

Aljomar José Vechiato Filho

Análise superficial e resistência de união entre zircônia e cimentos resinosos após tratamento de superfície com plasma de baixa temperatura e/ou primer metálico.

Araçatuba – SP

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Orientadora: Profa. Ass. Dr. Daniela Micheline dos Santos

Co-orientadora: Profa. Adj. Elidiane Cipriano Rangel

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Dedicatória

Dedicatória

A minha família, dedico esta Tese de Doutorado. O trabalho tem um papel muito importante em minha vida, assim como a minha família. Portanto, da mesma forma que dediquei a vocês todos os títulos acadêmicos que consegui até hoje, encerro este ciclo da minha vida dedicando também o resultado final da minha trajetória no curso de Doutorado. Este gesto simboliza toda a minha gratidão por tudo o que vocês fizeram por mim. Muito obrigado por terem sido fundamentais para a formação da minha personalidade e pelos exemplos de caráter a serem seguidos. Sem vocês nada disso seria possível!

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“A felicidade só é verdadeira quando compartilhada”

(Frase retirada do filme "Na Natureza Selvagem")

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"As you continue to advance your education, find your voice, and seek out opportunities to make the world a better place"

(Parte de uma carta escrita pelo Presidente Barack Obama)

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Agradecimentos

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Epígrafe

Epígrafe

Em minha tese de doutorado, mantereí a mesma epígrafe da minha dissertação de mestrado, pois acredito profundamente nas seguintes palavras:

“Seu trabalho vai preencher uma parte grande na sua vida e a única maneira de ficar realmente satisfeito é fazer o que você acredita ser um ótimo trabalho. E, a única maneira de fazer um excelente trabalho é amar o que você faz. Se você ainda não encontrou o que é, continue procurando. Não sossegue. Assim como todos os assuntos do coração, você saberá quando encontrá-lo. E, como em qualquer grande relacionamento, só fica melhor e melhor à medida que os anos passam. Então continue procurando até você achar. Não sossegue.”

(Steve Jobs)

Resumo

Vechiato Filho AJ. **Análise superficial e resistência de união entre zircônia e cimentos resinosos após tratamento de superfície com plasma de baixa temperatura e/ou primer metálico** [Tese]. Araçatuba: Faculdade de Odontologia da Universidade Estadual Paulista; 2016.

RESUMO

Devido ao alto conteúdo cristalino na composição da zircônia, o condicionamento com ácido hidrofluorídrico não é capaz de promover as alterações topográficas necessárias na superfície da zircônia para promover adequadamente retenção micromecânica com os cimentos resinosos. Esse fato faz com que adesão da zircônia com tais cimentos seja pequena e problemática. Atualmente, não existe um protocolo bem estabelecido para a cimentação da zircônia (Y-TZP) com cimentos resinosos. Os plasmas de baixa temperatura (PBT) podem ser uma alternativa para os problemas clínicos relacionados à adesão. O objetivo do presente estudo foi caracterizar a superfície da Y-TZP exposta ao tratamento com plasmas de metano (CH₄) ou submetida à aplicação de primer para ligas metálicas e ainda a associação de ambos os métodos, além de avaliar o efeito do tratamento com PBT na força de adesão da Y-TZP com dois cimentos resinosos. Um total de 235 discos de Y-TZP (8 × 2 mm) foram divididos em 5 grupos: Co (controle, sem tratamento de superfície), Pr (primer), PBT (plasma de metano), Pr + PBT e PBT + Pr. O efeito do tipo de tratamento na energia de superfície, morfologia, topografia e composição química da Y-TZP foi investigado. Os discos foram cimentados com substratos de resina composta utilizando Panavia F2.0 e Rely X U200. A análise de força de união (n = 10) foi realizada em uma máquina de ensaio universal com velocidade de 1mm/min, antes e depois da termociclagem (5-55°C, 2.000 ciclos) nos espécimes cimentados. Os resultados foram analisados com ANOVA um e três fatores e teste de Bonferroni ($\alpha = .05$). PBT alterou a energia de superfície e rugosidade dos discos de Y-TZP. As análises de MEV-EDS e XPS mostraram a presença de um filme fino orgânico, o

qual melhorou os resultados de adesão quando o Rely X U200 foi utilizado, sendo que o tratamento com primer foi mais efetivo para o Panavia F2.0. A termociclagem reduziu significativamente os resultados de adesão dos grupos PBT e Pr + PBT cimentados com Rely X U200 e Pr e dos grupos PBT + Pr cimentados com Panavia F2.0. O plasma de metano melhoraram a força de adesão entre Rely X U200 e os discos de Y-TZP e também demonstraram ser resistentes à hidrólise da água, sendo que o Panavia F2.0 demonstrou melhores resultados quando associado ao primer.

Palavras-chave: Zircônio; Cimentos de resina; Resistência ao cisalhamento.

Abstract

Vechiato Filho AJ. Surface analysis and shear bond strength of zirconia on resin cements after non-thermal plasma treatment and/or primer application for metallic alloys

[Thesis]. Araçatuba Dental School – Univ Estadual Paulista; 2016.

ABSTRACT

The desirable morphologic modifications for a proper adhesive retention with resin cements is not obtained through the etching promoted by hydrofluoric acid gel because of the high crystalline content present in the composition of zirconia material. This fact leads to a problematic and deficient adhesion between such ceramic material and resin cements. There is no established protocol for bonding zirconia (Y-TZP) with resin cements. Non-thermal plasma (NTP) may be an alternative for the clinical problems related to adhesion. The aim of the present study was to characterize the surface of Y-TZP exposed to methane (CH₄) NTP or coated with a layer of primer for metal alloys and the association between the two methods and to evaluate the effect of NTP treatment on bond strength between Y-TZP and two resin cements. A total of 235 Y-TZP discs (8 × 2 mm) were distributed into five groups: Co (no surface treatment), Pr (primer), NTP (methane plasma), Pr + NTP and NTP + Pr. The effect of the treatment type on the surface free energy, morphology, topography and chemical composition of the Y-TZP discs was investigated. The discs were cemented to composite resin substrates using Panavia F2.0 or RelyX U200. Shear bond strength (n=10) analyses were performed on a universal testing machine at a cross-head speed of 1 mm/min, before and after thermocycling (5-55°C, 2 000 cycles) on the bonded specimens. The data were analyzed with one and three-way ANOVAs and Bonferroni tests ($\alpha = .05$). NTP affected surface energy and roughness of the Y-TZP discs. SEM-EDS and XPS analyses showed the presence of the organic thin film, which significantly improved the bond strength results when Rely X U200 was used, whereas the primer treatment was more effective with Panavia F2.0. Thermocycling significantly reduced the bond strength results of the NTP and Pr + NTP groups cemented with Rely X U200 and the Pr and NTP + Pr groups cemented with Panavia F2.0. CH₄-nonthermal plasma improves the bond strength between

Rely X U200 and Y-TZP and also seems to have water-resistant behavior, whereas Panavia F2.0 showed better results when associated with primer.

Keywords: Zirconium; Resin cements; Shear strength.

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Lista de Abreviaturas

Zr = Elemento zircônio

C = Elemento carbono

O = Elemento oxigênio

N = Elemento nitrogênio

H = Elemento hidrogênio

Ar = Elemento argônio

Au = Elemento ouro

S = Elemento enxofre

Y-TZP = Molécula de zircônia policristalina tetragonal estabilizada por ítrio.

