Influence of different surface treatment protocols on the bond strength of itrite stabilized polycrystalline zirconia Itry stabilized polycrystalline tetragonal

Influência de diferentes protocolos de tratamento superficial na resistência de união da zirconia tetragonal policristalina estabilizada por itria

Influência de diferentes protocolos de tratamiento de superficies en la fuerza de unión de la zirconia policristalina estabilizada con itrite

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Abstract

Evaluate the influence of different surface treatment protocols on shear bond strength in zirconia ceramics. A hundred zirconia cylinders were made using a CAD/CAM system. The specimens were divided into 10 groups: No treatment; Clearfil Ceramic Primer; Scotch bond Universal; Clearfil Ceramic Primer + Scotch bond Universal; 50% hydrofluoric acid + Scotch bond Universal; Airborne-particle abrasion; Airborne-particle abrasion + Clearfil Ceramic Primer; Airborne-particle abrasion + Scotch bond Universal; Airborne-particle abrasion + Clearfil Ceramic Primer + Scotch bond Universal; Airborne-particle abrasion+50% hydrofluoric acid + Scotch bond Universal. All specimens were cemented with Panavia F 2.0, stored in distilled water, and then thermo cycled. The shear bond strength test was performed in a universal testing machine. Fractographic and surface zirconia analysis was done with a stereomicroscope, SEM and WDS. Data were analyzed using Pearson's chi-square test, Fisher exact test, and the Kruskal-Wallis test. The highest shear bond strength values were observed in the groups treated with hydrofluoric acid, besides, these groups did not show pre-test failure. The predominant failure mode was adhesive. Among the surface treatment protocols evaluated, 50% hydrofluoric acid conditioning associated with the Scotchbond Universal adhesive system offers higher values of shear bond strength to the zirconia, regardless of the use of microblasting.

Keywords: Ceramic; Y-TZP Ceramic; Shear Strength; Resin Cements; Hydrofluoric Acid.

Resumo

O objetivo deste estudo laboratorial foi avaliar a influência de diferentes protocolos de tratamento de superfície na resistência ao cisalhamento de cerâmicas de zircônia. Cem cilindros de zircônia foram feitos, usando o sistema CAD / CAM. Os espécimes foram divididos em 10 grupos: Sem tratamento; Clearfil Ceramic Primer; Scotchbond Universal; Clearfil Ceramic Primer + Scotchbond Universal; Ácido fluorídrico a 50% + Scotchbond Universal; Abrasão por partículas transportadas pelo ar; Abrasão por partículas aéreas + Clearfil Ceramic Primer; Abrasão por partículas aerotransportadas + Scotchbond Universal; Abrasão por partículas aéreas + Clearfil Ceramic Primer + Scotchbond Universal; Abrasão por partículas

aerotransportadas + ácido fluorídrico 50% + Scotchbond Universal. Todos os corpos-de-prova foram cimentados com Panavia F 2.0, armazenados em água destilada e termociclados. O ensaio de resistência ao cisalhamento foi realizado em máquina de ensaio universal. As análises fractográficas e da superfície da zircônia foram feitas com estereomicroscópio, MEV e WDS. Os dados foram analisados por meio do teste qui-quadrado de Pearson, teste exato de Fisher e teste de Kruskal-Wallis. Os maiores valores de resistência ao cisalhamento foram observados nos grupos tratados com ácido fluorídrico, além disso, esses grupos não apresentaram falha pré-teste. O modo de falha predominante foi adesiva. Dentre os protocolos de tratamento de superfície avaliados, o condicionamento com ácido fluorídrico 50% associado ao sistema adesivo Scotchbond Universal oferece maiores valores de resistência ao cisalhamento à zircônia, independente do uso de microjateamento.

Palavras-chave: Cerâmica; Cerâmica Y-TZP; Resistência ao cisalhamento; Cimentos de resina; Ácido fluorídrico.

Resumen

El objetivo de este estudio de laboratorio fue evaluar la influência de diferentes protocolos de tratamiento de superficies en la resistencia al cizallamiento de cerámicas de zirconio. Fabricarónse cien cilindros de zirconio utilizando el sistema CAD/CAM. Las muestras se dividieron en 10 grupos: Sin tratamiento; Clearfil Ceramic Primer; Scotchbond Universal; Clearfil Ceramic Primer + Scotchbond Universal; ácido fluorhídrico (50 %) + Scotchbond Universal; Abrasión por partículas transportadas por el aire; Abrasión por partículas aéreas + Clearfil Ceramic Primer; Abrasión por partículas en el aire + Scotchbond Universal; Abrasión por partículas aéreas + Clearfil Ceramic Primer + Scotchbond Universal; Abrasión por partículas en el aire + ácido fluorhídrico (50 %) + Scotchbond Universal. Todas las muestras fueron cementadas con Panavia F 2.0, almacenadas en água destilada y termocicladas. La prueba de resistencia al cizallamiento se realizó en una máquina de prueba universal. Análisis fractográficos y de superficie de zirconia fueron realizados con estereomicroscopio, SEM y WDS. Los datos se analizaron mediante la prueba de chi-cuadrado de Pearson, la prueba exacta de Fisher y la prueba de Kruskal-Wallis. Los mayores valores de resistencia al cizallamiento se observaron en los grupos tratados con ácido fluorhídrico, además, estos grupos no presentaron falla previa al ensayo. El modo de falla predominante fue el adhesivo. Entre los protocolos de tratamiento de superficies evaluados, el acondicionamiento con ácido fluorhídrico (50%) asociado con el sistema adhesivo Scotchbond Universal ofrece valores maus altos de resistencia al cizallamiento a la zirconia, independientemente del uso de microarenado.

