UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

Guilherme Bönecker Valverde

Caracterização química e adesão de superfícies cerâmicas e metálicas após a aplicação de plasma atmosférico não térmico

Tese apresentada à Faculdade de Odontologia de Piracicaba, Universidade Estadual de Campinas, para obtenção do Título de Doutor em Clínica Odontológica Área - Prótese Dental

Orientador: Prof.Dr. Marcelo Ferraz Mesquita

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E ORIENTADA PELO PROF. DR. MARCELO FERRAZ MESQUITA

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Marcelo Ferraz Mesquita [Orientador]

Rafael Leonardo Xediek Consani

Guilherme Elias Pessanha Henriques

Gelson Luis Adabo

Nelson Renato França Alves da Silva

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Prof. Dr. MARCELO FERRAZ MESQUITA

Prof. Dr. GELSON LUIS ADABO

Prof. Dr. NELSON RENATO FRANÇA ALVES DA SILVA

Prof. Dr. GUILHERME ELIAS PESSANHA HENRIQUES

Prof. Dr. RAFAEL LEONARDO XEDIEK CONSANI

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Resumo

Um esforço considerável tem sido feito pelos fabricantes e pesquisadores em alterar a propriedade das superfícies de materiais odontológicos como a zircônia e o titânio, através de tratamentos químicos e mecânicos. A nova tecnologia de plasmas atmosféricos não térmicos (NTP) tem o potencial de alterar quimicamente a superfície tanto da zircônia quanto do titânio. A proposta dos trabalhos realizados foi analisar a possível alteração química promovida pelo NTP através da determinação dos níveis de energia das superfícies (SE) de Y-TZP e Ti após o tratamento com NTP (1), caracterização química de suas superfícies (2), avaliação dos parâmetros de rugosidade e níveis de SE de superfícies de Y-TZP jateadas e polidas antes e após a aplicação do NTP (3), e a resistência à microtração (MTBS) de palitos de Y-TZP com diferentes métodos de tratamento, cimentados em palitos de reina composta (4). Para tal, discos de Y-TZP e Ti foram obtidos, submetidos à aplicação de NTP e avaliados quanto ao nível de SE. A quantificação de elementos químicos de ambas as superfícies foi realizada via espectroscopia de fotoelétrons excitados por raios x (XPS), antes a e após a aplicação do NTP. Os parâmetros de rugosidade, Sa e Sq, para a superfície de Y-TZP jateada e polida, foram estabelecidos por interferometria (IFM), e níveis de SE, estabelecidas pelo emprego do medidor óptico de ângulo de contato. Amostras de Y-TZP sem e com aplicação de NTP receberam um dos quatro tratamentos a seguir: jateamento de Al_2O_3, aplicação de 10-metacriloiloxidecil dihidrogeno fosfato, jateamento + MDP; sem tratamento e submetidos ao MTBS. Os dados foram submetidos a análises de variância one way, modelo misto de anova, teste de comparação múltipla de Tukey e test-t. Foi observado aumento significativo nos valores de SE para todas as superfícies submetidas à aplicação de NTP. A análise de XPS detectou principalmente, aumento da presença do elemento O e diminuição do elemento C, tanto na superfície da Y-TZP quanto na do Ti. As superfícies polida e jateada da Y-TZP apresentaram o mesmo nível de SE após a aplicação do NTP e todas as superfícies de Y-TZP tratadas com NTP apresentaram valores mais elevados de MTBS. A tecnologia de NTP alterou quimicamente as superfícies de Y-TZP e do Ti. Os resultados mostram que a utilização de NTP no processo de adesão pode ser promissor, no sentido de aumentar a adesão de materiais cerâmicos e metálicos.

Palavras chave: Adesão, ângulo de contato, energia de superfície, microtração, plasma atmosférico não térmico, titânio, Y-TZP

Abstract

There have been considerable efforts by many manufacturers and researchers to modify the surface properties of zirconia and titanium, mechanically and chemically by various surface treatments. Novel non-thermal plasma (NTP) technology has the potential to address surface changes of Y-TZP and Ti surfaces. The aim of the following studies was (1) to determine the surface energy (SE) levels of Y-TZP and Ti surfaces after NTP treatment; (2) chemically characterize their surfaces; (3) evaluate roughness parameters and SE levels of roughened Y-TZP specimens before and after NTP treatment; and (4) test the microtensile strength (MTBS) of Y-TZP specimens after a combination of different surface conditioning methods. Y-TZP and Ti discs were obtained from the manufacturer and were treated with a handheld NTP device followed by SE evaluation. Survey scans and quantification of the elements were also performed via X-ray photoelectron spectroscopy (XPS) prior and after NTP. Roughness paramenters, Sa and Sq, for the roughened Y-TZP surfaces were determined by Interferometry (IFM) and SE levels evaluated by the optical contact angle meter OCA 20. Furthermore, Y-TZP specimens with and without NTP application received one of the four following treatments: sand-blasting, 10-methacryloyloxydecyl dihydrogenphosphate application (MDP), sand-blasting + MDP, or baseline (no treatment) and were submitted to MTBS. Data analysis was performed by one-way anova, mixed model, Tukey test and t-test. Significant augmentation of SE values was observed in all NTP treated groups. XPS detected a large increase in the O element fraction and a decrease in C element on both Y-TZP and Ti surfaces. Different roughness profiles of Y-TZP specimens showed the same SE levels after NTP treatment, and all Y-TZP NTP treated specimens showed higher bond strength than the untreated counterparts. The non-thermal plasma technology had the capability of changing the surface chemistry of the different substrates tested and it appears to be very promising in adhesion processes.

Key words: Adhesion; contact angle; microtensile; non-thermal plasma; surface energy; titanium; wettability; Y-TZP

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Introdução

A modificação da superfície de materiais cerâmicos e metálicos é comum quando estes são empregados na clínica odontológica. Normalmente a modificação da superfície altera a composição, estrutura e morfologia da camada mais externa, sem alterar as propriedades gerais dos materiais (Mehulić & Laus-Sosić, 2009). No processo de adesão entre materiais de naturezas diferentes, a modificação da superfície é um desafio para conseguir boa união entre o remanescente dentário e os diferentes materiais restauradores (Marshall & Bayne et al., 2010).

As cerâmicas, por sua capacidade óptica de mimetizar os tecidos dentários e alta biocompatibilidade, tem sido os materiais de escolha na confecção de próteses onde a estética é fundamental (Rekow & Thompson, 2007). A introdução da zircônia parcialmente estabilizada pela Yttria (Y-TZP), ampliou o limite do design e o potencial do uso dos materiais cerâmicos em várias especialidades na área da saúde, como por exemplo, em aparelhos ortopédicos (Chevalier, 2006), implantes endósseos (Silva & Coelho et al., 2008), copings para coroas e estruturas para próteses fixas (Aboushelib & Kleverlaan et al., 2007).

A cimentação de cerâmicas puras tem recebido atenção especial devido às propriedades inerentes desse tipo de material, e devido ao sucesso adesivo de cimentos resinosos na restauração estar relacionado com o emprego de meios químicos e/ou micromecânicos (Dias de Souza & Thompson et al., 2011). O procedimento adesivo para cerâmicas feldspáticas, de dissilicato de lítio e leucita já estão bem estabelecidos, devido as características estruturais desses materiais (Chai & Chu et al., 2011). Porém, a estrutura policristalina da Y-TZP não apresenta fase vítrea, desqualificando o procedimento utilizado nas cerâmicas vítreas para o condicionamento de sua superfície (Kern & Swift, 2011). Tratamentos triboquímicos ou ainda, jatos abrasivos de partículas de alumina com o uso de primers, tem apresentado resultados controversos na literatura (Atsu & Kilicarslan et al., 2006;

Blatz & Chiche et al., 2007; Chai & Chu et al., 2011; Kern & Wegner, 1998; Piwowarczyk & Lauer et al., 2005; Tanaka & Fujishima et al., 2008), além de levantar questionamentos sobre a longevidade clínica da zircônia após a realização desses procedimentos (Zhang & Lawn et al., 2006; Zhang & Pajares et al., 2004).

Tem sido apresentadas na literatura novas possibilidades de tratamento de superfície (Aboushelib & Feilzer et al., 2010; Piascik & Swift et al., 2009; Piascik & Wolter et al., 2011), citadas nos capítulos que seguem, porém uma nova alternativa de fácil execução e com potencial de uso nos consultórios odontológicos, tem mostrado grande eficiência no processo de alteração da superfície tanto de materiais metálicos quanto cerâmicos. Esta tecnologia chama-se plasma atmosférico não térmico (NTP).

O plasma é um gás, geralmente provindo de um gás inerte (argônio, hélio, etc.), que quando submetido a certos níveis de energia e pressão, se torna ionizado. É frequentemente denominado como o quarto estado da matéria na sequência; sólido, líquido, gás e plasma, componente de mais de 99% da matéria do universo. Os plasmas ocorrem na natureza, e fazem parte da composição da ionosfera, da corona solar, dos ventos solares, assim como dos raios e da aurora boreal. Podem ser produzidos em laboratórios pelo homem e proporcionar numerosas oportunidades em diversas aplicações (Fridman, 2008). É um gás “eletrizado” com número diferente de elétrons, íons positivos e negativos, radicais livres, fótons, átomos e moléculas numa variação grande de temperatura e pressão (Fridman, 2008). As partículas leves são consideradas os elétrons e fótons, e os outros componentes são considerados as partículas pesadas (Boulos & Fauchais et al., 1994)

De maneira geral, duas categorias de plasma podem ser definidas, as de alta temperatura e de baixa temperatura, de acordo com as condições em que são criadas (energia X pressão), baseadas nos níveis energéticos dos elétrons e das partículas pesadas. Os plasmas de alta temperatura, ou térmicos, são obtidos por alta pressão ($\geq 10^5$ Pa) e altos níveis energéticos (acima de 50 MW), onde as partículas pesadas e leves apresentam o mesmo equilíbrio termodinâmico e consequentemente, o gás apresenta altíssimas temperaturas (5 to 20x10^3 K). Os plasmas de baixa temperatura são separados em dois grupos, os plasmas térmicos ou quasi-equilíbrio, e os plasmas não térmicos (NTP), ou ainda sem equilíbrio ou plasmas frios. Esses plasmas são obtidos com níveis energéticos e de pressão mais baixos, e são os elétrons que apresentam níveis energéticos bem mais altos que os outros constituintes do gás, e como conseqüência não apresentam equilíbrio termodinâmico (Moreau & Orange et al., 2008; Nehra & Kuma 2008).

Nas duas últimas décadas os NTPs tem sido amplamente empregados na engenharia ambiental, aeronáutica, aeroespacial, indústria química e têxtil, e devido às suas características, começaram mais recentemente a serem utilizados na área biomédica (Heinlin & Isbary et al., 2011).

Os NTPs são formados em pressões atmosféricas e níveis energéticos que estimulam prioritariamente os elétrons, deixando os íons e outros componentes, próximos à temperatura ambiente e consequentemente, possibilitando seu uso para diversas aplicações na área dos polímeros, nas áreas médicas, em procedimentos de desinfecção, cicatrização, doenças dermatológicas, e mais recentemente na área odontológica (Heinlin & Isbary et al., 2011; Ritts & Li et al., 2010; Rupf & Lehmann et al., 2010).

