

UNIVERSIDADE DE SÃO PAULO  
FACULDADE DE ODONTOLOGIA DE BAURU

ANGÉLICA FELTRIN DOS SANTOS

**Influence of the incorporation of TiO<sub>2</sub> nanotubes in a polycrystalline zirconia:  
synthesis of nanotubes, surface characterization and bond strength**

**Influência da incorporação de nanotubos de TiO<sub>2</sub> a uma zircônia policristalina:  
síntese de nanotubos, caracterização superficial e resistência de união**

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Orientador: Prof. Dr. Adilson Yoshio Furuse

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## FOLHA DE APROVAÇÃO



# DEDICATÓRIA

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## DEDICATÓRIA

*Dedico este trabalho à minha Mãe e ao meu Pai.*

*Mãe, você que me deu a vida e dedicou a sua para cuidar de mim e de nossa família, que abriu mão dos seus sonhos para que eu realizasse os meus. Eu te dedico este trabalho, este título, e tudo o que realizei até hoje. Sem você não seria possível.*

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## AGRADECIMENTOS

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# ABSTRACT

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## ABSTRACT

### **Influence of the incorporation of TiO<sub>2</sub> nanotubes in a polycrystalline zirconia: synthesis of nanotubes, surface characterization and bond strength**

Despite numerous advantages such as high strength, cementing zirconia is still critical. In the present study TiO<sub>2</sub> nanotubes were synthesized and applied over zirconia surface. This surface was characterized and after that the bond strength test was conducted to a resin cement. TiO<sub>2</sub> nanotubes were produced by alkaline synthesis, mixed with isopropyl alcohol (50 wt%) and applied on pre-sintered zirconia slices (IPS e.max ZirCAD). The ceramics were sintered and surfaces were characterized by confocal laser microscopy, scanning electron microscopy (SEM) and EDS analysis. For the bond strength, six groups (n = 16) were evaluated: 1) without application of TiO<sub>2</sub> and Single Bond Universal; 2) with the application of TiO<sub>2</sub> nanotubes and Single Bond Universal; 3) without application of TiO<sub>2</sub> nanotubes and Z-prime; 4) with application of TiO<sub>2</sub> nanotubes and Z-prime; 5) without application of TiO<sub>2</sub> and Signum Zirconia Bond; 6) with application of TiO<sub>2</sub> and Signum Zirconia Bond. After sintering, resin cement (RelyX Ultimate) cylinders with diameter of 1.40 mm and 1 mm in height were prepared and light cured for 40 s. The specimens were stored for 30 days in distilled water at 37°C and submitted to shear test. The nanotubes were incorporated in the zirconia surface and the EDS analysis has confirmed that the nanoagglomerates were composed of TiO<sub>2</sub>. The shear bond strength showed there was significant statistical difference among the analyzed groups. There was no significant statistical difference with the application of the nanotubes regardless of the analyzed group. It may be concluded that it was possible to incorporate nanotubes to the zirconia surfaces, however this incorporation did not improve the bond strength.

**Keywords:** Y-TZP. Shear bond strength. TiO<sub>2</sub> nanotubes.

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# RESUMO

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## RESUMO

### **Influência da incorporação de nanotubos de TiO<sub>2</sub> a uma zircônia policristalina: síntese de nanotubos, caracterização superficial e resistência de união**

Apesar de inúmeras vantagens, tal como alta resistência, a cimentação da zircônia ainda é crítica. No presente estudo nanotubos de TiO<sub>2</sub> foram sintetizados e aplicados sobre a superfície da zircônia, essa superfície foi caracterizada e posteriormete foi conduzido o teste de resistência de união a um cimento resinoso. Os nanotubos de TiO<sub>2</sub> foram produzidos por síntese alcalina, misturados com álcool isopropílico (50% em peso) e aplicados em fatias de zircônia pré-sinterizados (IPS e.max ZirCAD). As cerâmicas foram sinterizadas e as superfícies foram caracterizadas por microscopia confocal a laser, microscopia eletrônica de varredura (SEM) e análise de composição atômica por EDS. Para a resistência de união foram avaliados seis grupos (n = 16): 1) sem aplicação de nanotubos de TiO<sub>2</sub> e Single Bond Universal; 2) com a aplicação de nanotubos de TiO<sub>2</sub> e Single Bond Universal; 3) sem aplicação de nanotubos de TiO<sub>2</sub> e Z-prime; 4) com aplicação de nanotubos de TiO<sub>2</sub> e Z-prime; 5) sem aplicação de nanotubos de TiO<sub>2</sub> e Signum Zirconia Bond ; 6) com aplicação de nanotubos de TiO<sub>2</sub> e Signum Zirconia Bond. Após a sinterização, foram preparados cilindros de cimento resinoso (RelyX Ultimate) com um diâmetro de 1,40 mm e 1 mm de altura, fotopolimerizados por luz durante 40 s. Os espécimes foram armazenados durante 30 dias em água destilada a 37°C e submetidos a ensaio de microcisalhamento. Os nanotubos de TiO<sub>2</sub> foram incorporados na superfície de zircônia e a análise EDS confirmou que os nanoaglomerados eram compostos de TiO<sub>2</sub>. O teste de microcisalhamento mostrou diferença estatística significativa entre os grupos analisados. Não houve diferença estatística significativa com a aplicação dos nanotubos, independentemente do grupo analisado. Pode-se concluir que foi possível incorporar nanotubos às superfícies de zircônia, porém esta incorporação não melhorou a resistência de união.

**Palavras-Chave:** Y-TZP. Microcisalhamento. Nanotubos de TiO<sub>2</sub>.

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# INTRODUCTION

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## 1 INTRODUCTION

Ceramics have a prominent place in dentistry mainly due to incomparable features such as chemical stability, high compressive strength, excellent and lasting esthetics, biocompatibility and mimicry to tooth structure (Kelly *et al.*, 1996). Within the group of ceramics, the use of zirconia increased with the advance of CAD / CAM technology (Lee *et al.*, 2015). Therefore, zirconia has large number of indications in restorative dentistry, being used in monolithic restorations production as single crowns, inlay and onlay-bridges or frameworks fixed dental prostheses and implant abutments (Amaral *et al.*, 2016).

The great popularity of this ceramic material is related to its good esthetic characteristics and the superior mechanical properties when compared to other dental ceramics (Wang *et al.*, 2014) or to metal (Ban *et al.*, 2007). Furthermore, they have chemical stability (Aboushelib *et al.*, 2010), low thermal conductivity (Manicone *et al.*, 2007), biocompatibility (Josset *et al.*, 1999), good optical properties (Baldissara *et al.*, 2010) and high fractures toughness (Egilmez *et al.*, 2013). The last property is very interesting, because the zirconia can undergo martensitic transformation which is characterized by the change of tetragonal phase to the monoclinic, occupying a volume 3 to 5% larger than the tetragonal grains, producing compressive tension at the crack tip preventing actively the propagation and fracture of material (Denry *et al.*, 2008).