Palabras clave: Cerámica; Cerámica Y-TZP; Resistencia al cizallamiento; Cementos de resina; Ácido fluorhídrico.

1. Introduction

Among the dental ceramics, yttria-stabilized tetragonal zirconium polycrystalline (Y-TZP) is one of the highest flexural and fracture strengths (Dogan, et al., 2017; Zaher, et al., 2017.

As the Y-TZP ceramic is highly crystalline and due to the fact that, without glass, hydrofluoric acid, at concentrations between 4% and 10%, cannot effectively etch it, Y-TZP ceramic is regarded as an acid-resistant ceramic. The lack of silica in its composition makes it difficult to establish a suitable chemical bonding to methacrylate-based composites (Seabra, et al., 2014).

Several clinical protocols have been proposed to achieve Y-TZP ceramic bonding effectiveness, but there is no consensus in the literature on the most effective surface treatment method (Kern, et al., 2015).

Some of these protocols indicate mechanical treatments through airborne-particle abrasion or silicatization associated with silanization (Bielen, et al., 2015; Hallmann, et al., 2016).

Currently, the use of ceramic primers, adhesives, and/or resin cements containing phosphate monomers is indicated. Among them, the MDP (10-methacryloyloxydecyl dihydrogen phosphate monomer) has demonstrated a more effective and stable chemical bonding in an aqueous environment (Al-Harbi, et al., 2016). However, it is still not well-established whether greater benefit might be achieved by incorporating MDP in the ceramic primer, in the adhesive system, or the resin cement, or if a positive cumulative effect might be obtained when using all these MDP-containing products during the same cementing procedure.

A recent systematic review (Tzanakakis, et al., 2016) emphasized the need for further investigations regarding the superficial treatment of zirconia with hydrofluoric acid in strong concentrations and with longer application time.

This study aimed to evaluate the influence of differents surface treatment protocols on Y-TZP on shear bond strength. The hypotheses tested were that the association of primer, universal adhesive system, and resin cement, all containing MDP and etching with 50% hydrofluoric acid associated with a universal adhesive system, with or without airborne-particle abrasion treatment would not improve bond resistance to zirconia.

2. Materials and Methods

The specimens of this study were made according to International Standart Organization (ISO) 10477, second edition of 2018, for tests on ceramics.

The methodology and materials used in the present study are presented in Figure 1, and Table 1, respectively.

Figure 1. Flowchart of the laboratory steps.
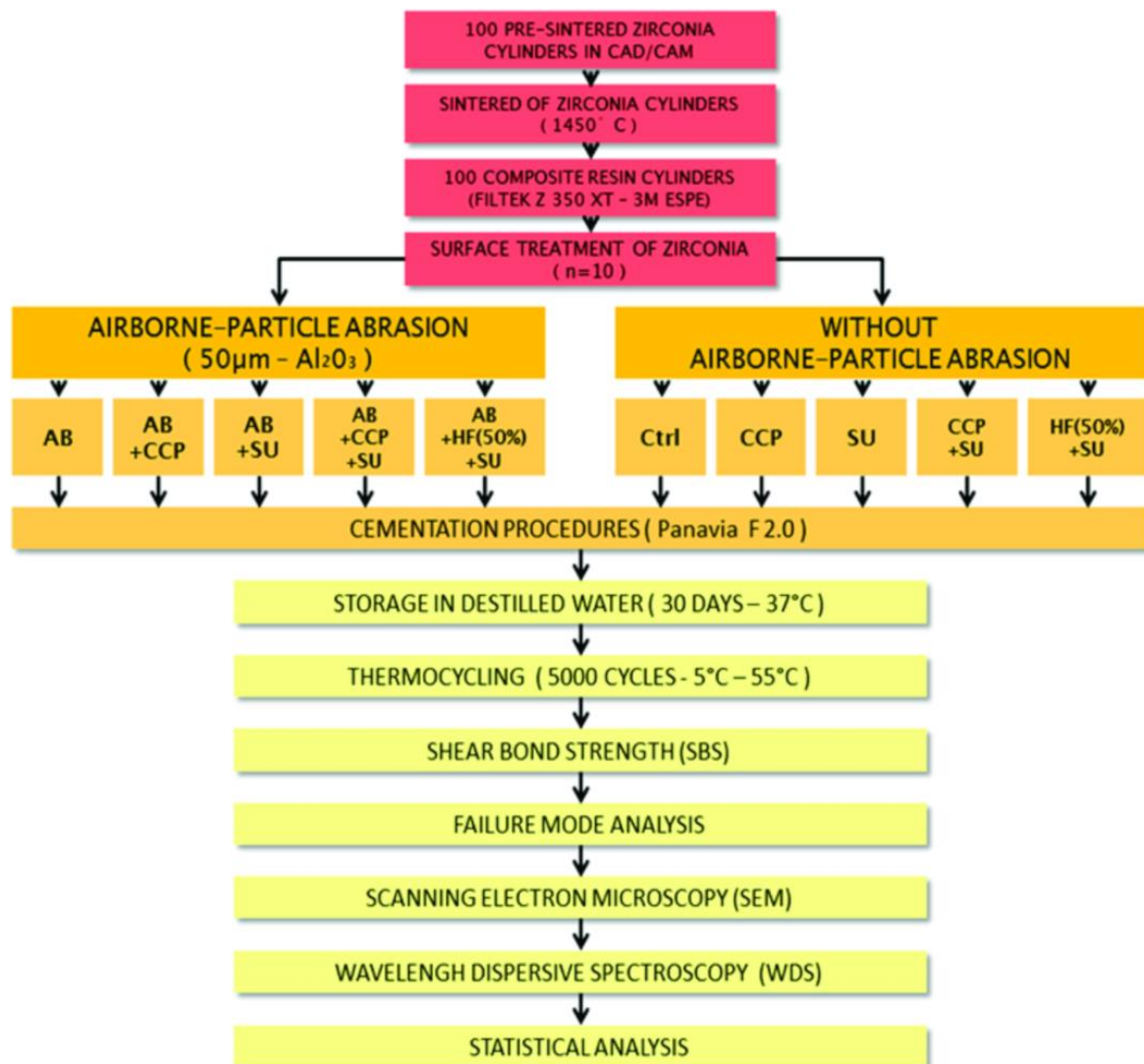
Representative scheme of the study methodology. Source: Authors.