CH₄ = Molécula de hidrocarboneto

O₂ = Molécula de oxigênio

Torr = Unidade de pressão

MEV = Microscopia eletrônica de varredura

EDS = Espectroscopia de energia dispersiva

XPS = Espectroscopia de fotoelétrons excitados por raios X

MHz = Mega-Hertz

Hz = Hertz

W = Volts

μs = Microsegundo

kV = Quilovolt

eV = Elétron-volt

μm = Micrômetros

nm = Nanômetros

$^{\circ}\text{C}$ = Graus Celsius

mbar = Unidade de pressão

Ra = Parâmetro que indica a média aritmética da rugosidade de superfície

Rq = Parâmetro que indica a média quadrática da rugosidade de superfície

Rt = Parâmetro que indica a altura total do perfil de rugosidade

Rz = Parâmetro que indica a distância vertical entre o perfil maior e menor dentro da área de avaliação

MPa = Megapascal

Sumário

Artigo: Surface analysis and shear bond strength of zirconia on resin cements after non-thermal plasma treatment and/or primer application for metallic alloys

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1. INTRODUÇÃO GERAL

Nas últimas duas décadas, devido à crescente valorização da estética, os sistemas cerâmicos sofreram modificações em sua composição na tentativa de melhorar suas propriedades físicas e mecânicas, tornando-os mais resistentes às fraturas.¹⁻³ Atualmente, a zircônia (poli cristalina com Ítrio tetragonal / Y-TZP) é o material mais comum utilizado na confecção de subestruturas protéticas devido a sua alta resistência a fratura, durabilidade química e excelente estética.^{4,5}

Por outro lado, o aumento do conteúdo cristalino da zircônia diminuiu a quantidade de matriz vítrea presente na composição da mesma, o que torna este tipo de sistema cerâmico resistente à ação do ácido hidrófluorídrico (HF).^{6,3} Dessa forma, o condicionamento com HF não produz alterações topográficas que possam promover adesão micromecânica efetiva com cimentos resinosos. Com isso, o protocolo estabelecido para o condicionamento de superfície de cerâmicas sensíveis a ação desse ácido não se aplica à zircônia e, sabendo que o sucesso clínico do tratamento é dependente também da qualidade da cimentação,⁴ a adesão da zircônia com os cimentos resinosos é problemática.^{2,7,8}

Como alternativas para modificar a superfície da zircônia e melhorar a adesão da mesma aos cimentos resinosos, existem basicamente três tipos de tratamentos: o jateamento com partículas de óxido de alumínio (Al_2O_3) revestidas ou não com sílica,^{7,8} a deposição de filmes finos por plasmas de baixa temperatura^{7,8,9} e o uso de primers para ligas metálicas.^{4,10,11} Contudo, estudos demonstram que a técnica do jateamento com partículas pode causar trincas na superfície do material e, ao longo do tempo, levar a prótese a fraturar, conduzindo o tratamento reabilitador ao insucesso.^{4,7,8,10-12}

Os plasmas de baixa temperatura (PBT) surgiram recentemente como opção bastante promissora para tratar a superfície da zircônia, pois de acordo com alguns autores possuem a capacidade de modificar superfícies inertes em quimicamente ativas sem causar danos na superfície da mesma.^{6,13,14} Plasmas de baixa temperatura são monômeros e/ou gases que, quando estimulados eletricamente, formam íons altamente reativos, os quais podem produzir modificações químicas e/ou físicas na superfície dos materiais melhorando a energia de superfície dos mesmos.^{6,7}

Os plasmas de baixa temperatura podem ser utilizados por meio de peças de mão, as quais produzem plasmas em pressão atmosférica,^{6,14} ou industrialmente, sendo os plasmas produzidos em

condições de vácuo.^{13,15} Contudo, alguns fatores como a distância da peça de mão e a superfície do substrato podem afetar a deposição de tais íons.¹³ Para que este parâmetro seja controlado, pode-se utilizar o tratamento por plasma de baixa temperatura em equipamento industrial.¹³ Nesses aparelhos, um gerador de alta frequência ajustado em kilohertz (kHz), megahertz (mHz) ou em microondas, é utilizado para ionizar os gases utilizados.¹³ Esse equipamento pode ser facilmente empregado nos laboratórios protéticos e apesar dessas vantagens, pouca atenção tem sido dada a este tipo de tratamento,^{16,19,20} apesar do mesmo ter demonstrado não agredir as propriedades físicas do material, diminuindo o risco de fratura das peças cerâmicas.^{7,8}

Em paralelo aos plasmas de baixa temperatura, outros estudos avaliam a utilização dos primers metálicos como alternativa bastante promissora para o tratamento da superfície de zircônia. Em um estudo prévio, a força de adesão entre a superfície da zircônia e cimentos resinosos foi melhorada após a aplicação de dois primers metálicos.¹⁰ Esta correlação tem sido demonstrada pela afinidade química que o monômero 10-metacriloxietil dihidrogenofosfato (MDP), substância presente na composição desse primer, possui com óxidos metálicos como, por exemplo, o óxido de zircônia (ZrO₂).^{3,5,6,10} Este monômero é encontrado tanto em primers metálicos quanto na composição de alguns cimentos resinosos.⁵

Sabe-se que alguns cimentos possuem maior capacidade de união do que outros quando se trata de zircônia, dependendo da sua composição⁵⁻⁷ e molhabilidade.¹³ Estudos prévios avaliaram o desempenho de alguns cimentos resinosos que possuem MDP em sua composição, e mostraram resultados bons e duradouros de adesão devido a presença de um grupo éster na molécula de MDP que possui afinidade química com óxidos metálicos.^{5,6} Além disso, estudos demonstram que cimentos autoadesivos, o qual possui monômeros éster-fosfórico metacrilato, possui grande afinidade com cerâmicas de alto conteúdo cristalino e, quando comparados com os cimentos com sistema de adesão via MDP, estes dois cimentos possuem os maiores resultados de valores de união.

Para que sejam elaborados novos tratamentos de superfícies, é necessário que se realize análises microscópicas quantitativas (rugosidade superficial) e qualitativas (microscopia eletrônica de varredura (MEV), espectroscopia de energia dispersiva (EDS) entre outros), visto que essas avaliações fornecem informações sobre as características estruturais dos materiais, composição e

propriedades físicas, por exemplo.²¹ Além disso, a modificação das características superficiais das cerâmicas pode promover maior molhabilidade de superfície (energia de superfície), que é o primeiro parâmetro a ser analisado para determinar protocolos de adesão.⁸

Para avaliar a força de união entre interfaces adesivas, alguns estudos afirmam que o envelhecimento in vitro por meio da termociclagem é um fator que afeta os valores de união, sendo condição testes necessária para se avaliar o bom desempenho das interfaces de união, sendo considerados parâmetros de envelhecimento clinicamente relevantes.^{2,13}

De maneira geral, pode-se observar que, de acordo com estudos prévios, o tratamento de superfície com plasmas de baixa temperatura ou mesmo a utilização de primers metálicos promovem resultados de adesão satisfatórios.^{6,7,13,14} Mas, até o presente momento, os autores desconhecem estudos que tenham avaliado a associação dos dois métodos.

Surface analysis and shear bond strength of zirconia on resin cements after non-thermal plasma treatment and/or primer application for metallic alloys*

* Este artigo está formatado de acordo com as normas do periódico *Materials Science and Engineering C: Materials for Biological Applications*.

2. INTRODUCTION

In recent years, dental ceramics with a high crystalline content have been widely used as a core material for fixed restorations because of their high fracture resistance, chemical stability and superior aesthetic properties when compared to other low-fusing ceramic systems [1-5,22,23]. However, as the crystalline content increases, the glass phase of the ceramic composition is reduced [4]. As a consequence, the etching effect caused by the hydrofluoric acid gel on the glass phase of low-fusing ceramic is not obtained, and this protocol cannot be recommended for yttria-tetragonal zirconia polycrystals (Y-TZP). Although the acid-resistant surface does not seem to be problematic when Y-TZP cores are cemented on ideally anatomic preparations, high bond strength may be required for milled restorations, which have with misfit of $\approx 100 \mu\text{m}$ and can be considered lesser retentive restorations [22]. Therefore, the development of any approach that could result in a stronger adhesive interface would be useful for those clinical scenarios.

