuraray Dental-Kurashiki, Okayama, Japan/000022	MDP, silane coupling agent, bisphenol A diglycidylmethacrylate, 2-hydroxyethyl methacrylate, hydrophobic aliphatic methacrylate, colloidal silica dl-camphorquinone, initiators and accelerators, water.	Clearfil Universal Adhesive applied in one coat with microbrush, left undisturbed for 5 s and gently air-dried for 5 s. Light cured for 10 s.

ultrasonically cleaned in acetone for 10 min, followed by thorough drying with oil-free compressed air for 10 s. One surface of each specimen was treated according to the experimental group: air abrasion with 45 μm alumina particles (Al – blasting, Polidental Ind., Cotia, São Paulo, Brazil) or air abrasion with 30 μm silica-coated alumina particles (C – blasting – Cojet, 3M ESPE Dental Products, Saint Paul, Minnesota), both at 2.5 bar pressure for 15 s at a working distance of 10 mm from the zirconia surface. Then, all specimens were ultrasonically cleaned for 10 min in distilled water and air oil-free was used to dry the specimens for 15 s. Samples treated with either Al or C were randomly distributed to five groups according to the following treatments: no chemical treatment (Al or C), Silane-containing ceramic primer (SP), MDP and silane-containing ceramic primer (MPS), MDP-containing primer (MP) and MDP and silane-containing adhesive system (MPA). The composition of the primer or adhesive solutions and treatment protocols for each experimental group are presented in Table 1.

2.1. *SEM/EDS analysis*

The analysis and characterization of Y-TZP surfaces grit-blasted with either silica-coated alumina particles or alumina particles was performed using SEM as well. Si and AL distribution on the surface of treated zirconia was quantified by Energy-dispersive X-ray spectroscopy analysis (EDS; X-Max, Oxford Instruments, United Kingdom) after sputter coating with carbon.

2.2. *Roughness corrected contact angle analysis using Theta topography system*

For the analysis of the roughness-corrected contact angle (θ_m), Y-TZP slabs were treated with either Al or C and randomly distributed to five groups according to the chemical treatments as previously mentioned (n = 5 — Table 1). The θ_m values were measured using an Attension Theta Topography (Biolin Scientific, New Jersey, USA) by the Fringe Projection Phase Shifting (FPPS) method. For this purpose, roughness parameters were measured with a LED light projected onto the sample surface and a sinusoidal fringe pattern slide (fringe project phase-shifting). Then, the Young contact angle (θ_Y) was measured by dropping one 5 μL drop of distilled water onto the treated zirconia surface. Multiple images were recorded during 10 s to obtain the dynamic contact angle. The Young contact angle (θ_Y) and surface roughness parameters were accurately measured from the same area, in the center of the sample.

The surface roughness parameter (increment of the interfacial surface area relative to a flat plane baseline - Sdr) was used in the Wenzel equation which calculated the roughness-corrected contact angle:

$$\cos\theta_m = r\cos\theta_Y \tag{1}$$

Where:

r (roughness ratio) = 1 + (Sdr/100)

Sdr = ratio between interfacial and projected area.

2.3. *Surface free energy*

Contact angles (CA_m) were measured to investigate the surface free energy (SFE) characteristics of the Y-TZP slabs treated by mechanical (Al or C) and chemical treatments (NC, SP, MPS, MP and MPA) as previously described ($n = 5$). The treated samples were subjected to surface free energy analysis with a goniometer (Easy Drop Contact Angle-Kruss Inc., Hamburg, Germany) using the sessile drop technique. Two liquids with different surface tensions were used: distilled water and diiodomethane, at room temperature. The SFE (mJ/m^2) was calculated using the harmonic average formula (Eqs (1) and (2)) of Owens and Wend, 1969 [25] and information relating to the liquids [26]. The contact angle was replaced to isolate the dispersive and polar constants of each solid. The sum of these constants corresponds to the SFE of zirconia surface (${\gamma_s}^{TOT}$).

$$\gamma_L^{TOT} = \frac{4\,\gamma_S^D\,\gamma_L^D}{\gamma_S^D + \gamma_L^D} - \frac{4\,\gamma_S^P\,\gamma_L^P}{\gamma_S^P + \gamma_L^P} \tag{2}$$

$$\gamma_S^{TOT} = \gamma_S^D + \gamma_S^P \tag{3}$$

Where:

γ_L^{TOT} corresponds to the SFE of the liquid $\cos\theta$ = cosine of the liquid CA_m for diiodo- methane or water.

γ_S^D corresponds to the dispersive energy of the solid.

γ_L^D corresponds to the dispersive energy of the liquid.

γ_S^P corresponds to the polar energy of the solid.

γ_L^P corresponds to the polar energy of the liquid.

γ_S^{TOT} correspond to the SFE of zirconia surface.

