UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

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**High-pressure vacuum application of TiO$_2$ nanotubes on a polycrystalline zirconia: influence on bond strength**

**Aplicação a vácuo de alta pressão de nanotubos de TiO$_2$ em uma zirconia policristalina: influência na força de adesão**

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Dissertação constituída por artigo apresentada a Faculdade de Odontologia de Bauru da Universidade de São Paulo para obtenção do título de Mestre em Ciências no Programa de Ciências Odontológicas Aplicadas, na área de concentração Dentística.

Orientador: Prof. Dr. Adilson Yoshio Furuse

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FOLHA DE APROVAÇÃO

# DEDICATÓRIA

*Dedico esse trabalho…*

*…aos meus pais Hernan e Miki e irmão Keni*

*pelo amor infinito e apoio incondicional*

*durante toda minha formação acadêmica.*

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*Agradeço à Universidad Peruana de Ciencias Aplicadas (UPC), por iniciar e cultivar meu interesse na odontologia. Em 6 anos de estudos aprendi a trabalhar com ética, respeito e paixão com meus pacientes, colegas e professores.*

*À faculdade de Odontología de Bauru, da Universidade de São Paulo, por multiplicar exponencialmente a vontade de aprender cada dia mais e iniciar meus primeiros passos como futuro docente.*

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*A meu tio, Daniel Watanabe, onde eu tive meu primeiro contato com a odontologia e me ensinou a trabalhar com ética e profissionalismo.*

# ABSTRACT

**Objective:** The purpose of this study was to evaluate the microshear bond strength of resin cement to Y-TZP ceramic after different application methods of $TiO_2$ nanotubes ($nTiO_2$) on pre-sintered Y-TZP surfaces.

**Material and methods:** $nTiO_2$ were produced by alkaline synthesis, mixed with either isopropyl alcohol or acetone and applied on pre-sintered zirconia. Surface characterization with scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) analysis was executed before and after nanotubes application and after shear bond strength evaluation. Six groups were evaluated according to the application method of $nTiO_2$ on the pre-sintered 1.4-mm-thick Y-TZP slices (n=15): 1) manual application of $nTiO_2$ mixed with isopropyl alcohol (MAL); 2) manual application of $nTiO_2$ nanotubes mixed with acetone (MAC); 3) application under high-pressure vacuum of $nTiO_2$ mixed with isopropyl alcohol (HPVAl) ; 4) application under high-pressure vacuum of $nTiO_2$ mixed with acetone (HPVAc); 5) control - $Al_2O_3$ sandblasting (OX); 6) control - Rocatec silicatization (ROC). After application Y-TZP were sintered. Ceramic slices of groups 5 and 6 had their surfaces treated after sinterization. Resin composite cylinders (1.4-mm-diameter and 1-mm-height) were cemented on the ceramic slices, stored in water at 37°C for 24h and were thermalcycled for 10.000 cycles before submitting to microshear bond strength evaluation. Data were analyzed by One-way ANOVA and Newman-Keuls tests (a=.05).

**Results:** SEM and EDS confirmed the presence of $TiO_2$ on $nTiO_2$-treated Y-TZP surfaces. There were significant differences between surface treatments (p<0.0001). HPVAl, OX and ROC showed higher shear bond strengths and where statistically similar (p > 0.05). MAC reached intermediary values and HPVAc and MAL presented a significant decrease in the shear bond strength, with a high percentage of premature debonding. HPVAl, OX and ROC had mixed failures (71.4%, 100%, and 92.7% respectively). MAC, HPVAc and MAL had 100% of adhesive failures.

**Conclusion:** The high-pressure vacuum application of $nTiO_2$ mixed with isopropyl alcohol showed the best results with shear bond strength values compared to conventional sandblasting methods.

**Keywords:** Dental ceramics, Zirconia, nanotechnology, nanotubes, titanium.

# RESUMO

**Objetivo:** O objetivo deste estudo foi avaliar a resistência ao cisalhamento de uma resina composta a uma cerâmica Y-TZP após diferentes métodos de aplicação dos nanotubos de TiO2 (nTiO2) na superfície da cerâmica..

