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**EFICÁCIA DO USO DE PLASMA EM PRESSÃO ATMOSFÉRICA NA
ADESÃO DE CERÂMICAS ZIRCÔNIA**

**Faculdade de Odontologia
Universidade Federal de Minas Gerais
Belo Horizonte
2018**

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EFICÁCIA DO USO DE PLASMA EM PRESSÃO ATMOSFÉRICA NA ADESÃO DE CERÂMICAS ZIRCÔNIA

Tese apresentada ao Programa de Pós-Graduação em Odontologia da Faculdade de Odontologia da Universidade Federal de Minas Gerais, como requisito parcial para obtenção do título de Doutor em Odontologia – área de concentração em Clínica Odontológica.

Linha de pesquisa: Propriedades físicas, químicas e biológicas dos materiais odontológicos.

Orientador: Prof. Dr. Nelson R. F. A. da Silva

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Belo Horizonte

2018

Ficha Catalográfica

N778 Nogueira, Lilian Capanema.
2018 Eficácia do uso de plasma em pressão atmosférica na
T adesão de cerâmicas zircônia / Lilian Capanema Nogueira. --
2018.

71 f. : il.

Orientador: Nelson Renato Alves França da Silva.

Coorientador: Marcelo Giannini.

Tese (Doutorado) -- Universidade Federal de Minas Gerais, Faculdade de Odontologia.

1. Plasma . 2. Pressão atmosférica. 3. Zircônio. I. da Silva, Nelson Renato Alves França. II. Giannini, Marcelo. III. Universidade Federal de Minas Gerais. Faculdade de Odontologia. IV. Título.

BLACK - D047



UNIVERSIDADE FEDERAL DE MINAS GERAIS

PROGRAMA DE PÓS-GRADUAÇÃO EM ODONTOLOGIA



FOLHA DE APROVAÇÃO

EFICÁCIA DO USO DE PLASMA EM PRESSÃO ATMOSFÉRICA NA ADESÃO DE CERÂMICAS ZIRCÔNIA

LILIAN CAPANEMA NOGUEIRA

Tese submetida à Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em Odontologia, como requisito para obtenção do grau de Doutor, área de concentração Clínica Odontológica.

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Belo Horizonte, 27 de julho de 2018.

Ao papai, **Carlos**, quanta saudade! Se hoje conquisto mais uma vitória, é porque um dia você esteve ao meu lado e me ensinou a lutar pelos meus sonhos. Viva sempre comigo em cada nova conquista!!!

À mamãe, **Helena**, pelas orações, por todo amor, educação, exemplo de simplicidade, caráter, persistência, carinho e dedicação que alguém pode necessitar.

À minha irmã, **Helen**, pela amizade sempre sincera e por ser presença tão marcante em minha vida. E por todos os dias me presentear com um lindo sorriso.

Ao meu filho, Gabriel, o maior presente que Deus poderia ter me dado nesta vida!

Amo muito vocês!

AGRADECIMENTOS

A *Deus* por me amparar nos momentos mais difíceis, dar-me força interior para superar as dificuldades, mostrar-me o caminho nas horas incertas e me suprir em todas as minhas necessidades.

Aos meus *familiares*, pelo apoio, incentivo e carinho.

Ao meu marido, *Antônio Carlos de Faria*, pela compreensão. O tempo todo ao meu lado, incondicionalmente. Nos momentos mais difíceis, que não foram raros neste último ano, sempre me fazendo acreditar que chegaria ao final desta difícil, porém gratificante etapa. Este período nos mostrou a verdade sobre nosso relacionamento: somos uma Família! Sou grata por cada gesto carinhoso, cada sorriso, e ansiosa por estar ao seu lado, com nosso filho, o resto da minha vida.

Ao Professor Dr. *Nelson Renato França Alves da Silva*, meu orientador, pela compreensão, pelos ensinamentos, confiança em meu trabalho, ou simplesmente pelo desejo de que tudo desse certo. Agradeço por cada palavra de apoio, por me incentivar a sempre buscar o melhor.

Ao Professor Dr. *Marcelo Giannini*, meu co-orientador, pelo acolhimento e disponibilidade na realização dos testes realizados no estudo, exemplo de competência, dedicação e profissionalismo.

Aos Professores, membros da banca, por enriquecerem este trabalho.

Aos Professores Dr. *Rodrigo Richard da Silveira* e Dr^a. *Karine Taís Aguiar Tavano*, por participarem da banca de qualificação e pela colaboração na execução do trabalho compartilhando o conhecimento.

Aos Professores e ao Programa de Pós-Graduação em Odontologia, pelos ensinamentos e por todos os momentos essenciais ao meu crescimento.

Às colegas Monize, Amanda, Marcela e Esther pela amizade, ajuda e por todos os momentos que passamos juntos.

À amiga, *Nayara Kelly Lyrio Ferraz*, pela agradável convivência, pela amizade e companheirismo, pelas conversas infundáveis, pelo conhecimento compartilhado e por ter em todos esses anos me proporcionado momentos de alegria e descontração.

Ao doutorando, *Gabriel Nima Bermejo*, pela disponibilidade, paciência e compreensão na realização dos testes realizados.

Ao funcionário do Laboratório, *Bruno*, pela disponibilidade em sempre ajudar.

A todos os meus amigos pelos bons momentos compartilhados.

À *Ivoclar Vivadent* pelo fornecimento dos materiais doados para a realização do estudo.

Ao Laboratório de Prótese Dentária, *Alexandre Franco*, pela atenção no serviço prestado.

A *UFMG*, Faculdade de Odontologia e ao Colegiado de Pós-graduação por terem fornecido as condições necessárias para realização desse trabalho...

À *Fundação de Amparo à Pesquisa de Minas Gerais (FAPEMIG)*, pela liberação de bolsas e recursos para o desenvolvimento da pesquisa.

E a todos que contribuíram direta ou indiretamente para a realização deste trabalho. O meu sincero MUITO OBRIGADA a todos!

*“Por vezes sentimos que aquilo que fazemos não é senão uma gota de água no mar.
Mas o mar seria menor se lhe faltasse uma gota.”*

Madre Teresa de Calcutá

Resumo

Um dos maiores desafios atuais da ciência dos materiais dentários é a obtenção de união efetiva e durável às cerâmicas de alto conteúdo cristalino. O objetivo do presente estudo foi avaliar a resistência de união, energia de superfície e tipos de fratura de dois sistemas cerâmicos após diferentes formas de tratamento de superfície associada à aplicação do plasma em pressão atmosférica. Para o estudo foram obtidas quarenta placas de zircônia (12 mm x 5 mm x 1,5 mm) de dois tipos de cerâmicas zircônia (E.max ZirCad e Calypso), polidas e limpas por ultrassom durante 5 minutos. Divididas aleatoriamente em 2 grupos de acordo com o sistema cerâmico e 4 subgrupos (n=5) de acordo com o tratamento de superfície, (I) controle (primer), (II) jateamento com partículas micrométricas de alumina (Al_2O_3) + primer, (III) jateamento com partículas micrométricas de alumina (Al_2O_3) + plasma + primer, (IV) plasma + primer. Foram confeccionados cento e vinte cilindros de resina composta (Z-100), utilizando matrizes cilíndricas (1,0 mm x 3,0 mm) cimentadas com cimento resinoso, Multilink N, sobre as placas de zircônia. Os espécimes foram armazenados em água destilada durante 24 horas a 37° C, depois testados para microcislamento em máquina de teste Shimadzu EZ a 1,0 mm/min. Os dados obtidos foram submetidos à análise estatística para comparação entre os grupos E.max e Calypso em relação à resistência à união (força/área – MPa), ângulo de contato e os tipos de fratura. Os dados foram analisados pelos testes ANOVA One-Way e Kruskal-Wallis para resistência de união ($p=0,003$) e ($p=0,005$) e ângulo de contato ($p<0,001$) e ($p<0,001$). Não houve diferença significativa para os dados de fratura ($p=0,145$), pelo teste qui-quadrado, com predomínio de fraturas mistas. Os valores de resistência de união das cerâmicas Y-TZP apresentaram maiores valores quando o plasma foi associado ao jateamento com óxido de alumínio e/ou primer e a aplicação somente do plasma não superou os valores alcançados pelas outras formas de tratamento da superfície. Essa associação resultou em menores valores dos ângulos de contato. Houve maior frequência de fraturas mistas quando realizado somente o tratamento com óxido de alumínio e quando em associação com o plasma.

Palavras-chave: Adesão. Microcislamento. Plasma em pressão atmosférica não térmico. Ângulo de contato. Energia de superfície. Y-TZP.

ABSTRACT

Efficacy of the use of plasma at atmospheric pressure in zirconia adhesion

One of the major challenges today in the science of dental materials is the achievement of effective and durable bonding to ceramics with high crystalline content. The objective of the present study was to evaluate the efficacy of plasma at atmospheric pressure in the adhesion of ceramic zirconia through the bond strength, surface energy and type of fracture of two ceramic systems after different forms of surface treatment associated with the application of plasma at atmospheric pressure. For the study forty zirconia plates (12 mm x 5 mm x 1.5 mm) were obtained from two zirconia ceramics (E.max ZirCad and Calypso), polished and cleaned by ultrasound for 5 minutes. Randomly divided into 2 groups according to the ceramic system and 4 subgroups (n = 5) according to the surface treatment, control (primer), primer + blasting with micrometric alumina (Al₂O₃) particles, primer + blasting with micrometric particles of alumina (Al₂O₃) + plasma, primer + plasma. One hundred and twenty cylinders of composite resin (Z-100) were made using cylindrical matrices (1.0 mm x 3.0 mm) cemented on the zirconia plates. The specimens were stored in distilled water for 24 hours at 37°C, then tested for microshear on a Shimadzu EZ test machine at 0.5 mm / min. The obtained data were submitted to statistical analysis for comparison between the E.max and Calypso groups in relation to the bond strength (strength / area - Mpa), contact angle and fracture types. The data were analyzed by ANOVA One-Way and Kruskal-Wallis tests for bond strength (p=0.003) and (p=0.005) and contact angle (p<0.001) and (p<0.001). There was no significant difference for the fracture data (p = 0.145), by the chi-square test, with a predominance of mixed fractures. The bond strength values of the Y-TZP ceramics showed higher values when the plasma was associated with blasting with aluminum oxide and / or primer and the application of only the plasma did not exceed the values reached by the other forms of surface treatment. This association resulted in lower values of contact angles. It is a higher frequency of mixed fractures when only aluminum oxide treatment is performed and when it is associated with plasma.

Keywords: Adhesion. Microshear. Plasma at non-thermal atmospheric pressure. Contact angle. Surface energy. Y-TZP.

