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AVALIAÇÃO DO SILICATO DE NIÓBIO COMO PARTÍCULA DE CARGA EM

CIMENTO RESINOSO FOTOPOLIMERIZÁVEL EXPERIMENTAL

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Orientador: Prof. Dr. Fabrício Mezzomo Collares

Porto Alegre, Março de 2019

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Dissertação apresentada ao Programa de Pós-Graduação em Odontologia da Universidade Federal do Rio Grande do Sul, como pré-requisito para obtenção do título de mestre em Odontologia.

Orientador: Prof. Dr. Fabrício Mezzomo Collares

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DEDICATÓRIA

Dedico esse trabalho aos meus pais, que sempre incentivaram e priorizaram os estudos e a educação. Vocês são meus maiores exemplos, tanto como pais quanto como profissionais. Minha eterna gratidão, carinho e amor.

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" Eu seguro minha mão à sua mão,

E uno o meu coração ao seu,

Para que juntos possamos fazer

Aquilo que sozinho eu não quero, não posso e não consigo.

Concedei-me a serenidade necessária

Para aceitar as coisas que eu não posso modificar,

Coragem para modificar as que eu posso, e

Sabedoria para distinguir umas das outras."

Autor Desconhecido

Resumo

O objetivo do presente estudo foi formular um cimento resinoso fotopolimerizável experimental utilizando silicato de nióbio (SiNb) como partícula de carga inorgânica e avaliar suas propriedades. A partícula de SiNb foi sintetizada pelo método sol-gel, e a caracterização da partícula SiNb foi realizada por meio dos ensaios de difração de raios-X, área de superfície e tamanho de partícula e espectroscopia de infravermelho. Foram formulados cimentos resinosos fotopolimerizáveis com bisfenol-a-glicidil metacrilato (BisGMA) na concentração de 50% em peso, dimetacrilato de trietilenoglicol (TEGDMA) 30% em peso, uretano dimetacrilato (UDMA) em 20% em peso e óxido bis-alquil fosfínico (BAPO) a 1% em peso. À essas formulações foram adicionados Vidro de Bário 50% ou 65% (grupos controle) e Silicato de Nióbio 50% ou 65% (grupos experimentais) como partícula de carga inorgânica. Os cimentos formulados foram caracterizados por meio de ensaios de índice de refração, grau de conversão e cinética de polimerização, amolecimento em solvente, radiopacidade, espessura de filme, estabilidade de cor, microcisalhamento e resistência à flexão. Os grupos SiNb obtiveram resultados satisfatórios nos ensaios de grau de conversão (SiNb50% = 65.07% e SiNb65% = 66,58%), espessura de filme (SiNb50% = 16.66μm e SiNb65% = 20 μm), amolecimento em solvente (SiNb50% = 7.32% e SiNb65% = 11.98%) e estabilidade de cor (SiNb50% = 4.3 e SiNb65% = 4.005), sendo todos esses estatisticamente mais satisfatórios quando comparados as grupos controle (p<0,05). Os ensaios de microcisalhamento e resistência à flexão foram avaliados imediatamente e após 6 meses, nos quais os grupos com Vidro de Bário obtiveram resultados mais satisfatórios na resistência à flexão, mas o

grupo SiNb65% obteve o melhor resultado no microcisalhamento, sendo de 36.83 após 6 meses. Os grupos com Vidro de Bário também apresentaram maior radiopacidade, variando entre 2.08 mmAl (50%) e 2.98 mmAl (65%). Concluiu-se que a adição de SiNb não agiu negativamente nos cimentos resinosos experimentais com resultados satisfatórios em relação às propriedades mecânicas e ópticas, podendo ser uma alternativa promissora no desenvolvimento de novos materiais odontológicos.

Palavras-chave: Cimentos resinosos, Sílica, Nióbio.