A química dos plasmas é complexa e envolve grande número de reações elementares, que podem ser separadas em homogêneas e heterogêneas. As reações homogêneas ocorrem como resultado de colisões inelásticas entre as partículas leves e pesadas do gás quando submetido a certos níveis de energia e pressão (i.e. excitação dos átomos e moléculas, de-excitação, ionização, dissociação, união dissociativa, ionização dissociativa, recombinação volumétrica, troca de carga, recombinação, recombinação de eletron-íon e recombinação íon-íon), enquanto que as reações heterogêneas ocorrem entre o plasma e a superfície do material que está em contato com o plasma (i.e. erosão, adsorção, deposição, recombinação, de-excitação metastática, remoção, e polimerização) (Nehra & Kuma 2008).

Os NTPs tem atraído mais atenção que os plasmas térmicos, pelo fato de não precisar de reatores à vácuo de alto custo. Os NTPs podem ser obtidos por diferentes descargas (energia) elétricas (i.e descarga de corona, descarga de tubos catódicos, jato de plasma atmosférico, etc.) através de aparelhos pequenos e portáteis com grande potencial de uso nos consultórios odontológicos.

Portanto, o objetivo dos estudos a seguir é entender como o NTP age na superfície de materiais metálicos e cerâmicos através da caracterização de elementos químicos e quantificação do nível da energia de suas superfícies, assim como avaliar os efeitos de sua ação no processo da adesão do Y-TZP.

Capítulo 1

Surface Characterization of Ti and Y-TZP following Non-Thermal Plasma Exposure

Artigo nas normas do periódico **Journal of Biomedical Materials Research: Part B – Applied Biomaterials**

Abstract

Novel non-thermal plasma (NTP) technology has the potential to address the bonding issues of Y-TZP and Ti surfaces. This study aims to chemically characterize and evaluate the surface energy (SE) of Y-TZP and Ti surfaces after NTP application. Y-TZP and Ti discs were treated with a handheld NTP device followed by SE evaluation. Spectra of Y-TZP 3d and Ti 2p regions, survey scans and quantification of the elements were performed via X-ray photoelectron spectrometer (XPS) prior and after NTP. Separate Y-TZP and Ti discs were NTP treated for contact angle readings using (10 – methacryloyloxydecyl dihydrogenphosphate) MDP primer. Significant augmentation of SE values was observed in all NTP treated groups. XPS detected a large increase in the O element fraction on both Y-TZP and Ti surfaces. Reduction of contact angle reading was obtained when the MDP primer was placed on NTP treated Y-TZP. Ti surface showed high SE prior to and after NTP application on Ti surfaces. NTP decreased C and increased O on both surfaces independently of application protocol. Wettability of MDP primer on Y-TZP was significantly increased after NTP. The high polarity obtained on Y-TZP and Ti surfaces after NTP applications appear promising to enhance bonds.

Key words: Adhesive; contact angle; non-thermal plasma; surface energy; titanium; wettability; Y-TZP

1.Introduction

Stable adhesion to ceramic and alloy surfaces remains as a goal for reliable clinical performance of restorative materials. Adequate bonding is known to be dependent on both micromechanical interlocking and physico-chemical treatments to assure wetting by the adhesive. [1] The physical treatment consists mainly in the creation of a rough and tribochemically altered surface and chemical treatment entails the application of ceramic and/or alloy primers to the surface. [2,3]

Since 1973, [4] alloys have been treated physically for bonding purposes in many different ways including electrolytic etching, [5,6] sandblasting, [7] deposition of a layer of silica [8-12] and laser-sintered cobalt chrome. [13] All these techniques, occasionally combined with the application of alloy primers, attempt to enhance the bond strength and bond stability for long-term clinical performance. However, some methods are alloy system dependent and effective bonding to less reactive metals such as titanium have presented a challenge, [14] pointing towards the need for a more universal and perhaps innovative approach to promote appropriate bonding to all alloys.

Similar efforts have been made for ceramics since the early 1980s [15,16] using glass ceramic systems etched with hydrofluoric acid followed by silane application. [17,18] While this procedure has been proven effective, the utilization of structural ceramics such as high strength yttrium stabilized tetragonal zirconia polycrystals (Y-TZP) with its chemical inertness and homogenous surface [1] has required revisiting of resin bonding cementation concepts previously applied to glass-based ceramic systems. [19,20] Other chemical and mechanical procedures were proposed in an effort to promote adequate bonds to Y-TZP. These included the combination of airborne particle abrasion with phosphate ester monomers, in particular, 10-methacryloyloxydecyl dihydrogenphosphate (MDP), which appears to result in the most effective bond response [20,21] for Y-TZP. Although being effective for bonding, airborne abrasion has been shown to induce micro-cracks on Y-TZP substrates at the intergrain level that might be detrimental for the longevity of the restoration. [22,23]

Moreover, examination of Y-TZP interfaces revealed the presence of microgaps and structural defects with the use of particle abrasion and MDP, thus calling into question its effectiveness on Y-TZP surfaces. [24,25] Thus, alternative approaches to improve the bonding mechanisms for Y-TZP-based materials are desirable.

Homogeneous and stable bonds depend on the optimal wettability of the adherent surface by the liquid adhesive, which is an important requirement to establish adhesion. [26-28] Wetting affects adhesion in two ways: (a) it determines the actual contact area between the adhesive and the solid, thus affecting the adhesion strength; and (b) it determines the energetics of the detachment of the adhesive from the solid. Wetting is assumed to be the first stage in adhesion. [29] However, to achieve optimal wettability, the surface energy (SE) of a substrate must be maximized relative to the liquid adhesive to lower the liquid contact angle on the substrate. Therefore, contact angle measurements are appropriate indicators of the interfacial tension and the wetting of a surface by the liquid phase. [30-33]

It is presumed that the currently employed methods of creating a rough surface for alloys and ceramics promote better wettability by increasing the surface area, thus strengthening the bond between the adhered surface and the adhesive. [34] However, literature results indicate the necessity of additional modifications and innovative strategies to enhance the SE of materials in order to maximize bonding properties. [35,36]

Plasmas have been used in different industrial applications as a viable option to modify chemically different material substrates.[37] The use of low-temperature plasmas, which are in essence ionized gases containing a mixture of electrons, ions and free radicals in a background of neutrals, [38] is currently experiencing spectacular growth in (bio)medical and biomaterials applications, in particular for surface modification and functionalization of restorative dental materials, such as ceramics. Non-thermal plasmas (NTPs) at atmospheric pressure and with gas temperatures around room temperature are commonly generated by supplying electrical energy to a gas, [39,40] using hand held devices that might be suitable for dental offices. These high electron temperature plasmas have the ability to induce chemical and/or physical reactions that enhance wettability through the SE changes of substrates without changing the nature of the bulk of the substrate. [41]

This investigation is aimed to: 1) determine the SE of Y-TZP and Ti surfaces exposed to 5-20 s of NTP treatment; 2) chemically characterize Y-TZP and Ti surfaces before and after NTP application via X-ray photoelectron spectroscopy and 3) measure contact angle of a commercial MDP primer dispensed on Y-TZP and Ti surfaces before and after plasma treatment. Three hypotheses were tested:

1) An increase in the SE levels of Y-TZP and Ti substrates is expected after 5, 10 and 20s NTP treatment.

2) For both Ti and Y-TZP substrates, surface chemistry will present increased levels of O species and decreased levels of carbon (C) after NTP.

3) A reduction in the contact angle of a MDP primer applied to both Ti and Y-TZP surfaces is expected after similar NTP exposure.

2. Materials and methods

2.1. The non-thermal plasma jet

The plasma device utilized in this study (KinPen 09, INP Greifswald, Germany) [42] consists of a hand-held unit (170 mm length, 20 mm diameter, weighing 170 g) connected to a high-frequency power supply (frequency 1.1 MHz, 2-6 kV peak-to-peak, 8 W system power) for the generation of a plasma jet at atmospheric pressure. The hand-held unit has a pin-type electrode (1 mm diameter) surrounded by a 1.6 mm quartz capillary. The plasma source can be operated either in a continuous mode or in a pulsed (burst) mode with a variable duty cycle. We used an operating gas consisting of Ar with an admixture of 30 standard cubic centimeters per minute (sccm) O_2 at a flow rate of 5 standard liters per minute (slm). The plasma plume emerging at the exit nozzle is about 1.5 mm in diameter and extends into the surrounding air for a distance of up to 5 mm.

2.2. Specimens and groups

Twelve Y-TZP (3M/ESPE, St. Paul, MN, USA) and grade IV commercially pure Ti (SIN, Sistema de Implante, São Paulo, S.P., Brazil) discs with dimensions of 10 mm in diameter and 2 mm thick were fabricated for the surface energy studies (Fig. 1A). These were ground to a 600 grit finish with SiC papers and dried in methanol. The discs were positioned 5 mm away from the exit nozzle of the plasma device (Fig. 1B), using a universal laboratory holder (Fisher Scientific, Waltham, MA, U.S.A.). The Ti and Y-TZP groups (n=3) were labeled according to the duration of the plasma exposure as follows:

Group TiB: (Baseline); Ti, no plasma treatment
Group Ti5: Ti, 5 s plasma treatment
Group Ti10: Ti, 10 s plasma treatment
Group Ti20: Ti, 20 s plasma treatment
Group YTZPB: (Baseline); YTZP, no plasma treatment
Group YTZP5: YTZP, 5 s plasma treatment
Group YTZP10: YTZP, 10 s plasma treatment
Group YTZP20: YTZP, 20 s plasma treatment

2.3 Surface Roughness Assessment

The roughness parameters were determined by optical interferometry (IFM) (Phase View 2.5, Palaiseau, France). Disks of each surface were evaluated at the flat (six measurements from each group) and S_a (arithmetic average high deviation) and S_q (root mean square) parameters determined. A filter size of 100μm x 100μm was utilized.

2.3. SE determination

All plasma treated discs were horizontally positioned into a contact angle meter (OCA 30, Data Physics Instruments GmbH, Filderstadt, Germany) for contact angle measurements (Fig. 1C) and SE calculations. Contact angle determinations were obtained via Young's equation:

$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$,

where θ is the measured contact angle and γ is the SE of the solid-vapor (sv), solid-liquid (sl) and liquid-vapor (lv) interface (Fig.1D)

The Owens-Wendt-Rabel-Kaelble (OWRK) method [43] was used for the SE determination by depositing 0.5 μl droplets of purified water, ethylene glycol and methylene iodide on the surface of each disk with a micro-pipette (OCA 30, Data Physics Instruments GmbH, Filderstadt, Germany). These solvents are typically used for the calculation of surface energies due to their wide range of intermolecular forces; non-toxicity; high surface tension, and known specific polarities. [44,45] Water being highly polar (properties in mN/m; γ_L=72.8; $\gamma^D{}_L$ =21.8; $\gamma^P{}_L$ =51), diiodomethane apolar (γ_L=50.8; $\gamma^D{}_L$ =48.5; $\gamma^P{}_L$ =2.3) and ethylene glycol in between the former two, (γ_L=48.0; $\gamma^D{}_L$ =29.0; $\gamma^P{}_L$ =19.0).[46]

Images were then captured and analyzed using software (SCA30, version 3.4.6 build 79). The relationship between the contact angle and SE was determined. The SE was calculated by $\gamma_L=\gamma^D{}_L + \gamma^P{}_L$, being γ_L the SE, $\gamma^D{}_L$ the disperse component and $\gamma^P{}_L$ the polar component.