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1 CONSIDERAÇÕES INICIAIS

A modificação da superfície de materiais cerâmicos é frequente quando estes são empregados na clínica odontológica, alterando a composição, estrutura e morfologia da camada mais externa, sem alterar as propriedades gerais dos materiais (Mehulic, Laus Susic, 2009). No processo de adesão entre materiais de naturezas diferentes, a modificação da superfície é um desafio para conseguir uma união efetiva entre o remanescente dentário e os diferentes materiais restauradores (Marshall et al., 2010).

As cerâmicas odontológicas reforçadas por óxido de zircônio possuem resistência e estética, mas são ácido-resistentes, ou seja, não são passíveis de condicionamento pelo ácido fluorídrico, como as porcelanas feldspáticas e vidros ceramizados (de Souza et al., 2010; Behr et al., 2011; Chen et al., 2013). Cerâmicas com baixo teor de sílica, especialmente a zircônia, tornaram-se um tópico de grande interesse no campo de próteses e implantes dentários (Thompson et al., 2011). Constatou ser um problema clínico o uso de componentes confeccionados de zircônia devido à dificuldade em conseguir adesão adequada com substratos sintéticos ou tecidos naturais. As estratégias adesivas tradicionais utilizadas com cerâmicas à base de sílica não tem a mesma eficácia com zircônia. Atualmente, várias alternativas estão sendo utilizadas para resolver este problema, e outras abordagens estão sob investigação (Piascik et al., 2009). O maior foco dos novos estudos relacionados à adesão da zircônia está principalmente na modificação de sua superfície inerte (Valandro et al., 2007; Amaral et al., 2008; Queiroz et al., 2012).

O tratamento de superfície consiste em modificar a superfície do substrato para melhorar o mecanismo adesivo destas cerâmicas ácido-resistentes. A utilização de tratamentos superficiais com base na retenção mecânica, adesão química ou ambas são propostos pela literatura (Della Bona et al., 2007; Thompson et al., 2011). Melhorar a durabilidade de união do cimento resinoso à zircônia ainda é um desafio para a comunidade científica, pois para que um tratamento seja efetivo, a mesma deve apresentar valores de resistência de união ≥ 20 Mpa (Papia et al., 2014).

Dentre os tratamentos que objetivam apenas modificar mecanicamente a superfície cerâmica, alterando a rugosidade superficial, apresenta-se o jateamento de micropartículas de alumina e o uso do laser (Thompson et al., 2011; Erdem et al., 2014). Há tratamentos de superfície que promovem a alteração química superficial, deixando o aderente mais reativo por meio de crescimentos de fluoretos, nitreto e

argônio a plasma (Külünk et al., 2013; Valverde et al., 2013). Outros tratamentos relatados na literatura consistem em tentar transformar a zircônia em uma cerâmica ácido-sensível, por meio de mecanismos adesivos mecânicos e químicos, a fim de utilizar o agente silano para gerar adesão entre o aderente e o cimento resinoso. Tal modificação superficial se dá com a implementação de sílica na superfície, por meio da ação de jateamentos de micropartículas de alumínio revestidas por sílica, *primers* cerâmicos e agentes silanos, uso da vitrificação e crescimento de sílica a plasma (Derand et al., 2005; Aboushelib et al., 2008; Ozcan et al., 2008; Smith et al., 2011; Thompson et al., 2011, Ntala et al., 2010; Lorenzoni et al., 2012). O agente de união silano é amplamente utilizado na clínica odontológica, constituído por moléculas bifuncionais, de natureza orgânica (reage com os cimentos resinosos e promove a formação de oligômeros) e inorgânica (reage com os óxidos metálicos da fase vítrea da cerâmica feldspática e produz ligações siloxanas), as quais são responsáveis pela união química cimento/cerâmica (Lung et al., 2012). A ação do silano não é eficaz nas cerâmicas de zircônia tetragonal policristalina estabilizada com ítrio (Y-TZP) sem a modificação da superfície, porque essas apresentam superfície relativamente apolar e quimicamente estável, comparado às cerâmicas ácido-sensíveis (Thompson et al., 2011; Valentino et al., 2012).

O jateamento de micropartículas de alumina revestidas por sílica consiste em um método de adesão mecânico/químico (tribosilicatização) que tem apresentado melhora significativa da resistência de união entre o substrato Y-TZP e o cimento resinoso (19,7 MPa), inclusive após condições de envelhecimento (Ozcan et al., 2008; Donassolo et al., 2009; Thompson et al., 2011). O efeito triboquímico gerado por este método cria uma camada de sílica, por meio do impacto da alta velocidade das partículas de alumina revestidas por sílica, que podem penetrar 15 µm no substrato; construindo um padrão topográfico de microrretenções para o embricamento mecânico com o cimento resinoso. A união química das superfícies recobertas por sílica e o material resinoso ocorre por meio do agente de união silano (Della Bona et al., 2007).

A limitação do tratamento supracitado é a formação de microfissuras na estrutura cerâmica (Thompson et al., 2011; Xie et al., 2013), induzindo a transformação da fase tetragonal para monoclinica, devido às camadas de tensão de compressão neutralizarem a propagação da falha (Della Bona et al., 2007). Assim ocorre a redução

da resistência mecânica e tenacidade à fratura deste material cerâmico, e risco de falha catastrófica prematura (Thompson et al., 2011; Xie et al., 2013). A difração de raio-x tem detectado que o jateamento de micropartículas de alumina revestidas por sílica (Rocatec TM Soft 30 µm, 3M ESPE, Seefeld, Alemanha) promove a alteração de fase tetragonal para monoclinica em 2,04% de volume da Y-TZP, enquanto que a zircônia não asperizada apresenta apenas 0,66% do volume em fase monoclinica (Yamaguchi et al., 2012); após 30 segundos essa mudança de fase aumenta em 9,11% do volume (CoJet 30 µm, 3M ESPE, Seefeld, Alemanha) (Turp et al., 2013).

Na tentativa da simplificação do uso desses promotores de adesão que apresentam silano e monômero fosfato em sua composição, adesivos universais são desenvolvidos para serem utilizados em diversos materiais restauradores. Tais agentes químicos podem promover a aderência às superfícies a base de sílica e/ou óxidos metálicos (Amaral et al., 2014). Novos agentes silanos com diferentes composições químicas são publicados na literatura (Aboushelib et al., 2008; Lung et al., 2012; Cheng et al., 2014). Entretanto, a resistência de união gerada pelo jateamento de micropartículas de alumina revestidas por sílica (CoJet 30 µm, 3M ESPE, Seefeld, Alemanha) (12,46 MPa) é superior aos valores encontrados pelos *primers* Z-Prime Plus (9,03 MPa) e Metal/Zirconia Primer (7,48 MPa) (Xie et al., 2013). *Primers* ou adesivos contendo MDP (metacriloiloxidecil dihidrogeno fosfato) e BisGMA (bisfenol glicidilmetacrilato) associados com jateamento parecem ser excelentes opções para a adesão da zircônia ao cimento resinoso (Lorenzoni et al., 2012; Chen et al., 2013; Amaral et al., 2014).

A vitrificação é um método de tratamento de superfície que utiliza o *glazer* cerâmico, adicionado de condicionamento ácido, para proporcionar uma superfície mais rugosa e porosa com a presença de sílica, que facilite a adesão de cimentos resinosos (Ntala et al., 2010). A literatura mostra que há superioridade de valores de resistência de união entre o uso da vitrificação associada ao condicionamento ácido (20,75 MPa) e ao jateamento (17,45 MPa) sem a ação do envelhecimento (Valentino et al., 2012); esta situação *in vitro* apresenta-se como uma tendência na literatura (Bottino et al., 2014). Em longo prazo, a vitrificação associada ao condicionamento ácido e cimento resinoso à base de MDP mostrou-se estável, sem alteração dos valores de resistência de união (Bottino et al., 2014). Uma falha deste tratamento de superfície é o destacamento entre a camada de *glazer* e a zircônia. Tal ocorrência se dá pela fraca união entre a camada de *glazer* e a zircônia, como também pode estar

relacionada com a incompatibilidade dos coeficientes de expansão térmica de ambas cerâmicas (Liu et al., 2014).

O crescimento de filmes finos a plasma, sobre a superfície da cerâmica Y-TZP, se mostra um tratamento de superfície promissor na resistência de união entre zircônia e cimento resinoso, embora poucas pesquisas abordem esse tipo de adesão química. Plasma é um gás total ou parcialmente ionizado, constituído por espécies carregadas (íons e elétrons), neutras (átomos e moléculas) e excitadas. De maneira geral, duas categorias de plasma podem ser definidas, os 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 (≥ 105 Pa) e altos níveis energéticos (acima de 50 MW), onde as partículas pesadas e leves apresentam o mesmo equilíbrio termodinâmico e conseqüentemente, o gás apresenta altíssimas temperaturas. Os plasmas de baixa temperatura são separados em dois grupos, os plasmas térmicos ou quasi-equilíbrio, e os plasmas não térmicos (PPA), 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 et al., 2008).

1.1 OBJETIVO GERAL

O objetivo deste estudo foi avaliar se diferentes formas de tratamento da superfície de dois sistemas cerâmicos de zircônia associada à aplicação do plasma em pressão atmosférica alteram a resistência de união e energia de superfície.

1.2 OBJETIVOS ESPECÍFICOS

- ✓ Avaliar a energia de superfície gerada sob a superfície de cerâmicas zircônia submetidas a diferentes formas de tratamento associada à aplicação do plasma em pressão atmosférica.
- ✓ Avaliar a resistência de união de superfícies cerâmicas submetidas a diferentes formas de tratamento de superfície associada à aplicação do plasma em pressão atmosférica.

- ✓ Avaliar diferenças nos modos de fratura dos espécimes após a aplicação do plasma em pressão atmosférica no teste de microcissalhamento.

2 METODOLOGIA EXPANDIDA

2.1 CÁLCULO DO TAMANHO AMOSTRAL

Considerando-se um nível de confiança de 95% e poder de 80%, realizou-se o cálculo amostral para comparação de duas médias utilizando como variável dependente do estudo a resistência de união do sistema de cimentação à cerâmica zircônia. Admitiu-se o desvio padrão de 7,4625²⁴ e uma diferença de 14,2 pontos na união das cerâmicas cimentadas utilizando o plasma em pressão atmosférica, diferença considerada clinicamente relevante. A amostra mínima necessária para o desenvolvimento do estudo foi de 4 espécimes por grupo. Para compensar possíveis perdas, foram acrescentados 20% ao cálculo, perfazendo um total de 5 espécimes por grupo, totalizando 40 espécimes para o estudo.