Several approaches have been investigated for enhancing the resin bond to zirconia-based restorations [4,7-11,22]. However, some studies have indicated that some of them may create critical flaws in the ceramic surface, leading to their catastrophic failure [4,8,10-12]. These findings may explain the reports of clinical failures [12,24-26], in spite of the fracture strength values being well above the stresses estimated for the posterior areas of the mouth [12]. Moreover, previous studies have suggested that some primers containing 10-methacryloyloxydecyl dihydrogen phosphate (MDP) showed no significant benefit compared to zirconia bonding because this surface treatment does not create a hydrolysis-resistant interface, which results in reductions in bond strength up to 87% for Panavia cements after 5 months of water storage [4,10].

In addition, nonthermal plasma (NTP) treatments have been considered an alternative solution for clinical problems related to adhesion [14,27,28]. In summary, the plasma technique may improve the adhesion by creating new reactive sites onto a substrate surface, which chemically bond to another substrate [14,27-29]. A previous study demonstrated that thin films created by methane (CH_4) plasma

indeed reduce the contact angle and increase free surface energy of some materials used in biomedical devices [17,19,29].

Considering that the plasma may be generated containing reactive and energetic species and that the exposure of a material to this environment will inevitably change the properties of the outermost layers, it is speculated that organic films deposited from methane may improve the adhesion between zirconia and resin cements because they would be well connected to the ceramic and possess an affinity to cement. However, to the best of the authors' knowledge, no study has evaluated CH₄-based NTP to improve the chemical bonding of Y-TZP to resin cements. Moreover, the association of promising surface treatments has already been investigated by an *in vitro* investigation, but not for MDP-based primers and plasma methods [7]. Undoubtedly, the durability of this new interface has to be tested through artificial aging [22,30]. A thermocycling challenge in an aqueous environment is commonly used to simulate mechanical fatigue in the wet oral environment [19,22,31-34]. Indeed, the hydrolytic stability of the bonding may affect the clinical performance of an indirect restoration because the humidity of the oral environment accelerates the degradation of the adhesive interface. Therefore, thermocycling is considered to provide clinically relevant information [19,22,31-34].

Thus, the aims of this study were: (1) to characterize the surface of Y-TZP discs with or without CH₄-nonthermal plasma or primer and the association of both based on surface energy, surface roughness, scanning electronic microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray dispersive spectroscopy (XPS) analyses, and (2) to evaluate the bond strength between Y-TZP-treated surfaces and two resin cements before and after thermocycling. The null hypotheses were that surface treatments and their combinations would not modify the surface characteristics of Y-TZP and not affect the bond strength between this ceramic system and tested resin cements.

3. MATERIALS AND METHODS

3.1. Experimental design

The materials used in the present study are listed in Table 1.

Table 1. Characteristics of materials used in the present study

Materials	Composition	Fabricant
Ceramill zi system	99% of Y ₂ O ₃ /HFO ₂ /Al ₂ O ₃ /1% of other oxides	ARMANGIRRBACH
Z100 composite resin	Bis-GMA/TEDGMA/ zirconia/silicon	3M ESPE
Rely X U200 (Base Catalyzt)	Vitreous powder/ silicon/ calcium hydroxide/ methacrylate phosphatide ester/di methacrylate/initiators.	3M ESPE
Panavia F2.0 (Paste A Paste B Oxyguard II)	BPEDMA/MDP/DMA/silica/barium sulfate/dibenzoylperoxide N,N-Diethanol-p-toluidine/silica sodiumfluoride Polyethyleneglycol/glycerine/sodium benzenesulfinate cont. gel 3-Methacryloxypropil trimethoxy silane/MDP/ethanol phosphoric acid	Kuraray America Inc.
Alloy primer	MDP, VBATDT, 98.5% acetone.	Kuraray America Inc.
CH ₄ , O ₂ and Ar	Methane, Oxygen and Argon	White Martins

*Information provided by the manufacturer: Bis-GMA: bis-phenol-A diglycidyl dimethacrylate; TEDGMA: Triethyleneglycoldimethacrylate; BPEDMA: bisphenol-A-polyethoxy dimethacrylate; DMA: aliphatic dimethacrylate; MDP: 10-methacryloxydecyl dihydrogen phosphate; VBATDT: 6-(4-vinylbenzyl-n-propyl)amino-1,3,5-trizaine-2,4-dithiol.

A total of 235 discs of Y-TZP (8 mm diameter × 2 mm thickness) were cut and sintered according to manufacturer's instructions. The treatment applied to the Y-TZP disc surfaces were: control (Co), alloy primer application (Pr), non-thermal plasma treatment (NTP), primer application followed by non-thermal plasma treatment (Pr + NTP), and non-thermal plasma treatment followed by primer application (NTP + Pr). Seven discs per group (n=7) were used for surface energy (n=3) and surface roughness (n=3), SEM-EDS and XPS (n=1) analyses immediately after surface treatment. Forty discs per group were used for the shear bond strength test, distributed as follows: 20 discs cemented with MDP-based resin cement (Panavia F2.0) and 20 cemented with ester phosphoric methacrylate-based cement (Rely X U200). Ten discs from each group were tested after the bonding procedure, and the remaining 10 were aged by means of thermocycling before being tested for shear bond strength. The flowchart shown in Fig. 1 schematizes the experimental procedures adopted here.

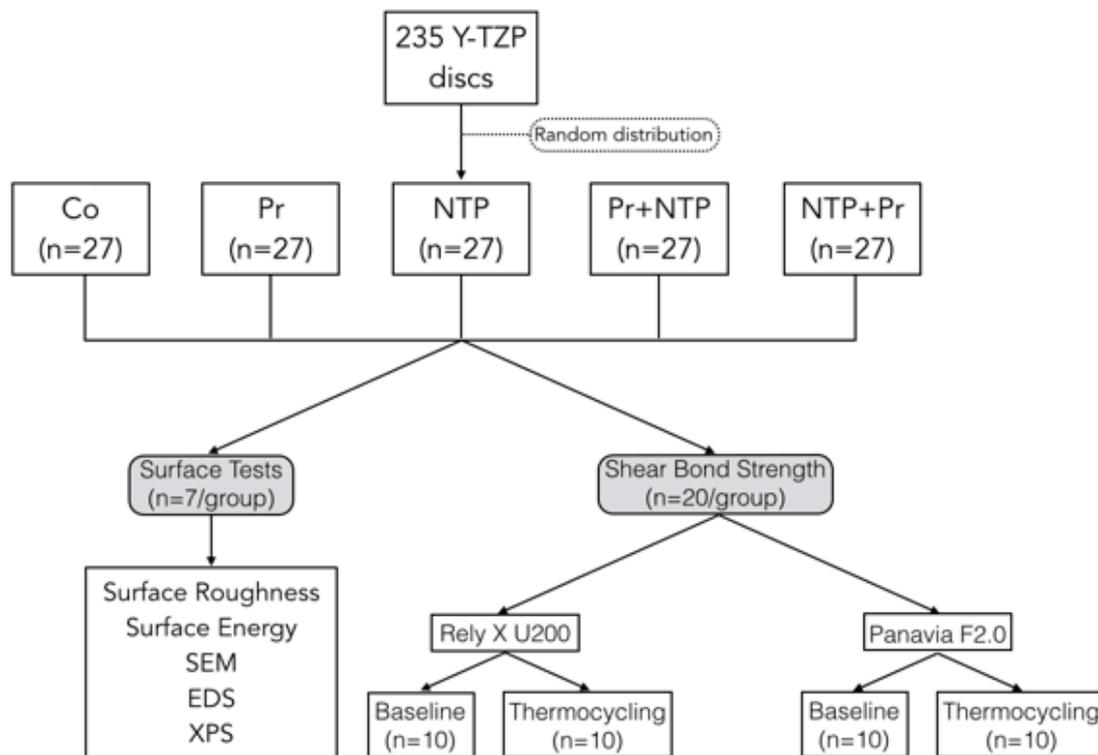


Fig. 1. Flowchart of experimental procedure.

