

UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
FACULDADE DE ODONTOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ODONTOLOGIA
MESTRADO EM ODONTOLOGIA ÁREA DE CONCENTRAÇÃO CLÍNICA
ODONTOLÓGICA - MATERIAIS DENTÁRIOS

LAISA CRUZETTA

AVALIAÇÃO DA INFLUÊNCIA DO TRATAMENTO
DE SUPERFÍCIE DE PARTÍCULAS DE CARGA
COM PLASMA NÃO TÉRMICO NAS
PROPRIEDADES FÍSICO-QUÍMICAS DE UM
CIMENTO RESINOSO EXPERIMENTAL

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LINHA DE PESQUISA: BIOMATERIAIS E TÉCNICAS TERAPÊUTICAS EM
ODONTOLOGIA

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PARTÍCULAS DE CARGA COM PLASMA NÃO TÉRMICO NAS
PROPRIEDADES FÍSICO-QUÍMICAS DE UM CIMENTO RESINOSO

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Dentários.

LAISA CRUZETTA

ORIENTADOR: PROF. DR. VICENTE CASTELO BRANCO LEITUNE

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“What I am saying then is just because you don’t know how you manage to be conscious, how you manage to grow and shape your body, doesn’t mean that you’re not doing it. Equally, if you don’t know how the universe shines the stars, constellates the constellations, or galactifies the galaxies – you don’t know but that doesn’t mean that you aren’t doing it just the same way as you are breathing without knowing how you breathe.”

Death- Allan Watts.

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RESUMO

CRUZETTA, L. **Avaliação da influência do tratamento de superfície de partículas de carga com plasma não térmico nas propriedades físico-químicas de um cimento resinoso.** 2020. Dissertação – Faculdade de Odontologia da Universidade Federal do Rio Grande do Sul, Porto Alegre, 2020.

As propriedades mecânicas dos compósitos resinosos são influenciadas pela adequada interação entre as suas duas fases, orgânica e inorgânica, e influenciam diretamente no desempenho clínico desses materiais (AYDINOĞLU, 2017, HABIB, 2016). A limpeza de superfícies com plasma não-térmico (PNT) é uma forma de aumenta a energia livre de superfície e molhamento da superfície tratada, melhorando a interação entre dois materiais (VECHIATO,2014; VALVERDE, 2013; PIEST, 2018). O objetivo do presente estudo foi avaliar a influência do tratamento com PNT em cargas inorgânicas nas propriedades físico-químicas de um cimento resinoso experimental. Uma resina base experimental foi formulada com BisGMA, UDMA e TEGDMA em concentrações de 50%, 25% e 25%, em massa, respectivamente. Fluoreto de itérbio e vidro de bário foram utilizados como partículas de carga a uma concentração de 65%, em massa. Os grupos com vidro de bário (G_{VB}) e fluoreto de itérbio (G_{FY}) receberam tratamento com PNT (G_{VBP} e G_{FYFYP}); PNT e silanização (G_{VBPS} e G_{FYFYS}); apenas silanização (G_{VBS} e G_{FYS}) e um grupo não recebeu tratamento de carga (G_{VB0} e G_{FY0}). As cargas foram caracterizadas quanto ao tamanho de partícula, área de superfície e espectroscopia de infravermelho por transformada de furrier (FTIR). Os cimentos foram avaliados quanto ao grau de conversão, à resistência à flexão e à resistência da união ao microcisalhamento (μ SBS). Não houve diferença no grau de conversão entre os diferentes tipos de tratamento no mesmo grupo de carga. Os grupos G_{VB} apresentaram maiores valores de grau de conversão do que os grupos G_{FY} . No entanto, o grupo G_{VBS} não apresentou diferença estatística em relação ao grupo G_{FY0} ($p=0.063$). No teste de resistência à flexão, a aplicação de PNT na carga de fluoreto de itérbio aumentou a resistência dos cimentos ($p=0,006$). A silanização e o tempo de 6 meses de armazenamento da carga de fluoreto de itérbio diminuíram a resistência à flexão ($p=0,004$) e ($p<0,001$), respectivamente. Na carga de vidro de bário, o PNT não demonstrou ter influência na resistência à flexão ($p=0,0427$), enquanto a sinalização da carga mostrou um aumento significativo ($p<0,001$) na resistência à flexão do cimento. No teste de μ SBS, ambos os tratamentos de carga (PNT e silanização) aumentaram os valores de μ SBS dos cimentos com fluoreto de itérbio como carga ($p=0,045$ e $p=0,046$, respectivamente). Nos cimentos com vidro de bário, o tratamento da carga com PNT não mostrou ter influência nos valores de μ SBS ($p=0,087$). Já a silanização aumentou os valores de μ SBS significativamente ($p<0,001$). O tratamento com PNT de cargas inorgânicas foi possível e demonstrou melhorar as propriedades dos cimentos resinosos com fluoreto de itérbio.

Palavras-Chave: Palavras-Chave: cimento resinoso; Plasma de pressão atmosférica não térmica; enchimento de vidro de bário; fluoreto de itérbio.

ABSTRACT

CRUZETTA, L. **Evaluation of the influence of non-thermal plasma surface treatment of filler particles on the physical-chemical properties of a resin cement.** 2020. Dissertation – Faculdade de Odontologia da Universidade Federal do Rio Grande do Sul, Porto Alegre, 2020. Portuguese.