2.2 MATERIAIS

Para a realização deste estudo, foram utilizadas duas cerâmica à base de dióxido de zircônia estabilizada por ítrio (IPS e.max Zir-CAD – Ivoclar Vivadent e Calypso – Dental Direkt GmbH), jateamento com partículas micrométricas de alumina, primer monobond N (Ivoclar Vivadent, Schaan, Liechtenstein), plasma em pressão atmosférica, resina composta Filtek Z-100 (3M ESPE Dental Products, St. Paul, MN, USA), cimento resinoso (Multilink Speed – Ivoclar/Vivadent). As marcas comerciais e suas características estão apresentadas na Tabela 1.

Tabela 1 – Marca comercial, tipo do material, composição química e fabricante dos materiais que foram utilizados na pesquisa.

Marca comercial	Tipo do material	Composição química	Fabricante
IPS e.max Zir-CAD	Cerâmica	Óxido de zircônio (ZrO_2) 94,4%, ítrio (Y_2O_3) 5,4%, outros 0,2%	IPS e.max Zir-CAD blocks; IvoclarVivadentAG, Schaan, Liechtenstein
Calypso	Cerâmica	ZrO_2 (88-96%) , HfO_2 (1-5%) , Y_2O_3 (4-6%) , Al_2O_3 , outros óxidos < 0,25%	Dental Direkt GmbH, Germany
Óxido de alumínio 100 μm	Partículas	Óxido de alumínio	Micro-etcher ERC, Danville Engineering, San Ramon, CA, EUA
Multilink Speed	Cimento resinoso auto-adesivo	Matriz de monomer: dimetacrilatos e monômeros ácidos. Partículas inorgânicas: vidro de bário, trifluoreto de itérbio, copolímero e dióxido de silicone altamente disperso. Componentes adicionais: iniciadores, estabilizadores e pigmentos coloridos (<1%).	Ivoclar Vivadent, Liechtenstein
KinPen 09	Plasma em pressão atmosférica	Íons e elétrons Gás Argônio	Greifswald, Germany
Filtek Z-100	Resina composta	Micro-híbrida, matriz Orgânica Bis-GMA e TEGDMA, parte inorgânica possui Zircônia-Sílica	3M ESPE Dental Products, St. Paul, MN, USA
Monobond N	Primer	Solução alcoólica de metacrilato de silano, metacrilato do ácido fosfórico e metacrilato de sulfeto.	Ivoclar Vivadent, Schaan, Liechtenstein
Ácido fosfórico	Ácido	H_3PO_4	3M ESPE Dental Products, St. Paul, MN, USA

2.3 MÉTODO

O método adotado nesta pesquisa foi dividido em quatro etapas: Etapa 1- Confeção dos espécimes, tratamentos de superfície e cimentação; Etapa 2- Análise do ângulo de contato das superfícies cerâmicas à base de zircônia antes e após os tratamentos de superfície e a aplicação do plasma; Etapa 3- Análise da

resistência de união do conjunto zircônia e cimento resinoso; e Etapa 4 - Análise da superfície de fratura.

2.3.1 ETAPA 1: CONFECÇÃO DOS ESPÉCIMES, TRATAMENTOS DE SUPERFÍCIE E CIMENTAÇÃO

2.3.1.1 Confecção dos Espécimes

Para a realização do trabalho foram utilizados blocos de zircônia estabilizada por ítrio comercializadas IPS e.max Zir-CAD (blocks; Ivoclar Vivadent AG, Schaan, Liechtenstein) e Calypso (Dental Direkt GmbH, Germany), cimento resinoso auto-adesivo Multilink Speed (Ivoclar Vivadent).

Blocos desses sistemas na forma pré-sinterizada, foram seccionados com auxílio da máquina de corte (ISOMET 1000, Buehler Ltd., IL, EUA) e disco de alta concentração de diamante (Buehler Ltd., IL, EUA), sob constante refrigeração, a fim de obter 20 espécimes de cada sistema cerâmico com dimensões aproximadas de 12 x 5 x 1,5 mm. Em seguida os espécimes foram enviados a um laboratório credenciado pelas empresas fabricantes para o processo de sinterização, em forno específico para esta finalidade.

Após o processo de sinterização, os espécimes foram regularizados com lixas d'água em ordem decrescente de granulação 400, 600, 800, 1200 (3M, Sumaré, SP, Brasil), sob irrigação constante em politriz (Automet 250, Buehler Ltd., IL, EUA), para padronização da rugosidade inicial. Após o processo de polimento seguiu-se com limpeza em ultrassom (Lavadora Ultrassônica Digital Soni Clean 2PS, Santa Rita da Sapucaí, MG, Brasil) por 5 min em água destilada e por fim secagem em temperatura ambiente. Os corpos de resina composta totalizaram cento e vinte cilindros de resina composta (Z-100, 3M / ESPE, Sumaré, SP, Brasil), utilizando-se matrizes cilíndricas

de 1,0 mm de diâmetro e 3,0 mm de altura. Sobre uma placa de vidro, a resina composta foi introduzida na matriz em incremento único e fotoativada por 40s na porção superior e inferior, utilizando-se o fotoativador Bluephase (Ivoclar Vivadent), previamente calibrado. Depois de remover a matriz, o cilindro de resina composta foi novamente fotoativado por 4 sequências de 40s nas laterais. Estes espécimes sofreram o mesmo tratamento de regularização dado aos corpos de cerâmica. Em seguida houve uma distribuição aleatória dos cilindros de resina, de acordo com os sistemas cerâmicos e tratamentos de superfície. Para a aleatorização, os espécimes foram numerados de 1 a 40 e oito sequências aleatórias de 5 números foram geradas por um programa de computador (Excel).

2.3.1.2 Tratamento de superfície

Jateamento

Para os blocos cerâmicos que receberam o jateamento com partículas de óxido de alumínio (Al_2O_3) (100 μm) (PG 400; Harnisch&Rieth, Winterbach, Alemanha) foi realizado a 0,55 MPa pressão (SU-Alustral; Schuler-Dental, Ulm, Alemanha) durante 15 segundos a uma distância de 10 mm. Após o jateamento, as amostras foram limpas em ultrassom em água destilada por 5 minutos e secas.

Plasma em pressão atmosférica

Para o tratamento da superfície das cerâmicas com plasma em pressão atmosférica, o dispositivo PPA utilizado neste estudo consiste de uma unidade de mão (170 mm de comprimento, 20 mm de diâmetro, pesando 170 g) (Figura 1) ligado a uma fonte de alimentação de alta frequência (1,1 MHz, 06/02 kV pico-a-pico, a energia

do sistema 8W) gerando uma nuvem de plasma em pressão atmosférica. A unidade de mão tem um pino tipo eletrodo (1 mm de diâmetro) rodeado por um quartzo (1,6 mm capilar). A fonte PPA opera com argônio (Ar) um gás com taxa de fluxo de massa de 2 litros padrão por minuto (SLM). A nuvem de plasma emerge do bico de saída apresentado 1,5 mm de diâmetro e estendida para o ar circundante, para uma distância de 15 mm (Figura 2). Cada grupo recebeu 20 segundos de aplicação para o tratamento.

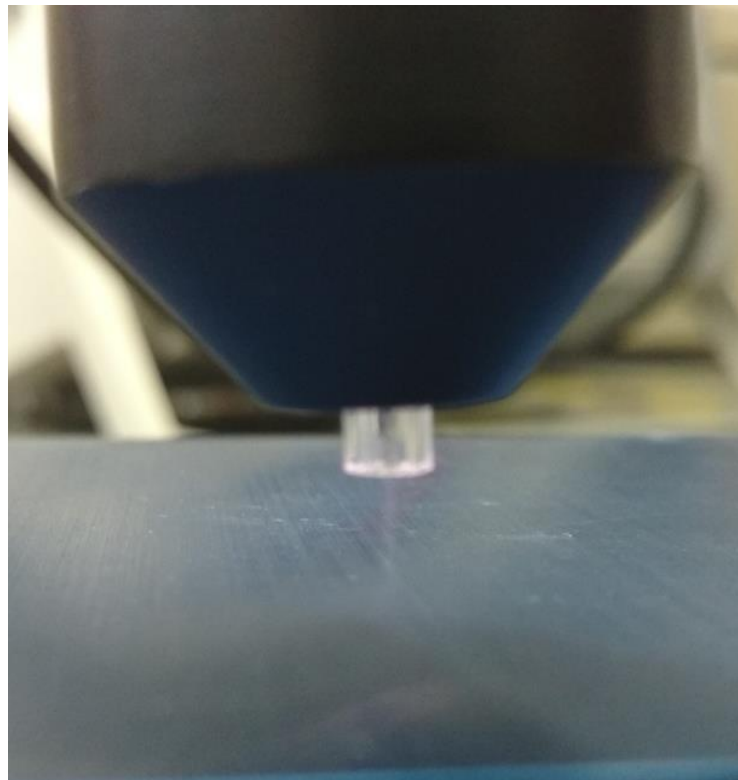


Figura 1 – Dispositivo do plasma em pressão atmosférica.

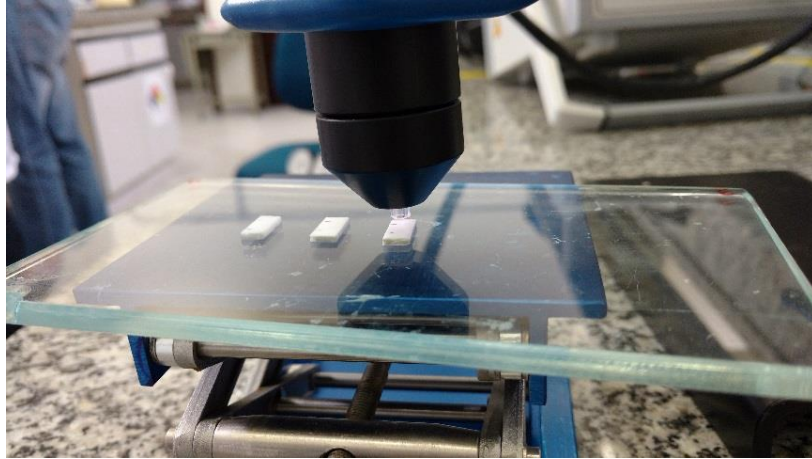


Figura 2 - Imagem mostra a caneta de plasma posicionada a 1,5 cm de distância da amostra. Distância de aplicação igual pode ser observada.

Aplicação do agente de união

A aplicação do agente de união (*primer*) foi realizada à temperatura de 20°C e umidade relativa do ar mantida em 40%. Foi aplicado o Monobond N (Ivoclar Vivadent, Schaaan, Liechtenstein) a todas as superfícies cerâmicas com um *microbrush* (KG Sorensen, Cotia, SP, Brasil) em contato friccional com a superfície cerâmica por 20s. O *primer* foi deixado em contato com a superfície por 60s (conforme recomendação do fabricante) para permitir reações químicas com a cerâmica. Após esse período, o excesso de *primer* foi removido com jato de ar livre de óleo a 2,8 bar por 10s antes da cimentação dos cilindros de resina composta.