Abstract

The aim of the present study was to formulate an experimental photopolymerizable resin cement using Niobium Silicate (SiNb) as an inorganic filler particle and to evaluate its properties. The SiNb particles were synthesized by sol-gel route. The characterization of the SiNb particle was performed by X-ray diffraction, surface area and particle size and infrared spectroscopy tests. The experimental resin cements were formulated with bisphenol A-glycidyl methacrylate (BisGMA) in a concentration of 50% by weight, triethylene glycol dimethacrylate (TEGDMA) 30%, urethane dimethacrylate (UDMA) 20% and phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) 1% by weight. To these formulations were added 50% or 65% of Barium Glass (control groups) and Niobium Silicate 50% or 65% (experimental groups) as inorganic filler particles. The resin cements were characterized by refractive index, degree of conversion and polymerization kinetics, softening in solvent, radiopacity, film thickness, color stability, micro shear bond strength and flexural strength. The SiNb groups obtained satisfactory results in the tests of degree of conversion (SiNb50% = 65.07% and SiNb65% = 66,58%), film thickness (SiNb50% = 16.66µm e SiNb65% = 20 µm), softening in solvent (SiNb50% = 7.32% and SiNb65% = 11.98%) and color stability (SiNb50% = 4.3 and SiNb65% = 4.005), all of those with results statistically higher than the control groups. The micro shear bond strength and flexural strength tests were evaluated immediately and after 6 months, in which the Barium Glass groups obtained better results for flexural strength, but the SiNb 65% group obtained the best result in the micro shear bond strength test (36.83 MPa). The Barium Glass groups also presented higher radiopacity, varying from 2.08 mmAl (50%) and 2.98 mmAl (65%) . It was

concluded that the addition of SiNb did not act negatively on experimental resin cements and improved its mechanical and optical properties, becoming a promising alternative in the development of new dental materials.

Sumário

1. Introdução

A prática da Odontologia restauradora passou por diversas mudanças a partir da introdução de técnicas e materiais inovadores. A utilização dos laminados cerâmicos têm aumentado ao longo dos anos, pois apresentam resultados clínicos favoráveis, com uma taxa de sobrevivência estimada de 90% entre 12 e 13 anos. O apelo estético, estabilidade e biocompatibilidade das facetas laminadas de porcelana as tornam uma opção segura para restaurar e reabilitar dentes anteriores.[1]

A durabilidade em ambiente oral, capacidade de adesão à estrutura dental, disponibilidade de cores semelhantes ao substrato dentário, bem como a possibilidade de serem diretamente inseridos ao dente preparado fazem dos cimentos resinosos o material de escolha para a cimentação de restaurações cerâmicas.[2-4] Além das propriedades estéticas favoráveis, os cimentos resinosos possuem também propriedades mecânicas como resistência à flexão e compressão, resistência de união à tração e ao cisalhamento superiores aos demais agentes de cimentação.[4]

Os sistemas autopolimerizáveis ou puramente químicos são pouco utilizados em relação aos cimentos resinosos de polimerização por luz ou dual, pois uma de suas desvantagens é o controle sobre o tempo de trabalho, podendo comprometer a reação de polimerização. Sendo assim, Os sistemas de ativação por meio de energia luminosa foram introduzidos para superar essa desvantagem.[5]

A principal virtude do sistema fotopolimerizável em relação aos cimentos duais é a maior estabilidade de cor, [6,7] sendo principalmente utilizado para cimentação de laminados cerâmicos, enquanto os cimentos duais são

utilizados para cimentação de restaurações do tipo onlay, inlay, coroas e pontes fixas cerâmicas e pinos intracanal.[8]

O sucesso clínico das restaurações cerâmicas é determinado pela resistência e durabilidade da união adesiva do cimento ao dente e à cerâmica,[9,10] e a natureza adesiva dos cimentos resinosos promove uma retenção superior, bem como a resistência a fratura das restaurações.[11]

Os cimentos resinosos contém partículas inorgânicas revestidas por um agente de união dispersas na matriz resinosa orgânica, que comumente é composta por uma mistura de monômeros metacrilatos. Tais monômeros, quando associados a fotoiniciadores adequados, geram polímeros em uma rede polimérica de ligações cruzadas não solúveis em água [12] e apresentam propriedades mecânicas desejáveis, tais como resistência à flexão e resistência de união longitudinal.[13]