For the sample preparation, the Y-TZP discs were embedded in the center of cylinder cups (SamplKups, Buehler) fabricated by using autopolymerizing acrylic resin (JET, Classico). After its polymerization, the embedded Y-TZP discs were polished with 32-grit sandpaper. Discs were then cleaned and degreased with a sequence of alternate ultrasonic bath [27]. The primer was applied onto the Y-TZP surface of the Pr, Pr + NTP and NTP + Pr groups using microbrushes (Microbrush; Microbrush International) for 60 seconds. Then, the solvent was removed with gentle air jets.

3.2. NTP treatment

The Y-TZP discs from the NTP, Pr + NTP and NTP + Pr groups were subjected to NTP treatment. Plasma treatment was performed inside a stainless steel chamber. The system was evacuated to a background pressure of 3.6×10^{-2} Torr. Before the CH_4 plasma depositions, argon (Ar) gas was admitted into the chamber, and cleaning plasmas were prepared at a radiofrequency of 13.56 MHz (70 W) and applied in the sample-holder for 600 seconds under a constant work pressure of 1.67

$\times 10^{-1}$ Torr. The depositing plasma, maintained for 1800 s, were then established by applying a radiofrequency signal (13.56 MHz, 70 W) to the top electrode while biasing the sample holder with negative pulses (3.12 kV, 299 Hz, 25 μ s and 0.75% of duty cycle). Under these conditions, positive ions from the plasma were attracted by the negative potential and implanted on the surface and subsurface region of the samples placed in the biased electrode simultaneously to the film deposition and according to the Plasma Immersion Ion Implantation and Deposition (PIIID) approach. In the first stages of the process, ion bombardment produced a dilution of the Y-TZP surface with the film constituents, resulting in a diluted film-substrate interface with improved adhesion, mechanical and tribological properties. After the conclusion of the PIIID time, the CH₄ flow was interrupted while that of Ar was maintained, generating a non polymerizable ion bombardment procedure named Plasma Immersion Ion Implantation (PIII), which was maintained for 480 s. The discs were removed from the stainless glass chamber at a temperature of 33 °C.

3.3. Surface energy and roughness

Three Y-TZP discs from each group were subjected to surface energy analysis with a goniometer (Ramé-Hart 100-00; Ramé-Hart Instrument) using the sessile drop technique. The Owens-Wendt-Rabel-Kaelble method was used to calculate the surface energy by measuring the contact angle between drops of two liquids with different polarities and the Y-TZP disk [8,9,18,20]. Surface roughness analysis was performed with a profilometer (Dektak D150; Veeco). Three discs from each experimental group were evaluated. Four parameters of surface roughness were obtained (Ra, Rq, Rz and Rt), following configurations of previous studies [27,29]. Then, the average was calculated in nanometers (nm) [27,29].

3.4. SEM–EDS and XPS analyses

For SEM analysis, images were captured at 3000 \times and 10000 \times magnifications (JSM 610LA; JEOL). Simultaneously, elemental chemical composition analysis was conducted through EDS. The configurations used for EDS analysis followed previous studies [27,29]. The oxide layer of Y-TZP disks was also measured by using x-ray photoelectron spectroscopy (XPS). The spectrometer

(Vacuum Science Workshop, VSW HA100) with a hemispherical analyzer was operated in constant transmission mode (line width of 1.6 eV for Au 4f7/2). Excitation was achieved by using Al K α (1486.6 eV) radiation. Measurements were conducted at a pressure less than 2×10^{-8} mbar. The C 1s line at 284.6 eV was fixed for surface charging.

3.5. Shear bond strength test

For the bonding procedures, composite resin (Z100; 3M-ESPE) cylinders (5 mm in diameter \times 2.5 mm in length) were fabricated. For bonding, resin cements were manipulated according to the manufacturer's instructions and placed onto the bottom of the composite resin cylinders with a syringe (Centrix; Nova DFL). Then, composite cylinders with the cement were placed onto Y-TZP discs. Afterwards, a weight of 1000 g was applied on top of the resin disc for 40 seconds with a custom-made device. Then, the excess cement was removed, and the discs were polymerized at 4 different locations for 60 seconds each. Afterwards, half of the specimens were immersed in 37°C distilled water for 24 hours, and the other half were thermocycled (MSCT-3 Plus; Nucci ME) with alternated baths (30 seconds each) in distilled water between 5°C and 55°C for 2000 cycles [29]. The bonded disks were attached to a custom-made holder and tested with a shear bond strength test in a universal testing machine (Instron Model 4400 Universal Testing System, Instron Corporation). A uniaxial tensile force was applied to the adhesive interface through a razor at a constant crosshead speed of 1 mm/min until failure of the sample. Shear bond strength results were determined in MPa considering the area of the adhesive interface.

3.6. Analysis of bonding failure

The mode of failure between the composite resin cylinder and the Y-TZP discs was evaluated and quantified using a stereomicroscope (SteREO Discovery V20, Carl Zeiss) at 150 \times magnification.

3.7. Statistical analysis

Surface energy and surface roughness data were examined by one-way analysis of variance (ANOVA) (factor: surface treatment). Shear bond strength data were analyzed by three-way ANOVA

(factor 1: surface treatment; factor 2: resin cement, factor 3: thermocycling). Bonferroni tests were used to compare the mean values among the groups ($\alpha = .05$) (SPSS version 20.0 – Statistical Package for the Social Sciences, Inc.). Partial Eta Squared was used for effect size measurement. With 10 samples per group in the shear bond strength test, a large size effect was obtained: $F(6.19) = 6.731$, $P < .0001$, $\eta_p^2 = .253$.

4. RESULTS

Surface treatment significantly affected the surface energy of the Y-TZP discs ($F=10.079$, $P < .002$). A significant difference of surface energy for NTP and Pr + NTP groups was observed when compared to Pr and NTP + Pr groups. Figure 2 displays the polar and dispersive components of the tested groups.

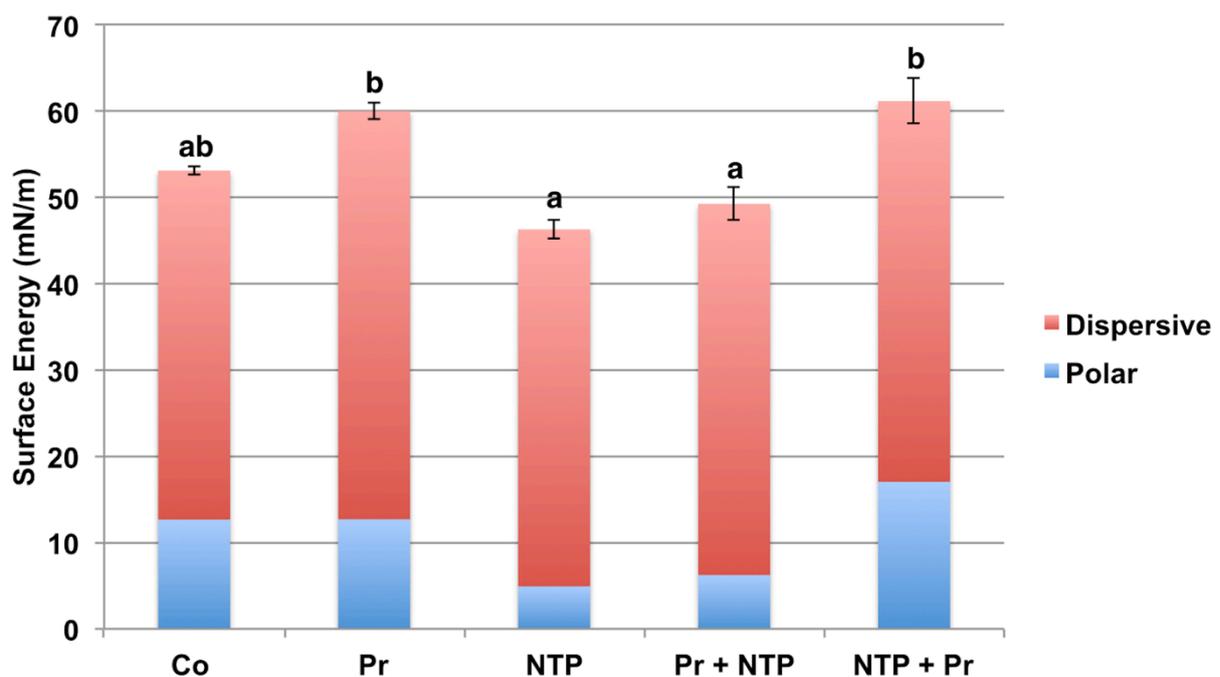


Fig. 2. Main polar and dispersive components of the Co, Pr, NTP, Pr + NTP and NTP + Pr groups. The different lower case letters represent significant differences ($P < .001$, Bonferroni test).