The preparation of minimally invasive restorations with smaller thickness and veneers is impossible due to the difficulties in obtaining reliable and lasting bonding to resin-based cements and, consequently, the dental structures (Cavalcanti *et al.*, 2009; Burgess *et al.*, 2010; Ozcane & Bernasconi, 2015; Qeblawi *et al.*, 2015). This is due to the absence of silica and glassy phase, which impairs the effectiveness of adhesive cementation procedures as application of hydrofluoric acid and coupling agent (Derand *et al.*, 2005; Ozcan *et al.*, 2008). In minimally retentive situations, resin cements might be a good option because of their improved mechanical properties when compared to zinc phosphate and glass ionomer cements (Piwowarczyk *et al.*, 2003; Koutayas *et al.*, 2009). Through of a reliable bonding of resin cements to restorative materials, more tooth structures may be preserved, and

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durable restorations can be produced (Akin et al., 2011). As a result of the adhesive cementation advantages, the researches has been focusing on different alternatives to improve the bonding of a resin cement to the zirconia inner surface through mechanical or chemical conditioning methods to optimize the bonding of the cement/ceramic interface.

Among the efforts of bonding to zirconia it has been suggested surface roughening by means of the aluminum oxide blasting before and after sintering (Abi-Rached et al., 2015), or particles of alumina-silica followed by silane application (Jevnikar *et al.*, 2010; Kirmali et al., 2015). Other alternatives are application of laser Er:YAG (Akin et al., 2015), grinding with diamond burs (Pereira et al., 2014) selective infiltration etching (De Munck et al., 2012), application of low fusing ceramic (Derand *et al.*, 2005), and application of fluoridric acid at 9,5% at 25°C for 1 hour (Sriamporn *et al.*, 2014). However, methods like these have shown different percentages of martensitic transformation in the treated surface (Sriamporn *et al.*, 2014; Abi-Rached *et al.*, 2015), causing the initiation and propagation of cracks in the material compromising the long-term durability of the piece made with zirconia (Guazzato et al, 2004; Hjerpe et al., 2010).

The use of cements, adhesives and primers that interacts chemically with the zirconia has shown promising results in bond strength (Ozcane & Bernasconi, 2015; Xie et al., 2016; Pilo et al, 2016). These materials exhibit phosphate monomers such as MDP (10 methacryloxy decile dihydrogen phosphate). The terminal phosphate group can react with the hydroxyl group (-OH) on the surface of the zirconia forming chemical bonds between oxygen and zirconium (Yoshida *et al.*, 2006). However none of these methods have been proven to be effective in bonding resin cements to zirconia, since the bond strength tends to decrease between resin cement and zirconia after thermal cycling treatment, demonstrating that the union undergoes hydrolytic degradation (Ozcan et al., 2003; Lee et al., 2015).

A possibility of bonding the zirconia that has not been studied refers to its association with TiO<sub>2</sub> nanoparticles. The decrease of the particle size to nanometer scale has favored the appearance of a broad range of applications in different materials, since its behavior changes as compared to the microscopic scale (Cheng *et al.*, 2013). The incorporation of nanostructures titanium dioxide (TiO<sub>2</sub>) has shown

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good results when added to polymeric materials (Xia *et al.*, 2008; Sun *et al.*, 2011; Poosti *et al.*, 2013). Nanoparticles can be easily agglomerated when mixed with the resinous material (Arruda, 2015), and promote better results in flexural strength properties and hardness, degree of conversion (Sun *et al.*, 2011; Arruda, 2015) and the antibacterial properties (Poosti *et al.*, 2013). Oxides at the nanoscale as TiO<sub>2</sub> may have unique physical and chemical properties due to their small size and high density of surface sites (Rodriguez & Fernández-García, 2007). The particle size can influence the properties of material increasing the surface free energy by an increase in the number of surface atoms and interface (Samsonov *et al.*, 2003). In nanoscale, the structures can vary not only in size but also in morphology such as nanospheres, nanorods, nanowires, nanotubes and nanosheets. In particular, the oxide nanotubes as TiO<sub>2</sub> are interesting mainly because of its large surface area, which can give rise to strong interactions with the solid matrix in which they can be incorporated, chemical stability, electrical properties and high index refraction (Arruda *et al.*, 2015). These characteristics can contribute to better interaction and reaction with the medium in which they are (Roy *et al.*, 2011). Thus, it is important to evaluate new forms/possibilities of application of nanotubes in Dentistry. They can be associated to zirconia as a treatment of surface aiming to improve the bond strength with the resin cement, since there is not any literature with this purpose.

## PROPOSITION

The aim of this study was to evaluate the infiltration of TiO<sub>2</sub> nanotubes into the surface of a partially yttrium-stabilized tetragonal zirconia and if the bond strength a resin cement to the infiltrated ceramics may be improved. This study was divided in two stages: 1) synthesis of TiO<sub>2</sub> nanotubes and characterization of ceramic surfaces using confocal laser microscopy and scanning electron microscopy (SEM) and EDS analysis; 2) shear bond strength evaluation with cement resin and different zirconia primers and adhesives.

Null hypotheses: (1) no infiltration would be detected; (2) the infiltration TiO<sub>2</sub> nanotubes would not influence the shear bond strength; and (3) there would be no difference between commercially available adhesives and zirconia primers used in the bond strength evaluation.

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## **2 ARTICLE**

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## **2 ARTICLE**

Article - The article presented in this Dissertation was written according to the Dental Materials instructions and guidelines for article submission

## **Influence of the incorporation of TiO<sub>2</sub> nanotubes in a polycrystalline zirconia: synthesis of nanotube, surface characterization and bond strength**

### **ABSTRACT**

**Objective:** To evaluate the infiltration of TiO<sub>2</sub> nanotubes into zirconia and the bond strength of a resin cement to infiltrated ceramics.

**Methods:** TiO<sub>2</sub> nanotubes were produced by alkaline synthesis, mixed with Isopropyl alcohol (50 wt%) and applied on pre-sintered zirconia discs (IPS e.max ZirCAD). The ceramics were sintered and surfaces were characterized by confocal laser microscopy, scanning electron microscopy (SEM) and EDS analysis. For the bond strength six groups (n = 16) were evaluated: 1) without TiO<sub>2</sub> and Single Bond Universal; 2) with TiO<sub>2</sub> nanotubes and Single Bond Universal; 3) without TiO<sub>2</sub> nanotubes and Z-prime; 4) with TiO<sub>2</sub> nanotubes and Z-prime; 5) without TiO<sub>2</sub> and Signum Zirconia Bond; 6) with TiO<sub>2</sub> and Signum Zirconia Bond. After sintering, resin cement cylinders (RelyX Ultimate) with a diameter of 1.40 mm and 1 mm in height were prepared and light cured for 20 s. Specimens were stored in water at 37°C for 30 days and submitted to shear test.

**Results:** The nanotubes were incorporated in the zirconia surface and the EDS analysis has confirmed that the nanoagglomerates were composed of TiO<sub>2</sub>. The shear bond strength showed there was significant statistical difference among groups. There was no significant difference with the application of the nanotubes regardless of the analyzed group.