O monômero Bisfenol A-glicol dimetacrilato (BisGMA) possui alta reatividade devido às duas duplas ligações de carbono reativas, porém apresenta alto peso molecular, resultando em um monômero de alta viscosidade, hidrófobo e de baixa solubilidade em água. Estas duplas ligações se quebram durante a reação, permitindo que o monômero se una a outros na reação de polimerização.[14] Os dimetacrilatos também dão origem a formação de uma rede polimérica, resultando em efeitos favoráveis como o aumento da taxa de polimerização, das propriedades mecânicas e da resistência à solubilização da matriz polimérica em água.[15] Assim, para a obtenção de polímeros com maior grau de conversão, a associação com um monômero de baixo peso molecular e baixa viscosidade é requerida.[16,17] Monômeros como o

trietilenoglicol-dimetacrilato (TEGDMA) e o Uretano dimetacrilato (UDMA) podem ser misturados ao monômero Bis-GMA a fim de possibilitar a obtenção de materiais que possam ser manipulados mais facilmente, pois a quantidade de diluente irá ditar a sua fluidez.[18] O TEGDMA é uma molécula linear, relativamente flexível e apresenta ligações instauradas de carbono nas suas extremidades.[17] O UDMA é sintetizado a partir da reação entre o 2-hidroxietil metacrilato e 2,4,4 Trimetil hexametileno diisocianato, de baixa viscosidade e devido a flexibilidade de ligações uretanas, produz polímeros com alta resiliência.[14]

Os fatores intrínsecos e da estrutura química dos cimentos resinosos podem pigmentar e amarelar os cimentos a longo prazo, comprometendo assim a estética das restaurações.[19,20] A mudança de cor além de ser afetada por fatores relacionados diretamente ao material, como o tipo de carga e fotoiniciador adicionados, composição da matriz resinosa, do sistema de polimerização e da taxa de conversão de ligações duplas de carbono,[21,22] também pode ser afetada por fatores extrínsecos que incluem manchas que podem ser causadas por fumo, comidas e bebidas.[23,24] A descoloração causada pelos fatores intrínsecos é acelerada pela irradiação ultravioleta e por mudanças de temperatura.[25]

A canforoquinona (CQ) é o fotoiniciador mais utilizado na composição dos cimentos resinosos, e a alteração de cor dos cimentos é diretamente afetada pela quantidade de CQ e amina presentes na formulação. Os cimentos resinosos fotopolimerizáveis que polimerizam apenas através da ação da luz mostram maior estabilidade de cor ao longo do tempo, e agentes cimentantes livres de amina terciária apresentam valores de mudança de cor menores

independente do modo de polimerização.[19,26] A estrutura química e o modo de polimerização do cimento afetam a estabilidade de cor ao longo do tempo.[6] Sendo assim, os cimentos adesivos fotopolimerizáveis são recomendados para a cimentação de restaurações em dentes anteriores.[7]

A conversão dos monômeros dos cimentos resinosos fotopolimerizáveis ocorre através da adição de fotoiniciadores em sua composição.[27] Devido a essa desvantagem em relação a estabilidade de cor dos cimentos resinosos, surgiram novos fotoiniciadores alternativos à CQ, como o óxido bis-aquil fosfínico (BAPO). Esses são fotoiniciadores que não precisam de co-iniciador (amina terciária) para iniciar o processo de polimerização.[28]