There was a reduction of the polar component for the NTP and Pr + NTP groups, whereas this component was maintained in the Pr group. However, polar and dispersive components were slightly

increased in the NTP + Pr group when compared to the control group. Moreover, the one-way ANOVA for surface roughness indicated that surface treatment significantly affected the Ra ($F=55.947$, $P<.001$), Rq ($F=67.384$, $P<.001$), Rt ($F=140.430$, $P<.001$) and Rz ($F=34.580$, $P<.001$) parameters. The Pr group exhibited the greatest surface roughness, whereas all the other groups were statistically similar to the control (Fig. 3).

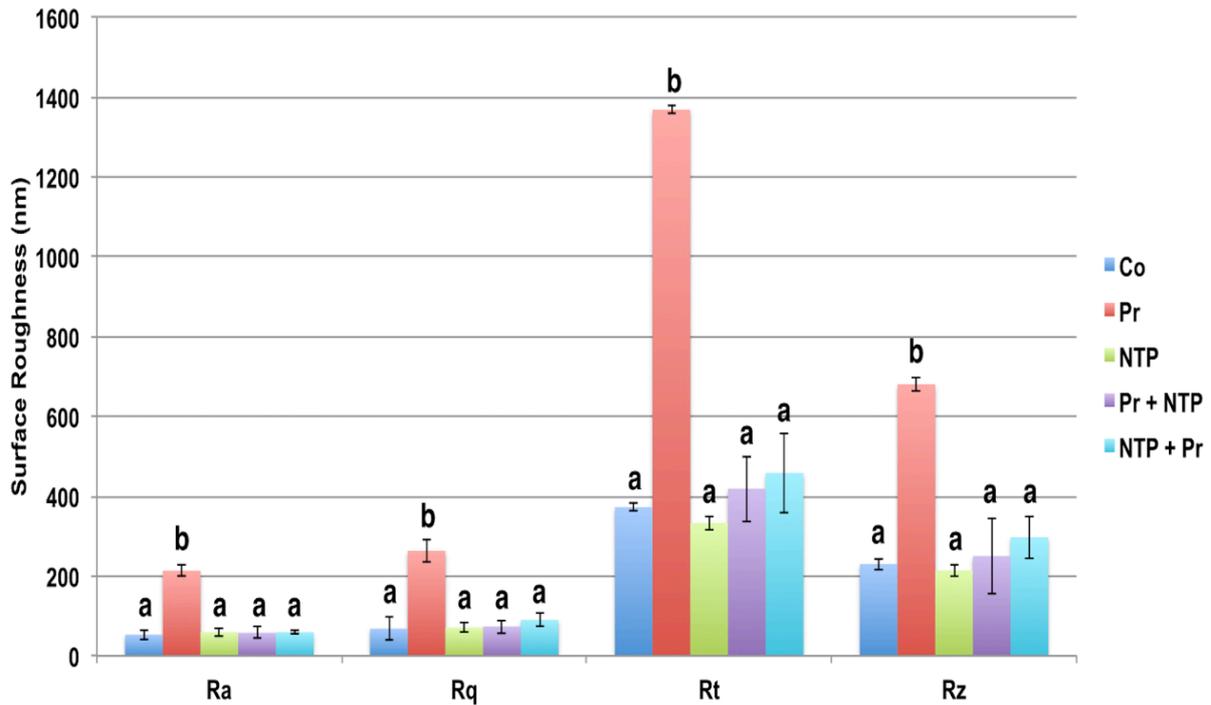


Fig. 3. Main surface roughness (Ra, Rq, Rt and Rz) of the Co, Pr, NTP, Pr + NTP and NTP + Pr groups. The different lower case letters represent significant differences within each roughness parameter ($P<.001$, Bonferroni test).

SEM-EDS images are displayed in Fig. 4.

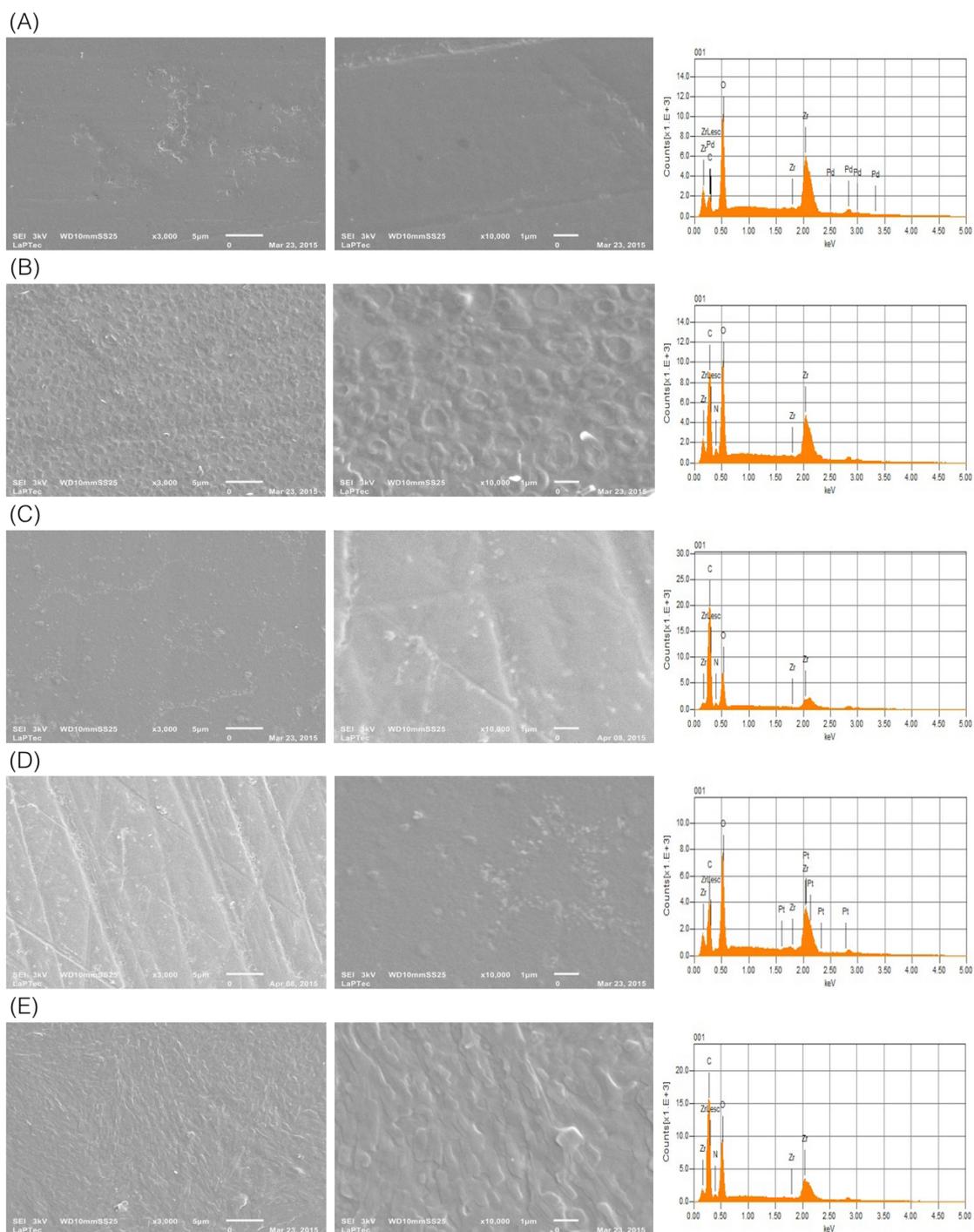


Fig. 4. Representative scanning electron microscopy images (original magnification at 3000 \times , bar = 5 μ m, 3 kV, WD = 10 mm) and energy-dispersive spectroscopy analysis of the Co (A), Pr (B), NTP (C), Pr + NTP (D) and NTP + Pr (E) groups.