**Material e métodos:** $nTiO_2$ foram produzidos por síntese alcalina, misturados com álcool isopropílico ou acetona e aplicados em zircônia pré-sinterizada. A caracterização da superfície por microscopia confocal a laser, microscopia eletrônica de varredura (MEV) e espectroscopia de dispersão de energia por raios X (EDS) foi realizada antes e após a aplicação dos nanotubos e após a avaliação da resistência ao cisalhamento. Seis grupos foram avaliados de acordo com o método de aplicação do $nTiO_2$ nas fatias de Y-TZP pré-sinterizadas com 1,4 mm de espessura (n = 15): 1) aplicação manual de $nTiO_2$ misturado com álcool isopropílico (MAL); 2) aplicação manual de nanotubos de $nTiO_2$ misturados com acetona (MAC); 3) aplicação sob vácuo de alta pressão de $nTiO_2$ misturado com álcool isopropílico (HPVAl); 4) aplicação sob vácuo de alta pressão de $nTiO_2$ misturado com acetona (HPVAc); 5) controle - jato de areia Al2O3 (OX); 6) controle - silicatização de Rocatec (ROC). Após a aplicação, o Y-TZP foi sinterizado. As fatias de cerâmica dos grupos 5 e 6 tiveram suas superfícies tratadas após a sinterização. Cilindros de resina composta (1,4 mm de diâmetro e 1 mm de altura) foram cimentados nas fatias de cerâmica, armazenados em água a 37 ° C por 24h e foram termociclados por 10.000 ciclos antes de serem submetidos à avaliação de resistência ao cisalhamento. Os dados foram analisados pelos testes teste ANOVA e Newman-Keuls (a = 0,05).

**Resultados:** MEV e EDS confirmaram a presença de $TiO_2$ nas superfícies de Y-TZP tratadas com $nTiO_2$. Houve diferenças significativas entre os tratamentos de superfície (p <0,0001). HPVAl, OX e ROC apresentaram maiores resistências ao cisalhamento e estatisticamente semelhantes (p> 0,05). O MAC atingiu valores intermediários e o HPVAc e o MAL apresentaram uma diminuição significativa na resistência ao cisalhamento, com alta porcentagem de descolamento prematuro. HPVAl, OX e ROC apresentaram falhas mistas (71,4%, 100% e 92,7%, respectivamente). MAC, HPVAc e MAL tiveram 100% de falhas adesivas.

**Conclusões**: A aplicação de vácuo de alta pressão de $nTiO_2$ misturado com álcool isopropílico apresentou os melhores resultados com valores de resistência ao cisalhamento em comparação com os métodos convencionais de jateamento.

**Palavras-chave:** Ortodontia, Terceiro Molar, Classificação, Epidemiologia.

# LIST OF ILLUSTRATIONS

# LIST OF TABLES

# LIST DE ABBREVIATIONS AND ACRONYMS

SEM        scanning electron microscopy

EDS        energy-dispersive x-ray spectroscopy

$nTiO_2$        $TiO_2$ nanotubes

MAL        manual application of $nTiO_2$ mixed with isopropyl alcohol

MAC        manual application of $nTiO_2$ mixed with acetone

HPVAl        high-pressure vacuum of $nTiO_2$ mixed with isopropyl alcohol

HPVAc        high-pressure vacuum of $nTiO_2$ mixed with acetone

OX        $Al_2O_3$ sandblasting

ROC        Rocatec silicatization

# TABLE OF CONTENTS

# 1 INTRODUCTION

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Zirconia is a crystalline dioxide of zirconium. It has been used in dentistry due to its high mechanical and physical properties in comparison with other dental ceramics. For being a metallic oxide, it has been called "ceramic steel" and it can be classified in three different patterns: monoclinic, cubic and tetragonal. For achieving greater molecular stability, other metallic oxides were mixed, such as MgO, CaO or $Y_2O_3$. Yttria-stabilized tetragonal zirconia polycristal (Y-TZP) is nowadays on of the most used in dental prosthetics ceramics. Besides its mechanical properties, it is well-known that zirconia ceramics presents chemical stability, biocompatibility, low thermal conductivity and phase modification when a stress is applied.[1]

Because of these optimal properties, zirconia has been used for monolithic crowns, implant abutments and core material for crowns and extensive fixed dental prosthetics. However, unlike glass-based ceramics, polycristalline zirconia is an etch-resistant ceramic; and conventional hydrofluoric acid application will not have any effect. In glass ceramics, acid is applied to remove a superficial layer of silica, which will promote a micromechanical retention. In lack of adhesion, various zirconia surface treatments have been described in the literature to improve bond strength.[2] Methods like aluminum oxide airborne particle abrasion, silicatization, laser application and surface roughening with diamond rotary instrument were tested with inconclusive results.[3-7] All these surface treatments are based on the mechanical removal of superficial layer to create micromechanical retention. The mechanical removal of superficial layer, however, creates problems in Y-TZP due to martensitic transformation. It occurs when a high stress is applied and cracking energy induces a transition of tetragonal phase to monoclinic phase of the particles around the crack.