Table 1: Materials used and their characteristics.

| Use	Brand Mark	Manufacturer	Batch no.	Chemical Components
Universal adhesive	Scotchbond Universal	3M ESPE SAINT PAUL, MN, USA	582957	BisGMA, Organophospate monomer (MDP), Vitrebond™ Copolymer, HEMA, Ethanol, Water, Charge particles, Silane, Initiators.
Resin cement	Panavia® F2.0	KURARAY MEDICAL INC, OKAYAMA, JAPAN	9V0114 9R0026	Pasta A: Hydrophobic and hydrophilic dimethacrylates, 10-MDP, Colloidal silica, Silanized silica, Camphorquinone, benzoyl peroxide. Pasta B: Hydrophobic and hydrophilic dimethacrylates, Silanized barium glass, Silanized titanium oxide, Sodium fluoride, Colloidal silica, Sodium sulfinate benzene salt 2,4,6 Triisopropyl, n, n-diethanol p-toluidina and pigments.
Zirconia Blocks	VIPI BLOCK ZIRCONN	VIPI PIRASSUNUNGA, BRAZIL	00S304315 B	Stabilized zirconium oxide with 3 mol% of ytrio (ZrO_2-3%Y_2O_3)
Composite Resin	Filtek Z350 XT	3M ESPE Saint Paul, MN, USA	455134 564691	Organic part: Bis-GMA (Bisphenol A-diglycidyl ether dimethacrylate), TEGDMA (triethylene glycol dimethacrylate), UDMA (dimethacrylate urethane) and bisEMA (6) (Bisphenol A - polyethylene glycol diethyl methacrylate).Inorganic part: charge particles (Zirconia / Silica 60% - 0.01 to 3.5 micrometers)
Alumina Oxide	Aluminum Oxide	BIO-ART SÃO CARLOS, SP, BRAZIL	42883	Al_2O_3 particles (50 μm)
Silicone	Futura AD Denso	DFL RIO DE JANEIRO, RJ, BRAZIL	15111726	Polymethylsiloxane, Silicon Dioxide, Hydrocarbon, Methylhydrogenosiloxane, Lilac Dye, Yellow Dye, Blue Dye and Organoplatinum Complex
Ceramic primer	Clearfil ceramic primer	KURARAY MEDICAL INC, OKAYAMA, JAPAN	240009	3-metacriloxipropiltrimetoxisilano (3-MPS), 10-MDP, Ethanol
Hydrofluoric acid at 50%	*	*	*	HF 50%
Phosphoric acid	Condac 37	FGM Joinville, SC, Brazil	250216	Phosphoric acid at 37%

* Manipulated in the Laboratory of Chemical Analysis of the Department of Mechanical Engineering of UFPE – Brazil. Source: Authors.

A hundred Y-TZP zirconia cylinders of 4mm diameter and 5mm height Vipiblock-Zirconn (Vipi Produtos odontológicos, Pirassununga, Brazil), were prepared using the Ceramill map 400 (CAD) and Ceramill motion 2 (CAM) (Amann Girrbach-Dürrenweng, Pforzheim, Germany) and densely sintered, at a temperature of 1,450°C, for 10 hours, in a kiln for ceramics (Ceramill Therm, Amann Girrbach, Pforzheim, Germany), following the manufacturers' recommendations. Zirconia cylinders were embedded in cylindrical tubes (25mm diameter x 20mm height) filled with colorless Epoxy resin (Redelease, Barueri, Brazil). After polymerization of epoxy resin, the zirconia free surface was sandpapered Silicon carbide abrasive sandpapers, 150 and 280μm, (Norton Saint-Gobain, Guarulhos, Brazil). The specimens were cleaned in an ultrasonic tub for 5 minutes at 50°C and then washed with distilled water and dried at room temperature for 30 minutes.

For the preparation of composite resin cylinders, one of the zirconia cylinders was molded with polyvinylsiloxane impression material Futura AD (DFL Indústria e Comércio S.A, Rio de Janeiro, Brazil), to obtain a standardized mold which was filled with composite resin Filtek Z350 XT (3M ESPE, St Paul, USA) in increments of 2mm, and each increment was light-cured for 20 seconds using a LED light-curing unit 1,200 mW/cm² Radii-cal (SDI, Bayswater, Victoria, Australia).