**Conclusions:** It may be concluded that it was possible to incorporate nanotubes to the zirconia surfaces. However, this incorporation did not improve the bond strength.

**Keywords:** Y-TZP, Shear bond strength, TiO<sub>2</sub> nanotubes.

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## **1 - INTRODUCTION**

In order to replace the metallic frameworks of fixed dental prostheses, zirconia has been introduced in dentistry, where it was widely regarded as the main alternative to replace them [1]. Recently, zirconia has gained great popularity in the field of dentistry because it has good optical and aesthetic characteristics and superior mechanical properties compared to other ceramics and metal [2]. Furthermore, it presents chemical stability, low thermal conductivity and biocompatibility [3], which expanded its applicability being used for manufacturing monolithic restorations such as individual crowns, inlays and onlays, as well as implant abutments [4].

Other ceramic materials such as glass-ceramics may have their surfaces etched with hydrofluoric acid, associated with a silane coupling agent, resulting in high bond strength [5]. However, the traditional adhesive technique for silica-based ceramics is not effective in zirconium dioxide due to the high crystalline content of its composition (no silica), which is resistant to etching with hydrofluoric acid [6]. Given the difficulty in obtaining a reliable and long-lasting bonding to between resin-based luting agents and acid-resistant ceramics such as zirconia, various methods have been proposed to increase the bond strength between the zirconia and resin cements, among them the standard treatments as the surface sandblasting with aluminum oxide [7] or silica-alumina particles followed by silanization [8]. Nevertheless, the effectiveness of these methods is controversial. Other attempts as laser application [9] roughening with diamond burns [10], selective acid infiltration [11], and low fusing ceramic application [12] have been also described. It is also reported these kinds of methods have shown different percentages of martensitic

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transformation in the treated surface [13], leading the initiation and propagation of cracks in the material compromising the long-term durability of the restoration made with zirconia [14,15].

It has been shown that the addition of phosphate monomers such as 10 metacriloxidecil dihydrogen phosphate (MDP) in primers or cements can increase the bonding to zirconia. They interact chemically through the phosphate terminal group (P) which reacts with the hydroxyl group (-OH) on the zirconia surface forming chemical bonds between oxygen and zirconium (P-O-Zr) [16]. The use of these materials that chemically interact with zirconia has shown promising results of bond strength. However, the bond strength tends to decrease after aging treatments [17].

A possibility of bonding to zirconia that has not been studied refers to its association with TiO<sub>2</sub> nanostructures. The decrease of the particle size to nanometer scales has favored the appearance of a broad range of applications in different materials, since its behavior changes as compared to the microscopic scale [18]. Nanostructures can be easily incorporated when mixed with resin-based materials [19], besides providing better results in flexural strength, hardness, degree of conversion [20] and antibacterial properties [21]. Nanoscale oxides such as TiO<sub>2</sub> may have unique physical and chemical properties due to their small size and high density of surface sites [22]. The particle size can influence the properties of material increasing the surface free energy by an increase in the number of surface atoms and interface [23]. In particular, the oxide nanotubes as TiO<sub>2</sub> are interesting mainly because of its large surface area, which can originate strong interactions with the solid matrix in which they can be incorporated, chemical stability, electrical properties and high refractive index [19]. These characteristics could contribute to a better interaction and reaction with the environment in which they are [24]. TiO<sub>2</sub> nanotubes

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associated to MDP monomers which have affinity with metallic oxides could improve the bond strength because there are binding sites. Thus, it is important to evaluate new forms/possibilities of application of nanotubes in Dentistry. They can be associated to zirconia as a treatment of surface aiming to improve the bond strength with the resin cement, since there is not any literature with this purpose

The aim of this study was to evaluate the infiltration of TiO<sub>2</sub> nanotubes into the surface of a partially yttrium-stabilized tetragonal zirconia and if the bond strength a resin cement to the infiltrated ceramics may be improved. This study was divided in two stages: 1) synthesis of TiO<sub>2</sub> nanotubes and characterization of ceramic surfaces using confocal laser microscopy, scanning electron microscopy (SEM) and EDS analysis; 2) shear bond strength evaluation with resin cement and different zirconia primers and adhesives.

Null hypotheses: (1) no infiltration would be detected; (2) the infiltration TiO<sub>2</sub> nanotubes would not influence the shear bond strength; and (3) there would be no difference between commercially available adhesives and zirconia primers used in the bond strength evaluation.

## **2 - MATERIALS AND METHODS**

### **2.1 - Preparation of ceramic sample**

For this study, slices were obtained from partially yttrium-stabilized tetragonal zirconia (Y-TZP) blocks. These blocks (IPS e.max Zircad (Ivoclar Vivadent, Schaan, Liechtenstein) were sectioned under water irrigation with a cutting machine (Isomet

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1000, Buehler, LakeBluff, IL, EUA), with a double-face diamond disk (Extec Dia, Wafer blade 5"x. 015x1/2, Extec Corp, Enfield, CT, EUA) to obtain 1.5-mm-thick specimens.

The ceramic slices were submitted to finishing and polishing with #800 and #1200 silicon carbide sandpapers (Carbimet, Buehler, Lake Bluff, IL, EUA) in a polishing machine (Aropol 2V, Arotec, Cotia, SP, Brasil). The polishing was performed with fine-grained felt discs associated with diamond solution of 1  $\mu\text{m}$  (Buehler, Lake Bluff, IL, EUA).

The ceramic slices were then placed in ultrasound deionized water bath (USC 750 - Unique Group, Indaiatuba, SP, Brazil) for 5 min.

## **2.2 - Synthesis of TiO<sub>2</sub> nanotubes**

The TiO<sub>2</sub> nanotubes were synthesized from 10 g of a commercial mixture of TiO<sub>2</sub> anatase powder (Aldrich, 99%) and 120 ml of alkaline solution of NaOH (10M), as described by Arruda et al [19]. The mixture was kept at 120°C for 24 h in a Teflon open container. This container was heated by glycerin bath using a heating mantle as thermal source. The whole process of synthesis was carried out at ambient atmospheric pressure.

After the alkaline treatment, the mixture was washed with 0.1 M hydrochloric acid (HCl) and deionized water repeatedly to remove the sodium ions and until neutralize the pH (pH 7.0). Finally, the solution passed through a drying process at 200°C for 24 h in atmospheric air to eliminate the liquid part and obtaining the final powder and nanotubes with a diameter and length of approximate 10 nm and 200 nm, respectively

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### **2.3 - Nanotubes application on the zirconia surface**

The TiO<sub>2</sub> nanotubes were mixed with isopropyl alcohol in a 50% concentration to obtain a paste. This paste was actively applied by rubbing the surface of the ceramic slice with a microbrush to obtain a uniform thin layer. Then, light air jets at a distance of 15 cm were used to evaporate all alcohol. Nanotubes excesses were removed with a dry microbrush. As control, the nanotubes were not applied. The ceramics were synthesized at a suitable oven following the cycle recommended by the manufacturer.