The Co group had a smooth surface with defects characteristic of the finishing provided to the ceramic surface. This morphology was substantially changed after alloy primer application with an increase in micrometric granular structures dispersed throughout the surface. The NTP treatment also altered the morphology of the pristine material, with the regular matrix being replaced by a fine-grained structure. The Pr + NTP group had an intermediary morphology that did not resemble the film nor the primer, indicating that plasma cleaning (Ar) prior to film deposition may have affected the overall characteristic of the primer surface. In the NTP + Pr group, the surface consistently recovered the aspect of the Pr-containing Y-TZP. Zirconium (Zr), carbon (C) and oxygen (O) were observed in the spectrum of all samples, whereas nitrogen (N) was detected in the Pr, NTP and NTP + Pr groups. For the NTP treated groups, the CH₄-based thin film showed no discontinuity and seemed to be adhered to the Y-TZP surface. Fig. 5 displays the XPS spectra of tested groups.

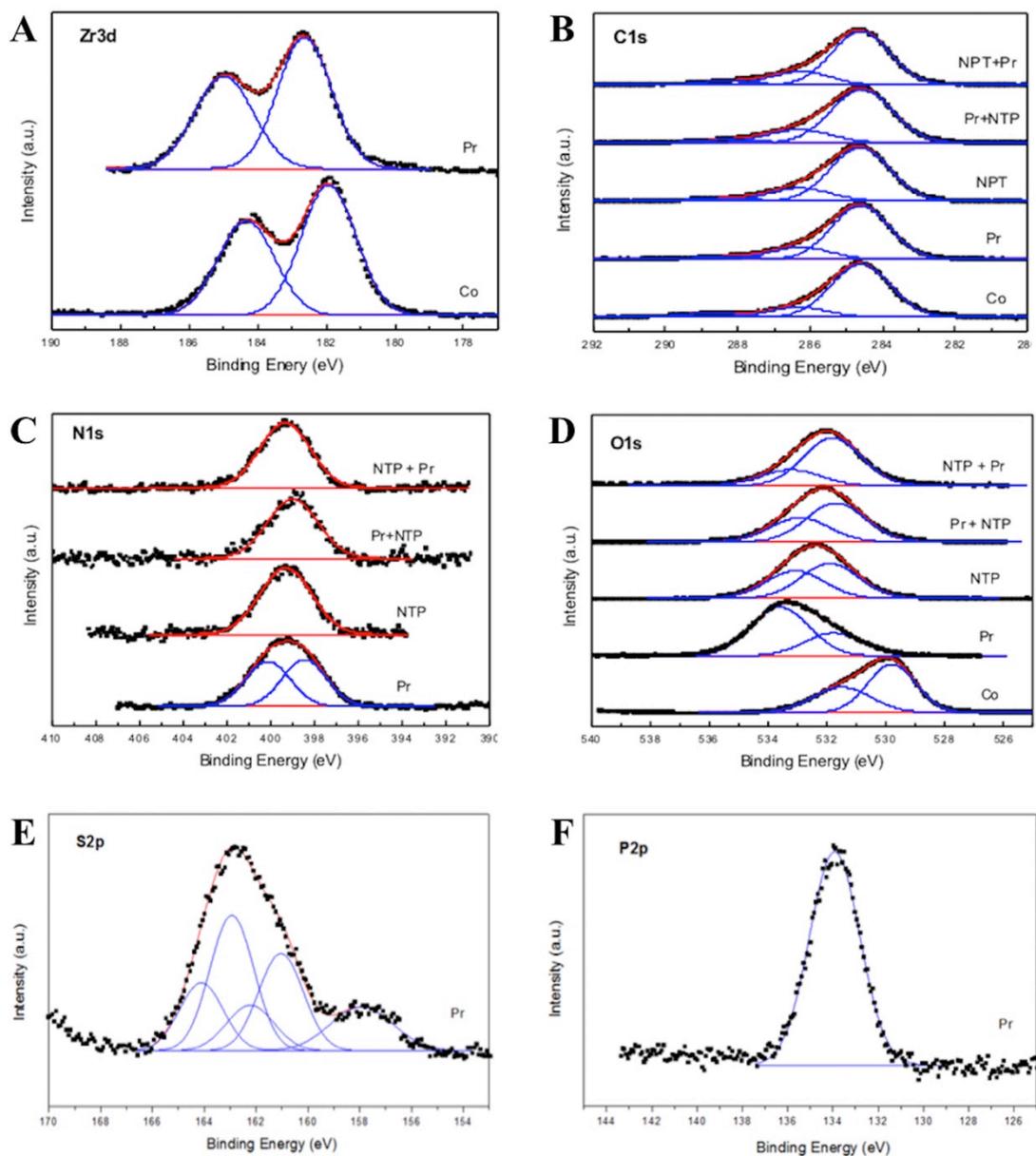


Fig. 5. XPS spectra of (A) Zr 3d, (B) O 1s, (C) C 1s, (D) P 2p, (E) S 2p and (F) N 1s spectra for the experimental groups.

Only the Co and Pr groups exhibited the Zr 3d spectrum, where peaks were centered approximately at 182 eV (Fig. 5A). Additionally, for O 1s spectra, peaks can be observed at 530-534 eV for all groups (Fig. 5B). Binding energies at 284-285 eV were seen in the C 1s spectrum in all groups (Fig. 5C). For the Pr group, the peak centered approximately at 134 eV may be associated with phosphor (P) ions, whereas the peak next to 163 eV may refer to sulfur (S) ions (Fig. 5D-E). Finally,

for the N 1s spectra, a peak centered approximately at 399 eV was found for groups subjected to tested surface treatments (Pr, NTP, Pr + NTP and NTP + Pr) (Fig. 5F).

For the shear bond strength, a three-way ANOVA revealed a significant effect of surface treatment ($P<.001$), resin cement ($P<.001$), thermocycling ($P<.001$) and their interactions ($P<.001$) (Table 2).

Table 2. Results of three-way analysis of variance (ANOVA) for shear bond strength

Source	Sum of Squares	df	Mean Square	F	P
Surface (S)	180.361	4	45.090	13.534	.001*
Cement (C)	46.918	1	46.918	14.082	.001*
Thermocycling (T)	130.739	1	130.739	39.241	.001*
S × C	127.976	4	31.994	9.603	.001*
S × T	74.697	4	18.674	5.605	.001*
C × T	16.771	1	16.771	5.034	.026*
S × C × T	181.187	4	45.297	13.596	.001*
Error	566.393	170	3.332		
Total	7314.767	190			
Corrected Total	1348.637	189			

* $P<.05$ denotes statistically significant difference

Fig. 6 displays the shear bond strength results.