The zirconia specimens were divided into 10 groups (n = 10), according to the surface treatment (Figure 2).

Figure 2. Surface treatment groups division.
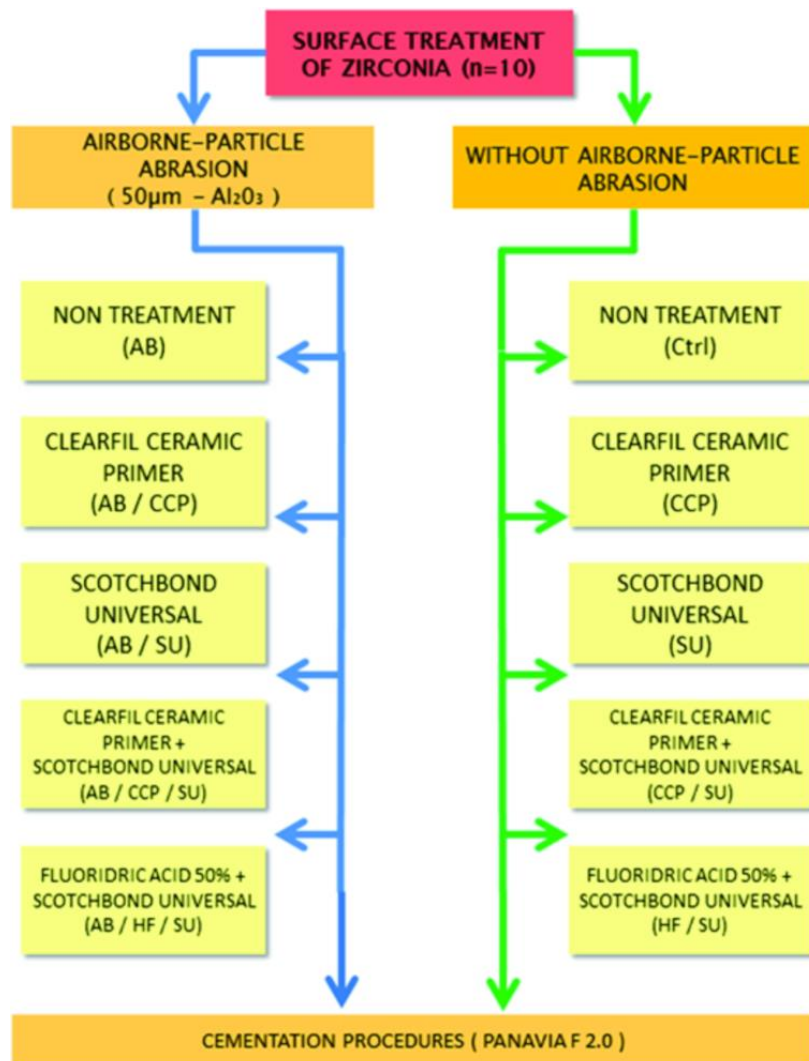
Shear bond strength (SBS) Mean (MPa) and standard deviation (±). Source: Authors.

Airborne-particle abrasion 50µm–Al_2O_3 (AB) (Bio-art Equipamentos Odontológicos LTDA, São Carlos, Brazil) was performed with horizontal and vertical movements, perpendicular to the zirconia surface, at a distance around 10mm and with pressure from 3.92 to 5.39 bars, for 15 seconds. Then, each specimen was washed with distilled water for 30 seconds and air-dried.

The application of the CCP (Kuraray Medical Inc, Kurashiki, Japan) and SU (3M ESPE, St Paul, USA) followed the manufacturers' recommendations. In the specimens from groups HF/SU and AB/HF/SU, 50% of hydrofluoric acid (Laboratório de Análises Químicas da Universidade Federal de Pernambuco, Recife, Brazil) was applied for 180 seconds using micro applicators Microbrush (Coltene, Rio de Janeiro, Brazil), then washed with distilled water for 1 minute, and air-dried for the same time.

After the surface treatment, all groups were cemented with resin cement Panavia F 2.0 (Kuraray-Medical-Inc, Kurashiki, Japan), according to the manufacturers' instructions. Composite resin cylinders had their bonding surface etched with 37% phosphoric acid Condac 37 (FGM Produtos Odontológicos Ltda, Joinville, Brazil) for 30 seconds, washed with water for the same time and dried with absorbent paper. ED primer, which is included in the Panavia F 2.0 kit, was applied for 30 seconds on the surface of composite cylinders, dried for 15 seconds, and the excess was removed with absorbent paper. Then, the Panavia F 2.0 pastes were mixed for 20 seconds and placed on the zirconia surface. The resin cylinders were placed on cement and a 500-gram weight was placed on the zirconia-cement-resin set for 20 seconds, in order to avoid air bubble formation. Cement excesses were carefully removed using micro applicators (Microbrush) and No. 5 explorer probe. Prior to photopolymerization, the water-soluble oxyguard II gel from the Panavia F 2.0 kit was applied to prevent non-polymerization of the cement surface layer by exposure to air, followed by two photopolymerization sessions of 40 seconds.