The mechanical properties of resin composites are influenced by the appropriate interaction between its two phases, organic and inorganic, and directly influence the clinical performance of these materials (AYDINOĞLU, 2017, HABIB, 2016). Cleaning surfaces with non-thermal plasma (PNT) is a way of increasing the free surface energy and wetting of the treated surface, improving the interaction between two materials (VECHIATO, 2014; VALVERDE, 2013; PIEST, 2018). The aim of the present study was to evaluate the influence of treatment with non-thermal plasma (NTP) on inorganic particles on the physical-chemical properties of an experimental resin cement. An experimental base resin was formulated with 50 wt% of BisGMA, 25 wt% of UDMA and 25 wt% of TEGDMA. Ytterbium fluoride or barium glass were used as filler particles at a concentration of 65 wt%. Cements were formulated with a 65% filler particle. The groups with barium glass (G_{BG}) and ytterbium fluoride (G_{YF}) received treatment with NLP (G_{BGP} and G_{YFP}); NTP and silanization (G_{BGPS} and G_{YFPS}); only silanization (G_{BGS} and G_{YFS}) and one group did not receive particle treatment (G_{BG0} and G_{YF0}). The particles were characterized in terms of particle size, surface area and FTIR. Cements were evaluated for degree of conversion, flexural strength and bond strength to microshearing (μ SBS). There was no difference in the degree of conversion between the different types of treatment in the same group of particles. The G_{BG} groups showed higher values of degree of conversion than the G_{YF} groups. However, the G_{BGS} group showed no statistical difference in relation to the G_{YF0} group ($p = 0.063$). In the flexural strength test, the application of NTP to the ytterbium fluoride particle increased the strength of the cements ($p = 0.006$). Silanization and the 6-month storage time of the ytterbium fluoride particle decreased flexural strength ($p = 0.004$) and ($p < 0.001$), respectively. In the barium glass particle, NTP has not been shown to influence flexural strength ($p = 0.0427$), while particle silanization has shown a significant increase ($p < 0.001$) in cement flexural strength. In the μ SBS test, both particle treatments (NLP and silanization) increased the μ SBS values of cements with ytterbium fluoride as filler particle ($p = 0.045$ and $p = 0.046$, respectively). In barium glass cements, the treatment of the particle with NTP did not show any influence on the μ SBS values ($p = 0.087$). Silanization increased μ SBS values significantly ($p < 0.001$). NLP treatment of inorganic particles was possible and has been shown to improve the properties of resin cements with ytterbium fluoride.

Key words: Key words: resin cement; Non-thermal atmospheric pressure plasma; barium glass filling; ytterbium fluoride.

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1. INTRODUÇÃO

Os compósitos resinosos desempenham um papel fundamental no avanço da Odontologia por apresentarem a possibilidade de adesão ao substrato dentário, fácil manipulação, excelente estética e biocompatibilidade aceitável (XU, 2002; L. MUSANJE, 2004). Para que possuam um adequado desempenho clínico, esses materiais precisam atender alguns requisitos como possuir propriedades mecânicas satisfatórias, alta resistência ao desgaste e baixa degradação hidrolítica (HABIB, 2016). São formados por uma matriz orgânica, composta principalmente de monômeros de resina, e uma fase inorgânica composta por carga inorgânicas de carga, além do sistema ativador/iniciador e do agente de união entre as partículas de carga e a matriz orgânica (FERRACANE, 2011).

A fase inorgânica influencia diversas propriedades dos compósitos resinosos, tendo em vista que altera a distribuição das tensões dentro do material, diminui a quantidade relativa de matriz polimérica, diminuindo a contração de polimerização e a degradação hidrolítica (CONDON, 2000; ANDRZEJEWSKA, 2001). Além disso, influencia a resistência à abrasão, o módulo de flexão, o coeficiente de expansão térmica e a radiopacidade do material (MOSZNER, 2005). O efeito da partícula de carga depende do tipo, forma, tamanho, quantidade utilizada e da existência de um acoplamento eficiente entre a carga inorgânica e a matriz resinosa (IKEJIMA, 2003). Cargas inorgânicas como vidro de bário, a sílica, o dióxido de zircônio, e o fluoreto de itérbio são amplamente utilizadas em compósitos resinosos (ILIE, 2009; NOVAIS, 2017). Cargas sem união com a matriz orgânica podem gerar

diferentes problemas como aglomeração das partículas, concentração de tensões, desprendimento da matriz e infiltração de água no material (RAHIM, 2011; XAVIER, 2015). Para suplantar esses problemas, lança-se mão da funcionalização das cargas com sílica para promover união à matriz orgânica (CARREÑO, 2012)

As cargas de silicato são passíveis de funcionalização com organossilanos, tal como o 3-(Trimethoxysilyl)propyl methacrylate (γ -MPTS) utilizado para criar ligações covalentes entre as partículas de carga inorgânicas e a matriz resinosa orgânica por copolimerização radicalar (MOSZNER, 2005). Enquanto uma extremidade da molécula de γ -MPTS copolimeriza com a matriz de resina, a outra extremidade pode estabelecer ligações de siloxano (Si-O-Si) com os grupos hidroxila na superfície da carga, melhorando a distribuição das tensões entre as duas fases (AKOVALI, 1993; SHAH, 2009). Na ausência de silanização, as cadeias poliméricas interagem com a superfície da partícula de carga por meio de ligações secundárias, que são muito menos estáveis e mais fracas do que as ligações siloxano. (XAVIER, 2015). O γ -MPTS possui três grupos metoxi (-OCH₃) e pode estabelecer ligações siloxano não só com a partícula de carga, mas também com outras moléculas de silano. Essas ligações entre grupos silanóis são mais suscetíveis à degradação hidrolítica do que as ligações covalentes formadas entre o silano e a matriz orgânica (MOSZNER, 2005).

Atualmente sabe-se do efeito positivo da silanização nas propriedades mecânicas dos compósitos (AYDINOĞLU, 2017). Propriedades mecânicas de compósitos que são produzidos com modificação de cargas inorgânicas com silano são melhores em comparação a compósitos contendo cargas não

modificadas (LUNG, 2012; ZHANG, 2009). Tais resultados são devido à melhora na interação da fase inorgânica e a rede de matriz orgânica. Porém, algumas partículas de carga utilizadas não possuem grupos hidroxilas disponíveis para fazerem ligações siloxano com o silano, como o caso do fluoreto de itérbio (YbF_3), utilizado em alguns materiais compósitos comerciais (NOVAIS, 2017) e experimentais (COLLARES, 2010).