### **2.4 - Surface Characterization**

For the surface characterization step, two zirconia samples were used: one sample without application of nanotubes and the other with application of nanotubes. Both specimens were submitted to analysis in confocal microscopy (Leica Microsystems, Wetzlar, Germany) for the average surface roughness measurement. Three readings were performed at different points of each sample under 50x magnification and dimensions of 254.64x190.90  $\mu\text{m}^2$ . The values were expressed in Ra. Images were generated through the Scanning Electron Microscope (SEM) by variable pressure APEX Express (APEX Corporation, Delmont, PA, USA). And the surface atomic composition of the ceramic samples was evaluated by EDS analysis. (EDS, energy-dispersive x-ray spectroscopy.)

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## **2.5 - Bond strength**

### **2.5.1 - Specimens Preparation**

After preparation, the ceramic slices were divided in six groups: 1) without application of TiO<sub>2</sub> nanotubes and Single Bond Universal; 2) with application of TiO<sub>2</sub> nanotubes before ceramic sintering and Single Bond Universal; 3) without application of TiO<sub>2</sub> nanotubes and Z-prime; 4) with application of TiO<sub>2</sub> nanotubes and Z-prime; 5) without application of TiO<sub>2</sub> nanotubes and Signum Zirconia Bond; 6) with application of TiO<sub>2</sub> nanotubes and Signum Zirconia Bond. The slices were sintered at a suitable oven according to the manufacturer recommendation.

Then, the slices were fixed in 10-mm-height 3/4 PVC tubes" with acrylic resin (Jet, Dental Articles Classic, Campo Limpo Paulista, SP, Brazil). After that, the slices received the application of the adhesive systems according to the groups previously described following each manufacturer recommendations and were light-activated by a LED light-curing device (Valo Cordless, Ultradent, South Jordan, UT, USA) with irradiance of 1000 mW/cm<sup>2</sup>. Surgical catheters with inner diameter of 1.40 mm and 1 mm height were used to produce resin cement cylinders (RelyX Ultimate 3M Espe, Seefeld, Germany). Four cylinders per ceramic slice were made, totalizing 16 cylinders per group (n = 16). The cement was handled according to the manufacturer recommendations and light-activated for 20 s with the same LED device previously described. After 10 min the surgical catheters were removed with #12 scalpel blades to expose the resin cement cylinders. Specimens were then stored at 37°C in deionized water for 30 days.

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### **2.5.2 - Shear bond strength**

After 30 days of water aging, the prepared specimens were submitted to shear test in a universal testing machine (Instron 3342, Illinois Tool Works, Norwood, MA, USA). The measurement of the force during the test was made using a 50 kgf (500 N) load cell. The samples were subjected to shear bond strength evaluation using a 0.2-mm wire-loop positioned as close as possible of the adhesive interface to shear at a crosshead speed of 0.5 mm/min.

### **2.6 - Failure analysis**

After the completion of the shear test, the surfaces of the samples were analyzed in stereomicroscope (Modular Stereomicroscope Leica MZ6, Wetzlar, Germany) for determination of the failure type involved. The failures were classified into adhesive, cohesive or mixed.

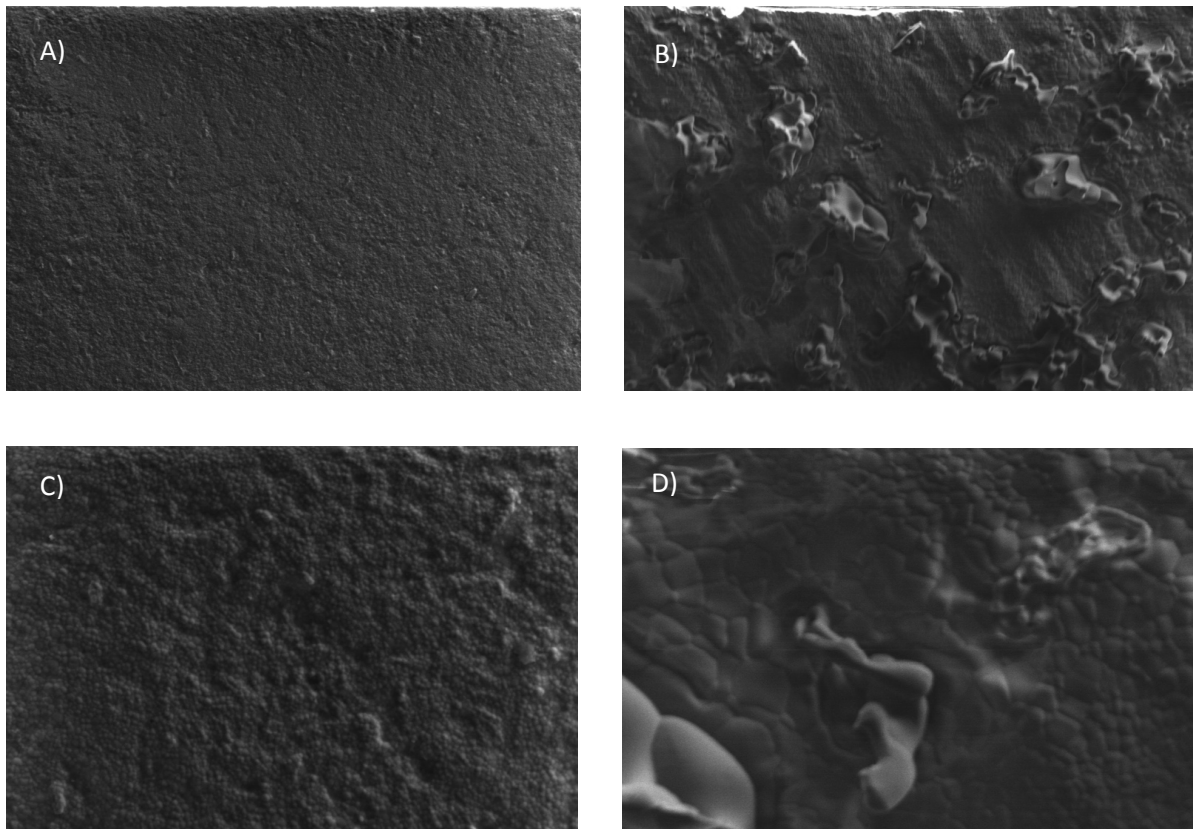
### **2.7 - Statistical analysis**

The shear bond strength data were submitted to the Bartlett test to check the homogeneity of variances. When verified the homogeneity, the data were analyzed by two-way ANOVA followed by Tukey. A global level of significance of 5% was adopted.