Estudos recentes testam e comparam o uso de diferentes fotoiniciadores com a CQ, bem como avaliam seus desempenhos e propriedades.[28-32] O hexafuoroantimonato de p-octiloxi-fenil-fenil iodônio (OPPI), quando adicionado a resina composta, apresentou maior estabilidade de cor, enquanto a CQ se mostrou amarelada e escurecida.[32] A CQ também mostrou um maior amarelamento quando comparada ao BAPO e ao óxido de difenil (2,4,6-trimetilbenzoil) fosfínico (TPO).[30] Quando comparada a fenilpropanodiona (PPD) em cimentos resinosos, a CQ também se apresentou mais amarelada e a adição da PPD não comprometeu a adesão e nem a polimerização.[30] Quando adicionada uma maior concentração de TPO em relação a CQ em resina composta, o amarelamento e a mudança de cor após a cura foram reduzidas.[9] As resinas formuladas com o fotoiniciador BAPO geralmente atingem um grau de conversão mais alto do que os formulados com CQ.[33] Além disso, não é tóxico na concentração necessária para uso clínico, sendo bem tolerados por células semelhantes a osteoblastos.[34,35]

Além dos monômeros resinosos e dos fotoiniciadores, as partículas de carga também são fundamentais às propriedades mecânicas dos cimentos resinosos, pois aumentam a resistência mecânica e reduzem a solubilidade e contração volumétrica do cimento resinoso.[36] No entanto, também aumentam a viscosidade do material, o que pode reduzir seu potencial de escoamento e aumentar a espessura de película, podendo dificultar o assentamento da peça protética e ocasionar desadaptação marginal.[36] As partículas de carga mais comumente utilizadas na composição dos cimentos resinosos atualmente disponíveis no mercado são a sílica (Si) e o Vidro de Bário, por conta de suas propriedades mecânicas favoráveis, bem como biocompatibilidade.[4]

O Nióbio (Nb) é um metal que, mesmo quando aplicado em pequenas quantidades, confere um aumento na resistência, além de apresentar alta biocompatibilidade, mostrando potencial para melhorar as propriedades de diferentes materiais.[37-42] O Nióbio, ao ser adicionado à resinas compostas experimentais, apresentou aumento no índice de refração após a polimerização das mesmas.[39] A adição de nióbio aos materiais biológicos vem sendo considerada por conta de sua associação à redução da citotoxicidade e aumento da atividade da fosfatase alcalina,[43] aumentando a calcificação em defeitos ósseos e melhorando propriedades biológicas.[44,45]

A adição de partículas de nióbio obtidas pelo método de síntese sol-gel juntamente com a sílica poderia representar uma alternativa de partícula de carga para cimentos resinosos. Devido ao possível potencial do Silicato de Nióbio (SiNb) em melhorar as propriedades mecânicas dos cimentos resinosos, o objetivo deste trabalho foi desenvolver um cimento resinoso fotopolimerizável

experimental e avaliar a influência da adição do SiNb nas propriedades do mesmo.

2. Objetivo

Formular um cimento resinoso fotopolimerizável experimental contendo Silicato de Nióbio como partícula de carga e avaliar suas propriedades.

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

NIOBIUM SILICATE AS FILLER PARTICLE ON EXPERIMENTAL PHOTOPOLYMERIZABLE RESIN CEMENT

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Abstract

The aim of the present study was to formulate an experimental photopolymerizable resin cement using Niobium Silicate (SiNb) as an inorganic filler particle and to evaluate its properties. The SiNb particles were synthesized by sol-gel route. The characterization of the SiNb particle was performed by X-ray diffraction, surface area and particle size and infrared spectroscopy tests. The experimental resin cements were formulated with bisphenol A-glycidyl methacrylate (BisGMA) in a concentration of 50% by weight, triethylene glycol dimethacrylate (TEGDMA) 30%, urethane dimethacrylate (UDMA) 20% and phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) 1% by weight. To these formulations were added 50% or 65% of Barium Glass (control groups) and Niobium Silicate 50% or 65% (experimental groups) as inorganic filler particles. The resin cements were characterized by refractive index, degree of conversion and polymerization kinetics, softening in solvent, radiopacity, film thickness, color stability, micro shear bond strength and flexural strength. The SiNb groups obtained satisfactory results in the tests of degree of conversion (SiNb50% = 65.07% and SiNb65% = 66,58%), film thickness (SiNb50% = 16.66µm e SiNb65% = 20 µm), softening in solvent (SiNb50% = 7.32% and SiNb65% = 11.98%) and color stability (SiNb50% = 4.3 and SiNb65% = 4.005), all of those with results statistically higher than the control groups. The micro shear bond strength and flexural strength tests were evaluated immediately and after 6 months, in which the Barium Glass groups obtained better results for flexural strength, but the SiNb 65% group obtained the best result in the micro shear bond strength test (36.83 MPa). The Barium Glass groups also presented higher radiopacity, varying from 2.08 mmAl (50%) and 2.98 mmAl (65%) . It was