All cemented specimens were stored in distilled water at 37°C for 30 days and thermocycler between 5 and 55°C ($\pm$ 3°C) in water with a 30-s dwell time at each temperature and transfer time of 2 seconds on average, following a regimen of 5,000 cycles.

Subsequently, the specimens were submitted to shear bond strength (SBS) test at a speed of 1mm/min in a universal test EMIC DL 10000 (EMIC Equipamentos e sistemas de ensaio LTDA, São José dos Pinhais, Brazil) (Figure 3) (Zhao, et al., 2016).

Figure 3. Shear bond strength test.
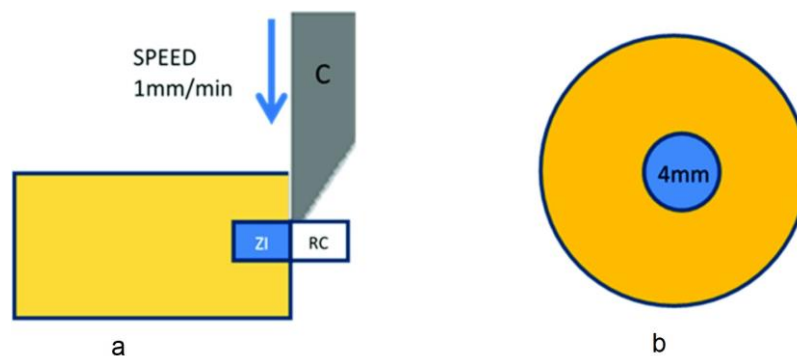
(a) Specimen in a jig. Zi, Zirconia. CR, Composite Resin. C, chisel. (b) Diameter of the zircônia specimen. Source: Authors.

Shear bond strength was calculated by dividing the maximum fracture load by the circular cementation area, using the circular area formula ($\pi.r^2$, where π is equal to 3,1416 and the radius is equal to 2mm) because the diameter of the sample was 4mm. The results were expressed in Megapascal (MPa) (Cristoforides, et al., 2012).

The surface morphology of the specimens was evaluated with a binocular stereo microscope Q744S (QUIMIS, Diadema, Brazil), with a 40x magnification and the failure mode was classified as: adhesive (<1/3 of the cementing material bound to zirconia); cohesive (>2/3 of the cementing material bound to zirconia); and mixed (>1/3 and <2/3 of the cementing material bound to zirconia) (Lung, et al., 2012; Matinlinna, et al., 2011).

A scanning electron microscope SEM-JSM 6460 (JOEL Ltd, Akishima, Japan) was used to analyze the zirconia surface and the resin cement. Two specimens from each group were carbon-coated by Cressington Carbon Coater-108 Carbon/A (TED PELLA INC, Redding, USA) using the sputtering technique. The acceleration voltage used by SEM was 30 kV. To check the chemical elements observed on the zirconia surface and the resin cement, an X-ray was used for wavelength dispersive spectroscopy WDS (Oxford Instruments, Abingdon, United Kingdom). The wavelength of the chemical element was obtained through diffraction by means of a monocrystal with a variable positioning angle.

The data were submitted to Pearson's chi-square test or Fisher exact test, to compare groups regarding categorical variables and the Kruskal-Wallis test for the bonding resistance variable SPSS v23, (IBM, Chicago, USA) ($\alpha = 0.05$).

3. Results

The shear bond strength results are presented in Table 2.

**Table 2.** Shear bond strength (SBS) Mean (MPa) and standard deviation (±).

Without Airborne-Particle Abrasion	
Groups	Mean
Ctrl	$4.1 \pm 0.5^{A\ddagger 1}$
CCP	5.9 ± 1.9^{AC}
SU	4.7 ± 1.3^{AE}
CCP/SU	$0.00 \pm 0.00^{\dagger}$
HF/ SU	12.7 ± 2.6^{BF}
Airborne-Particle Abrasion (50µm – Al_2O_3)	
Groups	Mean
AB	6.8 ± 2.6^{CE}
AB/CCP	7.5 ± 2.3^{C}
AB/SU	11.0 ± 3.3^{FG}
AB/CCP/SU	9.7 ± 3.00^{DG}
AB/HF/SU	14.1 ± 2.2^{B}

[a] Ctrl - Control Group only cement; CCP - Clearfil Ceramic Primer + cement; SU - Scotchbond Universal + cement; CCP/SU - Clearfil Ceramic Primer + Scotchbond Universal + cement; HF/SU - 50% hydrofluoric acid etching + Scotchbond Universal + cement; AB - Airborne-Particle Abrasion + cement; AB/CCP - Airborne-Particle Abrasion + Clearfil Ceramic Primer + cement; AB/SU - Airborne-Particle Abrasion + Scotchbond Universal + cement; AB/CCP/SU - Airborne-Particle Abrasion + Clearfil Ceramic Primer + Scotchbond Universal + cement; AB/HF/SU - Airborne-Particle Abrasion + 50% hydrofluoric acid etching + Scotchbond Universal + cement.
[b] If the letters are all different, there is a significant difference between the corresponding groups. The variability expressed through the variation coefficient has not increased, since the highest value was 38.21% (<50%).† Specimens lose spontaneously. ‡Significant difference (Ctrl, P<0.01). (1) Through the Kruskal-Wallis test with comparisons of the test concerned. Source: Authors.