Na busca por uma melhor interação entre materiais orgânicos e inorgânicos, estudos avaliaram a limpeza da superfície cerâmica com PNT na melhora da adesão a cimentos resinosos (VECHIATO, 2014; VALVERDE, 2013; PIEST, 2018). O PNT tem sido utilizado como alternativa ao ácido hidrofluorídrico para modificar o comportamento químico de uma superfície cerâmica sem danificá-la devido à sua capacidade de transformar superfícies inertes em quimicamente ativadas (VECHIATO, 2014).

O plasma é conhecido como o quarto estado físico da matéria. Trata-se de um gás ionizado, ou seja, um gás cujas moléculas tiveram seus elétrons arrancados (BLOGLE, 2007). Estima-se que os plasmas naturais representem mais de 99% do universo visível, e como exemplos de plasmas naturais há o sol e as estrelas, a coroa solar, os ventos solares, as nebulosas, a ionosfera da Terra, além de fenômenos conhecidos na Terra, como relâmpagos e auroraborealis (HEILIN, 2011). Em plasmas térmicos, todas as temperaturas de elétrons, íons e neutros são iguais, de modo que a temperatura do gás é normalmente muito alta (HAERTEL, 2014). Já nos plasmas não térmicos não há equilíbrio térmico entre os elétrons livres e as demais partículas do plasma, enquanto os elétrons movem-se a altas velocidades em altas temperaturas.

Nesse tipo de plasma, as demais partículas encontram-se em temperaturas próximas à temperatura ambiente (HEILIN, 2011).

O tratamento de superfícies com plasma não térmico fornece uma grande quantidade de espécies quimicamente ativas, como elétrons e radicais O_2^- , NO_2^- , OH^- , com temperatura entre 30-60°C com potenciais de limpeza da superfície tratada (HEINLIN, 2011; SILVA, 2011, MISRA, 2011). Assim, aumenta a energia livre de superfície e molhamento do material (MATTHES, 2019; VALVERDE, 2013).

O objetivo da limpeza de superfícies com PNT é remover a contaminação que se forma na superfície do material. Qualquer material que tem sua superfície exposta na atmosfera ambiente possui contaminação por espécies de carbono-oxigênio, espécies contendo hidrogênio, e incluem, por exemplo, óxidos na superfície de metais, adsorção de água e de vários compostos contendo carbono (BELKIND, 2008). O PNT possui aplicações em diversas áreas tecnológicas, como na indústria alimentícia, na esterilização de materiais na área biológica, remoção de contaminantes atmosféricos em motores de escape, entre outros (MIZUNO, 2009; KULAWIK, 2018).

O PNT aplicado em cargas inorgânicas pode realizar a remoção de impurezas da superfície, promovendo um aumento da energia livre de superfície e do molhamento das partículas. Assim, poderia melhorar a interação com a matriz orgânica, criando compósitos com melhores propriedades mecânicas e conseqüentemente, melhor desempenho clínico.

2. OBJETIVO

O objetivo do presente estudo foi avaliar a influência do tratamento com plasma não térmico nas cargas inorgânicas de vidro de bário e fluoreto de itérbio nas propriedades físico-químicas de um cimento resinoso experimental.

3. ARTIGO

A presente dissertação de mestrado apresenta-se na forma de um manuscrito escrito nas normas do periódico **Dental Materials**, para o qual será submetido.

Original paper

EVALUATION OF THE INFLUENCE OF NON-THERMAL PLASMA SURFACE TREATMENT OF FILLER PARTICLES ON THE PHYSICAL-CHEMICAL PROPERTIES OF A RESIN CEMENT

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ABSTRACT

Objective: The aim of the present study was to evaluate the influence of treatment with non-thermal plasma (NTP) of inorganic particles on the physical-chemical properties of an experimental resin cement. Methods: An experimental base resin was formulated with 50wt% of BisGMA, 25wt% of UDMA and 25wt% of TEGDMA. Ytterbium fluoride or barium glass were used as filler particles at a concentration of 65wt%. The groups with barium glass (G_{BG}) and ytterbium fluoride (G_{FY}) received treatment with NTP (G_{BGP} , G_{FYF}); NTP and silanization (G_{BGPS} , G_{FYPS}); only silanization (G_{BGS} , G_{FYS}) and no treatment (G_{BG0} , G_{FY0}). The particle size, surface area and FTIR of particles were evaluated. Cements were evaluated for degree of conversion (DC), flexural strength (FS) and microshear bond strength (μ SBS). Results: The surface area and particle size were 10.97 m²/g and 13.0 μ m (barium glass), respectively, and 6.87m²/g and 6.4 μ m (ytterbium fluoride), respectively. There was no difference in the DC between the different types of treatment for the same particle. The application of NTP to increased the FS of the cements with G_{FY} ($p=0.006$) and showed no difference to G_{BG} ($p=0.043$). Silanization decreased the FS for G_{FY} ($p=0.004$) and increased for G_{BG} and ($p<0.001$). In the μ SBS test, both particle treatments (NTP and silanization) increased the μ SBS of cements with ytterbium fluoride ($p=0.045$ and $p=0.046$, respectively). In G_{BG} , the treatment of the particle with NTP showed no influence on the μ SBS values ($p=0.087$). Silanization increased μ SBS values significantly ($p<0.001$). Significance: NTP could be an alternative to silanization of particles without silica.

Key words: Key words: resin cement; Non-thermal atmospheric pressure plasma; barium glass filling; ytterbium fluoride.