This can be the initial site of propagation of cracks and compromise the longevity of restoration.[8, 9]

New methods are being seeked for establishing stable bond for zirconia materials. Materials containing 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) have promising results when a 10-MPD primer was used in conjunction with 10-MDP containing resin cement.[10] These can be explained due to the chemical interactions between the polycrystalline ceramic and a resin-based material.[11, 12] 10-MDP monomer has two functional groups: a terminal divalent phosphoryl group and the other is a methacryloyl group.[13] The phosphate group can establish a chemical bond with metal oxides of the ceramic and the methacryloyl copolimerizes with the monomers of the adhesive and resin cement.[3, 14, 15]

In addition of chemical bond with 10-MDP resin-based materials, $TiO_2$ nanostructures have being studied in dentistry due to good results when utilized with polymeric materials.[16, 17] Specifically, $TiO_2$ nanotubes ($nTiO_2$) presents chemical stability, optimal electric properties, upstanding refractive index and large surface area. This larger surface area may amplify connections sites to found stronger and more stable bond. A recently published study demonstrated a new method of applying $nTiO_2$ nanotubes on the surface on a pre-sintered Y-TZP material.[18] This method is interesting, however, more application protocols must be evaluated. With this method two bonding mechanisms could in theory be achieved: micromechanical retention with the addition of a superficial layer of $nTiO_2$ and a chemical bonding of the metallic oxides of Y-TZP and $nTiO_2$ to the phosphate group of the 10-MDP monomer.

While evaluating the bond strength to ceramics, it is important to consider how their microstruture and opacity affect the light transmission for activating the resin cement. This is an important issue because direct light activation only occurs at the

margins of the restorations and it has been shown that the light attenuation caused by different ceramics plays and important role in the properties of resin-based cements.[19, 20] Thus, the shear bond strength method should consider the influence of the light attenuation caused by the ceramic material. The purpose of this study was to evaluate and establish a protocol of incorporation of $nTiO_2$ on a Y-TZP ceramic and its influence on the microshear bond strength of a resin cement to the ceramics. The null hypotheses evaluated were that no $nTiO_2$ infiltration would be achieved and the addition of $nTiO_2$ would not influence the shear bond strength in comparison of conventional surface treatments.

# 2 ARTICLE

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The article presented in this Dissertation was written according to The Journal of Prosthetic Dentistry instructions and guidelines for article submission.

# HIGH-PRESSURE VACUUM APPLICATION OF TIO2 NANOTUBES ON A POLYCRYSTALLINE ZIRCONIA: INFLUENCE ON BOND STRENGTH

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While evaluating the bond strength to ceramics, it is important to consider how their microstruture and opacity affect the light transmission for activating the resin cement. This is an important issue because direct light activation only occurs at the margins of the restorations and it has been shown that the light attenuation caused by different

ceramics plays and important role in the properties of resin-based cements.[19, 20] Thus, the shear bond strength method should consider the influence of the light attenuation caused by the ceramic material. The purpose of this study was to evaluate and establish a protocol of incorporation of $nTiO_2$ on a Y-TZP ceramic and its influence on the microshear bond strength of a resin cement to the ceramics. The null hypotheses evaluated were that no $nTiO_2$ infiltration would be achieved and the addition of $nTiO_2$ would not influence the shear bond strength in comparison of conventional surface treatments.

## MATERIALS AND METHODS

Ten grams of commercially available $TiO_2$ anatase powder (Aldrich, 99%) was mixed with 120 mL of alkaline solution of NaOH (10M), and kept in a Teflon container at 120°C for 24 hours. The container was heated a glycerine bath at ambient atmospheric pressure. After 24 hours of alkaline treatment, deionized water and hydrochloric acid solution (HCl) (0.1M) were used to sequentially and repeatedly wash the NaOH alkaline solution and the $TiO_2$ powder. The solution then undergone a drying process at 200°C for 24 hours in air atmosphere, to eliminate the liquid part and obtain the final powder with nanotubes of 20 nm in diameter and 200 nm in length.[21]

Six groups were evaluated according to the application method of $nTiO_2$ on the pre-sintered 1.4-mm-thick Y-TZP slices (n=15): 1) manual application of $nTiO_2$ mixed with isopropyl alcohol (MAI); 2) manual application of $nTiO_2$ nanotubes mixed with acetone (MAc); 3) application under high-pressure vacuum of $nTiO_2$ mixed with 100% isopropyl alcohol (HPVAI); 4) application under high-pressure vacuum of $nTiO_2$ mixed with acetone (HPVAc); 5) control - $Al_2O_3$ sandblasting (OX); 6) control - Rocatec silicatization (ROC). All commercially available materials used in the study are described on Table 1.