2.3.1.3 Cimentação

Após aplicação do *primer*, o cimento resinoso auto-adesivo Multilink Speed (Ivoclar Vivadent) foi utilizado seguindo as recomendações do fabricante para cimentação dos cilindros de resina composta (Z-100) aos blocos de cerâmica zircônia previamente preparados.

Posteriormente, foi realizada a cimentação dos cilindros de resina composta sobre as placas zircônia em regiões delimitadas (Figura 3), com o auxílio de um bloco de papel e uma espátula plástica, sendo a pasta base e a pasta catalisadora manipuladas como sugerido pelo fabricante. Imediatamente após a total homogeneização da mistura, o cimento resinoso foi aplicado ao cilindro de resina e posicionado sobre a superfície de zircônia tratada, durante 5 minutos, sob pressão digital. O excesso de cimento foi removido e a fotoativação foi perpendicular à interface adesiva em 4 posições (40s cada a 600 mW/cm^2). Cada bloco cerâmico recebeu três cilindros de resina composta em sua superfície de forma equidistante.

Após a cimentação, os espécimes foram armazenados em água destilada e armazenados em estufa a $37^\circ\text{C} \pm 1^\circ\text{C}$ durante 24 horas.



Figura 3 - Cerâmica zircônia com regiões delimitadas para a cimentação dos cilindros de resina composta.

2.3.2 ETAPA 2: ANÁLISE DO ÂNGULO DE CONTATO DAS SUPERFÍCIES CERÂMICAS A BASE DE ZIRCÔNIA ANTES E APÓS OS TRATAMENTOS DE SUPERFÍCIE

Em cada subgrupo foram realizadas leituras, passo a passo do ângulo de contato segundo a Tabela 2.

Tabela 2 - Grupos experimentais de acordo com o tratamento de superfície para análise do ângulo de contato.

Grupos experimentais	Cerâmica	Tratamentos de superfície
Grupo 1	IPS e.max ZirCAD	Controle – sem primer
Grupo 2		Primer
Grupo 3		Jateamento com partículas micrométricas de alumina (Al_2O_3)
Grupo 4		Jateamento com partículas micrométricas de alumina (Al_2O_3) + primer
Grupo 5		Jateamento com partículas micrométricas de alumina (Al_2O_3) + plasma
Grupo 6		jateamento com partículas micrométricas de alumina (Al_2O_3) + plasma + primer
Grupo 7		Plasma + primer
Grupo 8		Plasma
Grupo 9		Calypso
Grupo 10	Primer	
Grupo 11	Jateamento com partículas micrométricas de alumina (Al_2O_3)	
Grupo 12	Jateamento com partículas micrométricas de alumina (Al_2O_3) + primer	
Grupo 13	Jateamento com partículas micrométricas de alumina (Al_2O_3) + plasma	
Grupo 14	jateamento com partículas micrométricas de alumina (Al_2O_3) + plasma + primer	
Grupo 15	Plasma + primer	
Grupo 16	Plasma	

A determinação do ângulo de contato foi realizada a temperatura ambiente (20°C) e sob controle da umidade relativa do ar (40%) sobre a superfície das cerâmicas zircônia após 5 segundos da gota de água destilada ter sido dispensada sobre o bloco de cerâmica. Esta análise foi realizada por um goniômetro (GBX

Instrumentation Scientifique, Romans, France) (Figura 4). As imagens foram então capturadas e o ângulo de contato determinado.

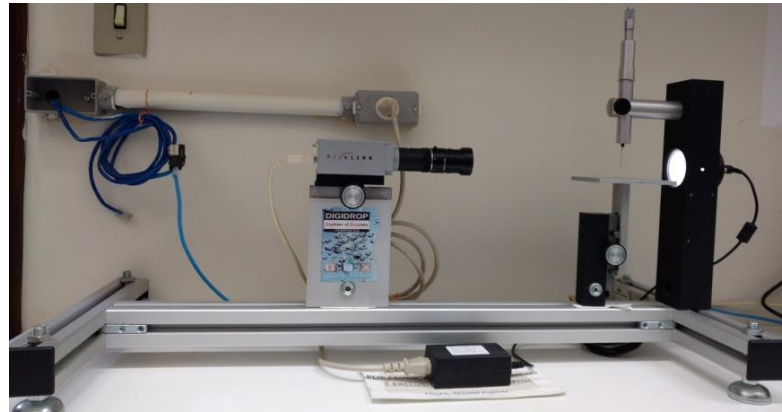


Figura 4 – Goniômetro (GBX Instrumentation Scientifique, France)

2.3.3 ETAPA 3: ANÁLISE DA RESISTÊNCIA ADESIVA DO CONJUNTO CERÂMICA ZIRCÔNIA E CIMENTO RESINOSO

Esta etapa do estudo foi composta por 8 grupos experimentais, cada qual com cinco espécimes ($n=5$), que representaram o tipo de sistema cerâmico (IPS e.max ZirCAD e Calypso), submetidos aos tratamentos de superfície (Grupo 1 - controle - primer / Grupo 2 - jateamento com partículas micrométricas de alumina + primer / Grupo 3 - jateamento com partículas micrométricas de alumina + plasma + primer / Grupo 4 - plasma + primer), aplicação do plasma em pressão atmosférica 20 segundos e cimentação com o cimento resinoso Multilink Speed.

Tabela 3 – Grupos experimentais conforme os fatores de estudo

Grupos experimentais	Cerâmica	Tratamentos de superfície	Cimento resinoso
Grupo 1 – controle	IPS e.max ZirCAD	controle – primer	MultilinkSpeed
Grupo 2		jateamento com partículas micrométricas de alumina (Al_2O_3) (SB) + primer	
Grupo 3		jateamento com partículas micrométricas de alumina (Al_2O_3) (SB) + PPA + primer	

Grupo 4		PPA + primer	
Grupo 5 – controle	Calypso	controle – primer	MultilinkSpeed
Grupo 6		jateamento com partículas micrométricas de alumina (Al_2O_3) (SB) + primer	
Grupo 7		jateamento com partículas micrométricas de alumina (Al_2O_3) (SB) + PPA + primer	
Grupo 8		PPA + primer	

Ensaio de Microcisalhamento

Para a realização do teste de microcisalhamento os espécimes foram posicionados em uma máquina de ensaio universal (EZ Test-S Shimadzu, Tokyo, Japão) e submetidos à aplicação de uma carga com velocidade de 1,0 mm/min perpendicular à interface adesiva até ocorrer a falha. O teste foi realizado utilizando-se um fio metálico de 0,20 mm de diâmetro e a resistência de união (em MPa) foi calculada dividindo-se a força (N) pela área aderida (mm²) (Figura 5).



Figura 5 – Espécime acoplado à máquina de ensaio universal (EZ Test - S Shimadzu, Tokyo, Japão)

2.3.4 ETAPA 4: ANÁLISE FRACTOGRÁFICA

Os modos de falha foram classificados da seguinte forma: falha adesiva quando a falha apresentou menos de 1/3 do material de cimentação na superfície da cerâmica, falha coesiva quando a fratura ocorreu no corpo do cimento cobrindo mais que 2/3 da superfície da cerâmica e falhas mistas quando as falhas adesiva e coesiva ocorreram simultaneamente e as fraturas demonstraram mais de 1/3 do material de cimentação e menos de 2/3 na superfície da cerâmica (Lung *et al.*,2012). Espécimes representativos de cada grupo foram montados em *stubs* e revestidos com ouro em metalizadora (BAL-TEC SCD 500, Sputter Coater, Liechtenstein) e caracterizados por microscopia eletrônica de varredura (MEV) (SEM; VP-435; Leo, Cambridge, Reino Unido).

2.4 ANÁLISE ESTATÍSTICA

Os dados obtidos foram tabulados utilizando-se o Software StatisticalPackage for Social Science (SPSS for Windows, version 24.0; SPSS Inc., Chicago, Ill., USA), submetidos à análise estatística para comparação entre os grupos dos sistemas cerâmicos E.max e Calypso em relação à resistência à união, ângulo de contato e os tipos de fratura. A resistência à união foi relacionada com a força/área (MPa) aplicada aos espécimes.

Os dados para ângulo de contato foram analisados por meio do teste ANOVA um fator seguido pelo teste de Tukey para múltiplas comparações nos grupos G1, G2, G3, G5, G6, G7, G9, G10, G11, G12, G14, G15. E Kruskal-Wallis seguido pelo teste de Mann-Whitney para os grupos G4, G8, G13 e G16. O nível de significância adotado foi de 5%.

Os dados para resistência à união também foram analisados pela ANOVA um fator seguido pelo teste de Tukey para múltiplas comparações nos grupos G1, G2, G4, G5, G6 e G7. E Kruskal-Wallis seguido pelo teste de Mann-Whitney para os grupos G3 e G8. O nível de significância adotado foi de 5%.

Os tipos de fratura das superfícies cerâmicas foram analisados pelo teste qui-quadrado.

**3 ARTIGO SUBMETIDO À REVISTA JOURNAL OF BIOMEDICAL MATERIALS
RESEARCH – PART B – APPLIED BIOMATERIALS**

***Efficacy of using atmospheric pressure plasma in zirconia-based ceramic
adhesion***

TITLE PAGE

**Efficacy of using atmospheric pressure plasma in zirconia-based ceramic
adhesion**

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Efficacy of using atmospheric pressure plasma in zirconia-based ceramic adhesion

Abstract

Aim: To assess the bond strength and surface energy of two ceramic systems after different treatments combined with applying non-thermal atmospheric pressure plasma.

Materials and Methods: Forty ceramic system plates (12×5×1.5 mm) of two zirconia-based ceramics (E.maxZirCad/Calypso) were prepared. Were randomly divided into 2 groups by ceramic system and 4 subgroups (n=5) by surface treatment. One hundred twenty composite resin cylinders were prepared using cylindrical matrices cemented onto zirconia plates.

Results: The findings were statistically analyzed to compare the ceramics groups for bond strength, contact angle and fracture types. The data were subjected to one-way analysis of variance (ANOVA) and the Kruskal-Wallis test, with $p=0.003$ and $p=0.005$, respectively, for bond strength and $p<0.001$ for contact angle. Significant differences were observed for both tests; the chi-squared test showed no significant differences in the fracture data ($p=0.145$), which were predominantly mixed fractures.