1. INTRODUCTION

Resin composites are materials widely used for direct dental restoration and cementation of indirect restorations. In the case of resin cements, the mechanical properties of these materials also influence the fracture resistance of teeth restored with indirect restorations.¹ To achieve effectiveness clinical performance, these materials are expected to have adequate mechanical properties, low hydrolytic degradation and high wear resistance.² These requirements are usually met by introducing inorganic filler particles into the organic matrix.³ The effect of the filler particle depends on the type, shape, size, amount used and the existence of an efficient coupling between the inorganic particle and the resin matrix.⁴

There are several inorganic particles that are added to resin composites for different purposes, but mainly to improve the physical-mechanical properties and increase the radiopacity of the composite.³ Barium silicate glass is inorganic filler with refractive index 1.58.⁵ It also has a high barium content, which increases its x-ray opacity. Its composition consists of 49% silicon dioxide (SiO_2) and 46% barium oxide (BaO).⁵ Micro-sized barium silicate glass fillers are widely used in conventional composite resins, resin-based luting cements and resin-modified glass ionomers.⁶ Another used filler particle is the ytterbium fluoride (YbF_3). Ytterbium is an element of the lanthanide series, with a high atomic number ($z = 71$).⁷ YbF_3 has refractive index of approximately 1.5.^{8,9}

Non-functionalized charges tend to agglomerate and it can act as a place of stress concentrator decreasing mechanical properties of the material.^{10,11} Thus, they decrease the homogeneity of the mixture affecting as material

properties as reduction of degree of conversion and mechanical resistance.^{12,13} Silane provides a crucial link between the resin matrix and the fillers that can have a significant effect on the overall performance of composites.¹⁴ This link has been reported to improve distribution and stress transition from the flexible organic matrix to the stiffer and stronger inorganic filler particles.^{14,15} Particles containing silica, such as barium glass, receive treatment with (Trimethoxysilyl)propyl methacrylate (γ -MPTS), which can bond to inorganic silica and organic polymer surfaces.^{16,17} This bonding occurs via condensation reactions between silanol groups of the filler surface and hydrolyzed silane molecules.¹⁸ γ -MPTS has three methoxy groups (-OCH₃) and can establish siloxane bonds with barium glass silica (Si-O-Si).¹⁹ The mechanical properties of composites that have been silanized are greater compared to unmodified composite compounds.^{20,21,22, 4} However, some elements that normally promote radiopacity for resin composites do not have a well-established signaling mechanism.²³ Thus, the interaction between these particles and the organic matrix is weaker, which can affect the stress distribution within the material.

The success of silanes is due to the hydrolysis and reformation of oxane bonds between silanes and silica, but at the same time hydrolysis without oxane bond reformation is a potential degradation mechanism of dental composites, what is a disadvantage of using the silane.^{24,25} With a hydrolytic degradation, water and other fluids are absorbed by the resin matrix, which results in a change in the color of the compound over time, leading to the pigmentation of the margin of ceramic restorations, in the case of resin cements.^{26,27}

One way to improve the interaction between organic and inorganic materials is by surface cleaning with NTP. Studies have evaluated the cleaning

of the ceramic surface with NTP, in the search for a better interaction resin cements.^{22,28,29} Plasma is known as the fourth physical state of matter. It is an ionized gas, that is, a gas whose molecules had their electrons pulled out.³⁰ It is estimated that natural plasmas represent more than 99% of the visible universe, and as examples of natural plasmas there are the sun and stars, the solar corona, solar winds, nebulae, the Earth's ionosphere, in addition to known phenomena in the Earth, like lightning and auroraborealis.³¹ In thermal plasmas, all electron, ion and neutral temperatures are equal, so that the gas temperature is normally very high.³² In non-thermal plasmas, on the other hand, there is no thermal balance between the free electrons and the other particles of the plasma, while the electrons move at high speeds at high temperatures. In this type of plasma, the other particles are at temperatures close to room temperature.³¹ NTP has been used as an alternative to hydrofluoric acid to modify the behavior of a ceramic surface without damaging the surface due to its ability to transform inert surfaces into chemically activated surfaces.²² NTP surface cleaning is a low-cost, environmentally friendly and effective method as the material properties can be unchanged or well maintained after NTP treatment.³³

When NTP gas interacts with the surface of various materials, the following effects can occur: removal of organic materials, cross linking via activated species of inert gases, ablation, and surface chemical restructuring.²⁹ It is known that the NTP are able to remove organic matter via breaking of C-C and C-H bonds. Organic composites present on the surface of inorganic particles can be degraded into low-molecular-weight oxidized material, or even volatile species by NTP.³⁴ There by, it increases the surface energy and

wettability of the treated surface.^{28,35} There are no studies in the literature that perform cleaning of inorganic fillers with NTP. Thus, this treatment could improve the interaction between inorganic particles with the organic matrix leading to a material with better mechanical and physical properties.

Therefore, the objective of the present study is to evaluate the effect of the treatment of inorganic charges with NTP on the physicochemical properties of a resin cement.

2. MATERIALS AND METHODS

2.1 Particle characterization

2.1.1 Surface Area and Particle size

The surface area of the ytterbium fluoride and barium silicate glass powders were evaluated by the Brunauer-Emmett-Teller (BET) method, based on the nitrogen adsorption isotherm data. The nitrogen adsorption measurements were obtained by an Autosorb Quantachrome Nova 1200 (Quantachrome Instruments Corporate Headquarters, USA) instrument. The particle size range was obtained by a laser diffraction particle size analyzer (CILAS 1180, France).

2.2 Preparation of filler particles

2.2.1 Non-thermal Plasma cleaning

The NTP was in a custom made glass vacuum chamber. A 10kV high voltage generator, operating at 45kHz, was connected to two parallel aluminum electrodes with an area of 64.25 cm² separated by 22 mm. Ytterbium fluoride or barium glass particles were kept in stove at 37 ° C for 24 hours. The particles were deposited on a piece of aluminum foil that was placed over the lower electrode. A vacuum pump was activated to let the pressure inside the reactor decrease to 500 mTorr.