Table 1 - Materials and respective compositions.

| Adhesive (manufacturer) | Composition | Instruction for use |
| --- | --- | --- |
| Single Bond Universal (3M ESPE, Seefeld Germany) | MDP phospate monomer, dimethacrylate<br><br>resins, HEMA, Vitrebond copolymer, filler,<br><br>ethanol, water, initiators, silane | (a) Clean the surface with alcohol and dry it with<br><br>compressed air; (b) apply with a microbrush to the<br><br>surface for 20 seconds; (c) apply compressed free oil<br><br>air for five seconds; (d) light cure for 10 seconds |
| RelyX Ultimate (3M ESPE) Seefeld Germany) | Base paste: silane-treated glass powder, 2-propenoic acid,<br><br>2-methyl-, 1,10-[1-(hydroxymethyl)-1,2- ethanediyl] ester,<br><br>reaction products with 2-hydroxy-1,3- propanediyl<br><br>dimethacrylate and phosphorus oxide, triethylene glycol<br><br>dimethacrylate (TEGDMA), silane treated silica, oxide glass<br><br>chemicals, sodium persulfate, tert-butyl peroxy-3,5,<br><br>5-trimethylhexanoate, copper (ii) acetate monohydrate<br><br>Catalyst paste; silane-treated glass powder, substituted<br><br>dimethacrylate, 1,12-dodecane, dimethacrylate, silane treated<br><br>sílica, 1-benzyl-5-phenyl-barbic-acid calcium salt, sodium<br><br>p-toluenesulfinate, 2-propenoic acid, 2-methyl-,<br><br>[(3-methoxypropyl)imino]di-2,1-ethanediyl ester, calcium<br><br>hydroxide, titanium dioxide | (a) Mix base paste and catalyst paste for 20 s with spatula to<br><br>obtain homogeneous mixture; (b) avoid incorporation of air<br><br>bubbles |

Y-TZP blocks (IPS e.max Zircad; Ivoclar Vivadent, AG) were sliced with a thickness of 1.5 mm width with a double-faced diamond disk (Wafer blade, 5-inch x 0.15 inch x 0.15 inch; Extec) in a cutting machine (IsoMet 1000; Buehler) under constant water-cooling (Fig. 1). After cutting, Y-TZP slices were finished and polished with #600, #800 and #1200 Silicon carbide papers (Carbimet; Buehler) and 1 μm polishing diamond solution (MetaDi water-based suspension; Buehler) on fined-grained felt disk. After finishing and polishing, 1.2-mm-thick slices were obtained. Slices were cleaned in ultrasonic bath with deionized water for 5 minutes, and the dried in a incubator for 2 hours at 37ºC.
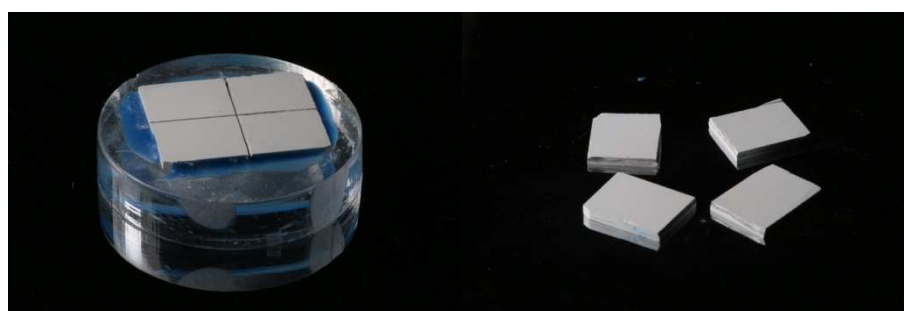


Figure 1 - Y-TZP slices.

For groups 1 and 2 a paste of $nTiO_2$ was made with isopropyl alcohol (group 1) or acetone (group 2) at 50%wt and applied with a flat point brush to create a uniform and thin layer. The alcohol/acetone was then evaporated with oil-free air with pressure of 40 psi, applied at 45° from a distance of 10 cm for 10 seconds (Fig. 2).