2.4. *Time-of-flight secondary ion mass spectrometry (ToF-SIMS)*

Y-TZP surfaces were treated using air abrasion with 45 μm alumina particles and were randomly distributed to five groups: no chemical treatment (NC), Silane-containing ceramic primer (SP), MDP and silane-containing ceramic primer (MPS), MDP-containing primer (MP) and MDP and silane-containing adhesive system (MPA). Then, the chemical analysis of the treated zirconia surface was carried with a dual beam PHI TRIFT V nano TOF (Physical Eletronics, Chanhassen, MN USA/ULVAC-PHI, Kanagawa, Japan) spectrometer equipped with 20 KeV $Bi3^+$ for the analysis and a 3 eV Cs^+ ion beam for the sputtering operated in ${G_{A1}}^+$ mode. TOF cycles of sputtering Argon and mass data acquisition were performed at surface, 100 nm and, 200 nm. The high-energy G_A gun (20 keV, DC current 750 nA) created a $500 \times 500\ \mu m^2$ crater on the coated layer in a sputter time of 300 s. Negative ions ${ZrO_2}^-$ (121.9) and $ZrO_2\ (OH)^-$ (138.9) were identified as the characteristic ions of zirconia substrate. A negative ion of trimethoxysilyl group ${SiO_3C_3H_9}^-$ (121) were the characteristic peak of MPS, while MDP was identified by ${PO_2}^-$ (63) and ${PO_3}^-$ (79) peaks [20].

2.5. *Microshear testing*

Samples treated with either Al or C were randomly distributed to five groups according to the chemical treatment applied (Table 1; $n = 10$). For the bonding experiments, two resin cement (RelyX Ultimate) cylinders were carefully built on the surface of each zirconia slab. For that purpose, a silicone mold (Express^{TM} Impression Material, 3M ESPE-Saint Paul, Minnesota, USA) with 1.0 ± 0.1 mm in diameter and 1.0 ± 0.1 mm in height was carefully positioned and stabilized, and then filled with resin cement. Each cylinder was light-cured using a one wave light emitting diode curing unit (Demi^{TM} Kerr Dental, mean irradiance of 1102 mW/cm^2) for 40 s from the top of the a silicone mold. The molds were removed after 5 min. The 40 cylinders built for each grit blasting treatment (Al or C) were randomly distributed into two groups, according to storage time: 24-h or 8 months. The specimens were stored in 100% relative humidity at 37 °C.

After the storage period, specimens were mounted in a metallic base and placed in a universal testing machine (Instron 4301, Norwood, MA, USA) and a shear load was applied at the interface between the resin cement cylinder and the zirconia surface with a thin wire (0.2 mm diameter) at a crosshead speed of 0.5 mm/min, until failure occurred. The microshear bond strength (μSBS) value for each resin cement cylinder was calculated based on the load at fracture and the sample dimensions at the interface and expressed in MPa.

2.6. *Data analysis*

Data normality was assessed using the Shapiro-Wilk test at a preset alpha of 0.05. The original corrected contact angle (θ_m) values, surface free energy (SFE) values (mN/m) and the surface roughness (Sdr) values were statistically analyzed using two-way ANOVA (grit blasting*chemical treatment).

The effect of grit blasting, chemical treatment, storage time and interaction between them on μSBS values was analyzed using three-way ANOVA and post hoc Tukey test (SPSS 20, SPSS Inc., Chicago, IL, USA), for that purpose, microshear bond strength for each sample was calculated as the mean values between the two cylinders built. The overall statistical significance was pre-set at 5%.

3. Results

3.1. *SEM/EDS analysis*

SEM images of the alumina-blasted (Fig. 1b) and silica-coated alumina-blasted (Fig. 1c) zirconia surface indicated that both surfaces exhibited similar topography with grooves irregularly distributed throughout the surface. EDS analysis revealed a scatter amount of silicon (Si) and aluminum (Al) over the Y-TZP surface after C - blasting treatment (Fig. 2b and c). As expected, Al was detected on the alumina-blasted surface (Fig. 2a).

3.2. *Roughness corrected contact angle analysis*

Table 2 shows the values of roughness-corrected contact angle (θ_m). ANOVA revealed that “chemical treatment” ($p < 0.001$) was significant for θ_m values, while “grit blasting” was not significant ($p = 0.071$). The highest θ_m values were presented when zirconia surface was grit-blasted (no chemical treatment) followed by blasted surface treated with MDP-based primer. The lowest θ_m values were observed for silane-based primer treated samples. For roughness parameters (Sdr),

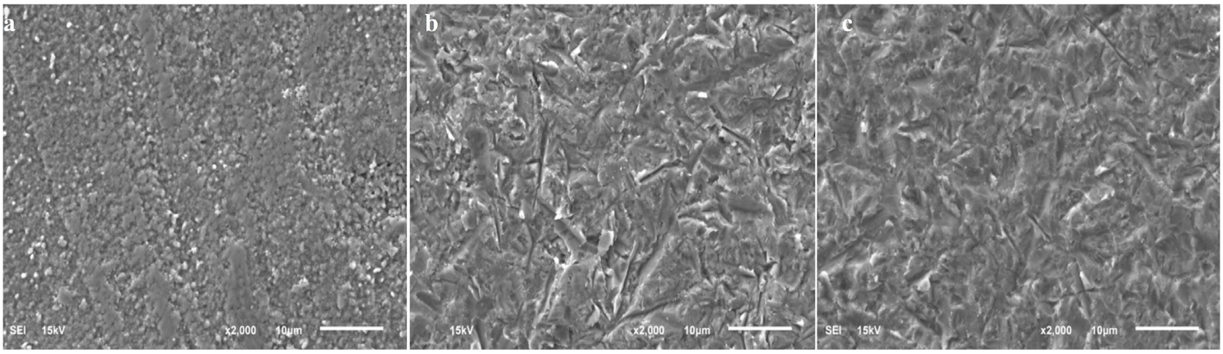

Fig. 1 – SEM micrographs of the Y-TZP surfaces: (a) control as received from CAD-CAM machining; (b) blasted with 45 μm alumina particles; (c) blasted with 30 μm silica-coated alumina particles (CoJet^{TM} Sand).