Three cycles of NTP cleaning were performed, each lasting 2 minutes. Between each cycle, the filler particles were hand mixed to increase the contact area with the plasma. Soon after NTP cleaning, the particles were mixed with the base resin or silanized. For FTIR analysis specimens were transported in dustproof containers before and after using NTP.

2.2.2 Silanization

The particles were mixed with 5 wt% of 3-(Trimethoxysilyl) propyl methacrylate, and 95 wt% acetone. They were kept at 37 °C for 24 hours for acetone evaporation.⁵

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements were performed in the VERTEX 70, Bruker Optics, Ettlingen, Germany. Particles with and without NTP treatment were dispensed over a diamond crystal of Attenuate Total Reflectance (ATR) accessory. A total of 64 scans were collected from 400cm⁻¹ to 5000 cm⁻¹ at a 4 cm⁻¹ resolution.

2.4 Preparation of experimental resin cements

Light-cured experimental resin cements were formulated by mixing the methacrylate monomers Bisphenol A-glycidyl Dimethacrylate (BisGMA), Urethane Dimethacrylate (UDMA) and Triethylene Glycol Dimethacrylate (TEGDMA) at 50 wt%, 25 wt% and 25 wt% respectively.

Ytterbium fluoride (YbF_3), (American Elements) and barium silicate glass (49% SiO_2 ; 46% BaO) (Esstech, Inc.) were used as filler particles at a concentration of 65 wt%. The groups received the following treatments: NTP; NTP and silanization; silanization, and one group received no treatment. All formulations were weighed on an analytical balance (AUW220D; Shimadzu, Kyoto, Japan), mixed manually and ultrasonicated processor with an ultrasonic tip (Sonic Vibra Cell. Sonic & Materials Inc., Newtown, U.S.A. Model: VCX 130).

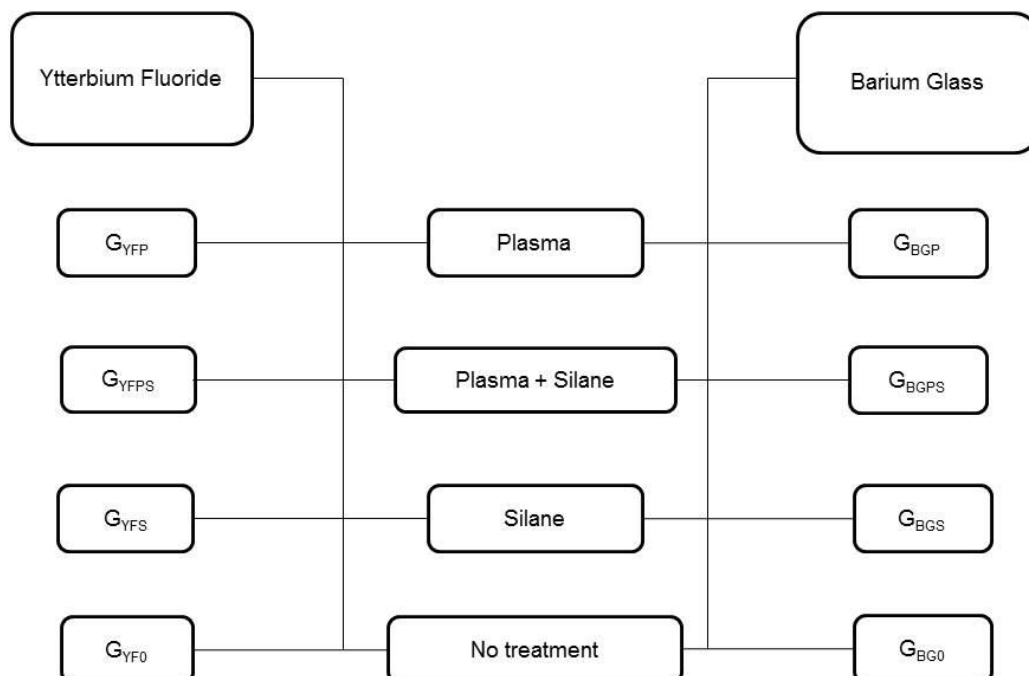


Figure 1. Experimental group diagram

2.5 Degree of conversion

The measurements were performed by Fourier Transform Infrared Spectroscopy (FTIR) on a spectrometer (VERTEX 70, Bruker Optics, Ettingen, Germany) equipped with an attenuated total reflectance (ATR) accessory composed of a horizontal diamond crystal forming an angle of 45° with the mirror. Three samples (n = 5) with 1mm of height and 4mm of diameter were performed for each group. Samples were photoactivated using LED equipment (Radii; SDI, Bayswater, Australia) for 60s, with standardization of 1mm distance between the tip of the equipment and the samples. Opus 6.5 software (Bruker Optics, Ettlingen, Germany) was used for processing the spectra, using the Blackman Haris 3-Term apodization, in a spectrum of 1750 to 1550 cm⁻¹, 4 cm⁻¹ resolution and mirror speed of 2.8mm/s. The analysis was performed in a room with the controlled temperature of 23°C and 60% relative humidity. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined by the quotient of the absorbance intensities between the aliphatic carbon double bonds (peak at 1640 cm⁻¹) and the internal standard (peak at 1610cm⁻¹), before and after the photoactivation of samples. To compute the resulting degree of conversion the following formula was used (1):

$$CG = 1 - \frac{\text{absorbance}(1640 \text{ cm}^{-1})/\text{absorbance}(1610 \text{ cm}^{-1})_{\text{polymer}}}{\text{absorbance}(1640 \text{ cm}^{-1})/\text{absorbance}(1610 \text{ cm}^{-1})_{\text{monomer}}} \times 100$$

2.6 Flexural Strength

For flexural strength analysis, 10 specimens from each group of resin cements were made through a metal matrix of 25 (± 0.1) mm x 2.0 (± 0.1) mm x