Figure 2 - Manual application of $nTiO_2$ alcohol/acetone mixtures.

Groups 3 and 4, high-pressure vacuum infiltration was employed with a Büchner flask for 5 minutes at 70 kPa. Initially, 10 mL of 100% alcohol (group 3) or 100% acetone (group 4) were mechanically mixed with 1 g of $nTiO_2$ with a vortex mixer (K45-2820, Kasvi) at 2800 rpm and 60 Htz on a 50-mL Falcon tube (Fig. 3). Pre-sintered ceramic slices were carefully placed inside the Büchner flask and the $nTiO_2$ mixture (with alcohol or acetone) was added to completely cover all slices. The vacuum was then applied with a compressor (DIA-PUMP 089/C; Fanem) (Fig. 4).



Figure 3 - Procedure for preparing the $nTiO_2$ mixtures.



Figure 4 - High-pressure vacuum application.

The ceramic slices were carefully placed on the bottom of the Büchner flask and the $nTiO_2$ mixture (with alcohol or acetone) was added to completely cover all slices. The vacuum was then applied with a compressor.

After the application of $nTiO_2$, treated slices were dried in an incubator for 24 hours at 37ºC.

After surface treatments, ceramic slices were sintered in a furnace (Programat S1, Ivoclar Vivadent, Schaan, Liechtenstein), following the manufacturer recommendations, and 1-mm-thick slices were obtained. Groups 5 and 6 received the surface treatment after the sinterization. For group 5, 50 µm aluminum oxide sandblasting was done at a 10 mm distance, 45° inclination, and 0.28 bar for 15 seconds. Group 6, 100 µm Rocatec Plus (3M Espe) sandblasting was employed with the same parameters as aluminum oxide groups. SEM images (EVO LS15; Zeiss) and EDS analysis were performed to evaluate the composition and presence of $TiO_2$ on the zirconia surface.

For the microshear bond strength evaluation, cylinders  (1.4 mm diameter and 1 mm height) were made using surgical catheters as molds with the resin composite Z350XT A2B (3M Espe) and kept in dark canisters at 37°C for seven days. These cylinders were cemented on the ceramic slices with a universal adhesive (Singlebond Universal; 3M Espe) and a dual-cured resin cement (RelyX Ultimate; 3M Espe). The universal adhesive was applied on the top of the ceramic slices as follows: adhesive was applied with a microbrush and remained untouched for 20 seconds; oil-free air with pressure of 40 psi was applied at 90° from a distance of 15 cm for five seconds to evaporate solvents; and the adhesive was light activated for 10 seconds with an LED device (VALO Cordless, Ultradent Products). The resin cement was mixed and applied on the top ceramic slice with a spatula and then the resin composite cylinder was carefully

placed and hand pressed. The excess of cement was removed with a microbrush and the light activation was conducted 5 minutes after mixing the two pastes to ensuring chemical curing of the resin cement and reproducing the clinical time needed for cementing the restoration.[20] The same operator cemented all cylinders and all procedures from $nTiO_2$ application to removing resin cement excesses were carried out under 4.3✕ magnification (EyeMag Pro F; Zeiss). To simulate a clinical condition in which the restoration is cemented on the tooth with the light activation occurring through the ceramic material, after removing resin cement excesses around the resin composite cylinders, the tip of the light-emitting diode device (Valo Cordless; Ultradent Products Inc) was positioned below the ceramic slice so the light could pass through the ceramics. For this purpose, a special device was made to place the ceramic slice and position the light source below it in a way that no light other then the one passing through the ceramics could reach the bonding interface (Fig. 5). All samples were light activated for 40 seconds with irradiance of 1100 mW/cm$^2$. Samples were submitted to artificial aging by thermocycling in deionized water for 10000 cycles at 5º - 55º water baths (Thermocycle; BioPDI).



Figure 5 - Device used to position the light source below the ceramic slice.

The ceramic slices were centered over an orange filter with a center role of 2 mm in diameter with the bonding interface on the opposite side of the light source.

Specimens were fixed in 19 mm diameter and 10mm height polyvinyl chloride tubes with acrylic resin (Jet; Dental Articles Classic). The shear bond strength was evaluated in a universal testing machine (Instron 3342, Illinois Tool Works), employing a 0.2mm wire loop and a 500-N-load cell at a crosshead speed of 0.5 mm/min. Soon after completing the shear test, failure type was analyzed under 70✕ magnification in a stereomicroscope (Citoval 2; Karl Zeiss Jena). Failures were classified as adhesive, cohesive or mixed. Data were analyzed by a One-way ANOVA and Newman-Keuls tests. A global level of significance of 5% was adopted.