The disperse component of the SE, characterizes the interaction between the surface and the dispensed liquid in terms of the non-polar interactions between molecules. [47] This component is determined by the roughness, unevenness, and the branching level of the surface. [48]

The polar component of the SE characterizes the polar interaction between the surface of the material and the working fluid. This component is determined by the presence of polar groups, electric charges, and free radicals on the surface such as those obtained by treatment in oxygen-containing plasma. [48]

2.4. Surface characterization

The immediate chemical surface composition was determined by X-ray photoelectron spectroscopy (XPS). The measurements were carried out with an AXIS Ultra DLD electron spectrometer (Kratos Analytical, Manchester, UK). The XPS data were recorded using monochromatic Al K_α excitation (1486 eV). Spectra were acquired by setting the instrument to medium magnification lens mode (field of view 2) and by selecting the slot mode, providing an approximately 250-µm diameter analysis area. Charge neutralization was implemented by low energy electrons injected into the magnetic field of the lens from a filament located directly on top of the sample. Wide scans and element spectra were recorded at a pass energy of 80 eV for the estimation of the chemical element composition and at a pass energy of 10 eV for the energetically highly resolved measurements of the C 1s peak. Three spots in different positions on each sample were analyzed and averaged. A relative standard deviation of up to 3 % was obtained. Data acquisition and processing were carried out using the CasaXPS software, version 2.14.dev29 (Casa Software Ltd., Teignmouth, UK).

2.5.Contact angle reading for MDP

Separate Y-TZP (n=4) and Ti (n=4) discs were obtained for this analysis. A droplet of a dental MDP primer (Clearfil Ceramic Primer, Kuraray medical Inc., Okayama, Japan) was dispensed on each surface before and after plasma treatment and the contact angle was measured. Three contact angle readings were performed and averaged for comparisons.

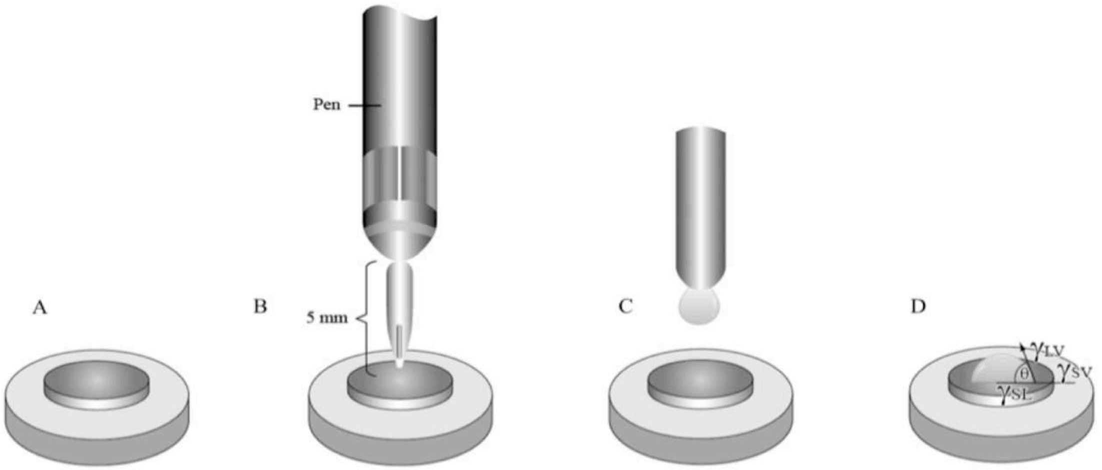

Figure1: (A) schematic showing the Y-TZP and Ti discs (10 X 2mm); (B) NTP jet being applied on a disc positing at 5 mm away from the handheld tip, (C) Drop of a liquid being prepared to be placed onto the disc using a micro-pipette. (D) Contact angle measurement (θ); γsv is the SE of the solid-vapor (SV), γsl solid-liquid (SL) and γlv liquid-vapor (LV) interface.

2.6 Statistical Analysis:

All Contact angle readings for MDP and surface roughness parameters were recorded and statistical evaluation performed by one-way ANOVA at 95% level of significance. Post-hoc multiple comparisons were performed by the Tukey's test.

Results

Surface roughness assessment showed significantly ($p<0.01$) higher S_a and S_q for the 600 grit abraded Ti control samples compared to the Y-TZP control samples (Figure 2).

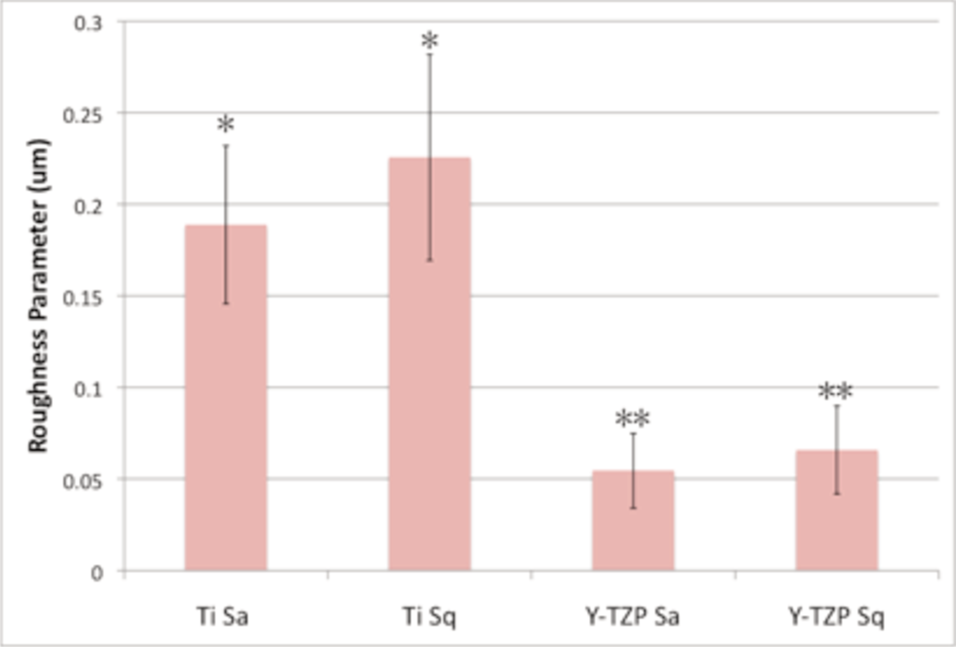

Figure 2: *, ** represent statistical differences. Surface roughness parameters Sa and Sq for the Ti and Y-TZP specimens. Significantly higher ($p<0.01$) roughness values were observed for the Ti specimens

Representative images of the contact angle before and after plasma treatment for both Ti and Y-TZP are presented in Figure 3. Significant increases ($p<0.01$) in the overall SE values were observed for all plasma treated groups relative to their untreated counterpart. Such increase in SE values were mainly due to the increase in the polar component of the SE between plasma-treated and non-treated samples, as proportionally smaller variations occurred for the disperse component of the SE between plasma-treated and non-treated samples (Figure 4).

No differences in SE values were observed within plasma-treated groups for both substrates at longer plasma exposure times and therefore 5, 10 and 20 seconds of NTP application had the same effect for Ti and Y-TZP substrates.

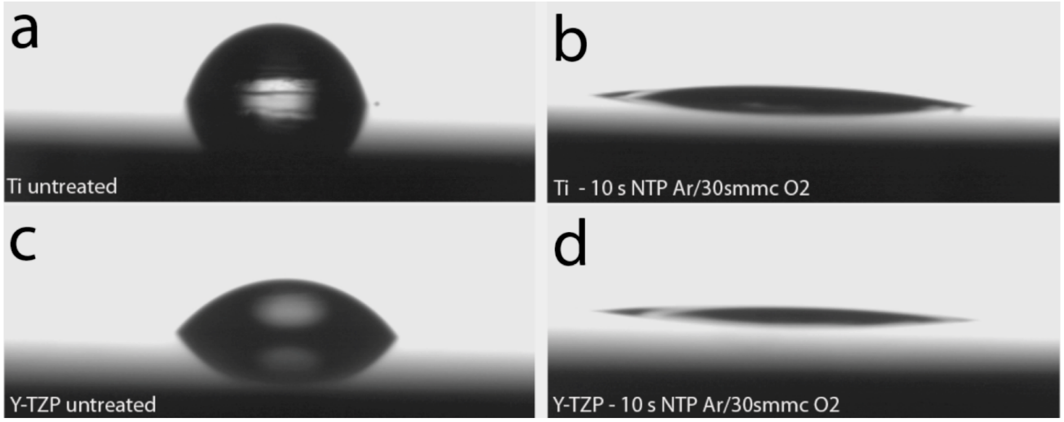

Figure 3: This series of images illustrates the contact angle of a drop of water dispensed on untreated (a and c) and plasma treated (b and d) Ti and Y-TZP surfaces. The contact angles were 82^{o} for Ti (a) and 57^{o} for Y-TZP (c) prior to plasma treatment. Note the significant reduction of the contact angle (~ 0^{o}) of the water on each material after 10 s of plasma exposure.

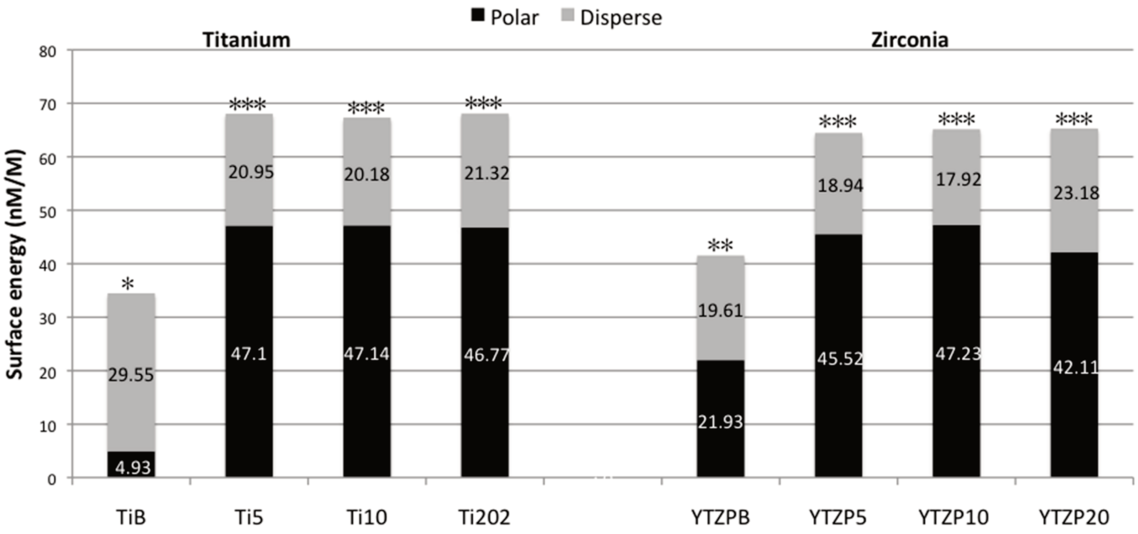

Figure 4: *, **, *** represent statistical differences. The polar and disperse components of Titanium and Y-TZP surfaces after 5, 10 and 20 s plasma treatment. The asterisks depict statistically homogeneous groups.