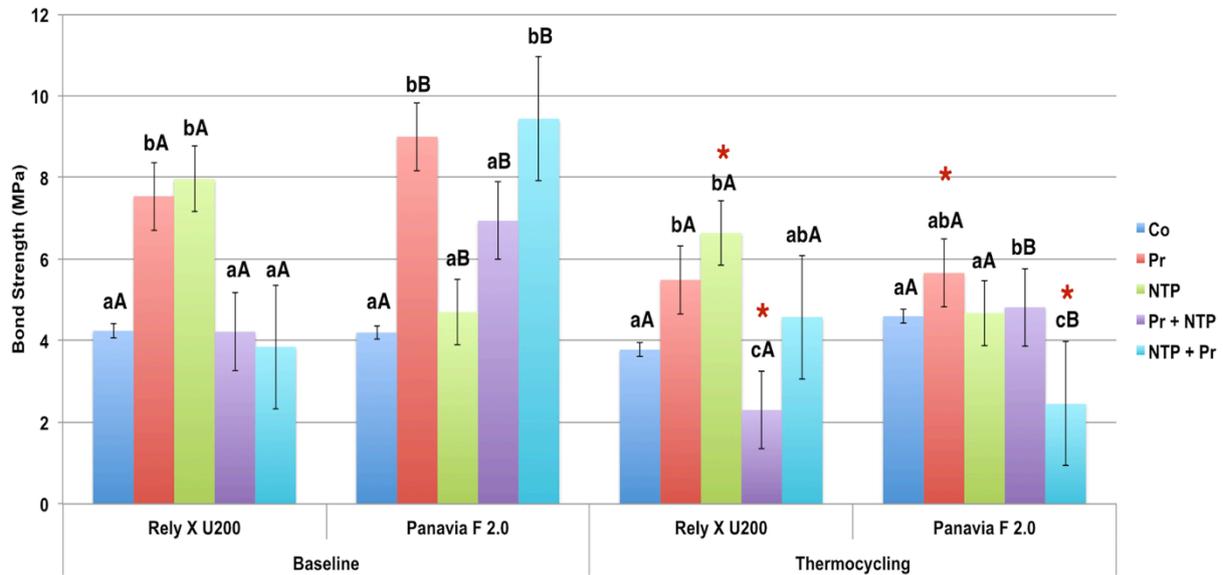


Fig. 6. Mean bond strength results of the Co, Pr, NTP, Pr + NTP and NTP + Pr groups before (baseline) and after thermocycling as a function of different resin cements. The different lower case letters represent significant differences within the same resin cement. The different upper case letters represent significant differences within the same surface treatment. * represents significant differences between periods.

The best bond strength results were numerically observed in the NTP group for the Rely X U200, regardless of testing period. For Panavia F2.0, the Pr and NTP + Pr groups showed higher bond strength results at the baseline. The bond strength of samples cemented with Rely X U200 and treated with NTP and Pr + NTP were significantly affected by thermocycling ($P=0.03$). On the other hand, samples cemented with Panavia F2.0 cement and treated with primer as their outermost surface treatment (Pr and NTP + PR) had significant decreases in bond strength after thermocycling ($P<0.001$).

The failure modes of all the groups are shown in Figs. 7 and 8.

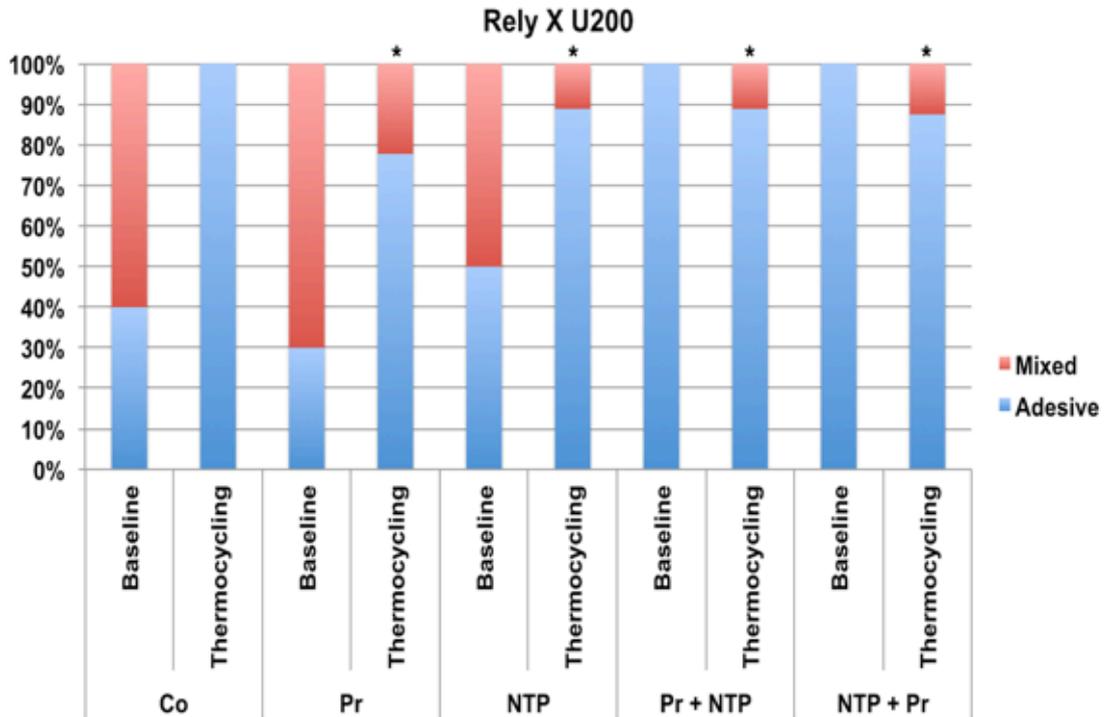


Fig. 7. Incidence of adhesive failure mode for all the samples submitted to the shear bond strength test for Rely X U200. * represents premature failure.

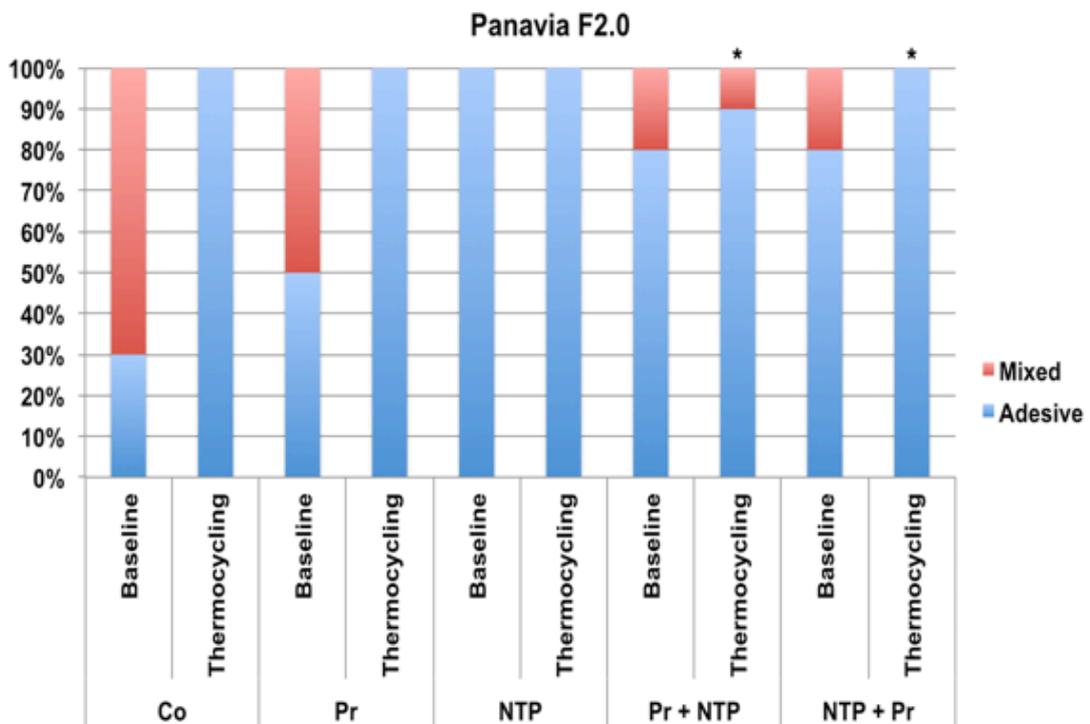


Fig. 8. Incidence of adhesive failure mode for all the samples submitted to the shear bond strength test for Panavia F2.0. * represents premature failure.