**RESULTS**

SEM images showed that $nTiO_2$ were effectively infiltrated in all $nTiO_2$-treated groups. The EDS analysis confirmed the presence of Ti on the treated ceramics (Fig. 6). Mean values and standard deviations for the shear bond strength data and number of lost samples for each group are shown in Table 2 and Figure 7. There were significant differences between surface treatments (p<0.0001). The OX group exhibited the highest shear bond strength, followed by HPVAl and ROC groups. These three groups obtained notably high shear bond strengths and there were no significant difference between them. The MAc group that reached intermediary shear bond strength. Contrarily, groups HPVAc and MAl presented a significantly decrease in the shear bond strength, with a high percentage of premature debonding. Group OX presented mixed failures (100%); while HPVAl shows a high amount of mixed failures (71.43%) and an equal number of adhesive and cohesive failure (14.29%). ROC group

presented a 92.86% mixed failure and a 7.14% cohesive failure. MAc, HPVAc and MAl had 100% of adhesive failures.

Table 2 - Mean values and standard deviations (SD) for the shear bond strength data and number of lost samples for each group.

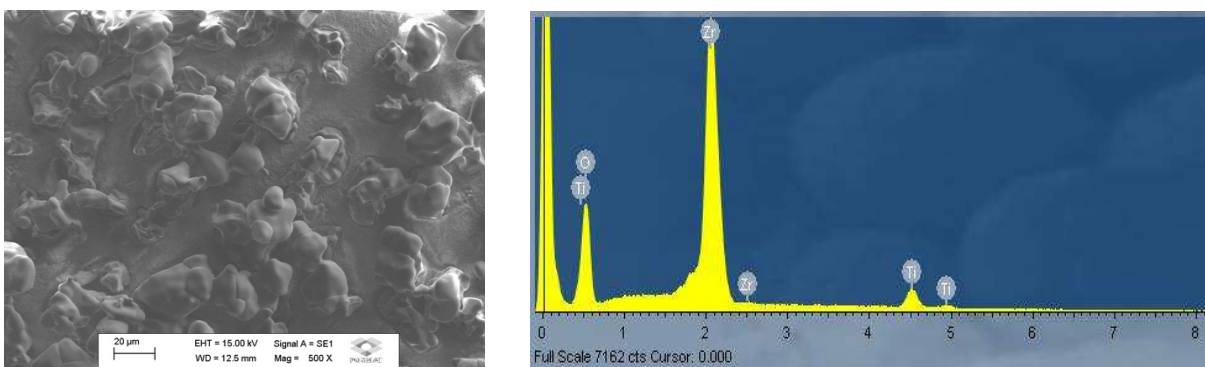| Groups | Shear bond strength (SD) | Sample losses (% out of 15 samples) |
|---|---|---|
| MAl | 1.22 (0.94)[c] | 8 (53.3%) |
| MAc | 9.6 (6.45)[b] | 8 (53.3%) |
| HPVAl | 22.96 (10.28)[a] | 1 (6.7%) |
| HPAc | 2.14 (3.34)[bc] | 7 (46.7%) |
| OX | 34.16 (7.91)[a] | 0 (0%) |
| ROC | 27.71 (9.42)[a] | 1 (6.7%) |
| *Different superscript letters represent statistically significant differences (p<0.05).* | | |