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### 3 - RESULTS

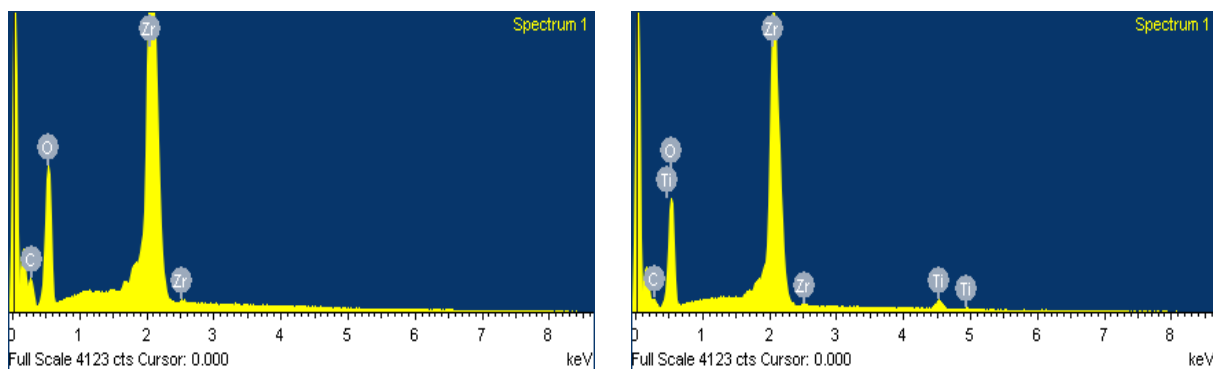
The SEM micrographs of the sintered zirconia samples with and without the application of nanotubes are illustrated in Figure 1. It is possible to observe that the nanotubes were incorporated in the zirconia surface. The EDS analysis has confirmed that the nanoagglomerates were composed of  $\text{TiO}_2$  (Figure 2). The confocal laser microscopy analysis showed an increase in the surface roughness with the application of nanotubes. Without the application of nanotubes the average of the surface roughness was 532.72 nm Ra and with the application 689.15 nm Ra. The images are shown in Figure 3.



**Figure 1:** A and B - images 1000x magnification demonstrating the surface of Y-TZP without and with incorporation of  $\text{TiO}_2$  nanotubes. Images C and D - surface of the Y-TZP without and with incorporation of  $\text{TiO}_2$  nanotubes 4000x magnification.

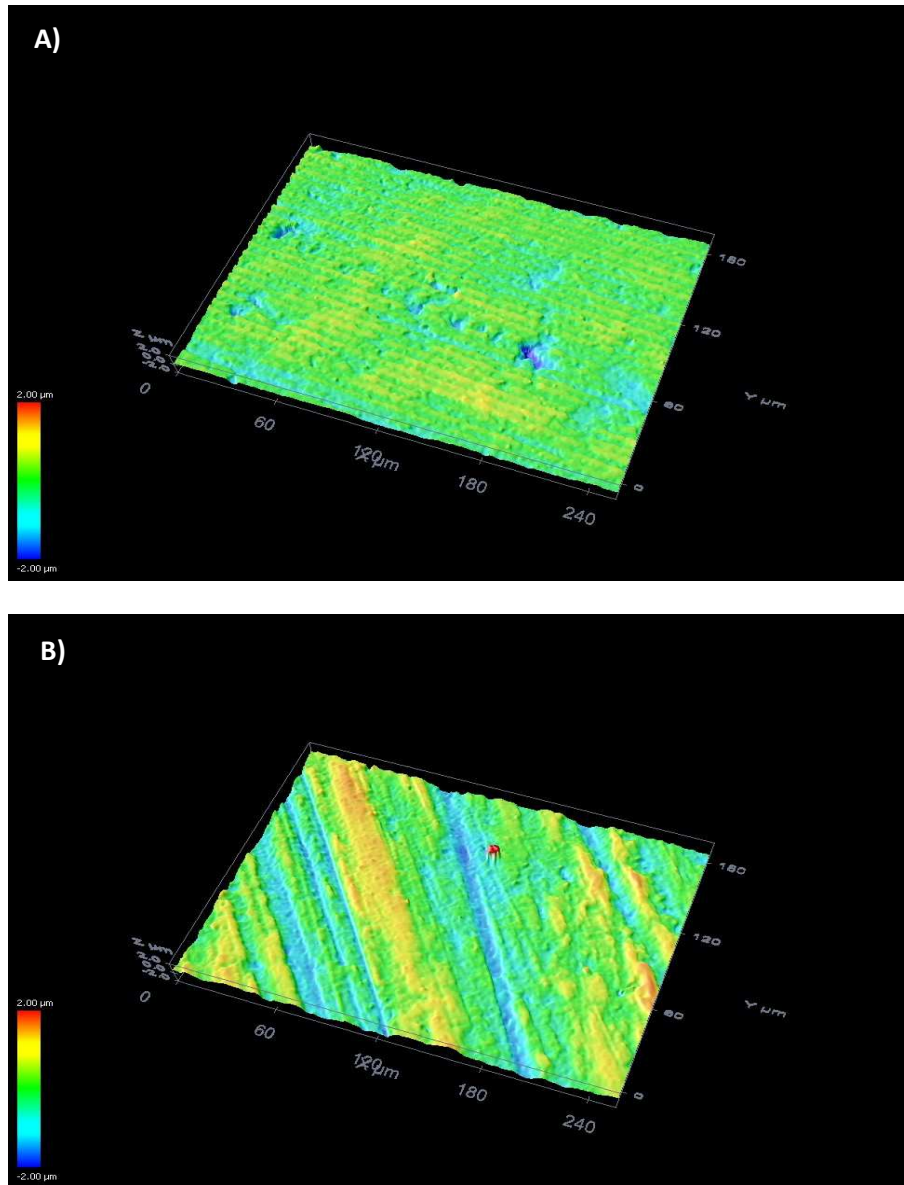
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Element	Weigh%	Atomic%	Element	Weight%	Atomic%
C K	15.11	32.07	C K	7.70	17.90
O K	33.62	53.59	O K	37.03	64.65
Zr L	51.27	14.33	Ti K	1.86	1.09
			Zr L	53.41	16.36
			Totals	100.0	
Totals	100.00				

**Figure 2:** Atomic composition evaluated by EDS analysis. Selected area of reading 700  $\mu\text{m}$  and 200x magnification.



**Figure 3:** The 3D representation of the analyzed surface. A) zirconia without application of TiO<sub>2</sub> nanotubes. B) zirconia after application of TiO<sub>2</sub> nanotubes. It is possible to observe an increase of superficial roughness through enhance of piks and vales represented by the colors red and blue respectively.

Mean values, standard deviations and statistical differences among the six groups for the shear bond strength test are shown in Table 1. There was significant difference among the analyzed groups ( $p = 0.025922$ ). The Signum Zirconia Bond group with nanotubes has shown the highest bond strength results ( $20.06 \text{ MPa} \pm 3.56$ ), and the Z-prime group without nanotubes has showed the lowest values ( $6.18 \text{ MPa} \pm 4.51$ ). No significant difference with the application of the nanotubes regardless of the analyzed group ( $p = 0.6882131$ ). Among the groups without the application of the nanotubes, there was a significant difference among the adhesives according to the following sequence: Signum Zirconia Bond > Single Bond Universal > Z-prime ( $p < 0.00001$ ). Within each adhesive the application of  $\text{TiO}_2$  nanotubes did not influence the bond strength ( $p > 0.05$ ). With the application of the nanotubes, the Single Bond Universal and Z- prime groups were equal to each other and were lower than the Signum Zirconia Bond.