2.0 (\pm 0.1) mm. The resin cements were dispensed, covered with a polyester matrix and photo activated with a light emitting diode (Radii Cal., SDI Ltda, Australia) each side of the sample was submitted to four overlapping photoactivation windows of 30s each. The specimens were stored in distilled water for 24h and 6 months and were fractured in a universal mechanical testing machine (EZ-SX Series, Shimadzu, Tokyo, Japan) at a crosshead speed of 1 mm/min. The force values were recorded in Newtons and transformed into megapascal (MPa) by the formula determined by ISO 4049:

$$\sigma = \frac{3LF}{2BH^2}$$

Where:

σ = Flexural strength (MPa)

F = Maximum load (N)

L = Distance (mm) between the holders (up to 0,01 mm)

B = Width (mm) at the center of the specimen measured just before the test

H = length (mm) in the center of the specimen measured just before the test.

2.7 Micro-shear Bond Strength (μ SBS)

To evaluate the μ SBS of the adhesive interface, 96 bovine incisors (n=12) were extracted, cleaned and stored in distilled water at 4°C. After cleaning and removal of the root, the vestibular enamel was removed and the superficial dentin was exposed. The teeth were embedded in acrylic resin. The superficial dentin of the buccal surface of each tooth was ground flat (600-grit)

under running water for 30s to produce a standardized smear layer. The dentin surface of each tooth was etched with 37% phosphoric acid for 15 seconds, rinsed off with distilled water for 15s and dried with absorbent paper. A commercial primer (Scotchbond Multi-Purpose Primer, 3M ESPE; St Paul, MN, USA) was actively applied for 20 s, and the solvent was evaporated. The commercial adhesive (Scotchbond Multi-Purpose Adhesive, 3M ESPE; St Paul, MN, USA) was applied and light cured for 20s. In order to make the cement tubes on the samples, each of the cements were deposited inside the matrix tubes. The specimens were photopolymerized (Radii Cal; SDI, Australia) for 40s. The samples were stored in distilled water at 37°C and were tested after 7 days.

The specimens were tested at universal mechanical testing machine (EZ-SX; Shimadzu, Japan). A 0.2mm diameter stainless wire was positioned close to the cement interface. Bond strength was determined at a crosshead speed of 1 mm/min. The μ SBS values were calculated by dividing the force value (MPa) by the section area of the cylinders. Failure modes were analyzed through a stereomicroscope at 40x magnification and classified as follows: adhesive failure between resin cement and dentin, cohesive failure within the cement and mixed failure type.

2.8 Statistical Analysis

The normality of the values obtained were tested using the Shapiro-Wilk test. one-way ANOVA was used for the degree of conversion test. The results of flexural strength and μ SBS were analyzed by multiple linear regression. All analysis were performed considering a significance level of 5%.

3. RESULTS

The surface area and particle size of the barium silicate glass particles was $10.97\text{m}^2/\text{g}$ and $13.0\mu\text{m}$, respectively. The surface area and particle size of the ytterbium fluoride was $6.869\text{ m}^2/\text{g}$ and $6.4\ \mu\text{m}$, respectively.

Figure 1A shows the spectrum of barium glass particle without surface treatment. The highest peak of the organic part of the material is 2351 cm^{-1} , close to the C = C bond peak. After NTP surface treatment this peak disappeared (Fig.1B). Figure 1C shows the spectrum of the untreated ytterbium fluoride particle. The peak of 1400cm^{-1} represents the C = C bond, the peak near 2250 cm^{-1} represents carbon to nitrogen bonds, and the peak near 3300 cm^{-1} represents the C = H bond, present in organic contamination on the particles.

Figure 1D shows the spectrum of the ytterbium fluoride particle after NTP treatment. There was a decrease in the peak representing the C = C bond. The peak carbon-nitrogen bond disappeared and the peak C-H bond had a small reduction in absorbance.

Table 1 shows the mean and standard deviation values of the degree of conversion. There was no statistical difference between the different types of treatment in the same particle group. The groups with the barium silicate glass particle had higher values of degree of conversion than the groups with the ytterbium fluoride particle. However, the G_{BGPS} group had no statistical difference from the G_{YF0} group.

Table 1 means and standard deviations of the values of the degree of conversion (%).

	DC (%)
G_{BGP}	59.32 (\pm 1.27) A
G_{BGPS}	58.99 (\pm 0.45) A
G_{BGS}	58.51 (\pm 0.85) AB
G_{BG0}	60.23 (\pm 1.10) A
G_{YFP}	56.06 (\pm 0.95) C
G_{YFPS}	55.78 (\pm 1.51) C
G_{YFS}	56.43 (\pm 0.29) C
G_{YF0}	56.91 (\pm 0.27) BC

*Different capital letters indicate statistically significant difference in the same column within each group ($P < 0.05$).

Table 2 Multiple linear regression results of the particles surface treatments of ytterbium fluoride and barium glass in the flexural strength test

	Constant	56.13 MPa	R ^{2*}
	NTP	6.16	p= 0.006
Ytterbium	Silane	- 6.33	p= 0.004
Fluoride	Time (6 months)	- 32.37	p<0.001
	Constant**	45.88 MPa	R ^{2**}
	NTP	2.76	p= 0.427
Barium Glass	Silane	41.31	p<0.001
	Time (6 months)	-15.69	p<0.001

*R²= 0,76; ** R²=0,68

In the flexural strength test, the application of NTP to the ytterbium fluoride particle increased the strength of the cements ($p = 0.006$). Silanization of the ytterbium fluoride particle decreased the flexural strength ($p = 0.004$). After 6 months there was a reduction in resistance in both types of treatment ($p < 0.001$). In the barium glass particle, the cleaning of the particle with NTP did not show to have an influence on the flexural strength ($p = 0.0427$), while the particle silanization showed a significant increase ($p < 0.001$) in the flexural strength of the cement (Table 2).