Figure 6 - SEM and EDS images showing the presence of $nTiO_2$ on Y-TZP surfaces.
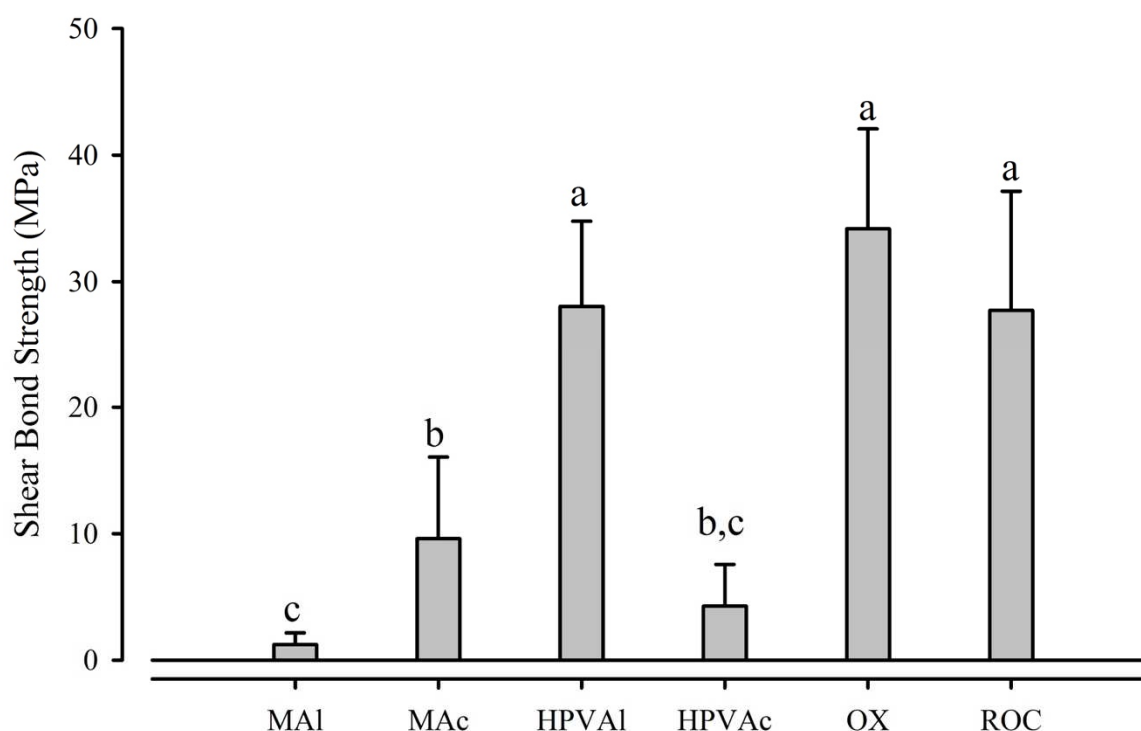
Figure 7 - Mean values and standard deviations for the shear bond strength. Similar letters above columns represent no significant difference ($p < 0.05$).

**DISCUSSION**

After confirming the presence of $nTiO_2$ with SEM images and EDS analysis , it can be inferred that under laboratory conditions, a higher surface roughness can be obtained. Thus the first null hypothesis that there will not be incorporation of $nTiO_2$ on the Y-TZP ceramic was rejected. The increase in the surface roughness has been recently described.[18] This can promote a micromechanical retention and could be a possible way of creating chemical bonding between zirconia and resin-based materials. In the present study, the influence of $nTiO_2$ incorporation was dependent of the method of application with higher bond strength values been observed for the application under high-pressure vacuum of $nTiO_2$ mixed with 100% isopropyl alcohol (HPVAl). This

method was not statistically different than the conventional sandblasting surface treatments with $Al_2O_3$ and Rocatec Plus. Thus the second hypothesis was accepted.

The Y-TZP evaluated in the present study is 97% tetragonal d 3% monoclinic zirconia. According to data provided by Ivoclar Vivadent the composition of IPS e.max ZirCAD has an approximately 87-95 wt.% $ZrO_2$, 4-6 wt.% $Y_2O_3$, 1-5 wt.% $HfO_2$, and 0.1-1 wt.% $Al_2O_3$; with a porosity of 47.3-49.3 vol%. Pre-sintered zirconia is porous and has low strength.[22] This characteristic of pre-sintered zirconia may allow the penetration of the nanostructures into the zirconia. As observed in the present study, the incorporation of $nTiO_2$ was effective, although some morphological changes were perceived. After sintering, $nTiO_2$ change to an amorphous configuration, possibly due to the high sintering temperature employed on Y-TZP sample. Even though it changed its morphology, its presence on the zirconia surface may be an available connection site to promote chemical bonding with functional monomers.

Chemical bonding with interaction of 10-MDP monomers and a polycrystalline zirconia ceramic has already been proven.[11, 12] The presence of 10-MDP monomer on the adhesive attained high bond strength values, while 10-MDP free adhesives obtained low bond strength values.[10] This monomer is amphiphilic, consisting of a hydrophilic phosphate group and a hydrophobic the vinyl group.[13]

As shown in a similar study, manual paste application lead to a non-homogeneous layer; obtaining sites with high percentage of nanotubes agglomerates and sites with low or non-presence.[18] On the other hand, another incorporation protocol was tried on this study. High-pressure vacuum was applied in previously dehydrated Y-TZP slices,with the intention of infiltrating the nanotubes into the interconnected porous structure. This new protocol submerging zirconia on solutions containing oxides is similar from the study done by Jevnikar et al. in 2010 with an alumina coating, in which

the zirconia samples are submerged in a mix of distilled water and alumina particles for 15 minutes and dehydrated for 2 hours at 110°C. [23] Jevnikar et al., however, did not use a high-pressure vacuum approach. In the present study, the fact of being submerged in $nTiO_2$ and isopropyl alcohol, resulted in a low concentration, although homogeneous layer, which was confirmed by SEM and EDS analyses.