The high polarity observed promotes electrostatic interactions between Y-TZP and Ti surfaces and molecules of, water, ethylene glycol and diiodomethane. The plasma treatment resulted in a uniform reduction in the disperse values of the SE for the Ti groups compared to baseline. For Y-TZP, the disperse component showed a slight reduction for the Y-TZP 5 and Y-TZP 10 groups and not significant small increase for the Y-TZP 20 group.

As time of NTP application showed no difference in SE, the surface chemistry evaluation by XPS of Y-TZP and Ti surfaces was made only after 10 s of NTP application and showed that NTP strongly influenced the concentration of O and C elements on both substrate surfaces. Regardless of substrate, an evident increase of O and decrease of C was detected (Table 1). Survey scans spectra (Figure 5 and 6) also showed the presence of Zr, Y and Si in the Y-TZP surface and the presence of and Ti in the Ti substrate before and after NTP treatment.

Table 1: Surface chemistry composition (in atomic percentage of each element) of Y-TZP and Ti surface before (Baseline) and after NTP application. Numbers in parentheses represent the standard deviation.

Surface	Y-TZP		Ti	
Chemical element	O	C	O	C
Baseline	47 (1)	33 (1)	42 (0.9)	37 (2.5)
NTP10 Ar/O_2	57 (0,9)	19 (1)	52 (0.6)	22 (0.2)

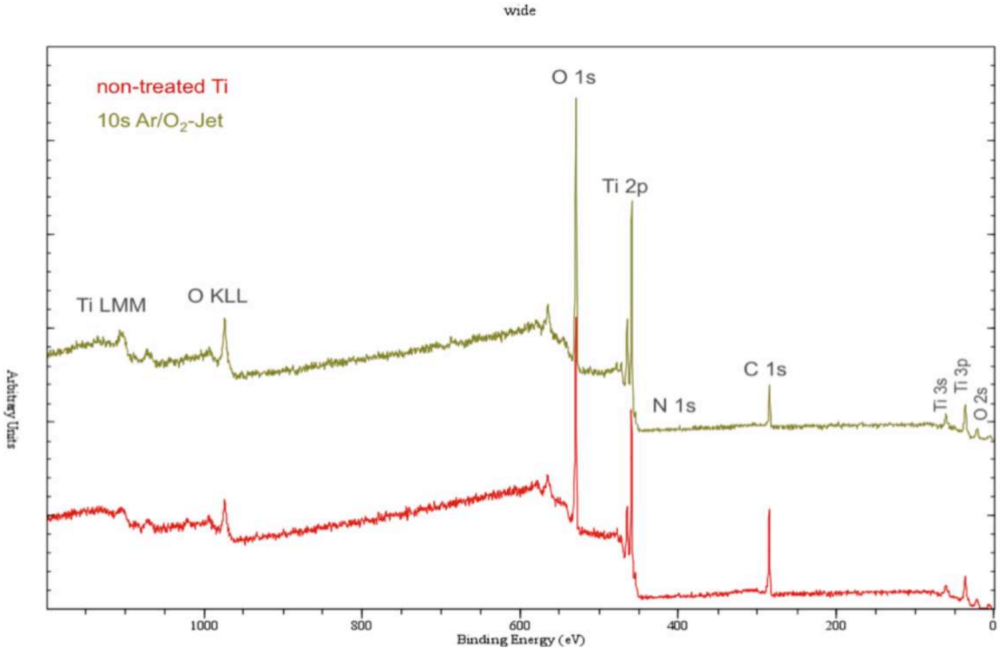

Figure 5. XPS spectra of Ti shows the differences in amounts of O and C prior and after NTP application

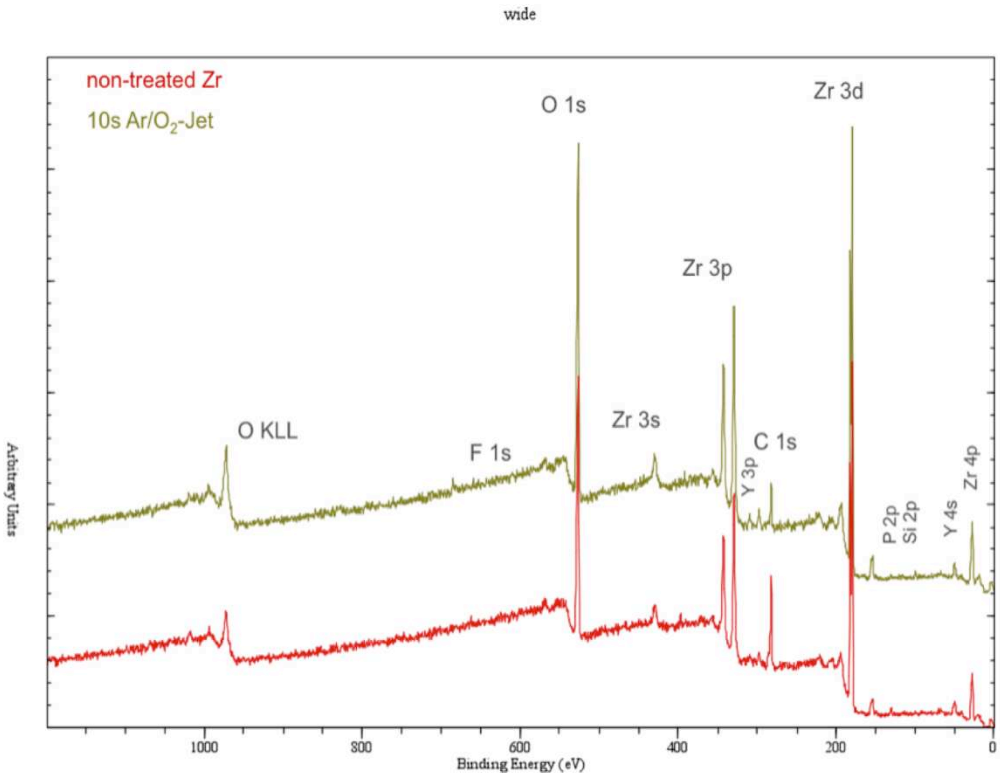

Figure 6. XPS spectra of Y-TZP shows the differences in amounts of O and C prior and after NTP application.

The MDP primer contact angle decreased from 15° (baseline, no plasma) to 0° after 10 s of plasma treatment for the Y-TZP specimens (Table 2). For the Ti substrate, on the other hand, a 0° contact angle was obtained when the MDP primer alone was dispensed on the Ti surface without plasma treatment and this value was maintained after 10 s of plasma treatment (Table 1).

Table 2. Results of contact angle measurements of the MDP primer on Ti and Y-TZP discs before and after plasma treatment. The asterisks depict statistically homogeneous groups.

NTP treatments	Y-TZP	Angle (θ)	Ti	Angle (θ)
Baseline	Y-TZPmdpB	$15\pm 2^{**}$	TimdpB	0^{*}
10s Argon 5slm+30 sccm O_2	Y-TZPmdpO_2	0^{*}	TimdpO_2	0^{*}

Discussion

The plasma pen utilized here with it associated physically small power supply could easily be employed clinically. Small cylinders of compressed argon gas and oxygen gas would be required. Ar is a commonly used operating gas in NTP technology because of its relatively low cost and high sputtering yield. [49] The presence of O_2 in the operating gas of the plasma device promotes the formation of active peroxide radicals (R-O-O-), which initiate chemical surface changes even on inert materials such as dense crystalline sintered ceramics.[49] The utilization of O_2 also promotes the incorporation of additional functional groups (C-O, C-OH) into the upper layer of the treated surface. Such observation was confirmed by our XPS data, which indicated a shift of the O1s to a binding energy located at 530 eV for both Y-TZP and Ti surface after the NTP application.

Excited particles, atoms, and UV radiation also stimulate chemical changes on the surfaces. The impact of electron and UV radiation causes the breaking of R-H (R: free organic radical), C-C bonds and initiates secondary reactions of atomic hydrogen. [49]

The presence of oxygen in the plasma also has a cleaning potential by removing organic contamination through the breaking of C-H and C-C bonds, thus reducing the surface adsorbed hydrocarbon content. This was observed as noted by a shift of C1s XPS spectra to a binding energy located at 285 eV for both Y-TZP and Ti substrates following the NTP application. Surface cleaning of metals can result in surface energies that approach 70 mN/m, which ensures excellent wettability. [38]

Since NTP treatments did result in high SE measurements (above 60 mN/m for both materials), it was not surprising that higher wettability was observed relative to non-treated substrates. Such results are in agreement with previous NTP related work concerning increase in surface wettability of other substrates. [38] However, our results showed that the increase in SE values was primarily due to the polar component increase on plasma-treated samples of Ti and Y-TZP composition. In fact, the disperse component, perhaps related to adsorbed –C-H moieties, was found to decrease after plasma treatment for Ti, but remained essentially unchanged for Y-TZP.

Although the surface modification is expected to depend, in addition to the operating gas and the pressure, on the plasma exposure time,[50] this study found no significant difference in the SE values for Y-TZP and Ti after 5, 10 or 20 s of plasma exposure.

The contact angle obtained for the MDP primer dispensed on the Y-TZP surface was reduced to 0° after plasma treatment, indicating that total wetting of the surface was achieved. Chemical bonding forces were reported to occur between the MDP monomer and metal ions present on restorative dental ceramics,[51,52] as Y-TZP contains metal oxides, the NTP treatment performed likely resulted in quantitative/qualitative alterations in the chemical bonds with these metal oxides via secondary forces such as Van der Waals or hydrogen bonds and the MDP primer. [53] A more specific mechanism may be related to population of the Y-TZP surface by the plasma with more basic –OH groups, increasing the acid base reaction between the surface and the acidic phosphate of the MDP molecule. This is supported by the XPS findings of increased O on the surface after treatment but requires further research for confirmation.

Unlike the observation for the non-treated Y-TZP, a 0° contact angle with MDP was observed for the non-treated Ti surface. Titanium is a highly reactive element, and various chemical elements such as oxygen have high affinity for titanium, spontaneously reacting resulting in an oxidized surface. [54] Such oxidation processes are expected to induce high wettability on the Ti surface and thereby is beneficial for the bonding mechanisms as the phosphate ester group of MDP seems to appropriately bond to the metal oxides. [55] It should be pointed, that the increase in wettability for the Ti might be related to its higher roughness after the 600 grit SiC preparation. These different roughness parameters are related to the difference in hardness between the Ti and Y-TZP.