Conclusion: The bond strengths of the zirconia (Y-TZP) increased when plasma was combined with aluminum oxide sandblasting and/or primer, and applying plasma and primer failed to exceed the values achieved by other surface treatments. This combination resulted in smaller contact angle values. The frequency of mixed fractures increased when aluminum oxide treatment was performed alone and when combined with plasma.

Keywords: Adhesion. Microshear. Plasma at non-thermal atmospheric pressure.
Contact angle. Surface energy. Y-TZP.

INTRODUCTION

A challenge in dental material science is to effectively and durably bond ceramics with a high crystalline content to the cementation system. Surface treatments aiming to increase chemical and micromechanical retention, such as acid etching and sandblasting, have been proposed, but these surface treatments are inapplicable to these types of ceramics due to the lack of a vitreous phase that can be attacked by acids or because they are too hard, which prevents effective abrasion by aluminum oxide particles.¹

Changing ceramic material surfaces is a common procedure when ceramics are used in dental clinics. This step usually changes the composition, structure and morphology of the outermost layer without affecting the general properties of the materials.^{2, 3}

Efficient bonding to ceramics is usually based on the combination of micromechanical retention and chemical bonding.⁴ Zirconia-based ceramic systems have shown promising results due to their physical properties for dental restorations;^{5,6} however, these systems fail to adequately respond to the proposed treatments for suitable bonding.⁷ A method was previously developed for simultaneously achieving micromechanical retention and chemical bonding based on the increased ceramic surface roughness by sandblasting with micrometric alumina (Al_2O_3) or silica-coated alumina (silicatization) particles.^{8,9} Studies show that silicatization combined with the use of silane and resin cement with the 10-methacryloyloxydecyl dihydrogen phosphate (MDP) monomer improves the bond strength between the zirconia and the cementing agent even after the interface is aged by thermocycling.¹⁰ Applying 30- μm silica-coated aluminum oxide particles to zirconia using the Cojet Intraoral Adhesive

Repair System (3M-ESPE) enhances silica incrustation in its structure, thereby strengthening the chemical bond to the agent silane agente.^{11,12}

The literature warns of the impact of sandblasting particles on ceramic zirconia, which can generate micro-cracks and structural defects, transforming tetragonal zirconia into monoclinic zirconia, thus partly compromising its strength in fatigue tests.¹³ Several authors focused on improving adhesion between the resin cement and the zirconia ceramic-based substrate with high crystalline content, proposing alternative surface treatments to modify the ceramic surface energy or the texture by abrasion to increase the adhesion area or improve mechanical microretention.¹³⁻¹⁷

Changes in adherent roughness yield changes in the outer area and wettability of the area subjected to abrasion. These changes are directly related to surface energy and adhesion potential.¹⁸ Substrate wettability is defined as the ability of a liquid component to effectively penetrate a substrate³ and is expressed as relative interfacial tension, in this case, between an adhesive and a solid substrate, resulting in a contact angle $< 90^\circ$. Perfect wetting ($\sim 0^\circ$) is the ability of a fluid to completely cover the substrate, thus maximizing the benefit from activating the adhesion mechanism because a smaller angle results in higher wettability and greater adhesion potential. Low wettability and reduced adhesion potential occur when the contact angle is larger than 90° .¹⁸

An alternative approach based on changing the zirconia surface is to use atmospheric pressure plasma (APP) to optimize chemical bonding at the zirconia ceramic interface for cementation procedures.¹⁹ Plasma is considered the fourth state of matter (in addition to solid, liquid and gas). More than 99% of matter in the universe consists of plasma, which has broad industrial and medical applications.^{20,21} The development of a new device that generates non-thermal atmospheric pressure

plasma (NTAPP) has expanded the potential applications of plasma, especially in biological and health sciences.^{20,21} Since 2000, this technology has attracted increasing interest and is widely used in biomedical applications, including sterilization processes, eukaryotic cell treatments, wound healing, blood coagulation, and dental applications.^{20,21}

APP is a partly ionized gas that provides many chemically active elements, such as O₃, OH, H₂O₂, NO and OH radicals, at low temperatures.^{22,23} By changing the functional groups of a material, these chemically active species can transform a non-reactive into a reactive surface without affecting the properties of the material.²⁴ Normally, the surface energy (SE) of a material increases after applying APP, and evidence shows that increased zirconia SE may enhance bonding without adversely affecting its structure.²⁵

Other adhesion strategies are necessary to improve the ceramic cementing method. Applying APP to the surface treatment of zirconia-based ceramics may be a promising approach because it is simple, modern and minimally invasive with no effect on the mechanical properties of the material. Therefore, this study assessed whether different surface treatments of two zirconia-based ceramic systems combined with APP application would change the bond strength and surface energy. Furthermore, this study tested the hypothesis that 20 s of APP increases (1) the surface energy of zirconia ceramics and (2) the bond strength of zirconia surfaces when subjected to different treatments with applied APP.

MATERIALS AND METHODS

Sample size calculation

Considering a 95% confidence level and 80% power, the sample size for comparing two means was calculated using the bond strength of the zirconia ceramic to the cementing system as the dependent variable. A 7.4625 standard deviation²⁴ and a 14.2 difference (considered clinically relevant) in cemented ceramic bonding using APP were admitted. The minimum required sample size was 4 specimens per group. To compensate for possible losses, the sample was increased by 20% (5 specimens per group), totaling 40 specimens for the study.

SPECIMEN PREPARATION, SURFACE TREATMENTS AND CEMENTATION

Specimen preparation

IPS e.max Zir-CAD yttria-stabilized zirconia blocks (blocks; Ivoclar Vivadent AG, Schaan, Liechtenstein) and Calypso (Dental Direkt GmbH, Germany) and Multilink Speed self-adhesive resin cement (Ivoclar Vivadent) were used to conduct the study.

Pre-sintered blocks from these systems were sectioned using a precision sectioning saw (ISOMET 1000, Buehler Ltd., IL, USA) and a high-concentration diamond disk (Buehler Ltd., IL, USA) under constant refrigeration to prepare 20 approximately 12 × 5 × 1.5 mm specimens of each ceramic system. The specimens were then sent to a laboratory accredited by the manufacturing companies for sintering in a purposed oven.

After sintering, the specimens were finished with 400-, 600-, 800-, and 1200-grit dental abrasive strips in descending order of granulation (3M, Sumaré, SP, Brazil) under constant irrigation using a grinder-polisher (Automet 250, Buehler Ltd., IL, USA) to standardize the initial roughness. After polishing, the specimens were cleaned in an

ultrasonic bath (Digital Ultrasonic Cleaner Soni Clean 2PS, Santa Rita da Sapucaí, MG, Brazil) for 5 min in distilled water and then dried at room temperature. In total, one hundred twenty cylinders of composite resin (Z-100, 3M-ESPE, Sumaré, SP, Brazil) were prepared using cylindrical matrices of 1.0 mm in diameter and 3.0 mm in height. On a glass plate, the composite resin was introduced into the matrix in a single increment and photoactivated for 40 s in the upper and lower portions using a previously calibrated Bluephase LED unit (Ivoclar Vivadent). After removing the matrix, the composite resin cylinder was photoactivated again in four 40-s sequences on the sides. These specimens were subjected to the same finishing treatment as the ceramic bodies. Next, the resin cylinders were randomly distributed by ceramic system and surface treatment. For randomization, the specimens were numbered from 1 to 40, and eight random 5-number sequences were generated using Microsoft Excel.

Surface treatments

Sandblasting

Ceramic blocks were sandblasted with aluminum oxide particles (Al_2O_3) (100 μm) (PG 400; Harnisch & Rieth, Winterbach, Germany) at 0.55 MPa (SU-Alustral; Schuler-Dental, Ulm, Germany) for 15 seconds at 10 mm. After sandblasting, the samples were cleaned in an ultrasonic bath in distilled water for 5 minutes and dried.

Non-thermal atmospheric pressure plasma

For surface treating ceramics with atmospheric pressure plasma, the APP device used in this study consisted of a handheld unit (170 mm in length, 20 mm in diameter, 170 g) (Figure 1) connected to a high-frequency power supply (1.1 MHz, 06/02 kV peak to peak, 8 W power) generating a plasma cloud at atmospheric pressure. The handheld unit had a pin electrode (1 mm in diameter) surrounded by a

quartz (1.6-mm capillary). The APP source operated with argon (Ar), a gas with a mass flow rate of 2 standard liters per minute (SLM). The plasma cloud jets from a nozzle of 1.5 mm in diameter and expands into the surrounding air up to 15 mm (Figure 2). Each group was treated for 20 seconds.

Bonding agent application

The bonding agent (primer) was applied at 20°C, and the relative humidity was maintained at 40%. Monobond N (Ivoclar Vivadent, Schaan, Liechtenstein) was applied to all ceramic surfaces with a microbrush (KG Sorensen, Cotia, SP, Brazil) in frictional contact with the ceramic surface for 20 s. The primer was left in contact with the surface for 60 s (as recommended by the manufacturer) to allow chemical reactions with the ceramic. Next, the excess primer was removed with oil-free air at 2.8 bar for 10 s before cementing the composite resin cylinders.

Cementation

After applying the primer, the Multilink Speed self-adhesive resin cement (Ivoclar Vivadent) was used per the manufacturer's recommendations for cementing the composite resin cylinders (Z-100) to the previously prepared zirconia ceramic blocks.

Composite resin cylinders were then cemented to zirconia plates in outlined sections using paper pieces and a plastic spatula, and the base paste and catalyst paste were handled per the manufacturer's instructions. Immediately after the blend was completely homogenized, the resin cement was applied to the resin cylinder and positioned on the treated zirconia surface under finger pressure for 5 minutes. The excess cement was removed, and the cylinder was photoactivated perpendicularly to

the adhesive interface at 4 positions (40 s each at 600 mW/cm²). Three composite resin cylinders were equidistantly cemented to each ceramic block surface.

After cementation, the specimens were stored in distilled water and incubated in an oven at 37 ± 1°C for 24 hours.

ANALYSIS OF THE CONTACT ANGLE OF THE ZIRCONIA-BASED CERAMIC SURFACES BEFORE AND AFTER SURFACE TREATMENTS

To analyze the contact angle, 2 readings were taken per specimen per group for both ceramic systems, as shown in Table 2. The contact angle was determined at room temperature (20°C) under controlled relative humidity (40%) on the zirconia ceramic surface 5 seconds after dispensing a drop of distilled water onto the ceramic block. This analysis was performed using a goniometer (GBX Instrumentation Scientifique, Romans, France). Images were acquired, and then the contact angle was determined.