Table 2 – Results (mean and standard deviation) of the roughness-corrected contact angle (θ_m), roughness parameter (Sdr), surface free energy ($\gamma^{TOT}{}_S$) and for groups tested.

Chemical treatment (primer/adhesive)	Roughness-corrected contact angle (θ_m) values	Roughness parameter (Sdr%)	$\gamma^{TOT}{}_S$(mN/m)
NC	85.9 (3.8)A	34.3 (8.3)B	20.6 (6.02)D
SP	50.5 (5.4)D	36.18 (9,8)B	48.2 (3.8)A
MPS	71.6 (2.1)B	110.5 (9.9)A	43.5 (3.7)B
MP	76.6 (3.3)B	35.1 (7.5)B	30.4 (3.2)C
MPA	65.7 (4.7)C	105.2 (15.8)A	42.3 (3.5)B

NC: abrasion with 45 μm alumina particles or 30 μm silica-coated alumina particles (no chemical); SP: Silane-containing ceramic primer; MPS: MDP and silane-containing ceramic primer; MP: MDP-containing primer; MPA: MDP-containing adhesive system. Values followed by different uppercase letters within the same column show significant differences between the chemical treatments ($p < 0.05$).

“chemical treatment” ($p < 0.001$) was significant, while “grit blasting” was not significant ($p = 0.51$). (Table 2). MPS and MPA groups showed higher Sdr values than others groups.

Images of the water contact angle of tested groups are shown in Fig. 3. Considering the samples that received chemical treatment, MPS and MP treatment showed the highest contact angles (Fig. 3c and d). In contrast, samples treated with either SP or MPA presented significantly lower contact angles (Fig. 3b and e).

3.3. *Surface free energy*

Table 2 shows the $\gamma^{TOT}{}_S$ values for all experimental chemical treatments. The analysis of the results (two-way ANOVA) indicated that “chemical treatment” ($p < 0.001$) was significant, while “grit blasting” was not significant ($p = 0.101$). There was no significant interaction between the two factors (grit blasting*chemical treatment ($p = 0.50$)). The lowest $\gamma^{TOT}{}_S$ values were observed for control (NC) samples, followed by MP, whereas SP-treated samples showed the highest values of $\gamma^{TOT}{}_S$.

3.4. *Time-of-flight secondary ion mass spectrometry (ToF-SIMS)*

The analysis of negative ion spectra was performed at three points: 0, 100 and, 200 nm from the zirconia surface. The negative spectra in 100 and 200 nm were identical for all experimental groups. All groups showed negative ions originating from the zirconium oxide surface such as ZrO_2^- (121.9) and ZrO^- (138.9). The OH^- (17) peaks appear in all the spectra and may correspond to the water adsorption. The SP group showed a peak at m/z 121 and/or 122 with more intense than other groups. This peak may be correlated to $SiO_3\ C_3\ H_9^-$ (121–122) from the silane-containing primer. The presence of phosphate-related ions after application of MDP-containing primer/adhesive is readily measured by means of the PO_2^- (63), PO_3^- (79), and $H_2PO_4^-$ (97) (Fig. 4).

The peak intensity of OH^- (17), PO_2^- (63), PO_3^- (79), and $H_2PO_4^-$ (97) differed in according to treatment group and depth analysis (Fig. 4). MPA group showed the greatest amount of PO_2^- (63), PO_3^- (79), and $H_2PO_4^-$ (97) in all depths (0, 100 and 200 nm). All primer and adhesive systems containing MDP demonstrated a decrease in amounts of phosphate-related ions at 100 nm and 200 nm compared to surface (0 nm) (Fig. 4). After application of MDP and silane-containing adhesive system, a higher amount of OH^- (17) was observed on the zirconia surface, decreasing this amount at 100 nm and 200 nm (Fig. 4). The presence of P–O–Zr bonds was evidenced by mass ions at m/z 185, 201, 265, 281 [20]. The MP group demonstrated the highest intensity for most of those in all depth analysis (Fig. 5).