An increase in mixed failures after thermocycling was noted for the Pr + NTP and NTP + Pr groups cemented with Rely X U200. There was an overall increase in adhesive failure for all tested groups after thermocycling. No premature failures were observed for either tested cements at baseline. However, 5 premature failures were observed for groups cemented with Rely X U200 and 4 for Panavia F2.0 groups during thermocycling.

5. DISCUSSION

This study evaluated the effect of the association between a thin film created by plasma and a primer on the bond strength between zirconia and two different resin cements. In accordance with the results, the null hypotheses of the present study were rejected once the NTP treatment modified the surface characteristics of Y-TZP and improved the shear bond strength of the tested ceramic to Rely X U200 cement before and after the thermocycling challenge.

The surface energy is a direct manifestation of intermolecular forces onto a solid surface, which is generally measured by the contact angle of two liquids with different polarities that refers to newer molecular interactions (polar or covalent bonds), such as dipole–dipole interactions, van der Waals forces (Keesom and Debye), hydrogen bonds, and dispersive forces of London [8,27]. The deposition of the thin film was responsible for a significant reduction in the surface energy of NTP and Pr + NTP groups, as well as a reduction in their polar and dispersive components when compared to groups that had the alloy primer as the outermost surface (Pr and NTP + Pr groups) [20]. These findings might be explained by the composition of the thin film. XPS analysis showed that the coating created by the NTP treatment is mainly composed of a tridimensional network of C atoms (peaks centered approximately at 284 eV/C 1s spectrum), which does not have chemical affinity to polar components [28,29]. This hypothesis can be explained by the ionic bombing during the film deposition. Such method provides sufficient energy to remove the H ions from C compounds, which will interact one another and result in a network of amorphous carbons. However, the presence of polar components is observed in all groups. For NTP and Pr + NTP groups, there is a non-intentional incorporation of N and O atoms that can be absorbed from the residual atmosphere into the reactor due

to unsaturated C bonds (C=C and C≡C) or the reticulation of the network (pending bonds), creating a low number of C-O, C=O, C-N, O-H interactions and a surface that has a low affinity to polar components. Nitrogen and oxygen incorporated in Y-TZP discs of Pr and NTP +Pr groups may result in a more hydrophilic surface because such molecules are in a higher quantity once the Alloy Primer has MDP and VBATDT (6-(4-vinylbenzyl-n-propyl)amino-1,3,5-triazine-2,4-dithiol) molecules in its composition [8]. The incorporation of nitrogen and oxygen to the discs from Pr, NTP, Pr + NTP and NTP + Pr groups is verified by the component centered next to 288 eV that can result from the overlapping nitrogen bonded to sp^3 hybridized carbon and peaks at 530-534 eV, respectively. Besides, peaks can be observed at 530-534 eV for all groups that probably correspond to Zr-O bonds and O^{2-} ions bonded to Al^{+3} ions to form Al_2O_3 , which can also be attributed to molecules derived from the Y-TZP native layer. Finally, the Zr 3d spectrum showed peaks that were related to Zr-O bonds in ZrO_2 and, interestingly, the XPS spectra did not show such binding energies for any groups subjected to NTP treatment, suggesting that the thin film completely covered the Zr surface.

In addition, the SEM images demonstrated that the NTP treatment applied in the present study showed no topographical alterations to the Y-TZP surface. As reported in a previous study [29], thin films created from CH_4 fragmented molecules were deposited at low temperatures [36]. SEM images revealed that NTP treatment did not induce critical defects (Fig. 4). Moreover, no relevant alterations were observed with regard to the surface roughness in the NTP groups compared to the other tested groups, except for the Pr group, in which a layer was created after primer drying. Therefore, misfit of NTP-treated Y-TZP-based restorations would not be observed in a clinical scenario. Thus, it can be assumed that this experimental treatment would be feasible for dental offices because it would not induce subcritical crack growth of the Y-TZP surface.

The bond strength results can be summarized in two main observations: (1) the thin film deposition had a positive effect on bond strength results when Rely X U200 cement was used, and (2) the alloy primer was more effective with Panavia F2.0. These findings suggest that there is a poor chemical affinity between thin films from Alloy Primer and Panavia F2.0, which might explain why the artificial aging affected the NTP groups more for this cement than the same groups cemented with

Rely X U200. XPS and EDS images showed that the thin film is composed of C-C, C-O and C-N bonds. It is possible that the inner surface of the thin film, which was in contact with the ceramic material, was composed mainly of C-O bonds, whereas its external surface (closer to the resin cement) had mostly C-C bonds. As a consequence, the effective bond between the acidic groups (phosphoric acid) from MDP did not occur because such molecules might have greater preference for oxides (ZrO) than C-C chains [4,10]. However, when an alloy primer was applied, MDP from Panavia F2.0 could bond to thiol groups (-SH) from the VBATDT monomer [4,10]. Some studies have reported the presence of carbon (C) and sulfur (S) over the Y-TZP surface after alloy primer application, which may explain this hypothesis [4,10].

This might also explain the better bond strength results of the NTP + Pr group when compared to the NTP group cemented with Panavia F2.0 once the thin film was under the primer layer. Therefore, it did not mask the effect of the outermost surface treatment. This works differently with the Rely X U200. Several studies reported that the ester phosphoric methacrylate from Rely X U200 had chemical affinity for the C-C bonds, which interacted directly with the C-C bonds of the thin film through secondary chemical interactions [27,29], resulting in an initially high bond strength that was also maintained after aging. Additionally, the presence of N elements is most likely due to the adsorption from the residual atmosphere [29,35,36]. Moreover, differences in chemical affinity might also explain the degradation of the bond at the cement/ceramic interface, which was demonstrated by the incidence of adhesive failures at both periods (Figs. 7 and 8).

With regard to the artificial aging, few significant differences were observed. Surprisingly, the best surface treatments for each tested cement (NTP for Rely X U200 and Pr for Panavia F2.0) and the two groups with combined treatments (Pr + NTP with Rely X U200 and NTP + Pr with Panavia F2.0) were significantly affected by thermocycling. However, the NTP group with Rely X U200 showed the highest bond strength results when compared to all tested groups after aging. Thermocycling is an approach used in several *in vitro* studies to evaluate the hydrolytic degradation of the resin-ceramic bond [19,22,30-34]. Thus, the results presented by CH₄ thin film-treated surfaces indicate that this treatment has great potential to fulfill the need for a standard treatment for the inner

surface of Y-TZP restorations because it induced no surface modification (damage) and seems to be chemically stable overtime.

Similar to other studies [3,22,23], this research used shear bond strength as the test method to evaluate the adhesion between zirconia and other materials because zirconia is a strong material, and it is extremely difficult to be sectioned. However, questions about the shear bond strength test have been raised because traditional shear protocols may underestimate shear stresses occurring in the clinical scenario, and stress distribution within the adherence zone was not uniform, which may result in significant variation in the mode of failure [22]. Fortunately, this approach provided the advantage of not failing cohesively when submitted to shear forces [3,37], which means that the values obtained represent the true bond strength between the adherent surfaces. Furthermore, it has also been demonstrated that microtensile and shear bond strength methods produce similar results when testing ceramics with a high crystalline content [3,37]. Other points to be considered in future studies would be the use of longer, and perhaps more clinically similar, aging protocols, such as a chewing simulation and the evaluation of the treatment efficacy when zirconia is bonded with other resin cements [22].

6. CONCLUSION

Within the limitations of this study, it was possible to conclude that: (1) thin films created from CH₄ fragmented molecules could be successfully deposited on a Y-TZP surface, (2) such films increase the resin bond strength of Y-TZP to Rely X U200 cement, and (3) the adhesive interface has water-resistant behavior. In contrast, Panavia F2.0 showed better results when associated with primer as its outermost layer.

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Anexo

8. ANEXO A

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*** Daniel D. Federman, Kathi E. Hanna, and Laura Lyman Rodriguez, Editors, Committee on Assessing the System for Protecting Human Research Participants, in: Responsible Research: A Systems Approach to Protecting Research Participants, The National Academies Press, 2002

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