The groups AB/HF/SU, HF/SU, and AB/SU showed higher shear bond strength values than the other groups. SEM analysis showed that when AB was not used, nor HF etching, the zirconia surface showed no irregularities, but specimens submitted to AB showed several surface irregularities (Figure 4).

Figure 4. Microphotography from scanning electron microscope (SEM).
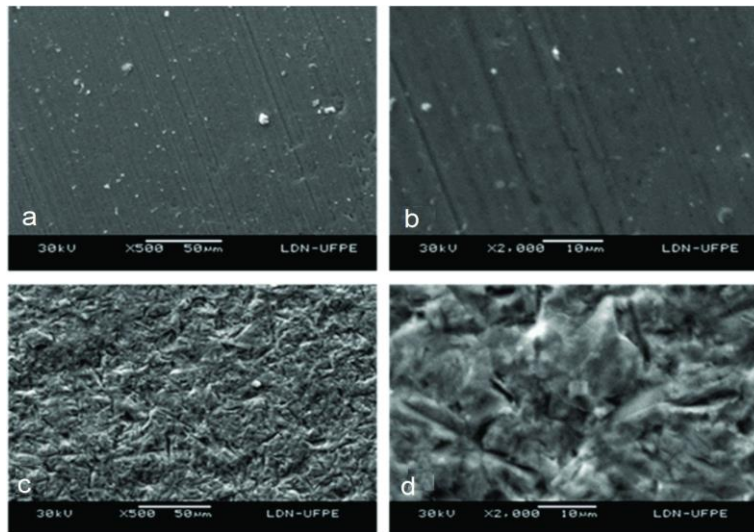
Images illustrating in (a) and (b) zircônia surface without airborne-particle abrasion and without etching with 50% hydrofluoric acid. Specimen from group CCP. (c) and (d) Surface treated with airborne-particle abrasion using 50 μm aluminum oxide. Specimen from the group (AB/SU). Source: Authors.

The chemical elements constituting these irregularities were confirmed by WDS analysis. In the areas treated with AB, high peaks having wavelengths compatible with zirconium oxide and aluminum oxide were detected and the lowest peaks referred to yttrium oxide and carbon (Figure 5).

Figure 5. WDS analysis of zircônia surface treated with airborne-particle abrasion.
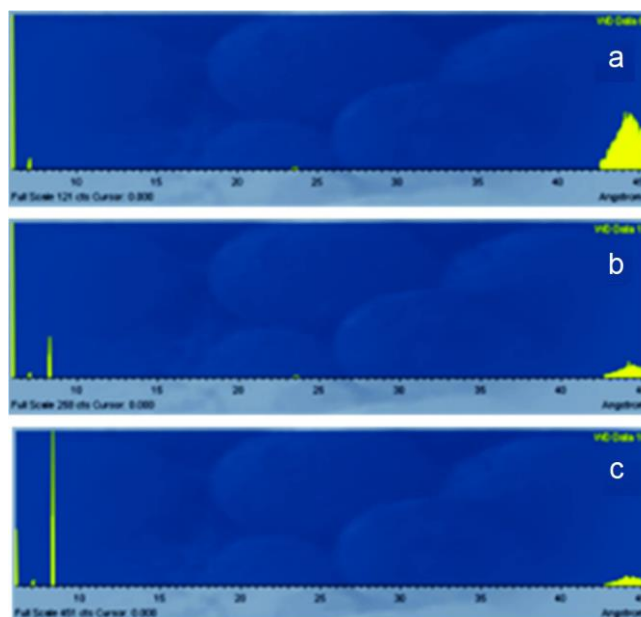
(a) Zirconium oxide peak. (b) Aluminum oxide peak. (c) Carbon and yttrium oxide peaks. Source: Authors.

The images resulting from the samples submitted to HF etching had surface irregularities with a different pattern from those created in the AB process. Some specimens had a discontinuous stretch-marked surface (Figure 6).

Figure 6. Microphotography from scanning electron microscope (SEM).
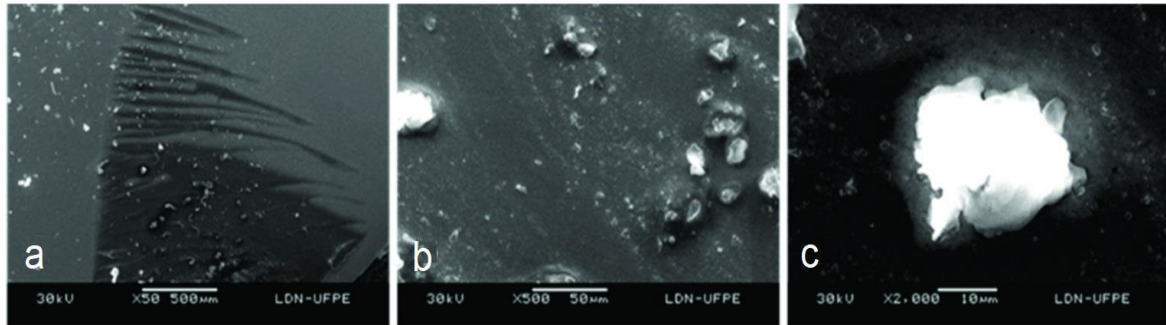
SEM images illustrating (a,b) the fracture pattern on the zircônia surface etched with 50% hydrofluoric acid for 180 seconds and (c) "Table-shaped" irregularity on the zircônia surface. Source: Authors.