Surface modification of biomaterials continues to be investigated and to improve the initial host response and improve biomaterial-biomaterial interactions and compatibility (such as bonding procedures in restorative dentistry). [49] Overall, all the proposed NTP regimes applied may be regarded as an attractive alternative for increasing the surface energy and wettability of two widely utilized biomaterials.

Conclusions

Non-thermal plasma treatment using a mixture of Ar and O_2 as the operating gas was found to be effective in enhancing the SE and wettability and of Ti and Y-TZP substrates. The NTP treatment of Ti and Y-TZP surfaces using Ar /30smmc O_2 for 5, 10 and 20 s resulted in an increase of the SE on Y-TZP and Ti surfaces supporting hypothesis (1). The surface chemistry evaluated by XPS demonstrated the reduction of C and increased O after NTP. Thus, hypothesis (2) was accepted. A significant reduction in the contact angle of MDP primer dispensed on Y-TZP surfaces was observed after 10 s plasma treatments. In the case of Ti, a 0^{o} contact angle of MDP primer was observed before and after a 10 s plasma treatment. Thus, hypothesis (3) was supported only for Y-TZP.

Acknowledgement

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Capítulo 2

Surface Characterization and Bonding of Y-TZP Following Non-Thermal Plasma Treatment

Artigo nas normas do periódico **Dental Materials**

Abstract

Objective**.** To characterize and evaluate the effect of Non-thermal plasma (NTP) application on roughened Y-TZP and to test the microtensile bond strength (MTBS) of zirconia, after a combination of different surface conditioning methods. Methods.Twenty-four Y-TZP discs, 4 mm in thickness and 13.5 mm in diameter, were obtained from the manufacturer and composite resin (Z-100) discs with similar dimensions were prepared. All discs were grounded to 600 grit and divided into 8 groups (n=3 disks each), four control (non-NTP treated) and four experimental (NTP treated) groups. All groups received one of the four following treatments: sand-blasting (SB group), a Clearfil ceramic primer (MDP group), sand-blasting + MDP (SBMDP group), or baseline (B group), no treatment. The experimental groups were added with NTP treatment for 10 s. SE readings and surface roughness parameters were statistically analyzed (ANOVA, Tukey's, $p < 0.05$) and a mixed model and a paired samples t-tests was used for the MTBS analysis. Results. SB and B groups showed the same SE levels after NTP treatment. An increase in O and decrease in C elements was detected in the NTP treated discs and all NTP groups showed higher bond strength than the untreated counterparts. Conclusion. NTP application greatly increased bond strength when it was applied in combination with treatments designed to improve bond strength.

Key words: Adhesion; contact angle; microtensile; non-thermal plasma; surface energy; wettability; Y-TZP.

1.Introduction

An efficient resin bond to a ceramic surface usually relies on the combination of micromechanical interlock and chemical functionalization [1]. While the high crystalline content of yttria-tetragonal zirconia polycrystals (Y-TZP) ceramic systems results in favorable physical properties for dental restorations, [2, 3] obtaining an adequate bonding performance to such polycrystalline structure has been proven difficult [4].

Effective methods to bond resin cements to zirconia substrates have relied on roughening the Y-TZP surface with either tribochemical silica coating or airborne Al_2O_3 particle abrasion followed by the application of the trialkoxysilane coupling agents [5] and/or phosphate ester monomer-containing primers such as 10–Methacryloyloxydecyl dihydrogen phosphate (MDP) [6, 7].

Particle abrasion increases the substrate surface roughness [8]. The inorganic alkoxy groups of the silane can form covalent siloxane bonds with the impregnated silica on the Y-YZP surface, and the organic functional portion can polymerize with the organic matrix of the composite material [9, 10]. Functional monomers (MDP) bond to metal oxides on the Y-TZP surface and molecular attraction at the resin–zirconia interface also arise from secondary forces such as Van der Waals forces or hydrogen bond [11-13].

These chemical bonding procedures aim to increase the surface energy and wetting ability of the Y-TZP surface to resin bond. Micromechanical roughening is indicated to clean and activate the surface [14, 15], enabling better wetting of the Y-TZP surface to primers [16]. Although these methods have been reported to promote effective bonding to Y-TZP substrates [12, 13], particle abrasion may create structural defects and mechanical damage that could potentially cause unreliable long-term performance [17]. Therefore, omitting air-abrasion completely might be advantageous to eliminate potential negative effects.

Few techniques have attempted to address the concerns of air-abrasion to ceramic materials by substituting it for other treatments. The selective infiltration etching (SIE) [8], chloro-silane combined with water vapor [4] and the fluorination vapor techniques [18] have shown different approaches for adhesive bonding of Y-TZP, but do require further investigation.

A possible alternative may be the utilization of non-thermal plasmas (NTP) to optimize the surface chemistry of the Y-TZP for bonding/cementation procedures. NTP technology consists of a partially ionized gas in nonequilibrium that provides a large amount of chemically active species such as O_3, OH, H_2O_2, NO, OH radicals, at low (even ambient) temperatures [19]. By changing functional groups on the surface of different materials, these chemically active species are able to transform nonreactive to reactive surfaces without affecting the bulk properties of the material [20]. Normally, the surface energy (SE) of a material is enhanced after the NTP application, leaving it better prepared for newer molecular interactions. Therefore, increasing the SE of Y-TZP surfaces might enhance bonding without deleterious effects to its structure.

This investigation tested the hypotheses that 10 s of NTP application: 1) increases the SE levels of roughened Y-TZP; 2) increases elemental O and decreases elemental C on Y-TZP surface; and 3) increases the microtensile bond strength (MTBS) to Y-TZP surfaces, when applied alone or in combination with known bonding facilitators.

2. Materials and methods

Sample preparation

Twenty-four fully sintered Y-TZP discs (Lava Frame, 3M Espe, St. Paul, MN), 4 mm in thickness and 13.5 mm in diameter, were obtained from the manufacturer, ground with 600 grit silicon paper (Buehler Ltd., Lake Bluff, IL) under water cooling for initial roughness standardization. Twenty four composite resin (Z-100 Universal composite resin, 3M/ESPE) discs with similar dimensions were prepared in a plastic mold and light cured according to the manufacturer's recommendation (Elipar FreeLight 2; 3M ESPE), and subsequently ground with 600 grit silicon carbide paper (Buehler Ltd.). The Y-TZP discs were randomly distributed in 4 groups according to surface treatment as follow: sand-blasting (SB group), a phosphate monomer application (MDP group), sand-blasting + phosphate monomer application (SBMDP group), or baseline (B group), no treatment.

The sand-blasting was achieved by airborne particle abrasion with 50 µm aluminum oxide particles (P-G 400; Harnisch & Rieth, Winterbach, Germany) at 0.55 MPa pressure (S-U-Alustral; Schuler-Dental, Ulm, Germany) for 10 sec. After SB, the samples were ultrasonically cleaned in 96% ethanol for 2 min. The phosphate monomer Clearfil ceramic primer (Kuraray Medical Inc., 1621 Sakazu, Kurashiki, Okayama, Japan) was applied with a disposable brush tip and the surface dried by blowing mild oil-free air (according to the manufacturer instructions). Half of the specimens from each group were randomly selected and received the additional NTP treatment (n=3).

Non-Thermal Plasma (NTP)

The NTP device utilized in this study (KinPen 09, INP Greifswald, Germany – [21] consisted of a hand-held unit (170 mm length, 20 mm diameter, weighting 170 g) connected to a high-frequency power supply (frequency 1.1 MHz, 2-6 kV peak-to-peak, 8 W system power) generating a NTP plume at atmospheric pressure. The hand-held unit has a pin-type electrode (1 mm diameter) surrounded by a 1.6 mm quartz capillary. The NTP source operated with Argon (Ar) gas at a mass flow rate of 5 standard liters per minute (slm). The NTP plume emerging at the exit nozzle presented 1.5 mm in diameter and extended into the surrounding air for a distance of 5 mm. Each NTP treated group received 10 s of NTP application.

The NTP-treated groups comprised: sand blasting + NTP (SBP group), a phosphate monomer application + NTP (MDPP group), sand-blasting + phosphate monomer + NTP (SBMDPP group), or only NTP treatment, baseline (BP group).

The surface roughness, energy, and chemistry of the SB, and B groups were assessed previously and after NTP treatment.

Surface Roughness

Prior to surface energy (SE) calculations, roughness parameters of the SB and B specimens were determined by optical interferometry (IFM) (Phase View 2.5, Palaiseau, France). Discs of each surface were evaluated at the flat (five measurements from each group) and S_a (arithmetic average high deviation) and S_q (root mean square) parameters determined. A filter size of 100µm x 100µm was utilized.

Surface energy (SE)

SE was calculated by measuring the contact angle of liquids with known values of surface tension. Values of polar and disperse components were obtained by $\gamma_L = \gamma^D_L + \gamma^P_L$, being γ_L the SE, γ^D_L the disperse component and γ^P_L the polar component. Discs from group B and SB were horizontally positioned into a contact angle meter (OCA 30, Data Physics Instruments GmbH, Filderstadt, Germany) for contact angle measurements and SE calculations performed. The Owens-Wendt-Rabel-Kaelble (OWRK) method [22] was used for the SE determination by depositing 0.5 μl droplets of purified water, ethylene glycol and methylene iodide on the surface of each disk with 50μl glass syringe (OCA 30, Data Physics Instruments GmbH, Filderstadt, Germany). Images were then captured and contact angle and SE determined by the use of the software (SCA30, version 3.4.6 build 79).

X-Ray Photoelectron spectroscopy (XPS)

XPS measurements were performed before and after NTP application using AXIS Ultra DLD electron spectrometer (Kratos Analytical, Manchester, UK). The XPS data were recorded using monochromatic Al K_α excitation (1486 eV). Spectra were acquired by setting the instrument to medium magnification lens mode (field of view 2) and by selecting the slot mode, providing an approximately 250µm diameter analysis area. Charge neutralization was implemented by low energy electrons injected into the magnetic field of the lens from a filament located directly on top of the sample. Wide scans and element spectra were recorded at a pass energy of 80 eV for the estimation of the chemical element composition and at a pass energy of 10 eV for the energetically highly resolved measurements of the C 1s peak. Three spots in different positions on each Y-TZP discs were analyzed and averaged. A relative standard deviation of up to 3 % was obtained. Data acquisition and processing were carried out using the CasaXPS software (Casa Software Ltd., version 2.14.dev29, Teignmouth, UK).

Microtensile bond strength test (MTBS)

A self-adhesive resin-based cement (Rely X Unicem 3M Espe, St. Paul, Minnesota, U.S.A.) was used following the manufacturer's instructions to bond the composite discs to treated Y-TZP discs.