The failure modes were adhesive in almost all specimens ( $94 = 97.9\%$ ). Mixed failures occurred in two samples ( $2.1\%$ ) which belong to the Signum Zirconia Bond with nanotubes group.

**Table 1:** Mean Values and SDs for Shear Bond Strength and number of sample losses.

Adhesive	Nanotubes	Shear bond strenght MPa	Sample losses (% of de 16 samples)
Single bond Universal	without	$11.42 \pm 5.81^b$	1 (6.25%)
Single bond Universal	with	$7.55 \pm 3.54^{cb}$	1 (6.25%)
Signum Zirconia Bond	Without	$18.71 \pm 3.23^a$	0 (0%)
Signum Zirconia Bond	with	$20.06 \pm 3.56^a$	0 (0%)
Z-Prime Plus	without	$6.19 \pm 4.51^c$	3 (18.75%)
Z-Prime Plus	with	$7.61 \pm 5.13^{cb}$	3 (18.75%)

Different superscript letters indicate statistically significant differences.

## 4 - DISCUSSION

The null hypothesis that no TiO<sub>2</sub> infiltration would be detected was rejected. The second null hypothesis, on the other hand, was accepted, because no statistically significant difference was found between application or not of TiO<sub>2</sub> nanotubes. The third null hypothesis was rejected, because there were differences between commercially available adhesives.

Zirconia has a very dense structure, which prevents the penetration of nanometric structures [25]. In the present study, a thin layer of the TiO<sub>2</sub> nanotubes was applied to the surface of the Y-TZP prior to sintering so that the two materials could be melted with the high temperature, known as the melting process. In the scanning electron microscopy, it is possible to observe that before the application of the nanotubes the surface showed only the microstructural characteristics of the zirconia where the grains that compose this structure could be observed. After application, the presence of nanostructures in the images between zirconia crystals could be noticed. Therefore, the nanotubes were incorporated in the surface of the material, but not in a uniform way, existing areas with higher concentration of nanoagglomerates than in others, and also regions in which there was no incorporation of the nanoagglomerates. In these regions the nanotubes could have been removed during the process of removing excesses and also because after the heat generated by the sintering the nanotubes melt losing their tubular conformation and with the cooling they agglomerate. This causes a greater concentration of these nanostructures in some regions.

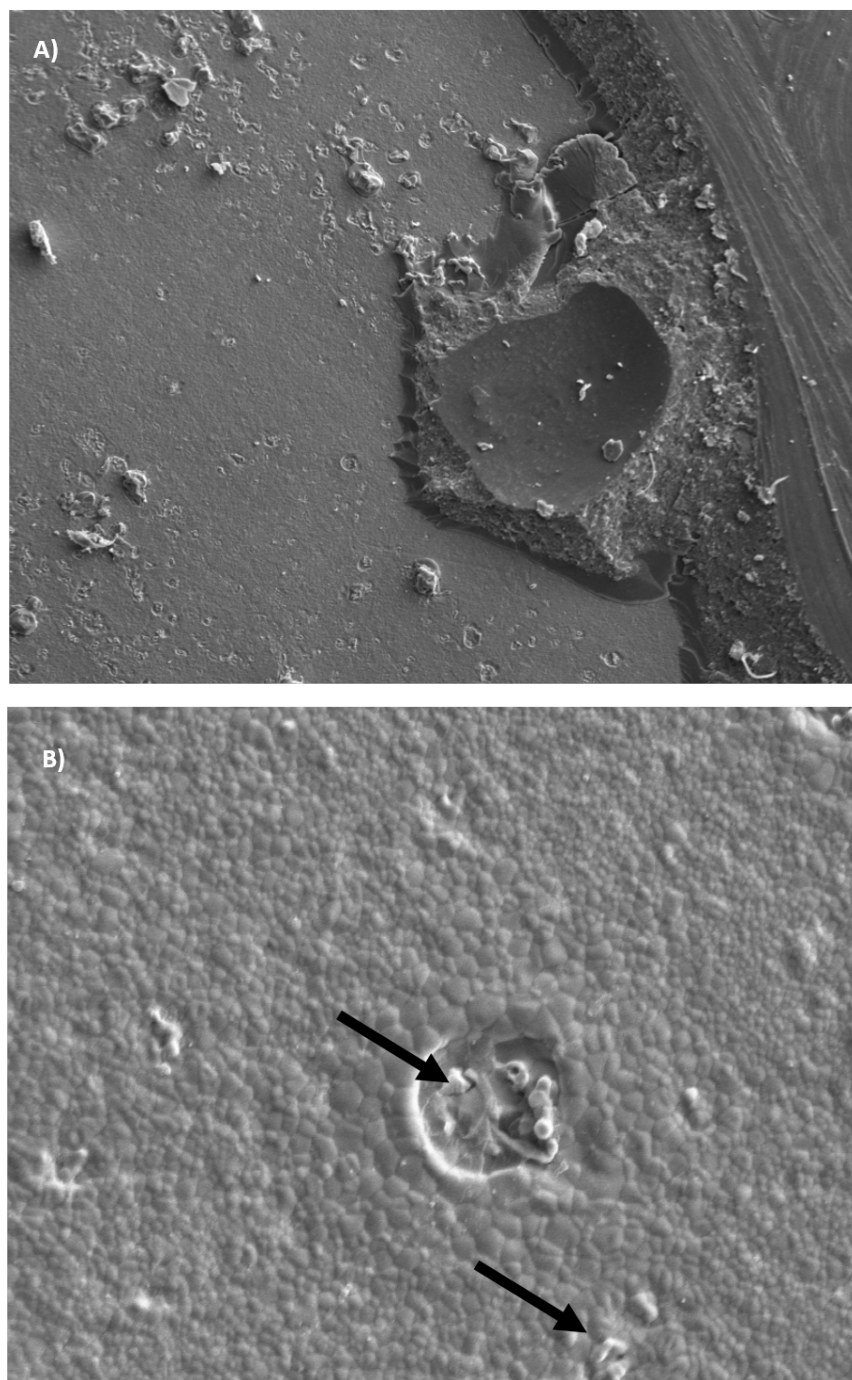
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In fact, the application of the nanotubes on the surface of the Y-TZP is a difficult process to obtain homogeneity, because it is the attempt to melting two materials in a solid state at room temperature. Two considerations must be made about this fact, the first is that the nanotubes were applied in this way because of the ease of the method, which can be strapped for laboratory practice. Where a layer of paste could be applied to the pieces of zirconia after the machining. The second is that the nanotube powder was not mixed with the zirconia powder and subsequently pressed, because the purpose of the study was not to make a modification in the material, which already has excellent mechanical properties, but a surface treatment that could improve the interaction with other materials.

It has already been demonstrated by Arruda et al [19] that the mixture of nanotubes to resinous materials is satisfactory and promotes improvements in its properties. Basically it is a powder material being added to a viscous material, making it easier to obtain a homogeneous mixture. This good interaction between titanium nanotubes and composite resin may also suggest a good interaction between  $\text{TiO}_2$  nanotubes and resin cement and promote improvement in bond strength.