In the μ SBS test, both particle treatments (NTP and silanization) increased the μ SBS values of cements with ytterbium fluoride as the filler particle ($p = 0.045$ and $p = 0.046$, respectively). In cements with barium glass, the treatment of the particle with NTP did not show to influence the values of μ SBS ($p = 0.087$). The silanization increased the values of μ SBS significantly ($p < 0.001$) (Table 3). The failure analysis showed that 47.64% of the failures were of the mixed type, 43.45% of the adhesive type and 8.90% the failure was cohesive in the cement.

Table 3 Multiple linear regression results of the particles surface treatments of ytterbium fluoride and barium glass in the μ SBS test.

	Constant	10.10 MPa	R^{2*}
Ytterbium fluoride	NTP	3.27	$p = 0.045$
	Silane	3.25	$p = 0.046$
	Constant	12.70 MPa	R^{2**}
Barium Glass	NTP	3.20	$p = 0.087$
	Silane	8.76	$p < 0.001$

* $R^2 = 0,16$; ** $R^2 = 0,37$

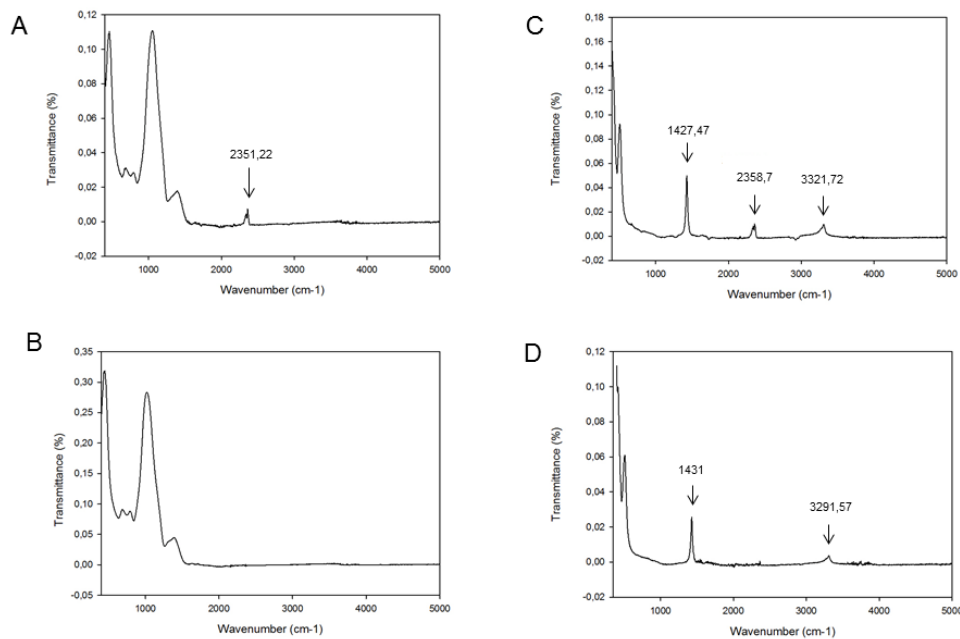


Figure 1. FTIR spectrum of the untreated barium glass particle (A); barium glass after NTP treatment (B); untreated ytterbium fluoride (C) and ytterbium fluoride after NTP treatment (D).

4. DISCUSSION

The adhesion between inorganic fillers and the organic matrix in composite resin is a crucial point for obtaining satisfactory physical and mechanical properties of dental composite.³⁶ In addition to affecting stress distribution, may act as a toughening agent, and can also affect light transmission within the composite.^{37,38} Previous studies have shown the use of barium glass and ytterbium fluoride particles to improve mechanical properties and radiopacity in conventional composite resins, resin-based luting cements and resin-modified glass ionomers.^{6,7,39,40,41,42} In the present study, the

cleaning of these inorganic particles with non-thermal NTP prior to mixing with the resin matrix showed a positive influence on the mechanical properties of experimental resin cements with ytterbium fluoride as a filler particle.

In this study, barium glass and ytterbium fluoride received three types of treatment prior to mixing with the organic matrix (NTP, NTP + silanization and silanization), and one group received no surface treatment. These particles were chosen because the ytterbium fluoride particle cannot be silanized, while barium glass can be silanized. The degree of conversion of barium glass cements was higher than in cements using ytterbium fluoride, and there was no difference between the different types of treatment within the same filler group. Compatibility in resin matrix and filler particle refractive indexes is known to be an important factor in the polymerization of composites.⁴³ Although both fillers have similar refractive indices (barium glass= 1,58; ytterbium fluoride = 1,50), while Bis-GMA, TEGDMA and UDMA have a refractive index of 1.55 and 1.46 and 1.48 respectively, the groups with barium glass as the filler particle had a higher degree of conversion than the group with ytterbium fluoride. It is reported that ytterbium fluoride has low solubility in composite resin which led to a higher particle agglomeration than in barium glass cements.⁶ Therefore, the agglomeration leads to decreased light transmission that could affected the polymerization. Nevertheless, the degree of conversion values of the ytterbium fluoride cements was compatible with that of commercial cements.⁴⁴

In the mechanical flexural strength test, the NTP factor had a positive influence on the mechanical performance of cements with ytterbium fluoride, while the silane factor had a negative influence. Ytterbium fluoride has no silica and no oxane bond formation, thus there was no improvement in the interaction

between the organic and inorganic phase of the composite. In addition, the presence of silane may have hindered the particle's interaction with the organic matrix. On other hand, NTP removes organic matter and possible impurities from the particle surface.^{45,46,47} Using this method, the number of oxygen-containing polar groups increases, leading to a surface with greater wettability and resulting in better resin-particle filler interaction.²⁹

In the barium glass particle, cleaning with NTP did not show to have any influence on the flexural strength values. However, the functionalization of the filler with silane has been shown to increase the flexural strength values. Silane can establish oxane bonds with the hydroxyl groups on the surface of the barium glass. Thus, there is a better stress distribution within the material, improving its flexural strength.³⁸ After 6 months of aging in water, there was a reduction in resistance in both fillers regardless of the factors. This shows that regardless of the treatment used, there is an expected hydrolytic degradation of the resin composite. Despite that, it is known that hydrolysis of the silane coupling agent is known to be accepted as one of the major causes of composite material degradation^{48,49} leading to a shortened service life of dental restorations.