After cementation steps, the specimens were serially cross-sectioned perpendicular to the adhesive interface with a diamond blade (Buehler Isomet with Buehler Diamond Wafering Blade—Series 15 LC Diamond, No 11-4255, Lake Bluff, IL) under constant irrigation, producing squared beams with approximately 0.8-1.0 mm^2 and 8 mm in length. Twenty beams from each disc were randomly selected, resulting in a total of 60 beams per group. The MTBS testing was performed by attaching each beam to the flat grips of a special jig using cyanoacrylate glue

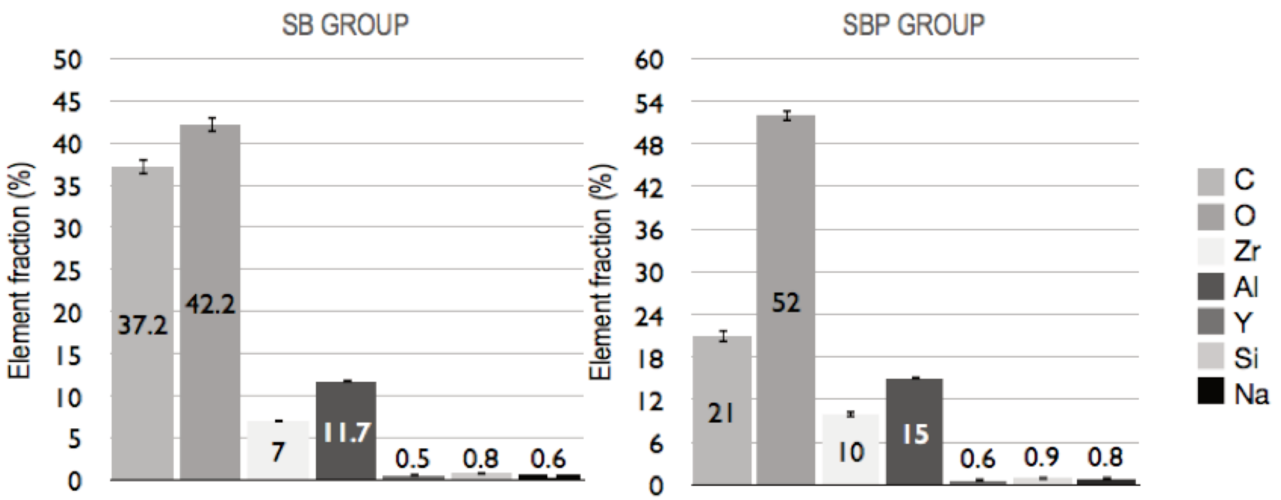


Figure 7: XPS of the sand blasted surfaces also showed that NTP strongly influenced the concentration of O and C elements. An evident increase of O and decrease of C was detected as well. Prior to NTP application, the SB group contained 37% of C element and 42% of O element and after NTP treatment, SBP group showed a decrease in the fraction of C to 21% and an increase in the fraction of O to 52%. The presence of 12% of Al element was also detected prior NTP application, together with 7% of Zr, 0.5% of Y, 0.9% of Si, and 0.6 of Na, and after NTP application, a slightly increase in the Al and Zr elements of 15% and 10%, respectively could be detected, while element s Y, Si and Na remained unaltered.

MTBS values for the non-NTP- and NTP-treated groups are shown in Tables 1. Before analysis, MTBS values were transformed to their logarithm (base10), which normalized those distributions, (However, to keep the interpretation straightforward, means are presented in raw units.) To avoid heterogeneity in error variances between several combinations of non-NTP and NTP treated groups, these two treatment conditions were analyzed separately. Looking first at the non-

(Scotch Super Glue Gel, 3M, St. Paul, MN, U.S.A.). The specimens were loaded to failure under tension at a crosshead speed of 1 mm/min [23] using a universal testing machine (Model 5566 - Instron Corporation, Norwood, MA, USA) equipped with a 100N load cell . The cross-sectional areas of all specimens were measured individually after testing using a digital caliper (Mitutoyo, 20-1 Sakado, Kawasaki, Kanagawa 213, Japan), and the MTBS values calculated in MPa for group comparisons.

Fractographic Examination

All tested specimens were examined using a stereomicroscope (Leica MZ-APO, Meyer Intruments, Inc., TX, U.S.A) at 63x magnification. Failure modes were classified as following: (A) adhesive failure at the Y-TZP surface, (B) cohesive failure in the luting composite resin or (C) mixed. Representative debonded specimens from each group were mounted onto a small stub and gold coated (Emitech K650 Sputter, Coater, London, UK) for scanning electron microscopic (S-3500N, Hitachi, Japan) evaluation.

Statistical Analysis

SE readings and surface roughness parameters were recorded and omnibus statistical evaluation performed by one-way ANOVA and Tukey at .05 level of significance. Overall differences in bond strength were evaluated within non-NTP and NTP groups with a mixed model ANOVA at a 5% confidence level. A mixed model was used to control for effects endowed to each microbeam by the unique characteristics of their parent disc, and perhaps different from those of other parent discs. Given significant overall results, group means were compared with the LSD procedure. Specific comparisons of each combination of conditions with and without NTP were accomplished with a paired samples t-tests.

3. Results

Surface roughness, S_a and S_q, was greater ($p<0.05$) for the SB group than the baseline (B) samples (Figure 1). IFM images are show in Figure 2

Surface energy (SE) was lower ($p< .05$) in the untreated (B) (12.18 mN/m) than the sand blasted (SB) group (27.85 mN/m). This change was most evident in the polar component, and proportionally smaller variations occurred for the disperse levels. The polar component of both substrates increased ($p<0.05$) after NTP application (Figure 3). Representative images of the contact angle readings using water, diiodomethane and ethylene glycol for SE calculations before and after NTP treatment for both B and SB treatments are presented in Figures 4 and 5.

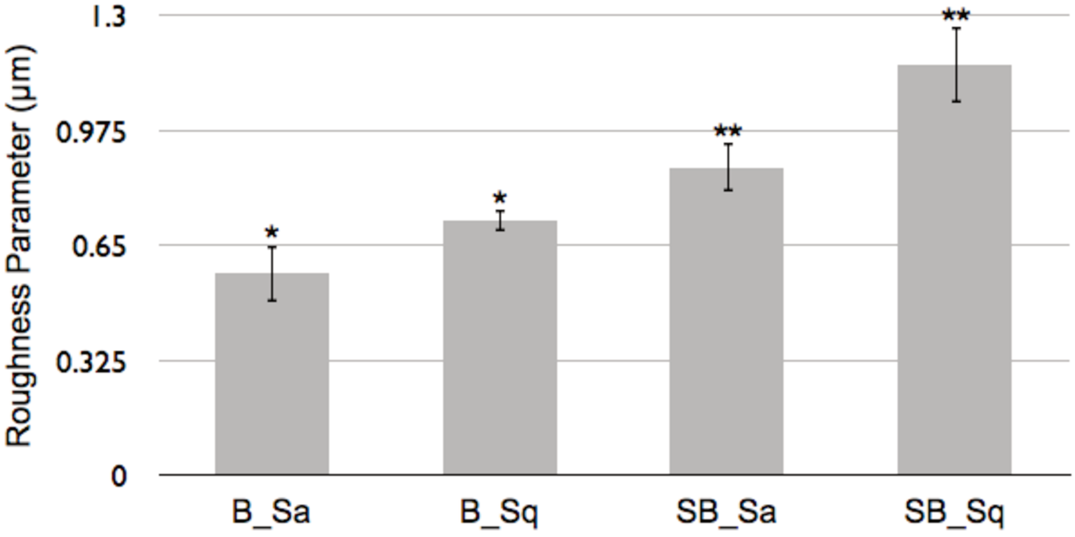


Figure 1: Mean measures of surface roughness parameters Sa and Sq for the SB and B groups. *, ** represent a difference at $p< .05$.

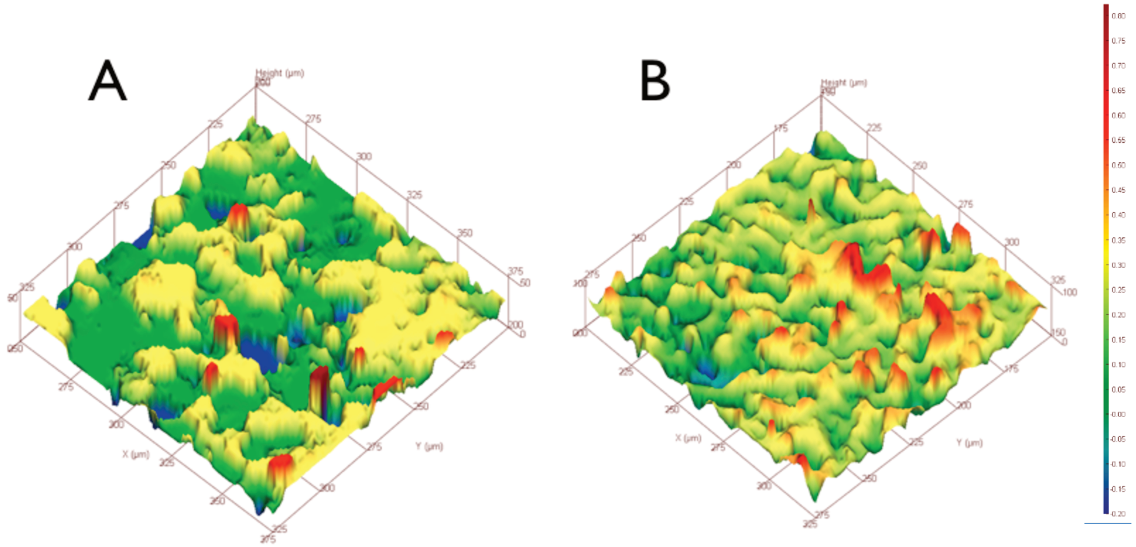


Figure 2: Representative IFM images of a B (A) and SB (B) surfaces respectively. Measurable roughness parameters (Sa and Sq) showed overall higher roughness profile for SB compared to B group.

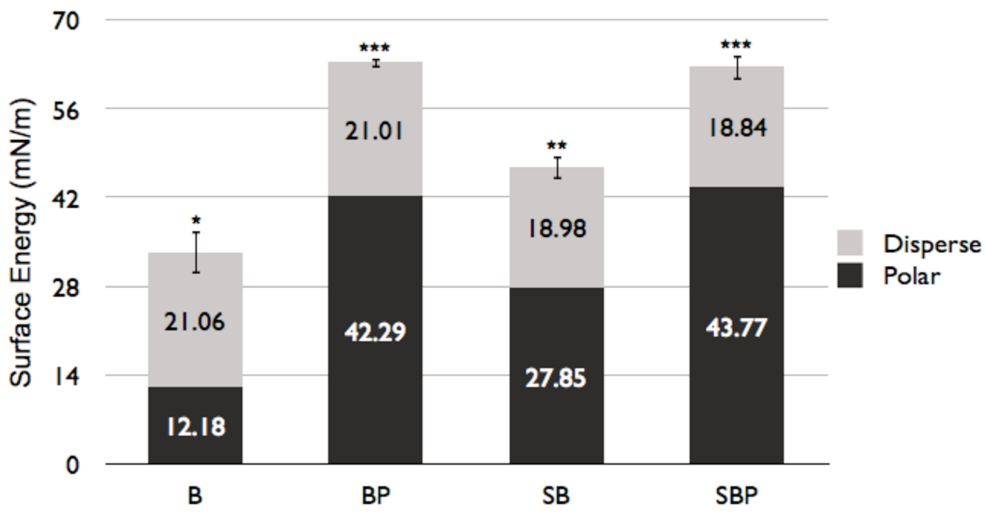


Figure 3: Mean levels of the polar and disperse components of the Baseline (B) and SB surfaces before and after a 10 s plasma treatment (SB and SBP). The numbers of asterisks represent statistically homogeneous groups.