ANALYSIS OF THE BOND STRENGTH BETWEEN THE CEMENT RESIN AND ZIRCONIA

This stage of the study consisted of 8 experimental groups, each with five specimens (n=5) representing the ceramic system type (IPS e.max ZirCad and Calypso), and subjected to surface treatments (Group 1 - control + primer; Group 2 - sandblasting with micrometric alumina particles + primer; Group 3 - sandblasting with micrometric alumina particles + plasma + primer; and Group 4 - plasma + primer), atmospheric pressure plasma application for 20 seconds and cementation with Multilink Speed self-adhesive, self-curing composite resin cement.

For the microshear test, the specimens were placed in a universal testing machine (EZ Test-S Shimadzu, Tokyo, Japan) and subjected to a 1.0-mm/min load

perpendicular to the adhesion interface until failure. The test was performed using a 0.20-mm diameter metal wire, and bond strength (in MPa) was calculated by dividing the force (N) by the adhesion area (mm²) (Figure 3).

FRACTOGRAPHIC ANALYSIS

Failure modes were classified as follows: adhesive failure occurred when the failure showed less than 1/3 of the cementation material on the ceramic surface, cohesive failure occurred when the fracture occurred in the cement body covering more than 2/3 of the ceramic surface, and mixed failure occurred when the adhesive and cohesive failures occurred simultaneously, and fractures showed more than 1/3 of the cementation material and less than 2/3 of the ceramic surface.²⁶ Specimens representative of each group were assembled in stubs, coated with gold in a metallizer (BAL-TEC SCD 500, Sputter Coater, Liechtenstein) and characterized by scanning electron microscopy (SEM) (SEM; VP-435; Leo, Cambridge, United Kingdom).

STATISTICAL ANALYSIS

Data were analyzed using the Software Statistical Package for Social Science (SPSS for Windows, version 24.0, SPSS Inc., Chicago, Ill., USA), and the E.max and Calypso ceramic systems were compared for bond strength, contact angle and fracture types. Bond strength considered the force/area (MPa) applied to the specimens.

Contact angle data were analyzed using a one-way analysis of variance (ANOVA) followed by the Tukey test for multiple comparisons among groups G1, G2, G5, G6, G7, G9, G10, G11, G12, G14 and G15 and the Kruskal-Wallis test followed by the Mann-Whitney test for groups G4, G8, G13 and G16. The significance level was set at 5%.

Bond strength data were analyzed by one-way ANOVA followed by the Tukey test for multiple comparisons among groups G1, G2, G4, G5, G6 and G7 and by the Kruskal-Wallis test followed by the Mann-Whitney test for groups G3 and G8. The significance level was set at 5%. The ceramic surface fracture types were analyzed using the chi-square test.

RESULTS

The comparison between contact angles in the E.max ceramic system outlined in Table 3, showed significant differences per one-way ANOVA ($p < 0.001$) and the Kruskal-Wallis ($p < 0.001$) test. The Tukey and Mann-Whitney tests showed significant differences between groups G1 and G5; G3 and G4; G4 and G5; G5 and G8; and G8 and G5.

In evaluating the mean contact angles of the Calypso ceramic system outlined in Table 4, one-way ANOVA ($p < 0.001$) and the Kruskal-Wallis ($p < 0.001$) test showed significant differences. The Tukey and Mann-Whitney tests showed significant differences between groups G9 and G 16; G10 and G16; G15 and G16; G16 and G9; G16 and G10; and G16 and G15.

Comparing the E.max and Calypso ceramic systems outlined in Table 5 showed significant differences on the one-way ANOVA ($p < 0.001$) and Kruskal-Wallis ($p < 0.001$) test. In the Tukey and Mann-Whitney tests, significant differences were detected between groups G1 and G13; G1 and G16; G2 and G16; G3 and G16; G4 and G13; G4 and G16; G5 and G9; G5 and G10; G5 and G12; G5 and G14; G5 and G15; G6 and G16; and G8 and G16.

Table 6 outlines the comparison of mean microshear bond strength (MPa) between the E.max and Calypso ceramic systems, which showed significant differences on the one-way ANOVA ($p=0.003$) and Kruskal-Wallis ($p=0.005$) test. The Tukey and Mann-Whitney tests showed significant differences in bond strength between groups G2 and G4; G3 and G4; G3 and G8; G4 and G3; G6 and G4; and G8 and G3.

Fractographic analysis enabled identifying the fracture type. The fracture mode distribution is outlined in Table 7. No significant differences were found between surface treatment ($p=0.145$) types per the chi-squared test. Mixed fractures prevailed in all groups (Figures 4 and 5).

DISCUSSION

These findings allowed the analysis of the postulated hypotheses. The accepted hypothesis was that applying non-thermal atmospheric pressure plasma combined with aluminum oxide sandblasting and/or primer on zirconia would increase the surface energy and bond strength of this ceramic, and the rejected hypothesis was that applying plasma on the zirconia ceramic surface alone would not be as effective as that when combined with other treatments. This study assessed surface energy by measuring contact angle, bond strength and fractography. No protocol has been established on the best surface treatment for zirconia (Y-TZP) bonding to resin cement; therefore, APP may be an alternative solution for adhesion-related clinical problems.^{25,27}

Treatment with plasma using argon, an inert gas, has been widely used to modify biomaterial surfaces. When activated electronically in the plasma state, argon

APP consists of several energetically and chemically reactive species, including high-energy electrons and electronically excited neutrons and free radicals.²⁸ These reactive species in argon plasmas can chemically modify substrate surfaces without affecting the properties of the material body. Treatment with argon plasma increases surface hydrophilicity and wettability.^{28,29}

Surface energy (SE) is a direct manifestation of intermolecular or interatomic forces, and the SE of a material is usually calculated by measuring the contact angles of liquids on those surfaces typically used with known surface tension values from which the surface energy of the solid can be measured. Thus, the values of polar and dispersive components from new molecular interactions, such as dipole-dipole interactions, hydrogen bonding and London dispersion forces, can be calculated.³⁰ Using atmospheric pressure plasma increases the zirconia surface reactivity, rendering it more hydrophilic and decreasing the contact angle by increasing the wettability relative to the zirconia without surface treatment.^{23,18,17,25} These data are consistent with those of the present study when using E.max zirconia and applying plasma combined with aluminum oxide (Al_2O_3) sandblasting (G5 - Al_2O_3 + plasma) (0.00 ± 0.00) and subsequently applying the monobond primer (G7 - primer + plasma) (25.72 ± 16.47). Conversely, not using plasma on the untreated control group, increased the mean contact angle (41.80 ± 8.44) (Table 3). Lower mean contact angles were observed in the Calypso zirconia groups both when applying plasma with aluminum oxide (G13 - Al_2O_3 + plasma) sandblasting (12.70 ± 19.01) and applying plasma (G16) alone (5.74 ± 12.83). The highest mean contact angle was found in the untreated control group (42.76 ± 8.54) (Table 4), possibly because plasma deposition enhances forming a reactive layer on the zirconia, rendering it more hydrophilic than zirconia without surface treatment^{24, 25,19,31}. The increased bond strength covers

zirconia with more reactive sites, which favor the adhesive potential of the ceramic, thereby increasing the number of covalent bonds to the resin cement.^{32,25} In addition, one report in the literature characterized the surface to assess the effects of exposure to APP on Ti and on Y-TZP and showed that plasma treatment increased the surface energy concomitantly with increased treatment time.^{23,33}

Because zirconia has no vitreous phase, it is not susceptible to etching from hydrofluoric acid. In contrast to feldspar porcelain, adhesion to zirconia ceramics is more difficult, and different surface treatments were tested to improve adhesion. Treatment with APP alters the surface in some materials, facilitating peroxide radical formation (R-O-O).^{34-36,23} Functional groups on the altered surface of the zirconia may combine with the phosphate radical (C=O) on the resin cement, thus increasing bond strength between the cement and zirconia.³⁷ Changes in the zirconia surface resulting from plasma deposition are promising, but they are affected by changes in the reactor, deposition parameters, precursor gas and reaction by-products,³² unlike the sandblasting method, which is easily applied and inexpensive, although sandblasting may cause or aggravate failures in the zirconia structure.¹³

In the present study, combining APP application + sandblasting with aluminum oxide + primer increased the bond strength values, as shown in the groups E.max zirconia G3 (71.87 ± 11.38) and Calypso zirconia G7 (62.21 ± 10.35) (Table 6). These data corroborate the study conducted by Valverde and colleagues in 2013, who detected a significantly increased bond strength of Y-TZP surfaces when applying APP alone or with aluminum oxide (Al_2O_3) sandblasting.^{25,33} This is likely explained by the presence of O_2 in the plasma device gas, which enhances forming active peroxide radicals (R-O-O-). These radicals promote chemical changes, even in inert materials,

such as high crystalline ceramics, and incorporate additional functional groups (C-O, C-OH) onto the top layer of the treated surface.²⁴

Higher bond strength values were also observed in groups treated with Al₂O₃ + primer both in E.max (G2 - 70.78 ± 16.36) and Calypso (G6 - 76.57 ± 10.66) zirconia (Table 6) because the sandblasting effect also involves physicochemical changes on the zirconia surface.³⁸ Other studies using APP treatment found significantly higher bond strengths in the APP treatment groups than in the untreated groups.^{4,39,34,40,41} Reports published in the literature show that applying sandblasting + primer and/or phosphate fails to improve bond strength when using plasma. Conversely, when APP was not applied, those adhesion agents played key roles in the resulting bond strength.^{34,4,39,40}

Bond strength varied as a function of the surface treatment; however, analyzing the fracture modes showed that most failures in the zirconia ceramic surface were classified as mixed failures, particularly in groups treated by combining aluminum oxide sandblasting and APP in both zirconia types (Table 7). This result is similar to previous findings in which mixed fracture modes observed in plasma-treated groups were higher than 95%.²⁵ Other studies showed higher rates of adhesion failure,^{33,41} although per Seker and colleagues (2015), mixed failures were more frequent in groups with the highest bond strength values on the microshear test.³³

Because this study was performed *in vitro*, there are some limitations, including adhesion to a flattened surface area and a lack of oral cavity moisture, shear test parameters and longitudinal bond strength data. These limitations may change the interpretation of the results, although these tests suggest scientific evidence for clinical practice. Based on the abovementioned findings, additional studies should be

conducted to address plasma application in controlled clinical trials in order to assess its clinical applicability in adhesion procedures.

CONCLUSION

Based on the method and findings of the present study, we conclude that wettability increased when APP was applied and when APP application was combined with aluminum oxide sandblasting and/or primer on E.max and Calypso zirconia surfaces. The bond strengths of both ceramics increased when plasma was combined with aluminum oxide sandblasting and/or primer, and treatment with plasma and primer failed to surpass the values reached by other zirconia surface treatments. Mixed fractures were more frequent in groups surface treated with aluminum oxide blasting and sandblasting combined with atmospheric pressure plasma.