In these groups, 'table-shaped' irregularities were also observed, as well as probable cement filler particles around these irregularities (Figure 6), which were confirmed by the WDS test (Figure 7).

Figure 7. WDS analysis of zircônia surface etched with 50% hydrofluoric acid ("table-shaped" irregularity area).
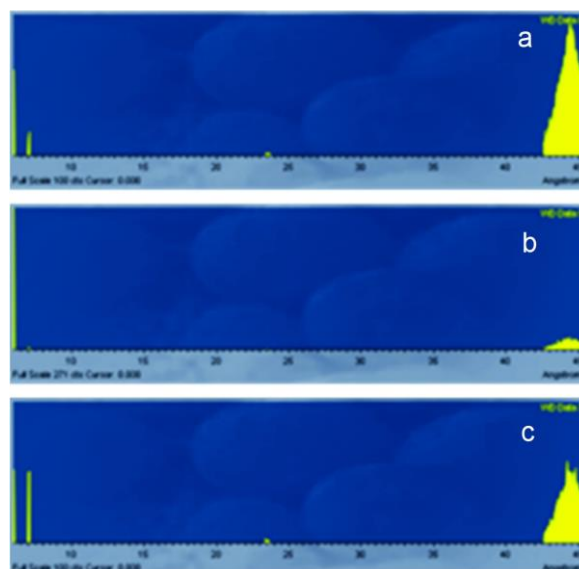

(a) Zirconium oxide peak. (b) Yttrium oxide peak. (c) Silicon oxide peak in the micro-retained particles around the zircônia irregularity. Source: Authors.

Except for the HF/SU and AB/HF/SU groups, all the other groups tested had pre-test failures. It means that some or all of their test specimens debonded, they did not withstand the aging simulation process by storage in water for 30 days associated with thermocycling.

As for the fracture mode, stereomicroscope analysis showed a predominance of adhesive failure (80%), followed by mixed failure (17%) and cohesive failure (3%) (Figure 8).

Figure 8. Microphotography from scanning electron microscope (SEM).
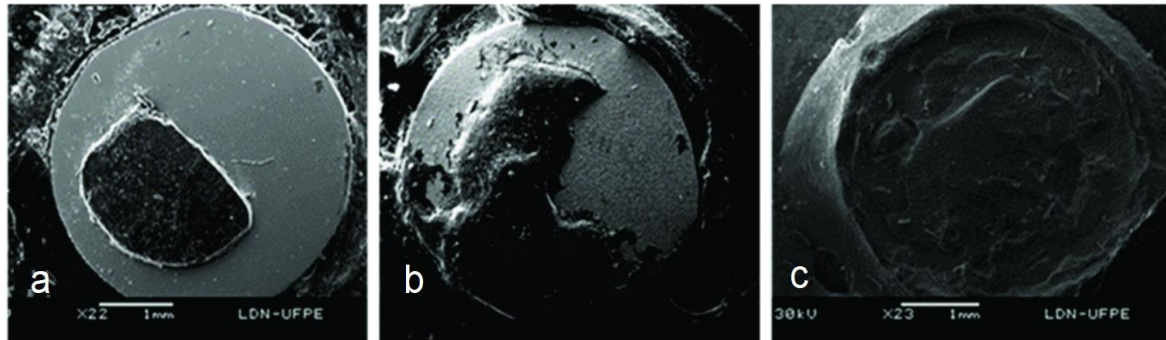
SEM images illustrating the failure modes. (a) Adhesive failure. (b) Mixed failure. (c) Cohesive failure. Clear areas – Zirconia. Dark areas – Resin Cement. Source: Authors.

4. Discussion

The hypothesis that the association of primer, universal adhesive system, and resin cement, all containing the MDP monomer, would not increase zirconia bond strength, had to be accepted, since the combination of these two bonding agents associated with the cement did not increase bond strength. Previous studies (Koizumi, et al., 2012) report that the MDP phosphate monomer is structurally formed by 2 functional groups, a methacrylate group and a phosphoryl divalent group. The latter is incorporated into the zirconia, and methacrylate copolymerizes with the other resin cement monomers. Therefore, MDP establishes a chemical bonding with metallic oxides, through Van Der Walls forces or hydrogen bonds in the composite/zirconia interface, improving the surface wettability, thus increasing bond strength, which could inhibit hydrolytic degradation (Koizumi, et al., 2012; Xie, et al., 2016).

Although MDP-containing materials have good zirconia bond strength results, the combination of a primer, universal adhesive system, and resin cement, all containing MDP, had not been tested, yet. This study demonstrated that the association of these materials did not improve shear bond strength (SBS). It may be explained by MDP saturation, where it is no longer possible to have an additional chemical bonding (adhesion) to the zirconium oxide layer, furthermore, even if a chemical bonding condition is established between primers with MDP,

and Y-TZP ceramic surface, hydrolytic sensitivity of the formed zirconia carboxylate salts can affect the interface bonding stability (Pilo, et al., 2016).

A group of searchers concluded that adhesives used to bond to Y-TZP ceramic, such as Scotch bond Universal and Signum Zirconia Bond, both containing MDP, showed the highest bonding values (Llerena-Icochea, et al., 2017). Another group reported that the combination of mechanical and chemical treatments (airborne-particle abrasion and single-step universal adhesive application, respectively) can promote a more stable bonding to zirconia. Similar results were observed in this study for the group AB / SU (Xie, et al., 2016).