The microshear bond strength test performed on this study has some known limitations due to the nonhomogeneous stress distribution at the bonding interface. Literature recommends microtensile test as the ideal bond strength evaluation test, due to the unidirectional vertical force applied.[24] The limitations founded on the shear bond strength test was diminished by reducing the bonding area, applying the force directly to the interface resin-ceramic and distribute the stress area with the usage of a wire loop that embraces entirely the resin sample. For the purpose of simulating the light attenuation caused by the microstruture and opacity of the ceramics in the present study a device was developed to allow light activation of the resin cement with light only passing though the ceramics. This idea would not be feasible if a microtensile evaluation were to be executed.

The shear bond strength test was performed after 10,000 cycles of thermal heat artificial aging, with intervals of 5-55°C. In spite of not having an established artificial aging to determine an in vivo functioning simulation, thermocycle was chosen for several reasons. Aging prostheses or specimens must receive stress/damage accumulation. For laboratory studies, mechanical, thermal and chewing cycles can be applied.[25] However, the size of the specimen limits the viability for mechanical and chewing simulations. Consequently, thermal aging, although maybe not the best approach, was employed for causing expansion/contraction stresses on the resin composite, Y-TPZ and adhesive interface. Nevertheless, a longer water storage and

higher number of thermal cycles could represent a more reliable data, without being clinically unrealistic. New forms of mechanical aging must be developed to increase validation of the artificial aging process.

Feltrin et al. (2018) first introduced the idea of the possibility incorporating $nTiO_2$ on pre-sintered zirconia surfaces, showing that even after the shear bond strength the $TiO_2$ structures remained fixed to the Y-TZP ceramics.[18] These authors, however, did not observed any increase the shear bond strength compared to the application of zirconia primers and evaluated only the manual application of $nTiO_2$ mixed with isopropyl alcohol, without submitting samples to thermocycling. In the present study, the same manual application showed a decreased bond strength after 10,000 cycles of thermocycling, while the manual application of $nTiO_2$ mixed with acetone showed intermediary results. These results mean that the solution used as vehicle is important and other solutions should be evaluated. On the other hand, the experimental group HPVAl (high-pressure vacuum application with alcohol) had similar results to ROC and OX; with relatively high values for all of them. This result may lead to a new form of surface treatment without causing a removal of a superficial layer by generating new sites of adhesion and an increase of the superficial roughness with the incorporation of $nTiO_2$. Without sandblasting the sintered Y-TZP martensitic transformation could be avoided on the affected area and the possibility of future fractures could be reduced. After the analysis of the data, it can be inferred that the type of application and solution vehicle are critical factors to attain positive results. High-pressure vacuum infiltrated with isopropyl alcohol showed better shear bond strength values than all manual application groups and high-pressure vacuum infiltrated with acetone. An advantage for applying $nTiO2$ by high-pressure vacuum is the low cost to assemble and a more homogeneous application capability. It should, however, be noted that other solutions,

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**CONCLUSION**

The high-pressure vacuum application of $nTiO_2$ mixed with isopropyl alcohol showed the best results with shear bond strength values compared to conventional sandblasting methods.

**ACKNOWLEDGMENT**

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# APPENDIX

## APÊNDICE A – DECLARAÇÃO DE USO EXCLUSIVO DE ARTIGO EM DISSERTAÇÃO/TESE

**DECLARAÇÃO DE USO EXCLUSIVO DE ARTIGO EM DISSERTAÇÃO/TESE**

Declaramos estarmos cientes de que o trabalho Levantamento epidemiológico dos terceiros molares em indivíduos da cidade de Bauru será apresentado na Dissertação do aluno **Franco Naoki Mezarina Kanashiro**, não podendo ser utilizado em outros trabalhos dos programas de Pós -Graduação da FOB/USP.

Bauru, 17 de Dezembro de 2018.

Franco Naoki Mezarina Kanashiro

Nome do autor                                    Assinatura

Adilson Yoshio Furuse

Nome do autor                                    Assinatura