ACKNOWLEDGMENT

The authors thank FAPEMIG (FAPEMIG Process nº 5.308/15) for their financial support for the study. Thanks to Prof. Dr. Marcelo Giannini (CNPq Process 307217 / 2014-0) and the doctoral student Gabriel Nima Bermejo, FOP - UNICAMP, for the reception and availability of the tests carried out in the study. The authors are grateful to Ivoclar Vivadent for providing the donated materials for the study.

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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Tables

Table 1: Experimental groups according to study factors

Experimental groups	Ceramic	Surface Treatments	Resin cement
Group 1 – control		control – primer	
Group 2	IPS	blasting with micrometric alumina particles	MultilinkSpeed
	e.max	(Al ₂ O ₃) (SB) + primer	
Group 3	ZirCAD	blasting with micrometric alumina particles	
		(Al ₂ O ₃) (SB) + PPA + primer	
Group 4		primer + PPA	
Group 5 – control		control – primer	
Group 6		blasting with micrometric alumina particles	
	Calypso	(Al ₂ O ₃) (SB) + primer	MultilinkSpeed
Group 7		blasting with micrometric alumina particles	
		(Al ₂ O ₃) (SB) + PPA + primer	
Group 8		PPA + primer	

Table 2: Experimental groups according to surface treatment for contact angle analysis

Experimental groups	Ceramic	Surface Treatments
Group 1		Control – primer
Group 2	IPS e.max	Primer
Group 3	ZirCAD	Blasting with micrometric alumina particles (Al_2O_3)
Group 4		Blasting with micrometric alumina particles (Al_2O_3) + primer
Group 5		Blasting with micrometric alumina particles (Al_2O_3) + PPA
Group 6		Blasting with micrometric alumina particles (Al_2O_3) + PPA + primer
Group 7		PPA + primer
Group 8		PPA
Group 9		Control – primer
Group 10		Primer
Group 11		Blasting with micrometric alumina particles (Al_2O_3)
Group 12		Blasting with micrometric alumina particles (Al_2O_3) + primer
Group 13	Calypso	Blasting with micrometric alumina particles (Al_2O_3) + PPA
Group 14		Blasting with micrometric alumina particles (Al_2O_3) + PPA + primer
Group 15		PPA + primer
Group 16		PPA

Table 3: Comparison of the contact angle between groups with the E-max ceramic by the one-way test Anova and post-hoc of Tukey.

Groups (n=5)	Contact angle											
	Contact angle (mean \pm SD ¹)	CJ ² at 95%		P value Post hoc								
		Lower	Upper	G1	G2	G3	G4	G5	G6	G7	G8	
E-max												
G1- Control without primer	41.80 \pm 8.44	31.3 1	52.2 8	-	0.99	0.95	1.00	0.00 2	1.00	0.92	1.0 0	
G2 – Primer	29.42 \pm 9.23	17.9 5	40.8 8	0.99	-	1.00	0.87	0.12	1.00	1.00	0.9 9	
G3 - Al₂O₃	26.60 \pm 9.05	15.3 5	37.8 4	0.95	1.00	-	0.69	0.24	1.00	1.00	0.9 6	
G4 - Al₂O₃ + primer¹	46.82 \pm 11.30	32.7 7	60.8 6	<0.001 <0.001*	0.22 **	0.56 **	0.03 6**	-	0.00 5**	0.04 7**	0.04 7**	0.1 7**
G5 - Al₂O₃ + PPA	0.00	0.00	0.00		0.00 2	0.12	0.24	<0.0 01	-	0.51	0.29	0.0 03
G6 - Al₂O₃ + PPA+ primer	32.76 \pm 11.66	18.2 8	47.2 3		1.00	1.00	1.00	0.97 1	0.05	-	1.00	1.0 0
G7 – PPA + primer	25.72 \pm 16.47	5.26	46.1 7		0.92	1.00	1.00	0.63	0.29	1.00	-	0.9 4
G8 - PPA¹	41.28 \pm 39.91	-8.28	90.8 4		0.17 **	0.67 **	0.83 **	0.17 **	0.00 5**	0.46 *	0.83 **	-

Non-normal distribution¹ Kruskal Wallis^{1*} Post hoc Mann-Whitney^{1**}

Table 4: Comparison of contact angle between groups with Calypso ceramics by the one-way test Anova and post-hoc of Tukey.

Groups (n=5)	Contact angle											
	Contact angle (mean ± SD ¹)	CI ² at 95%		P value	P value Post hoc							
		Lower	Upper		G9	G10	G11	G12	G13	G14	G15	G16
Calypso												
G9 - Control without primer	42.76 ± 8.54	31.31	52.28		-	1.00	0.99	1.00	0.10	1.00	1.00	0.013
G10 - Primer	38.74 ± 11.29	24.71	52.76		1.00	-	1.00	1.00	0.27	1.00	1.00	0.047
G11 - Al₂O₃	31.92 ± 8.03	21.95	41.89		0.99	1.00	-	0.53	0.76	1.00	1.00	0.27
G12 - Al₂O₃ + primer	35.06 ± 9.02	23.86	46.25		1.00	1.00	1.00	-	0.53	1.00	1.00	0.13
G13 - Al₂O₃ + PPA¹	12.70 ± 19.01	-10.90	36.30	<0.001*	0.045**	0.045**	0.072**	0.072**	-	0.045**	0.045**	0.52*
G14 - Al₂O₃ + PPA+ primer	37.86 ± 7.50	28.54	47.18		1.00	1.00	1.00	1.00	0.33	-	1.00	0.061
G15 - PPA + primer	39.16 ± 9.50	27.37	50.95		1.00	1.00	1.00	1.00	0.25	1.00	-	0.042
G16 - PPA¹	5.74 ± 12.83	-10.20	21.68		0.007**	0.013**	0.024**	0.013**	0.52*	0.013*	0.013**	-

Non-normal distribution¹ Kruskal Wallis^{1*} Post hoc -Mann Whitney^{1**}

Table 5: Comparison of the contact angle of the E-max and Calypso ceramics by the one-way test Anova and post hoc of Tukey.

Groups (n=5)	Contact angle								
	P value	P value Post hoc							
		G9	G10	G11	G12	G13 ¹	G14	G15	G16 ¹
G1- Control without primer		1.00	1.00	0.99	1.00	0.026* *	1.00	1.00	0.007**
G2 – Primer		0.98	1.00	1.00	1.00	0.16**	1.00	0.99	0.041**
G3 - Al₂O₃		0.92	0.99	1.00	1.00	0.24**	0.99	0.99	0.041**
G4 - Al₂O₃ + primer¹	<0.001	0.54**	0.076* *	0.076* *	0.076* *	0.015* *	0.11**	0.14**	0.013**
G5 - Al₂O₃ + PPA	<0.001*	0.002	0.007	0.065	0.025	0.13**	0.010	0.006	0.31**
G6 - Al₂O₃ + PPA + primer		0.99	1.00	1.00	1.00	0.11**	1.00	1.00	0.024**
G7 – PPA + primer		0.88	0.98	1.00	1.00	0.19**	0.99	0.99	0.058**
G8 - PPA¹		0.11**	0.29**	0.46**	0.25**	0.11**	0.25*	0.25**	0.041**

Non-normal distribution ¹ Kruskal Wallis ^{1*} Post hoc -Mann Whitney^{1**}

Table 6: Bond strength (MPa) for the two zirconia and different treatments

Microshear													
Groups (n=5)	Bond strength (mean ± SD ¹)	CI ² at 95%		P value		P value Post hoc							
		Lower	Upper	G1	G2	G3	G4	G5	G6	G7	G8		
Emax													
G1 - Control = primer	52.51 ± 14.44	34.58	70.43	-	0.38	0.31	0.95	1.00	0.10	0.93	1.00		
G2 - Al ₂ O ₃ + primer	70.78 ± 16.36	50.46	91.10	0.38	-	1.00	0.04	0.23	0.99	0.96	0.55		
G3 - Al ₂ O ₃ + PPA ¹ + primer	71.87 ± 11.38	57.74	86.00	0.09*	0.84*	-	0.008**	0.056**	0.54*	0.09*	0.008**		
G4 - Primer + PPA	43.41 ± 18.65	20.25	66.58	0.95	0.04	0.032	-	0.99	0.008	0.34	0.86		
Calypso													
G5 - Control = primer	50.04 ± 11.53	35.72	64.35	0.003	0.005*	1.00	0.23	0.18	0.99	-	0.056	0.82	0.99
G6 - Al ₂ O ₃ + primer	76.57 ± 10.66	63.35	89.82	0.10	0.99	0.99	0.008	0.05	-	0.67	0.18		
G7 - Al ₂ O ₃ + PPA + primer	62.21 ± 10.35	49.37	75.10	0.93	0.96	0.93	0.34	0.82	0.67	-	0.98		
G8 - PPA ¹ + primer	54.82 ± 8.71	44.00	65.65	0.54*	0.22*	0.008**	0.42*	0.42*	0.008**	0.31*	-		

Non-normal distribution ¹ Kruskal Wallis ^{1*} Post hoc Mann-Whitney^{1**}

Table 7: Analysis of the fracture pattern according to the types of surface treatments by the chi-square test

Groups (n=5)	Fracture standard			P value	
	Adhesive	Cohesive	Adhesive		
Emax					
G1- Control = primer	1 (20.0)	0 (0.00)	4 (80.0)	0.154 ^c	
G2 - Al₂O₃ + primer	0 (0.00)	0 (0.00)	5 (100)		
G3 - Al₂O₃ + PPA + primer	0 (0.00)	1 (20.0)	4 (80.0)		
G4 - Primer + PPA	2 (40.0)	0 (0.00)	3 (60.0)		
Calypso					
G5 - Control = primer	2 (40.0)	0 (0.00)	3 (60.0)		
G6 - Al₂O₃ + primer	0 (0.00)	0 (0.00)	5 (100.0)		
G7 - Al₂O₃ + PPA + primer	0 (0.00)	0 (0.00)	5 (100.0)		
G8 - PPA + primer	3 (60.0)	0 (0.00)	2 (40.0)		

^c chi-square test (p>0.05)