An important factor is that after the shear bond strength test, the nanoagglomerates that were incorporated in the Y-TZP surface were not removed, which was verified by scanning electron microscopy and analysis of the composition of the sample by EDS, as shown in Figure 4. However, it is possible to affirm that, despite the limitations of the technique of applying to nanotubes in the Y-TZP surface, when incorporated, they remain on its surface after the shear bond strength evaluation.

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**Figure 4** - Image A: 200x magnification demonstrating the presence of  $\text{TiO}_2$  nanoagglomerates after shear bond strength test. Image. B: 2000x magnification. The arrows indicate the  $\text{TiO}_2$  nanoagglomerates.

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Only one type of nanotube was analyzed. At the nanoscale, structures can vary not only in size but also in morphology (e.g. nanospheres, nanobastons, nanowires, nanofoils and nanotubes) [19]. After heating, the structure of the nanotubes changes, being no longer tubular showing amorphous way, but still remaining in nanometric scale, and with the same properties as chemical stability and large surface area [19]. These characteristics have contributed to a better interaction and reaction with the environment in which they are [24].

All the adhesives and zirconia primers tested in the present study contain monomers of 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), as shown in Table 2. These monomers bond chemically to metal oxides and also to dental substrates through the phosphate terminal group, and can also react with the hydroxyl group (-OH) on the surface of the zirconia forming chemical bonds between oxygen and zirconium [16]. Because it has the ability to chemically bond to metal oxides, MDP monomers could also bind to TiO<sub>2</sub> nanoagglomerates forming bonds with the oxygen of these structures as well as with oxygen on the surface of zirconia.

The results of this work have shown that after aging, the adhesive Single bond Universal with nanotubes and Z-Prime with and without nanotubes have obtained bond strength values below the minimum values of 10 to 13 MPa [26]. This is in agreement with other studies that showed that the effectiveness of chemical bonds between 10-MDP and zirconia decreases after periods of aging, suggesting that the bonding may undergo hydrolytic degradation [17-27]. In the groups that contained the Signum Zirconia Bond adhesive, the results showed higher values of bond strength even after aging, which it is also in agreement with other studies [28]. These good results may be related to the presence of methyl methacrylate in its composition that

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establishes primary bonds with the methacrylate present in the resin cements, thus improving the bonding strength [29].



**Table 2:** Materials and Composition.

<b>Materials (manufacture)</b>	<b>Composition</b>	<b>Instructions for use</b>
Single Bond Universal (3M ESPE, Seefeld, Germany)	MDP phosphate monomer, dimethacrylate resins, HEMA, Vitrebond copolymer, filler, ethanol, water, initiators, silane	(a) Clean the surface with alcohol and dry it with compressed air; (b) apply with a microbrush to the surface for 20 seconds; (c) apply compressed free oil air for five seconds; (d) light cure for 10 second
Signum Zirconia Bond (Heraeus Kulzer, Hanau, Germany)	Signum zirconia bond I <sup>a</sup> : Acetone, 10-MDP, acetic acid.  Signum zirconia bond II <sup>a</sup> : methyl methacrylate, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide. MMA, initiators	(a) Clean the surface with alcohol and dry it with compressed air; (b) Signum Zirconia bond I is dispensed and applied with a suitable brush to the entire surface and air dried for five seconds; (c) Signum Zirconia bond II is applied and light cured for 40 seconds
Z-Prime Plus (Bisco, Schaumburg, USA)	Biphenyl dimethacrylate, MDP, ethanol	(a) Clean the internal surface of the restoration, rinse and air dry; (b) Apply 1-2 coats of Z-Prime Plus uniformly wetting the bonded surface. Dry with an air syringe for 3-5 seconds
RelyX Ultimate (3M ESPE, St. Paul, USA)	Base Paste: silane treated glass powder, 2-propenoic acid, 2-methyl-, 1,1'-[1-(hydroxymethyl)-1,2-ethanediyl] ester, reaction products with 2-hydroxy-1,3-propanediyl dimethacrylate and phosphorus oxide, triethylene glycol dimethacrylate (TEGDMA), silane treated sílica, oxide glass chemicals, sodium persulfate, tert-butyl peroxy-3,5,5-trimethylhexanoate, copper (ii) acetate monohydrate  Catalyst Past; silane treated glass powder, substituted dimethacrylate, 1,12-dodecane, dimethacrylate, silane treated sílica, 1-benzyl-5-phenyl-barbic-acid calcium salt, sodium p-toluenesulfinate, 2-propenoic acid, 2-methyl-, [(3-methoxypropyl)imino]di-2,1-ethanediyl ester, calcium hydroxide, titanium dioxide	Mix the base paste and the catalyst paste for 20 seconds with a spatula so as to obtain a homegene mixture. Avoid the incorporation of air bubbles

In the present study, no pretreatment on the surface of zirconia was performed. Several pretreatments have been suggested and studied in the literature to increase the bonding strength between zirconia and resin cements. Many of these methods aim to increase surface roughness through mechanical treatments such as surface roughness with diamond burns and discs, application of Nd: YAG, CO<sub>2</sub> and Er: YAG lasers and aluminum oxide sandblasting, which is considered in the literature as gold standard [30]. In fact, these pretreatments can increase surface roughness, wetness and surface energy, which promote micromechanical retention [31-32]. On the other hand, these same treatments can cause microcracks and induce the transformation of phase from tetragonal to monoclinic, leading to compromise of the durability and properties of the material [14-15]. Since the present study was designed to evaluate the bond strength of a resin cement to zirconia with and without application of nanotubes through different coupling agents. The interference of the reported surface characteristics was eliminated without any pretreatment being performed. Additionally, a factor that it should be discussed is that Y-TZP slices were polished #800 and #1200 sandpapers and fine-grained felt discs associated with diamond solution of 1 µm before the sinterization which could made the incorporation of nanotubes more difficult.

It is important to note that in the present study, the bond strength test was conducted after a period of 30 days of storage in water. Results of bond strength to immediate zirconia are vast in the literature. The results are more valuable after aging, because the resistance to biodegradation is a factor that has great influence on the clinical performance of dental restorations. This study was according to the aging protocol of immersion in water. This artificial technique is common to predict the behavior of resin-based restorative materials, because the presence of water is

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crucial for its deterioration [33]. It should, however, be noted that only a 37°C-water-immersion for 30 days was used for aging purposes so the results of the present study could be different if long-term water storage, termocycling or mechanical cycling were used instead.

Since SEM images showed that the incorporation of nanotubes is not uniform, a suggestion for future studies is that the layer of nanotubes to be applied on the surface of the zirconia is denser and thicker, allowing the covering of its surface in the largest possible area. Moreover, new types of nanometric structures can be tested, characterized also by transmission electron microscopy and the adhesive interface placed under cyclic mechanical-thermal stress before the bond strength evaluation.