concluded that the addition of SiNb did not act negatively on experimental resin cements and improved its mechanical and optical properties, becoming a promising alternative in the development of new dental materials.

1. Introduction

The practice of restorative dentistry went through several changes with the introduction of innovative techniques and materials. The use of ceramic laminates has increased over the years as they present favorable clinical results, with an estimated survival rate of 90% between 12 and 13 years.[1] The aesthetic appeal, durability and biocompatibility of porcelain veneers make them an appropriate assortment to restore and rehabilitate anterior teeth.[1]

The durability in oral environment, ability to bond to dental structure, availability of colors similar to the dental substrate, as well as the possibility of being directly inserted to the prepared tooth make the resin cements the material of choice for the cementation of ceramic restorations.[2-4] In addition to the favorable aesthetic properties, the resin cements also have mechanical properties such as flexural strength and compression, tensile bond strength and shear bond strength superior to other cementing agents.[4] The photopolymerizable system is mainly used for cementing ceramic laminates, due to their greater color stability, while the dual cements are used for cementation of onlay, inlay, crowns and fixed bridges ceramic restorations and intracanal posts.[5-7] The clinical success of ceramic restorations is determined by the strength and durability of adhesive bonding of cement to tooth and ceramics, and the adhesive nature of resin cements promotes superior retention as well as fracture resistance of restorations.[8-10]

The intrinsic factors and chemical structure of the resin cements can pigment and yellow the cements in the long term, thus compromising the aesthetics of the restorations.[11,12] The color change is affected by factors

directly related to the material, such as the type of load and photoinitiator composition, the resin matrix composition, the polymerization system and the rate of conversion of carbon double bonds. It may also be affected by extrinsic factors that include stains that may be caused by smoking, food and drink.[13-16] The discoloration caused by intrinsic factors is accelerated by ultraviolet irradiation and temperature changes.[17]

Niobium (Nb) is a metal that, even when applied in small amounts, gives an increase in resistance, besides presenting high biocompatibility, showing potential to improve the properties of different materials.[18-23] The addition of Niobium to biological materials has been considered because of its association with the reduction of cytotoxicity and increased alkaline phosphatase activity, increasing calcification in bone defects and improving biological properties.[24-26]

The addition of niobium particles obtained by the sol-gel synthesis method together with silica could represent an alternative filler particle for resin cements. Due to the possible potential of Niobium Silicate (SiNb) in improving the mechanical properties of resin cements, the aim of this study was to develop an experimental photopolymerizable resin cement and to evaluate the influence of the addition of SiNb on its properties.

2. Materials and Methods

2.1 Synthesis of Niobium Silicate

The SiNb particles were synthesized by the sol-gel method, using Tethaethilorthosilicate (TEOS) as the silica precursor and Niobium Pentachloride (NbCl$_5$) as the precursor of Niobium. From the production of the sol and the hydrolysis of TEOS, 7 days were expected for its gelling at room temperature. Then, the mixture was subjected to heat treatments in the oven at 100ºC for 24 hours and 500ºC for another 24 hours for drying and stabilization. This resulted in Niobium Silicate, which was then ground and sieved in a 500 mesh sieve, where only particles smaller than 2.5µm could pass through, so that it could be silanized and used in the resin cement.