In the μ SBS test, the NTP and the silane were shown to increase the μ SBS values of cements with ytterbium fluoride. In the barium glass particle, the results coincided with the results of flexural strength, in which the NTP did not change the μ SBS values and the silane significantly increased the μ SBS values. It is known that luting cement properties affects the predictability and effectiveness of its bond strength with the tooth substrate.^{50,51} The silanization of the ytterbium fluoride particle showed controversial results in the flexural

strength test and in the μ SBS test. There is no chemical bond between the silane and the ytterbium fluoride particle, silane diffuse through the resin organic matrix, leading to the silane hydrolysis and degradation of the composite.⁶

According to the FTIR spectra of the particles before and after surface treatment with NTP, there was a reduction in the peaks corresponding to the carbon bonds, resulting from organic contamination on the surface of the particles. Previous studies analyzed surfaces such as dentin, enamel and ceramics after NTP application and concluded that there was a decrease in the amount of surface carbon.^{33,52,53} NTP is a state of matter composed of a large number of highly reactive species, such as electrons, electronically excited neutrons and free radicals.³³ When highly reactive NTP species react to the surface of the charge, the C-C and C-H organic bonds break down, reducing organic and protein content.^{34, 54} Thus, the surface becomes more reactive and with higher wetting, improving the interaction between the particle and the resin matrix. The particle sizes used were 13.0 μm for barium silicate glass and 6.4 μm for ytterbium fluoride. The surface area for barium glass was 10.97 m^2 / g and for ytterbium fluoride it was 6.86 m^2 / g . It is known that there is an inverse proportional proportion between a surface area and particle size.⁵⁵ However, particles with irregular surfaces have a larger surface area than particles with a smooth surface.⁵⁶ Thus, the higher surface area presented in the barium glass particle may be due to a higher irregularity of the surface compared to the ytterbium fluoride particle. Thus, this may have made it difficult to clean the barium glass with NTP because it is more irregular, which may explain the fact that the NTP did not influence the properties of the barium glass cements.

NTP particle cleaning has been shown to influence the mechanical properties of cements with ytterbium fluoride. However, it is possible that there is an influence of the particle morphology on the effectiveness of cleaning with NTP. With this, the NTP showed a promising treatment in improving the mechanical properties of composites with filler particles without the presence of silica, which is not possible to perform silanization.

5. CONCLUSION

The results obtained in the present study showed that NTP treatment of inorganic particles was possible, and was shown to reduce the amount of organic contamination of the particle surface. In addition, the treatment of inorganic particles with NTP can be an alternative to improve the interaction of the organic and inorganic phase of resin composites and obtain materials with better mechanical properties and consequently better clinical performance and restorative longevity.

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CONSIDERAÇÕES FINAIS

A limpeza de superfícies sólidas, como esmalte, dentina e cerâmica com plasma não térmico já tem se demonstrado eficaz na melhora da interação dessas superfícies com compósitos resinosos (VECHIATO, 2014 CHEN, 2013). Não há na literatura estudos que realizem limpeza de cargas utilizadas para a produção de compósitos com plasma. No presente estudo o plasma teve influência positiva nas propriedades mecânicas dos cimentos com fluoreto de itérbio como partícula de carga. Como o tamanho da carga de fluoreto de itérbio é aproximadamente a metade do tamanho da carga de vidro de bário, 6,4 e 13,0 μm , respectivamente, espera-se uma área de superfície maior na carga fluoreto de itérbio. Porém, a área de superfície do vidro de bário é de 10,97 m^2/g e para o fluoreto de itérbio, de 6,86 m^2/g . Isso demonstra que a carga do vidro de bário possui mais irregularidades na superfície, deixando a área de superfície maior. Essas irregularidades podem ter dificultado a ação do plasma na superfície, reduzindo seus efeitos de limpeza nas carga de vidro de bário.

Além disso, confirmou-se a importância da silanização em cargas com conteúdo de sílica nas propriedades mecânicas dos compósitos resinosos. A maioria das cargas radiopacas utilizadas em compósitos são compostos metálicos que não formam ligações covalentes com a matriz resinosa durante a polimerização (MOSZNER, 2005). A estabilização e modificação da superfície dessas cargas são cruciais e não tão simples como em cargas de sílica. (MOSZNER, 2005). A utilização do silano em cargas sem modificação de superfície por sílica pode ser prejudicial ao longo do tempo, pois sabe-se que a

hidrólise do silano é amplamente aceita como uma das principais causas de degradação de compósitos resinosos (FERRACANE, 1992; SODERHOLM, 1984). Nesse contexto, o plasma mostrou-se ser um método vantajoso na melhora da interação das partículas de carga sem presença de sílica com a matriz orgânica, mostrando ter impacto nas propriedades mecânicas dos compósitos resinosos. A ação do plasma é explicada pela redução no conteúdo orgânico na superfície das cargas utilizadas (Figura 1), o que está de acordo com a literatura prévia (PIEST, 2018).

Os resultados do tratamento de superfície das partículas inorgânicas com plasma não-térmico foram promissores e, por ser um método barato e prático, pode ser aplicado em cargas como coadjuvante à silanização ou de forma isolada nas cargas em que a silanização não é indicada. Mais ensaios precisam ser realizados para avaliar a eficiência do plasma em diferentes tipos de cargas.

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