3.5. *Microshear bond strength testing*

Analysis of microshear bond strength results showed that the factors “grit blasting” ($p < 0.001$), “chemical treatment” ($p < 0.001$), and “storage time” ($p < 0.001$) were significant for bond strength as well as the interaction between the fac-

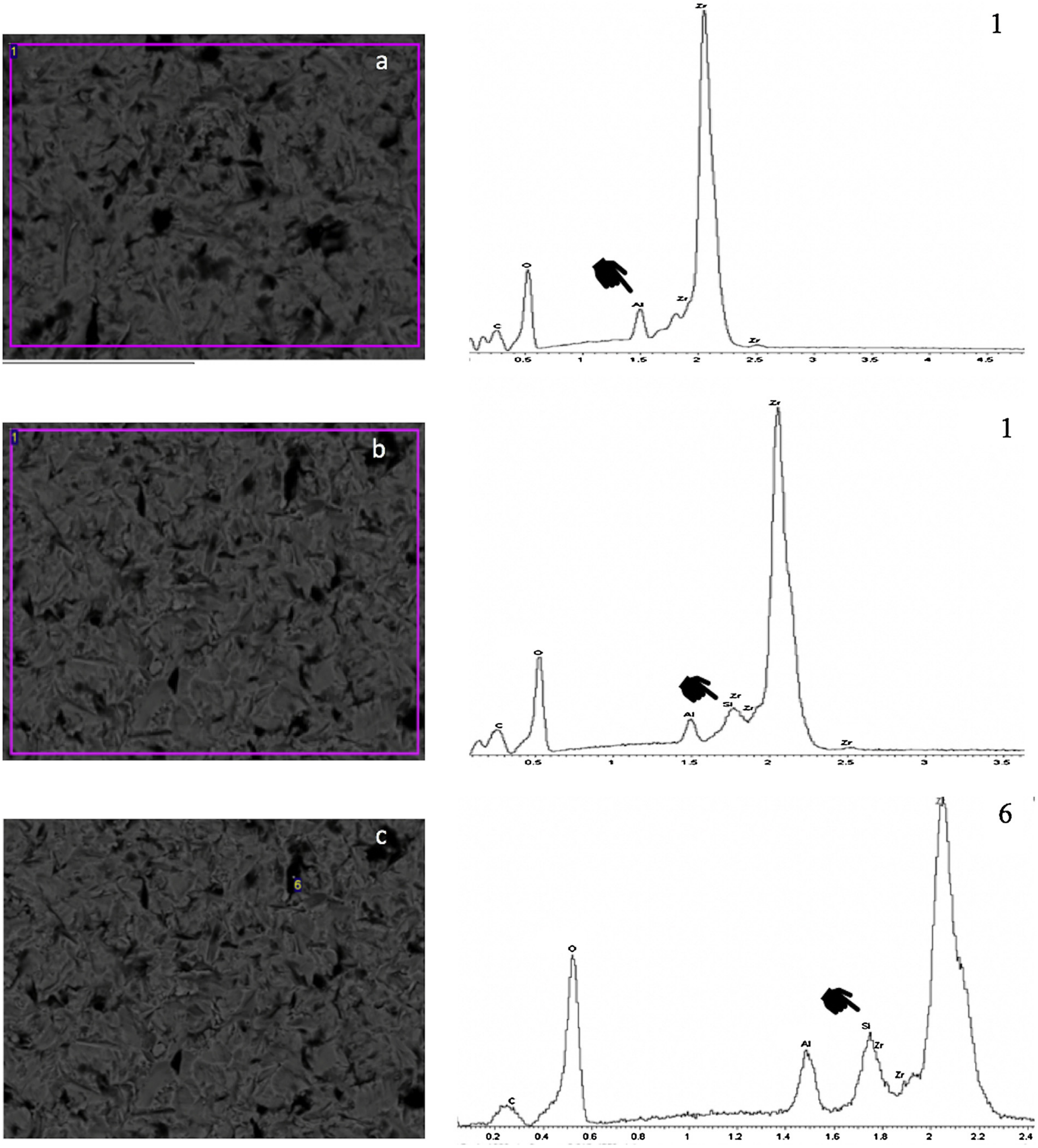

Fig. 2 – EDS analysis of grit blasted Y-TZP surfaces cleaned with water in ultrasonic bath (10 min): (a) alumina-blasted Y-TZP showing presence of some aluminum (finger point) throughout the surface (b) tribochemically-coated Y-TZP showing low concentration of silica throughout the surface (finger point) and (c) some silica was located in the deepest spots over the surface (finger point).

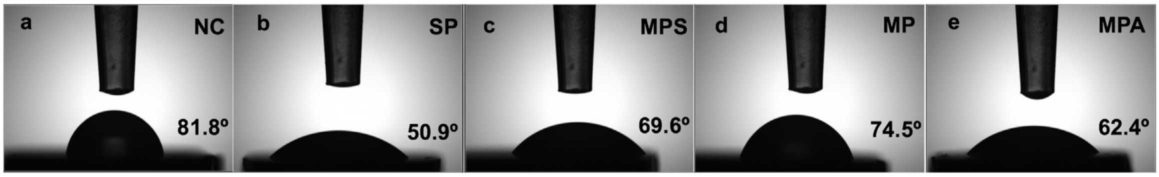

Fig. 3 – Representative images of water contact angles on the alumina-blasted (NC) surface (a), treated surface using silane-containing ceramic primer (SP) (b), MDP and silane-containing ceramic primer (MPS) (c), MDP-containing primer (MP) (d), MDP and silane-containing adhesive system (MPA) (e).