2.2 Particle Characterization

2.2.1 X-ray diffraction

The X-ray diffraction was performed for the SiNb powder by the diffractometer (X'PertPRO, PANalytical MPD, Netherlands). It was operated using CuKα radiation at 40kV - 40mA at the angular range between 5º and 100º, with the step size of 0.02 for 2 seconds (s).

2.2.2 Surface Area and Particle size

The surface area of the SiNb powder was calculated 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).

2.2.3 Infrared spectroscopy

The chemical groups of SiNb compounds were identified by micro-Raman spectroscopy equipment (VERTEX 70, Bruker Optics, Ettingen, Germany). The range of the analysis was 400-3000 cm^{-1}.

<u>2.3 Resin Cement Formulation</u>

Four experimental photopolymerizable resin cements were formulated by using the metacrylate monomers Bisphenol A-glycidyl Dimethacrylate (BisGMA), Urethane Dimethacrylate (UDMA) and Triethylene Glycol Dimethacrylate (TEGDMA) in concentrations of 50%, 30% and 20% by weight, respectively. The initiation system was the bis-alkyl phosphinic oxide (BAPO), added in the concentration of 1% by weight. The Butylated Hydroxytoluene (BHT) polymerization inhibitor was added at 0.01% by weight. In the Experimental groups, SiNb was added in the concentrations of 50% and 65% by weight. In the Control groups, Barium Glass particles (Esstech-Essington, Pennsylvania, USA) were added in the same concentrations. The particles were silanized with an acetone solution of 3-(Trimethoxysilyl)propyl methacrylate (Merck KGaA, Darmstadt, Germany) at 95wt% acetone concentration, and all formulations were weighed in an analytical balance (AUW220D; Shimadzu, Kyoto, Japan), mixed manually and ultrasonicated for 480s (L100; Schuster, Santa Maria, RS, Brazil).

2.4 Resin Cement Characterization

2.4.1 Refractive Index

The refractive index values of the monomers were evaluated by spectral ellipsometry before and after polymerization. Each sample (n = 3) was analysed using an ellipsometer (SOPRA GES-5E PUV) adjusted for the wavelength range of 380 - 450 µm.

2.4.2 Degree of Conversion and Polymerization Kinetics

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 45º with the mirror. Three samples (n = 3) 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 23ºC 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.[27]

2.4.3 Softening in solvent

Five specimens (5mm diameter and 1mm thickness) were prepared for each group. The specimens were photoactivated for 30s on each side, embedded in acrylic resin and polished with a felt disc containing alumina suspension (Alumina, 6μm, Arotec, Cotia, SP, Brazil). In each specimen, 5 indentations (25g/20s) were made in each sample, using a digital Knoop Hardness Tester (HMV 2, Shimadzu, Tokyo, Japan). The specimens were immersed in ethanol 70% for 2 hours. The samples were submitted to the hardness test before and after the immersion in ethanol solution (KHN1 and KHN2) and the percentual of the hardness reduction was recorded.[28]

2.4.4. Radiopacity

For the radiopacity analysis, 5 specimens (10mm diameter and 1mm thickness) were made for each group. All samples were covered with a polyester matrix and photoactivated with a light emitting diode (Radii Cal, SDI Ltda, Australia) for 30s on each side. Radiographic images were obtained on phosphor plates (VistaScan, Durres plus GmbH & Co. KG, Bietigheim-Bissingen, Germany) after 0.4s of exposure at a focal length of 40 cm. The X-ray source was operated at 70 kV and 8 mA. The test was performed by allocating each specimen from each group along an aluminum scale on each phosphor plate. The images were saved in tiff format and the pixel density of each specimen and each step of the aluminum scale (standard $25mm^2$ central area) was measured in the ImageJ software (Wayne Rasband, National Institutes of Health, USA). The pixel density values were converted to mmAl according to the pixel density in each image.