## **5 - CONCLUSION**

According to the results of the present study, it is possible to conclude that the TiO<sub>2</sub> nanotubes were incorporated in the surface of the Y-TZP. For the shear bond strength test, there was a significant difference between the adhesives tested, but the application of TiO<sub>2</sub> nanotubes in the zirconia surface had no significant effect on the bond strength.

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## **3 DISCUSSION**

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### 3 DISCUSSION

The null hypothesis that no TiO<sub>2</sub> infiltration would be detected was rejected. The second null hypothesis, on the other hand, was accepted, because no statistically significant difference was found between application or not of TiO<sub>2</sub> nanotubes. The third null hypothesis was rejected, because there were differences between commercially available adhesives.

Zirconia has a very dense structure, which prevents the penetration even of nanometric structures. In the present study, a thin layer of the paste formed by the TiO<sub>2</sub> nanotubes was applied to the surface of the Y-TZP prior to sintering so that the two materials could be melted with the high temperature, known as melting process. In the scanning electron microscopy it is possible to observe that the nanotubes were incorporated in the surface of the material, but not in a uniform way, existing areas with higher concentration of nanotubes than in others, and also regions in which there was no incorporation of the nanotubes, probably removed during the process of removing excesses. In fact, the application of the nanotubes on the surface of the Y-TZP is a difficult process to obtain homogeneity, because it is the attempt to melting of two materials in a solid state at room temperature. It has already been demonstrated by Arruda et. al., (2015) that the mixture of nanotubes to resinous materials is satisfactory and promotes improvements in its properties. Basically it is a powder material being added to a viscous material, making it easier to obtain a homogeneous mixture.

An important factor is that after the shear bond strength test, the nanotubes that were incorporated in the Y-TZP surface were not removed, which was verified by scanning electron microscopy and analysis of the composition of the sample by EDX, as shown in Figure 4 (in the previous article). However, it is possible to affirm that, despite the limitations of the technique of applying to nanotubes in the Y-TZP surface, when incorporated, they remain on its surface after the shear bond strength evaluation being the union of the two materials considered resistant.

Only one type of nanotube was analyzed. At the nanoscale, structures can vary not only in size but also in morphology (e.g. nanospheres, nanobastons,

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nanowires, nanofoils and nanotubes) (Arruda et al., 2015). After heating, the structure of the nanotubes changes, being no longer tubular, but still remaining in nanometric scale, and with the same properties as chemical stability and large surface area (Arruda et al., 2015). These characteristics have contributed to a better interaction and reaction with the environment in which they are (Roy et al., 2011).

All the adhesives tested in the present study contain monomers of 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), as shown in Table 2 (in the previous article). These monomers bond chemically to metal oxides and also to dental substrates through the phosphate terminal group, and can also react with the hydroxyl group (-OH) on the surface of the zirconia forming chemical bonds between oxygen and zirconium (Zhao et al., 2016). The results of this work have shown that after aging, the adhesive Single bond Universal with nanotubes and Z-Prime with and without nanotubes have obtained bond strength values below the minimum values of 10 to 13 MPa (Luty et al., 2006). This is in agreement with other studies that showed that the effectiveness of chemical bonds between 10-MDP and zirconia decreases after periods of aging, suggesting that the bonding may undergo hydrolytic degradation (Lee et al., 2015; Wegner et al., 2002). In the groups that contained the Signum Zirconia Bond adhesive, the results showed higher values of bond strength even after aging, which it is also in agreement with other studies (Pereira et al., 2014). These good results may be related to the presence of methyl methacrylate in its composition that establishes primary bonds with the methacrylate present in the resin cements, thus improving the bonding strength (Ural et al., 2011).

In the present study, no pretreatment on the surface of zirconia was performed. Several pretreatments have been suggested and studied in the literature to increase the bonding strength between zirconia and resin cements. Many of these methods aim to increase surface roughness through mechanical treatments such as surface roughness with diamond burns and discs, application of Nd: YAG, CO<sub>2</sub> and Er: YAG lasers and aluminum oxide sandblasting, which is considered in the literature as gold standard (Tzanakakis et al., 2016). In fact, these pretreatments can increase surface roughness, wetness and surface energy, which promote micromechanical retention (Della Bona et al., 2007; Karakoca et al., 2009). On the other hand, these same treatments can cause microcracks and induce the transformation of phase from tetragonal to monoclinic, leading to compromise of the

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durability and properties of the material (Guazzato et al., 2004; Hjerppe et al., 2010). Since the present study was designed to evaluate the bond strength of a resin cement to zirconia with and without application of nanotubes through different adhesives, the interference of the reported surface characteristics was eliminated without any pretreatment being performed. Additionally, a factor that it should be discussed is that Y-TZP slice were polished #800 and #1200 sandpapers and fine-grained felt discs associated with diamond solution of 1  $\mu\text{m}$  before the sinterization which could made the incorporation of nanotubes more difficult.

It is important to note that in the present study, the bond strength test was conducted after a period of 30 days of storage in water. Results of bond strength to immediate zirconia are vast in the literature. The results are more valuable after aging, because the resistance to biodegradation is a factor that has great influence on the clinical performance of dental restorations. This study was according to the aging protocol of immersion in water. This artificial technique is common to predict the behavior of resin-based restorative materials, because the presence of water is crucial for its deterioration (Amaral et al., 2007). It should, however, be noted that only a 37°C-water-immersion for 30 days was used for aging purposes so the results of the present study could be different if long-term water storage, termocycling or mechanical cycling were used instead.

Another point to be addressed is the fact that in the present study the photoactivation of the resin cement was conducted directly without the influence of a ceramic material between the light source and the cement. Although the Y-TPZ trademarks may exhibit different degrees of translucency, the attenuation of light caused by ceramic may influence the properties of resin cement (Calgaro et al., 2013; Watanabe et al., 2015). The interposition of ceramic materials between the light source and the cement has the effect of reducing the degree of conversion and the hardness of the cement (Calgaro et al., 2013). It has already been shown that the thickness of the interposing ceramic material influences the light transmittance and as the ceramic thickness increases, longer irradiation periods are required. It is known that the bond between the ceramic and the dental substrate also depends on the appropriate cure of the resin cement and factors such as resin cement type, characteristics of the light-activation device and the light-activation protocol could play an important role. For this reason, the results of the present study could be

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different not only if the ceramics were interposed but also if other cements and curing protocols were evaluated.

Since SEM images showed that the incorporation of nanotubes is not uniform, a suggestion for future studies is that the layer of nanotubes to be applied on the surface of the zirconia is denser and thicker, allowing the covering of its surface in the largest possible area. Moreover, new types of nanometric structures can be tested and the adhesive interface placed under cyclic mechanical-thermal stress before the bond strength evaluation.

## **4 CONCLUSION**

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## **4 CONCLUSION**

According to the results of the present study, it is possible to conclude that the TiO<sub>2</sub> nanotubes were incorporated in the surface of the Y-TZP. For the shear bond strength test, there was a significant difference between the adhesives tested, but the application of TiO<sub>2</sub> nanotubes in the Zirconia surface had no significant effect on the bond strength.





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