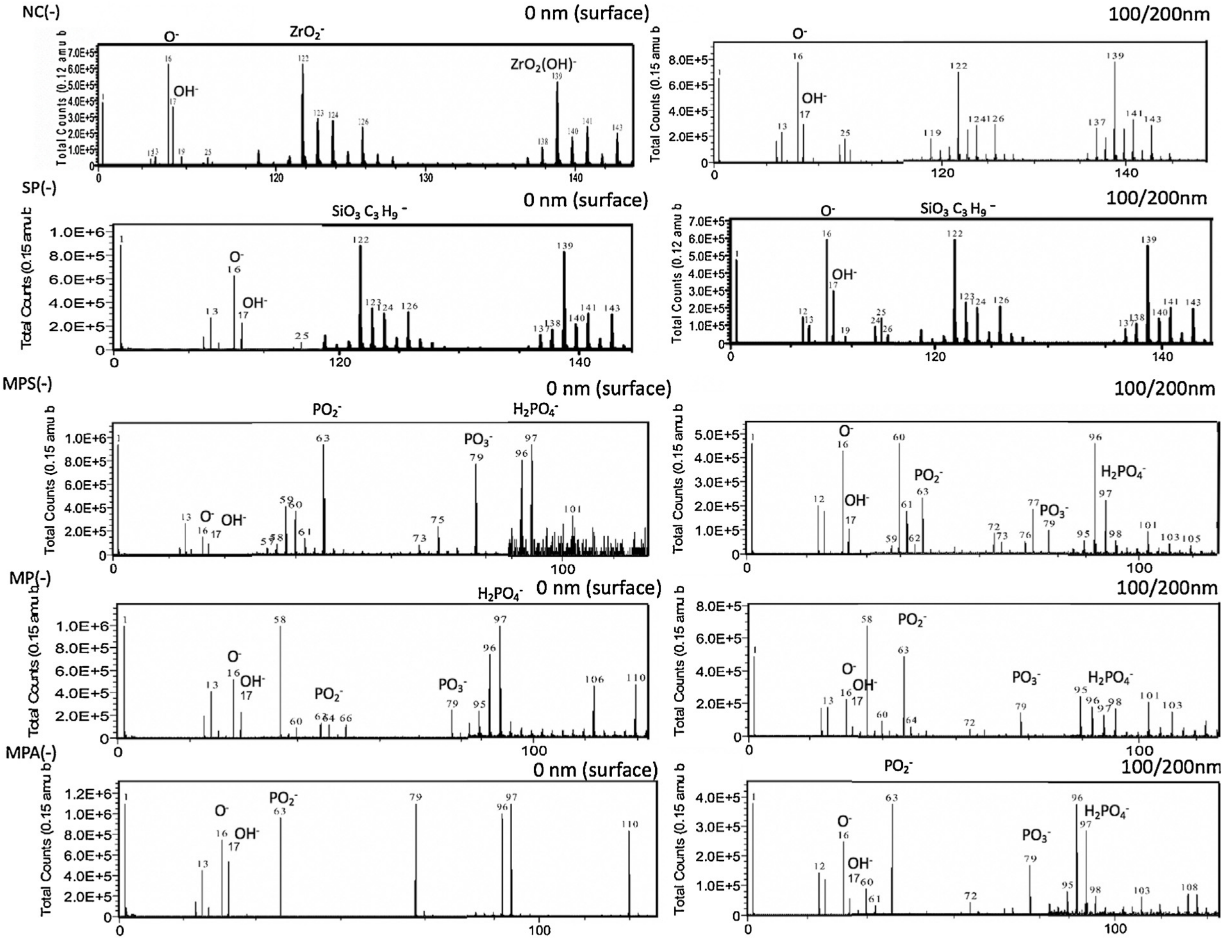

Fig. 4 – Negative secondary ions mass ToF-SIMS spectra for all experimental groups. ZrO_2^- and $ZrO_2(OH)^-$ at m/z 121.9 and 138.9 were revealed and are characteristic of zirconia. Groups coated with MDP (MPS, MP and, MPA) showed PO2– (63), PO3– (79).