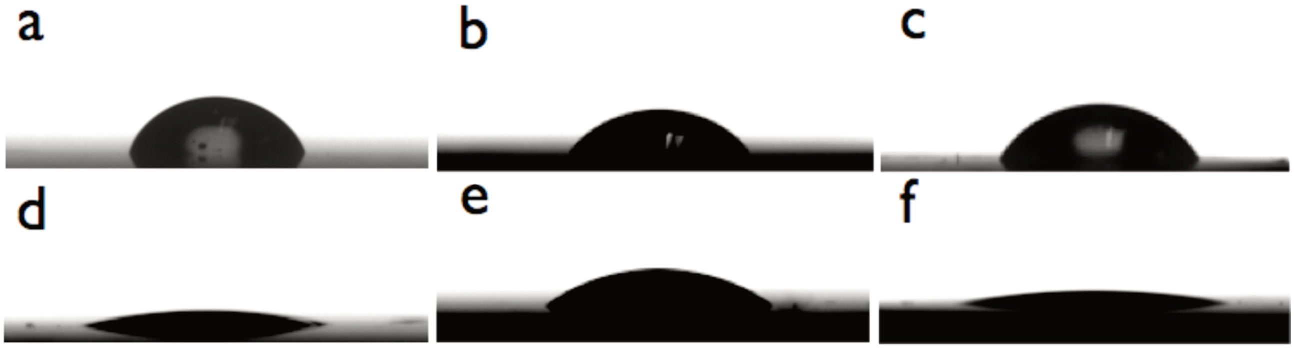


Figure 4: This series of images illustrates the contact angle of drops of water (a and d) Diiodomethane (b and e) and Etyhylene Glycol (c and f) dispensed on the untreated B (a,b and c) and on the plasma treated (BP) surfaces (d, e, and f). The contact angles were 76°, 56° and 64° respectively for a, b and c prior to NTP treatment. Note the significant reduction of the contact angle of 18°, 40° and 13 ° respectively for d, e and f after 10 s of NTP exposure.

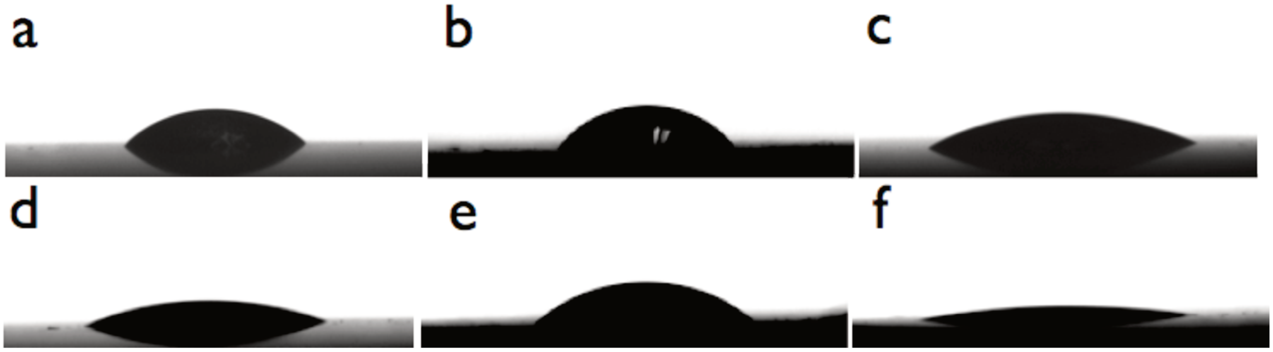


Figure 5: This series of images illustrates the contact angle of drops of water (a and d) Diiodomethane (b and e) and Etyhylene Glycol (c and f) dispensed on the sandblasted (a,b and c) and on the sandblasted plus plasma treated (d, e, and f) surfaces. The contact angles were 50°, 58° and 35 ° respectively for a, b and c prior to NTP treatment. Note the significant reduction of the contact angle of 16°, 47° and 13° respectively for d, e and f after 10 s of NTP exposure.

XPS surface chemistry assessment of B and SB groups before and after NTP application (BP and SBP) (Figure 7 and 8) showed that after NTP, it was observed in both groups an increase in the level O and a decrease in C content. BP group had also an increase in Zr and Si contents while no substantial alteration was detected for Y. SB group showed the presence of element Al due to sandblasting, which increased slightly after NTP application. Zr element also increased after NTP application and small traces of Na, Si and Y detected before NTP application, remained almost with the same percentages after NTP treatment.

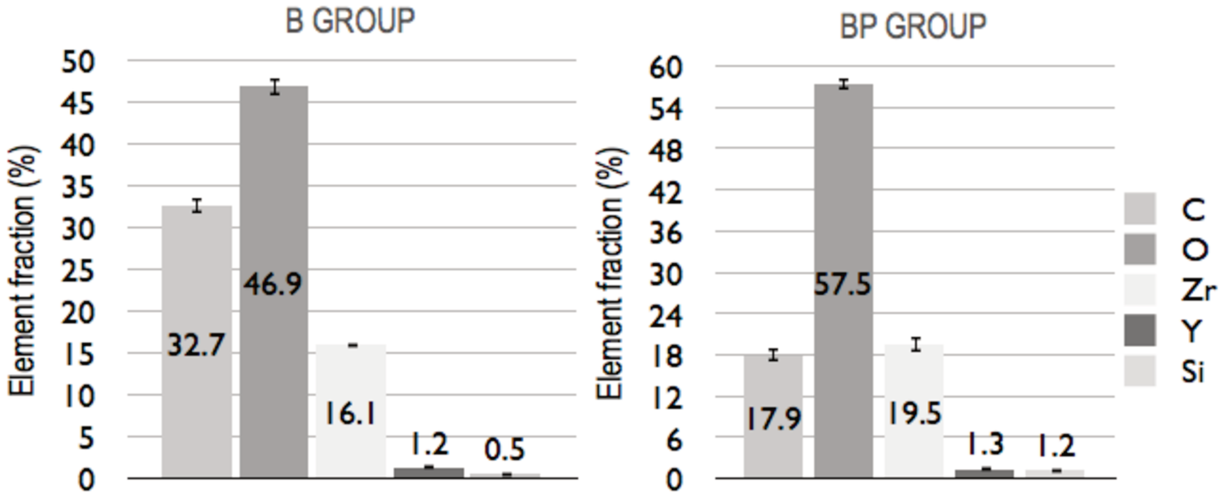
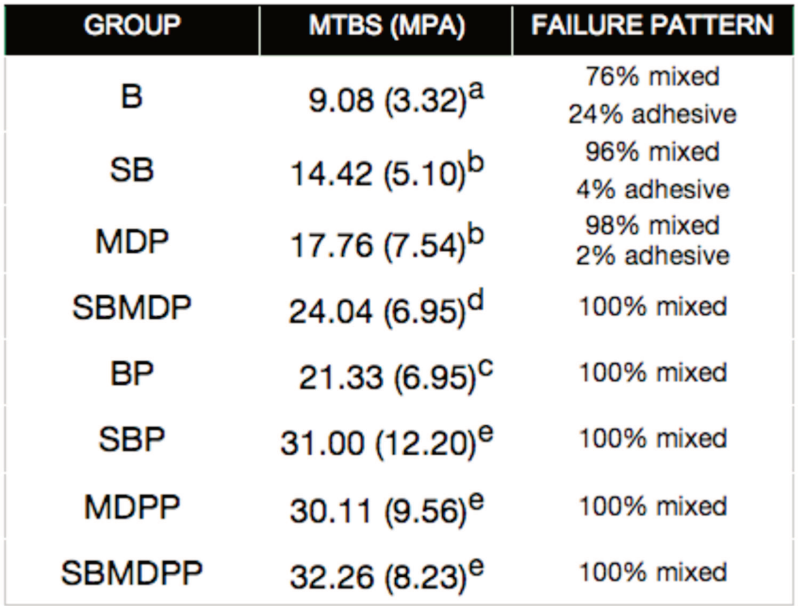


Figure 6: XPS of the baseline surfaces showed that NTP strongly influenced the concentration of O and C elements. An evident increase of O and decrease of C was detected. Prior to NTP application, the B group contained 33% of C element and 47% of O element and after NTP treatment, BP group showed a decrease in the fraction of C to 19% and an increase in the fraction of O to 57%. The presence of 16% of Zr element was also detected prior NTP application, together with 1% of Y and 0.5% of Si and after NTP application, a slightly increase in the Zr and Si elements of 20% and 1.2%, respectively could be detected, while Y element remained unaltered.

NTP groups, ANOVA revealed a group effect ($p<0.05$) in MTBS mean values. Table 1 shows that group SBMDP showed the highest bond strength, statistically greater than both the SB and MDP groups. These last two groups were statistically similar to one another ($P>0.05$), but they both showed higher bond strength than group B ($P< .05$). Thus, MDP seemed to strengthen the SB surface relative to either SB or MDP alone, and all three of these conditions led to greater bond strength than the untreated samples. Turning to the plasma treated samples, ANOVA showed no statistical difference between groups SBMDPP, SBP and MDPP, but each of these groups showed higher bond strength than the BP group, which showed the least strength. Thus, plasma treatment further increased the bond strength of each other treatment that is intended to increase bond strength. To isolate the specific improvement in bond strength attributable to NTP, we compared each Non-NTP treatment with their NTP counterparts. Pairwise comparions between respective plasma-treated and non-treated groups indicated that plasma treatment resulted in significant improve in bond strength ($p< .05$)

Table 1. Failure strength (in MPa) and failure mode of the Non-NTP and NTP groups. Groups with the same superscript letter were not significantly different.



GROUP	MTBS (MPA)	FAILURE PATTERN
B	9.08 (3.32)^{a}	76% mixed 24% adhesive
SB	14.42 (5.10)^{b}	96% mixed 4% adhesive
MDP	17.76 (7.54)^{b}	98% mixed 2% adhesive
SBMDP	24.04 (6.95)^{d}	100% mixed
BP	21.33 (6.95)^{c}	100% mixed
SBP	31.00 (12.20)^{e}	100% mixed
MDPP	30.11 (9.56)^{e}	100% mixed
SBMDPP	32.26 (8.23)^{e}	100% mixed

Failure modes observed in all groups are also presented in table. The light microscopy analysis demonstrated that almost all (> 95%) of the Y-TZP surfaces presented a mixed type of failure, except groups B, SB and MDP where failures of 24%, 4% and 2% respectively were adhesive. Representative SEM images of all groups are displayed in figure 8.