Figures

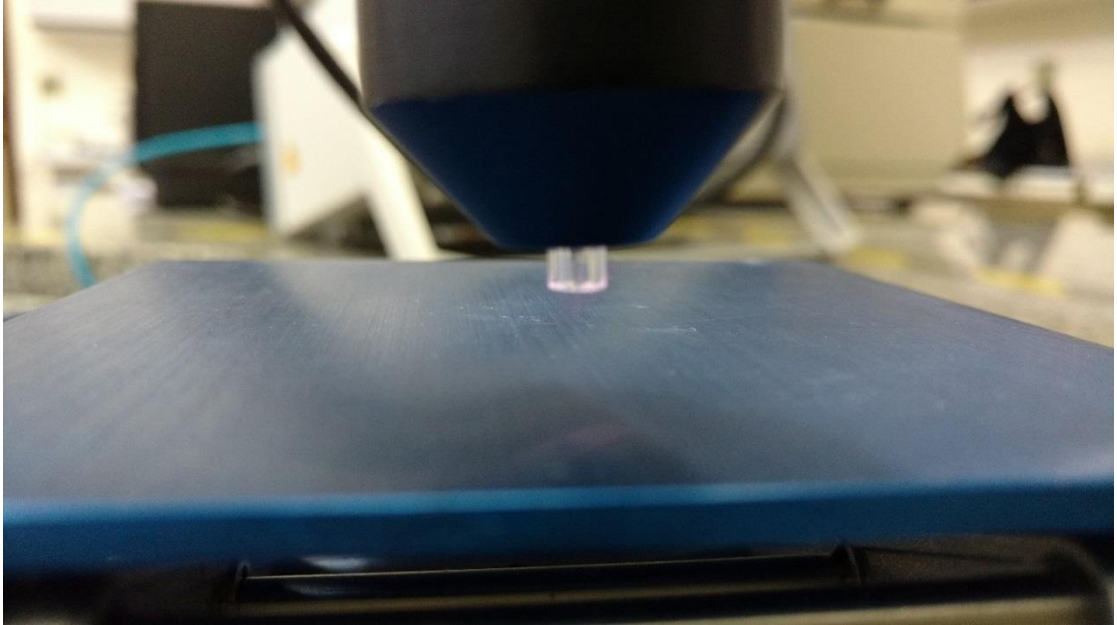


Figure 1: Device of plasma at atmospheric pressure.

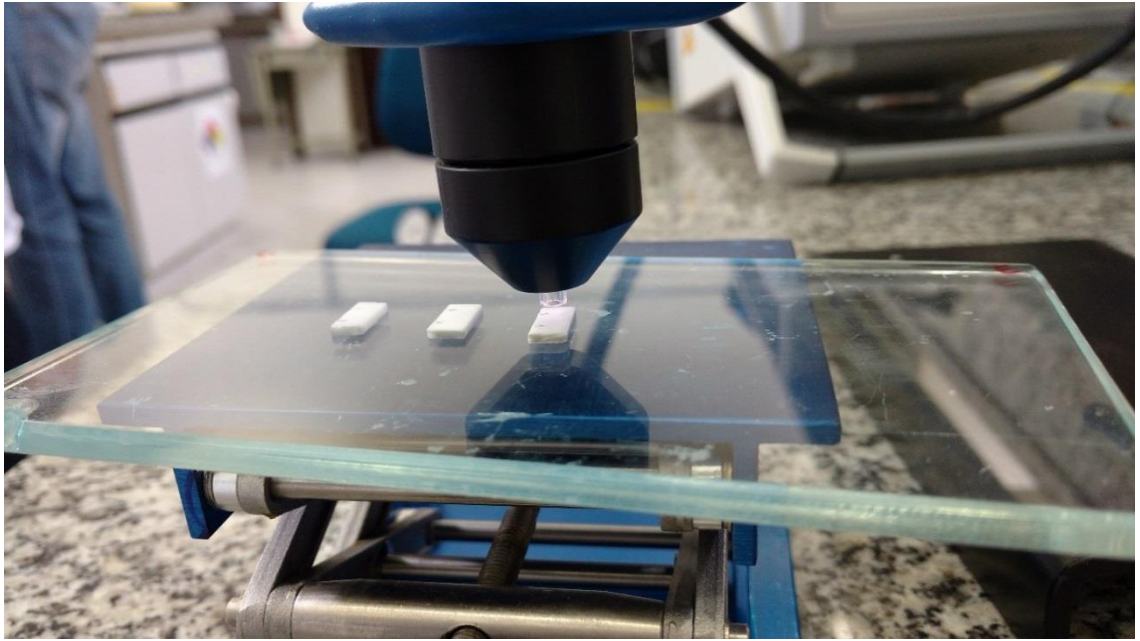


Figure 2: Image shows the plasma pen positioned at 1.5 cm distance apart from the sample.

Equal application distance can be noted.



Figure 3: Specimen coupled to the universal testing machine (EZ Test - S Shimadzu, Tokyo, Japão).

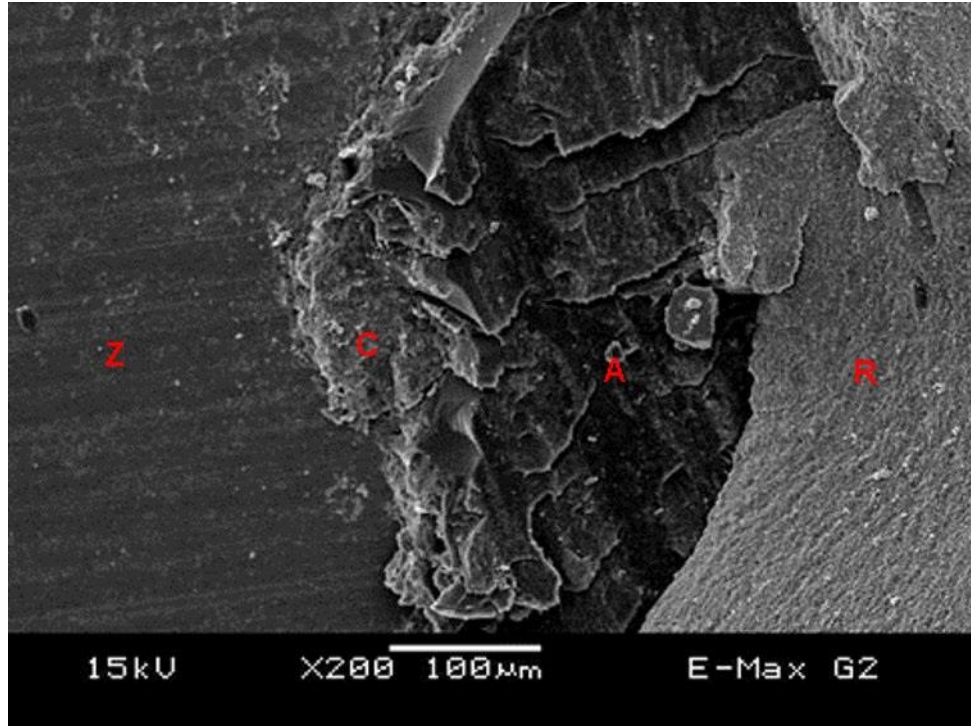


Figure 4: SEM image (200X) of the group ZrE.max (Al₂O₃ + Primer) mixed failure, Z) zirconia C) resin cement A) adhesive system R) composite resin.

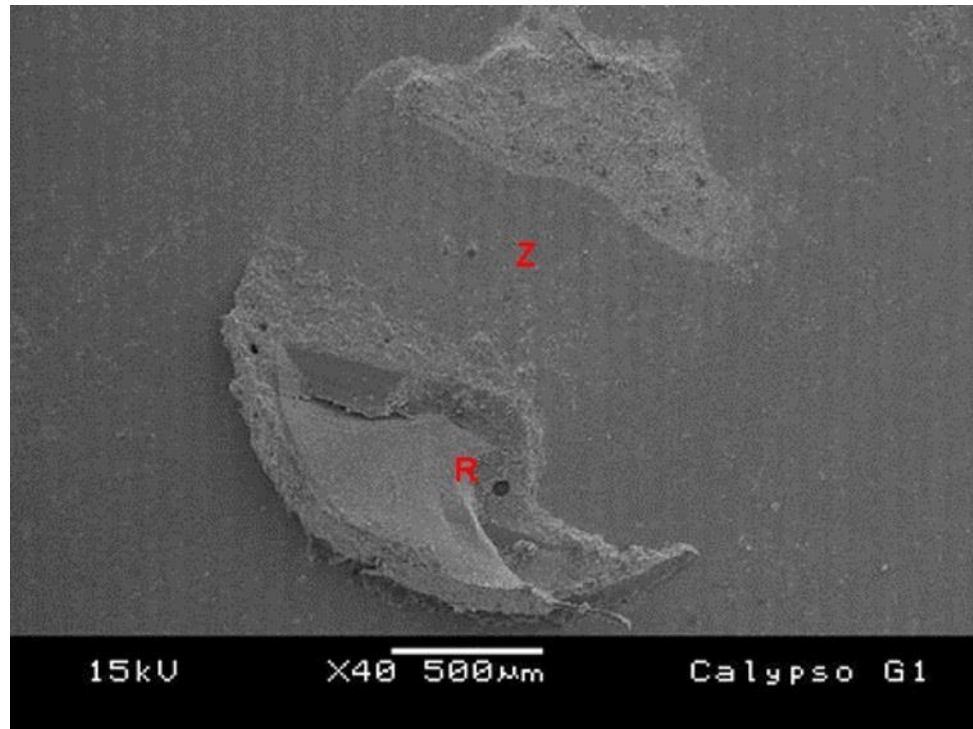


Figure 5: SEM image (40X) of the group Calypso (Primer) mixed failure, Z) zirconia R) composite resin.

CONSIDERAÇÕES FINAIS

A crescente utilização de cerâmicas na clínica odontológica deve-se ao fato de apresentar uma estética favorável, ser biocompatível e boas propriedades mecânicas. As cerâmicas à base de zircônia tetragonal parcialmente estabilizada por ítria (Y-TZP) apresentam além da estética, altos valores de resistência à fratura o que tem contribuído para a sua popularidade na Odontologia, no entanto, são cerâmicas ácido-resistentes podendo ser considerado como um problema clínico, devido à dificuldade em se conseguir uma união adequada com substratos sintéticos ou os tecidos naturais. Diante disso, várias alternativas para o tratamento de superfície têm sido utilizadas para que seja possível aliar suas boas propriedades mecânicas a uma adesão que seja favorável ao ambiente bucal, sendo que estudos relacionados à adesão da cerâmica zircônia estão na modificação química da superfície utilizando-se o plasma em pressão atmosférica não térmico. O plasma em pressão atmosférica não térmico consiste na deposição de filmes finos sobre a superfície da cerâmica Y-TZP, apresentando um alto potencial para o tratamento de superfície devido a modificação química que promove na superfície de um material, por meio de reações químicas que ocorrem entre os gases envolvidos na construção do revestimento/filme. Portanto, o propósito desse trabalho foi verificar a eficácia do plasma em pressão atmosférica e através do estudo realizado foi possível constatar que a associação do tratamento de superfície utilizando o plasma com o jateamento com óxido de alumínio resultou em aumento da molhabilidade da superfície devido à redução do ângulo de contato e melhores valores de resistência de união no ensaio de microcisalhamento.

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