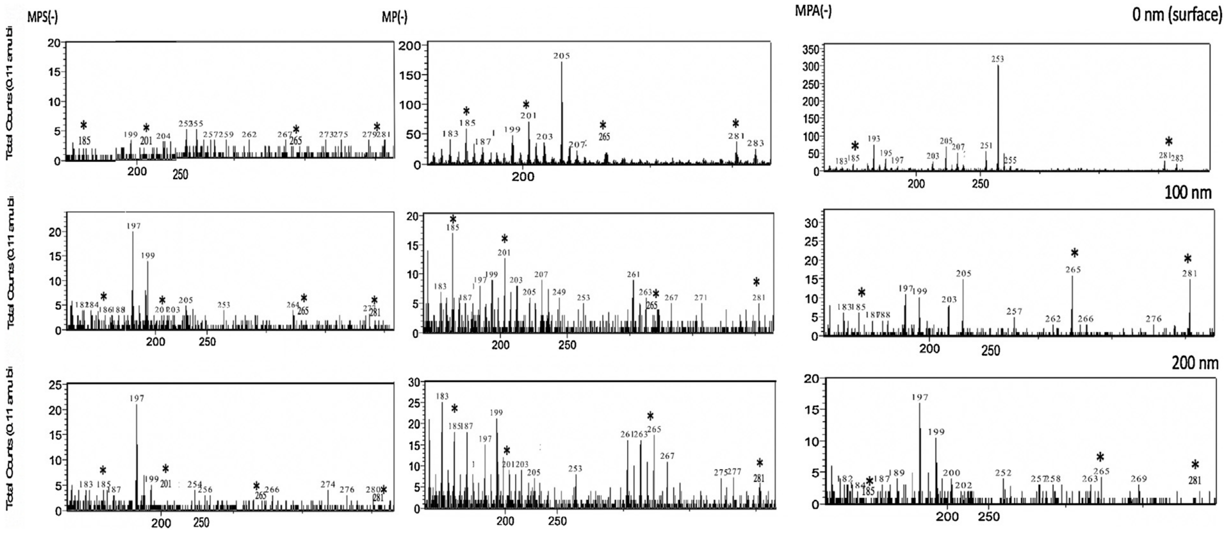

Fig. 5 – Expansion of negative ion mass spectrum (m/z 180–360 region) to illustrate the zirconia-phosphate bonding. Asterisks indicate the presence of P–O–Zr bonds.

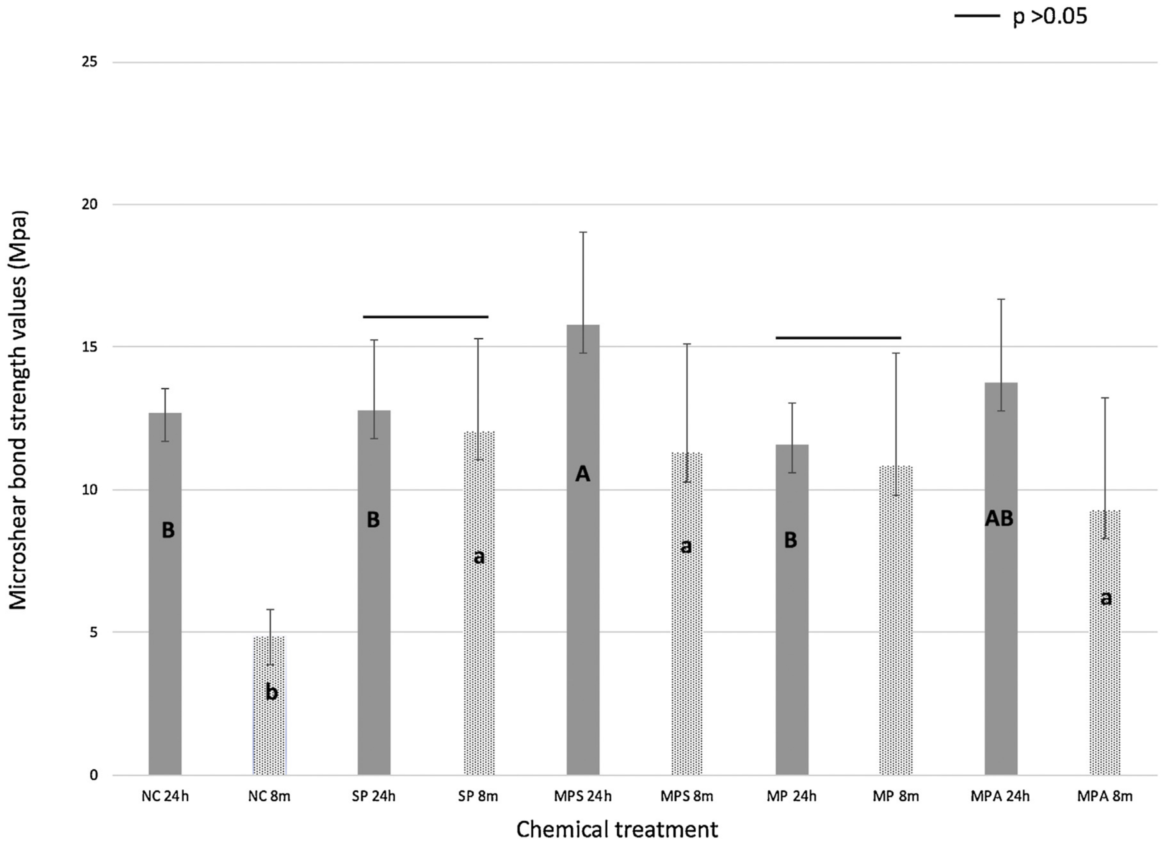

Fig. 6 – Means and standard deviation of μSBS values for groups tested after 24-h and 8-months storage in distilled water. NC: no-chemical treatment; SP: Silane-containing ceramic primer; MPS: MDP and silane-containing ceramic primer; MP: MDP-containing primer; MPA: MDP and silane-containing adhesive system. Values followed by different uppercase letters show significant differences between the chemical treatment after 24 h, while different lowercase letters show significant differences after 8 months ($p < 0.05$). The horizontal bars indicate no significant difference for microshear bond strength between both storage times ($p > 0.05$).

tors “chemical treatment*storage time” ($p = 0.000$). Overall, the alumina-blasted zirconia surfaces chemically treated presented higher μSBS values than C - blasted surfaces. Fig. 6 shows the μSBS values for the interaction between the factors “chemical treatment*storage time”. The results reveled that MPS and MPA groups showed higher μSBS values in 24-h compared to other groups. After aging (8 months), NC-treated samples presented the lowest μSBS values.