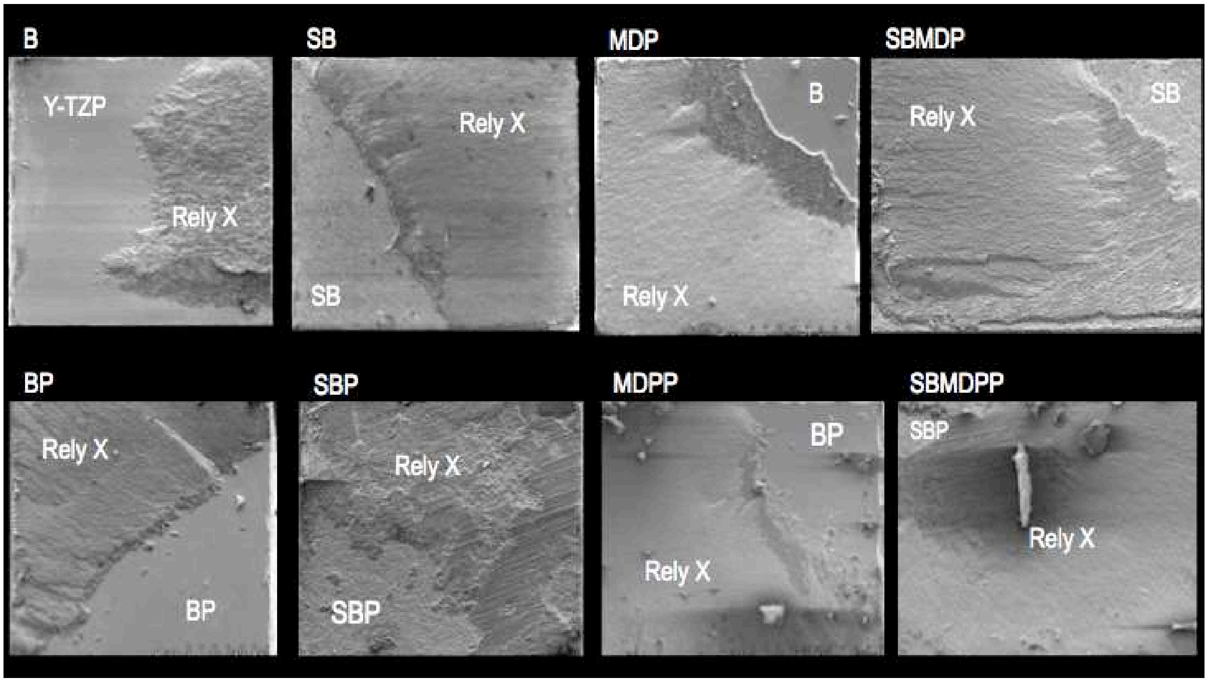


Fig 8. Representative SEM images (X 900) of Y-TZP sides of broken beams from each experimental group, demonstrating a different combination of cohesive and adhesive failure (mixed) in different proportion for the different tested groups. Note that group SBMDPP (highest bond strength) has a very small area of adhesive failure.

4. Discussion

Bonding properties to Y-TZP for dental applications are known to be problematic [1, 24, 25]. Although recent studies have reported that the bond strength between resin cement and zirconia would depend on the resin cement selection rather than on the surface treatment [26, 27], the present work showed that the novel NTP technology has potential to enhance bonding performance to Y-TZP surfaces.

In all NTP groups, significantly higher bond strength values were noted in comparison to their respective non-NTP. The application of sandblasting and/or phosphate primer did not matter to improve bond strength when plasma was used. Conversely, when plasma was not applied, the other bonding facilitators played a significant role on the resultant bond strength, as previously reported in the literature [1, 11, 28, 29].

The roughness readings of the Y-TZP surfaces showed higher Sa and Sq parameters for the SB group when compared to the Baseline (B). The surface, promoted by the air-abrasion, [1, 11, 13, 28, 30-34] is not only increased in area, thus improving wetting kinetics, but it is also cleaned, once organic contaminants are removed by the blasting [33-35]. Therefore, significant higher bond strength was noted for group SB when compared to the baseline [7, 36]. The increased surface area of Y-TZP due to sandblasting permits also more substantial surface reaction and greater contact among the hydrophilic monomers, cement and zirconia ceramics [37], explaining some of the general characteristics of adhesion to roughened surfaces. However, the sand blasting effect involves also physico-chemical changes that have been reported to affect SE and wettability [38].

SE is a direct manifestation of intermolecular forces and the common way of calculating the SE of a material is by measuring the contact angle of liquids, typically used for their known values of surface tension, from which the solid's surface energy can be extracted. Values of polar and disperse components can be obtained, referring to the newer molecular interactions such as dipole-dipole interactions, hydrogen bond and dispersive forces of London [39].

Prior to NTP application, the SE of the SB specimens was significantly higher than the baseline group, reinforcing the role of the sand blasting in the overall process of adhesion. After NTP application, it was noted that both SB and and B surfaces presented a higher content of O element according to the element fraction analyses and significant enhancement of SE (around 60 mN/m), particularly due to their high polar component. This high polarity is capable of promoting an excellent wettability, since polar interactions have a significantly greater influence on adhesion mechanisms regarding dental monomers [24, 40].

It is known that the gas of the plasma device promotes the formation of active peroxide radicals (R-O-O-), and incorporates additional functional groups (C-O, C-OH) into the upper layer of the treated surface, which initiate chemical surface changes even on inert materials such as Y-TZP [41]. This high SE of SB and B surfaces might explain the higher MTBS values for all NTP groups when compared to the Non-NTP groups and the equal MTBS values found among groups SBP (31 MPa), MDPP (30.11 MPa) and SBMDPP (32.26 MPa), since the reached hydrophilicity on the Y-TZP surface due to a higher presence of polar components after NTP application, might improve the bonding of Y-TZP surface to MDP primer and Rely X resin cement.

Rely X Unicem cement has a phosphate monomer with two phosphate groups, so some bond to zirconia after sandblasting can be achieved, [12] and after sand blasting plus NTP application, the Y-TZP surface becomes even more activated, so qualitative/quantitative alterations in the chemical bonds with these phosphate groups via secondary forces such as Van der Waals might occur. These qualitative/quantitative chemical alterations promoted by the NTP might also play a role in the interactions that occur with the hydroxyl groups in MDP primer and the hydroxyl groups on zirconia ceramic surface [16].

The mean MTBS value of the SBMDPP group showed no statistical difference towards groups SBP and MDPP. When NTP is not applied (group

SBMDP) the sum of the bonding facilitators (MDP + sandblasting) makes a difference in the overall bond strength. It could be speculated that in group SBMDPP, a saturation level in the bonding interactions between the surface of Y-TZP and MDP and Rely X Unicem occur, since the Y-TZP surface is highly activated, and both primer and cement present phosphate monomer in their compositions.

Furthermore, as the NTP application has also a cleaning potential, a reduction of adsorbed hydrocarbon content through the breaking of C-H and C-C bonds occurs [40]. A reduction of organic contaminants from the Y-TZP surfaces, as shown by the element fraction analysis, also might have played a role for a better bonding results obtained in all NTP treated groups.

Bond strength varied as a function of the surface treatment; however, analysis of failure mode showed that most failures in the Y-TZP surface were classified as mixed type (adhesive and cohesive in resin cement) observed complexly in most debonded specimens. The high standard deviation in MTBS values might have occurred due to the variations in the failure modes that included cases, such as in group SBMDPP, of almost cohesive failure (highest bond strength) and combination of cohesive and adhesive failure in different proportions, which created a large spread in bond strength values [3].

The present results demonstrated that Y-TZP ceramic surface was chemically modified by the 10-sec application of NTP, resulting in increased surface energy of both sand-blasted and as fired surfaces. This was associated with significant increases in elemental O and decreases in C elemental. NTP application greatly increased MTBS when it was applied as a single agent on both as fired and sand-blasted surfaces, as well as when it was applied in combination with other maneuvers designed to improve bond strength. NTP is a promising technique for increasing bond strength in this otherwise difficult to bond material and further study will address the effect of NTP on long-term durability of bonding to Y-TZP.

5. Conclusion

The following conclusions were drawn:

1. The same surface energy levels of sand-blasted and gritted Y-TZP were obtained after 10 seconds of Non-Thermal Plasma application.

2. An increase of ±30% of elemental O and a decrease of ±40% of elemental C was detected on Y-TZP surface after 10 seconds of Non-Thermal Plasma application.

3. An significant increase in the microtensile bond strength to Y-TZP surfaces was observed when Non-thermal Plasma was applied alone or in combination with Clearfil Ceramic primer and/or Al_2O_3 sand-blasting.

Acknowledgement

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Considerações finais.

O plasma atmosférico não térmico (NTP) apresenta um alto potencial no tratamento da superfície de materiais odontológicos. Através dos trabalhos apresentados, pode-se constatar que ele tem a capacidade de deixar a superfície de metais e principalmente da zircônia, repleta de grupos químicos funcionais polares (principalmente daqueles compostos por oxigênio), resultando numa superfície extremamente hidrofílica.

Esse mecanismo proporcionado pelo plasma, resulta num aumento de energia de superfície dos materiais testados, que nada mais é do que um aumento da possibilidade de novas interação moleculares do substrato e de soluções aplicadas sobre eles. Nesse sentido, é verificado que há um aumento do molhamento de monômeros hidrofílicos utilizados no processo de adesão da zircônia, após a aplicação do NTP, evidenciado por menores ângulos de contato obtidos durante sua aplicação.

O ensaio de microtração pode confirmar que o processo de adesão na superfície da zirconia tratada com NTP foi melhorado devido a valores de forças adesivas significativamente maiores do que quando não houve a aplicação do mesmo. Porém, é extremamente importante verificar o comportamento adesivo de monômeros e/ou cimentos resinosos em superfícies de zircônia com a aplicação de NTP, submetidos a certos períodos de envelhecimento imersos em água ou por ciclagem térmica, afim de confirmar seu real potencial em aplicações cínicas para essa finalidade, já que coroas e próteses fixas com esse tipo de material serão cimentadas no ambiente bucal.

Por fim, a aplicação de plasma atmosférico não térmico apresenta um potencial enorme e promissor em diversas áreas da Odontologia, como em procedimentos restauradores que envolvem a formação da camada híbrida (o molhamento e adesividade de adesivos dentinários), clareamento dentário, procedimentos obturadores endodônticos, desinfecção, colagem de braquetes na ortodontia e em processos reparadores ósseos na implantodontia.

Conclusão

1. A aplicação de plasma atmosférico não térmico por 10 segundos aumenta a energia de superfície dos materiais Y-TZP e Ti.
2. Y-TZP jateada com Al_2O_3 e polida com lixas de carboneto de silício (gramatura 600), apresentam a mesma energia de superfície após a aplicação de 10 segundos de plasma atmosférico não térmico.
3. Após 10 segundos da aplicação de plasma atmosférico não térmico, o molhamento do MDP sobre a superfície da Zircônia aumentou significamente.
4. 10 segundos de aplicação de plasma atmosférico não térmico, aumentou a resistência à microtração da união do cimento resinoso à superfícies de Y-TZP.

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