The results of this study show that the groups that were submitted to airborne-particle abrasion had higher bonding strength, corroborating other studies (Moradabadi, et al., 2014; Liu, et al., 2015). The current literature shows that additional mechanical retention, through surface irregularities promoted by airborne-particle abrasion with aluminum oxide particles, may be needed to provide zirconia restorations with durable bonding (Kern, et al., 2015; Tanis, et al., 2015).

However, when comparing the groups CCP and AB/CCP, no significant statistical difference was observed. This may be explained by the primer application and its solvent evaporation, which can affect chemical bonding in the interface. Besides, the aluminum oxide (Al_2O_3) used in this study may change chemical composition in the Y-TZP ceramic surface by deploying aluminum particles (Zinelis, et al., 2010). This was evidenced by the WDS test, which can further affect this bond.

The WDS test was used to confirm that the specimens tested surface was really zirconia, and not another chemical element or a degrades. In Figure 5, the chemical elements present were zirconium oxide, sandblasting aluminum oxide, the carbon from the metallization of the carbon specimens (a procedure required for SEM evaluation) and a small percentage of yttrium oxide from the zirconia itself. In Figure 7, the chemical elements found were zirconium oxide, yttrium oxide, and carbon from metallization. The aluminum oxide was not present in Figure 7, because the aluminum oxide micro blasting was not performed. This test is a substitute for EDX, which is used for the identification of the chemical elements present on the surface of the samples tested (Liu, et al., 2015; Samimi, et al., 2015).

On the other hand, the solvent (ethanol) of the CCP evaporates faster than the ethanol + water used in the SU chemical composition. And by showing slower evaporation than the primer, perhaps the adhesive system better penetrates and imbibes on the irregular surface resulting from AB inducing less intermolecular reactions between components. Accordingly, it constitutes less multiple layers and increases the formation of carboxylate salts and especially

of zirconia phosphate salts, increasing chemical bonding. Thus, the groups using SU and AB, together (AB/SU and AB/CCP/SU) had better SBS results than their counterparts, without previous AB (Zinelis, et al., 2010).

The hypothesis that a new protocol using HF etching associated with a universal adhesive system, with or without AB treatment, would not result in higher bond strength values, was rejected because the groups in which acid was used showed the highest resistance mean values, and there was no statistically significant difference between them. Also, these groups did not have pre-test failures, probably this was due to the surface treatment effectiveness with hydrofluoric acid.

These results confirm the findings of a study (Menani, et al., 2014) that obtained high bond strength values when using 40% hydrofluoric acid for 210 seconds as zirconia surface treatment. These high SBS values may be related to the hydrofluoric acid ability, at a stronger concentration, to promote irregularities in the zirconia surface, as evidenced by SEM analysis in this study. Thus, surface treatment with hydrofluoric acid increases energy and surface area, decreases surface tension, improves the adhesive system's wettability and permeability. This combined with MDP effectiveness in forming chemical bonding with zirconium oxide, by constituting zirconia carboxylate and zirconia phosphate salts, can provide effective and stable bond strength, according to the results obtained in this study with the groups HF/SU and AB/HF/SU.

The ISO Standard No. 10477 states that the minimum bond strength values so that material and/or surface treatment must be approved is 5.0 MPa, however, a study (Matinlinna, et al., 2011) considers these values low to maintain cemented zirconia restorations in the oral cavity. Another study (Behr, et al., 2011) reported that a 10 MPa tensile strength in tensile and shear tests may be sufficient to withstand mouth conditions, so this study considered as clinically feasible only those groups that had results higher than 10 MPa.

Another major factor is that bonding quality should not be evaluated by having only SBS data as a basis (Della, et al., 2000). The mode of failure evaluation by optical microscopy and fractographic analysis are essential to test the bonding protocols' performance. The predominant failure mode in this study was adhesive. This failure mode probably occurs due to water penetration in the composite/zirconia interface, causing hydrolytic degradation, which combined with thermal stress results in adhesive rupture (Cristoforides, et al., 2012; Lung, et al., 2012; Xie, et al., 2016; Liu, et al., 2015; Samimi, et al., 2015).

In this study, pre-test failures (debonding) were observed during the aging process by storage in water, for 30 days, followed by 5,000 thermocycles, in almost all groups, except in

the groups in which 50% hydrofluoric acid etching was used for 180 seconds. This shows lower susceptibility of these groups to water hydrolysis and thermal stress.

Despite some limitations, this study may indicate a possible and feasible clinical protocol for adhesive cementation of zirconia-based ceramics, obtaining safety and longevity in aesthetics rehabilitations through crowns and fixed partial prostheses. Further studies are needed to confirm the results obtained through zirconia etching by means of 50% hydrofluoric acid, for 180 seconds. Changes in acid concentration and etching time should be tested, in order to be reduced, providing greater safety and agility to the protocol tested, without losing its effectiveness.

5. Conclusions

Among the surface treatment protocols evaluated, the 50% hydrofluoric acid etching associated with the Scotch bond Universal adhesive system offers higher values of shear bond strength to the zirconia, regardless of the use of micro blasting. The combination of primers, adhesive, and cement, all with the MDP monomer, is not initiated in the zirconia bond strength, rejecting the hypothesis tested.

Further research is needed to test the influence of different types of hydrofluoric acid concentrations and application time, on the bond strength of the zirconia, associating or not with other methods of surface treatment.

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