4. Discussion

Several methods have been used to modify the zirconia surface as an attempt to improve zirconia’s reactivity, thus enhancing its bond strength to resin cement. Amongst the possible treatments, the association between grit blasting and chemical methods has been considered a reliable alternative. In this study, two types of grit blasting treatments were used, blasting with alumina oxide particles (45 μm - Al) or silica-coated alumina particles (30 μm - C). Cleaning with an ultrasonic bath for 10 min was performed after surface blasting, thus before application of the different primer or adhesive systems. The majority of the silica particles deposited was removed after ultrasonic bath cleaning, indicating that the silica particles are weakly attached to the zirconia surface, as previously suggested [14]. This fact can be confirmed by the EDS results, since no difference in the topographic features and a mild difference in silica distribution was observed on zirconia surface after grit blasting using either alumina particles (Fig. 2a) or silica-coated alumina particles (Fig. 2b). As a result, grit blasting was not a significant factor for the physicochemical properties analyzed such as wettability, surface free energy and bond strength.

Surface properties (wettability, roughness and surface free energy) were evaluated in this study after the application of surface grit blasting and chemical treatments. Results showed that the surface properties of zirconia (Table 2) were affected by the chemical treatment and, consequently, the first null hypothesis was rejected. The wettability of the treated-zirconia surface was determined by measuring the roughness corrected contact angle (θ_m). The θ_m parameter calculates the contact angle of a rough surface, using the Young contact angle for a smooth surface (θ_Y) and the roughness ratio ($r = 1/Sdr$). The Sdr parameter is sensitive to the surface slope and determines the additional surface area created by roughness compared with that of a totally flat plane substrate [15,27]. Table 2 shows that MPS and MPA-treated samples showed higher roughness values than other groups. Different explanations may be associated with the rougher surfaces encountered. MPA, for example, has colloidal silica in its composition and the presence of those filler particles seem to be enough to affect roughness parameters. Although MPS does not have filler particles in its composition, the application of the primer on the substrate with a microbrush may have incorporated bubbles and voids in the micro- and nano-scale range, affecting the final surface roughness of the substrate. Furthermore, variations in the monomer distribution and type of solvent used may have played a role in the lower roughness values presented by the other experimental groups. The surface energy and the wettability of treated Y-TZP surface varied according to the chemical changes caused by the application of a primer or adhesive. SP group showed the highest surface free energy values and the lowest θ_m contact angle values (Table 2). This may be explained by the hydrophilicity of the Y-TZP surface after silane agent treatment [28]. The high wettability was a consequence of the presence of both the silanol groups on the zirconia surface and the water in the silane coupling agent [29–31]. Although silane cannot contribute to the chemical bond to zirconia directly, the increase in the wettability of silane-treated surface has potential to enhance the initial bond strength of resin cements to zirconia restorations [21,23].

Regarding MPS and MPA groups, both materials used have silane and MDP molecules in their composition. The MDP and silane-containing adhesive uses water as a solvent. However, these groups showed lower surface free energy and higher contact angle values than SP-treated samples. This may be due to the chemical bond formed between the phosphates or phosphonates groups of MDP and the zirconium oxide (P–O–Zr), which decreases the density of dangling atomic bond on Y-TZP's surface [32,33]. For the samples treated with the MDP-based primer tested in this study, higher contact angle and lower surface free energy values were observed when compared to other chemical treatments (Table 2 and Fig. 3), indicating that a higher amount of P–O–Zr bonds were formed on the zirconia surface, as demonstrated by the ToF-SIMs analysis (Fig. 5). These findings show how the chemical treatment can modify the surface topography and surface physicochemistry of zirconia, affecting the ability of the resin cement to wet the ceramic surface, which may either positively or negatively affect the resin-mediated zirconia bonding [21,16]. The control group (no chemical treatment) presented low surface free energy and high contact angle values which can be attributed to hydrocarbon contamination of these surfaces after exposure to laboratory air [34,35]. Non-noble metal oxide materials, including zirconium dioxide (ZrO_2), are characterized by their superhydrophilicity, but after the physisorption of hydrocarbons to OH– groups and other energetically favorable sites present on the zirconia surface, modifications on the surface properties may occur [34,35].

The bonding mechanism of phosphate ester monomers to Y-TZP is based in hydroxylation-drive chemistry as observed in the silane-glass ceramic bonding [36]. In the present study, different commercial 10-MDP-coating primer/adhesive systems were used for pre-treating surface-roughened Y-TZP to better reflect the clinical situation. The chemical bond between these products and zirconia was analyzed using ToF-SIMS. All MDP-based products showed peaks of PO_2^- (63), PO_3^- (79), and $H_2PO_4^-$ (97), which are the elemental ions to yield the formation of P–O–Zr bonds and the ZrP compounds [20]. However, the peak intensity of these ions varied depending on the primer or adhesive applied and the analysis depth on the zirconia surface (Fig. 4). The greatest amount of PO_2^- (63), PO_3^- (79), and $H_2PO_4^-$ (97) were observed for the MPA group in all depths (0, 100 and 200 nm) (Fig. 4). However, these groups presented lower intensity of mass ions at m/z 185, 201, 265, 281 that correspond to P–O–Zr bonds (Fig. 5). Therefore, although the MDP and silane-based adhesive generated the highest amounts of PO_3^-, it is possible that the effect of the MDP monomer was inhibited by the different components in the adhesive, such as the silane molecules leading to the formation of Si–O–P bonds [22]. Moreover, the acid pH (<2.5) of this adhesive may have reduced the bonding capacity of the MDP monomer [14]. The MDP and silane-based adhesive system used in this study uses water as a solvent, which can influence the chemical affinity of MDP for Y-TZP because of the insolubility of the MDP molecule in water, which results in minimal deposition of MDP on the zirconia surface. Experimental primers using acetone as the solvent showed the highest percentage of P–O–Zr bonds in comparison to primers containing ethanol, as confirmed by the ToF-SIMS results of the present study [18].

Theoretically, phosphate groups in the MDP molecule can react with one or two zirconium atoms, forming two bonding configurations: “double coordinate” and “single coordinate” [3]. In this study, the chemical bonds between MDP and zirconia were identified as a single coordinate in the monodentate form and bridging bidentate or phosphates bridged at one zirconia atom (m/z 185, 201, 265, 281), as reported in a recent study [20]. The MP group showed the highest intensity of peaks (m/z 185, 201, 265, 281) correspondent to P–O–Zr compared to MPS group (Fig. 5). This may be attributed to the presence of silanols in the MDP and silane-based primer, which may impair the strength between MDP and zirconia surface, as previously mentioned for the MPA group. Although the chemical characterization using ToF-SIMS analysis indicated that the greatest amount of P–O–Zr bonds was obtained when the MDP-based primer was applied on the grit blasted zirconia surface (MP group), this primer did not produce the highest bond strength values for both storage times evaluated (Fig. 6). This may be due to the low sensitivity of the shear bond strength test. Nevertheless, the μSBS values did not decrease after storage time in distilled water (8 months) for MP group, suggesting that the P–O–Zr covalent bonds formed may help to resist the penetration of water and retain bond durability, as demonstrated by other studies [11,20,21,24]. Therefore, the type of chemical treatment used affected the strength of the resin-mediated zirconia bonding, leading to the rejection of the second null hypothesis. For the SP group, a decrease in the μSBS values was not also observed. However, this chemical method showed pre-test failures that were excluded from the statistical analysis, leading to an apparent higher bond strength for silane-based primer after aging time (Fig. 6). As observed in the results of shear bonding test, the silane molecule present in the primer or adhesive systems increases the wettability of the zirconia surface (Table 2), improving the initial values. However, all groups containing silane presented lower μSBS values after storage in water, as reported by other studies [23]. This was a clear indication of the hydrophilicity of the silane molecule, which has a deleterious effect on the longevity of the bonding due to the hydrolytic degradation of the interface [23]. As observed in Fig. 6, a significant decrease in μSBS values for NC group occurred after aging. This finding confirms that the combination of grit blasting and chemical pre-treatments is crucial to achieve a durable bonding to zirconia.

Although this study aimed at evaluating the effect of grit blasting protocol and chemical treatments on the surface of zirconia, the analysis of the real effect of tribochemical silica coating on the zirconia-bonding was limited since the majority of the silica coating was removed by a simple cleaning procedure. Therefore, further investigations that include physicochemical analyses of the combination of this tribochemical silica blasting with silica-coated particles and solutions containing MDP and silane molecules to improve resin-zirconia bonding should be conducted. Furthermore, the analysis of the effect of clinically-applied cleaning methods on the partial/total removal of silica also deems further investigation.

5. Conclusion

1 Chemical treatments (primer or adhesive application) affect the surface topography and physicochemistry (roughness, wettability, and surface free energy) of Y-TZP.
2 Bonding to zirconia may be affected by the chemical treatment. When the surfaces were blasted with particles, this study showed that the use of a MDP-only containing primer is the only treatment capable of promoting a stable bond to Y-TZP.
3 The effectiveness of the chemical interaction between MDP molecule and zirconium oxide can be compromised when this molecule is present in a multicomponent system.

Funding

This study was financed in part by the Coordenaçã̃o de Aperfeiçoamento de Pessoal de Ní́vel Superior - Brasil (CAPES) - Finance Code 001.

Acknowledgements

The authors are in debt to Dr. Shahram Karimi and Dr. Ricardo Cuello (Lambton College, Canada) for roughness corrected contact angle support. The authors would like to gratefully thank Department of Comprehensive Care, School of Dental Medicine, Case Western Reserve University for Ion Mass Spectrometry support. The research received financial support from CAPES (Coordination of Improvement of Higher Level).

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