2.4.5 Film Thickness

The film thickness test was carried out in accordance to ISO 4049: 2009. Three specimens were made for each group (n = 3). Two glass plates with a contact surface area of 200 ± 25 mm^2 each and with a thickness of at least 5 mm had their thicknesses measured (reading A). A portion of the experimental cement was dispensed in the center of the lower plate and placed on another plate where a force of 150 Newtons (N) for 180s was applied over the whole set. After this period of time, the force was removed and the sample was photopolymerized for 60s, and the thickness of the set was measured again (reading B). The difference between the 2 measured thicknesses was the result of film thickness (reading B - reading A). For each experimental group, the test was repeated 3 times, thus obtaining the average values of the film thickness.

2.4.6 Color Stability

The colorimetric evaluation was carried out with a spectrophotometer, using the CIELab (Comission Internationale de L'Eclairage) method. Five specimens per group (n = 5) were made with an elastomeric matrix (10mm diameter and 1mm thick) and each half of the specimen was photoactivated for 30s on each side. Each specimen was stored in distilled water in a stove at 37ºC and were tested after 24 h and 6 months. The spectrophotometer filters the radiation reflected by the test body and then separates the fractions corresponding to the red, green and blue wavelengths. Based on the relative intensity of each wavelength, 3 different color parameters were be calculated: ΔL tonality changes, tonality changes over the scale red/green Δa, and tonality changes over the yellow/blue scale Δb. From the values of each parameter, the

color difference (ΔE) was calculated between the resin cements by the equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

2.4.7 Micro-shear Bond Strength

Twenty ceramic discs based on lithium disilicate (IPS E.max, Ivoclar Vivadent, Schaan Liechtenstein) with 10mm diameter and 2mm high were manufactured and divided into 4 groups, according to the concentration of SiNb and Barium Glass in each resin cement formulation. Twenty ceramic discs based on lithium disilicate were sintered according to the manufacturer's recommendation. After sintering, the discs were embedded in acrylic resin through a metallic matrix and polished with a felt disc containing alumina suspension (Alumina, 6μm, Arotec, Cotia, SP, Brazil). Samples were randomly separated and divided into 4 groups: SiNb 50%, SiNb 65%, Barium Glass 50% and Barium Glass 65%. The surfaces of the samples were sandblasted and subsequently immersed in distilled water for 5 minutes (min) in an ultrasonic vessel.

For surface treatment, hydrofluoric acid 10% gel (Condac porcelana 10%, FGM, Joinville, SC, Brazil) was applied on the ceramics' surface for 20s, washed in running water and cleaned in an ultrasonic tank with distilled water for 5 min (L100; Schuster, Santa Maria, RS, Brazil). After the bonding agent, silane was applied (RelyXTM Ceramic Primer, 3M ESPE, Sumaré, SP, Brazil) and an adhesive layer (AdperTM ScotchbondTM Multiuso, 3M ESPE, Sumaré,

SP, Brazil) was also applied in the air-jet ceramics for 5s. On each disc, 6 cylinders of resin cement were made, using a matrix of 0.7 mm diameter and 1.0 mm height. In order to make the cement tubes on the ceramic samples, each of the cements were manipulated and deposited inside the matrix tubes with the aid of an exploratory probe and spatula. The specimens were photopolymerized (Radii Cal; SDI, Australia) for 60s. The samples were stored in distilled water in a 37°C stove and were tested after 7 days and 6 months.

The specimens were positioned in an universal test machine (EZ-SX; Shimadzu, Japan), used to apply a shear force through a 0.2 mm diameter steel cable positioned as close as possible to the cement interface. The bond strength was determined at a constant rate of 1 mm/min until the fracture occurred. Failure modes were analyzed visually through a stereomicroscope at a magnification of 40x and classified as: adhesive failure between resin cement and ceramic, cohesive failure inside the ceramic or cement and mixed.

2.4.8 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 ± 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) for 30s on each side. The specimens were stored in distilled water and after 24h and 6 months, were fractured in a universal mechanical testing machine (EZ-SX Series, Shimadzu, Tokyo, Japan) at a speed of 1 mm/min and

equipped with a 50N . The force values were recorded in Newtons and transformed into megapascal (MPa) by the formula determined by ISO 4049:

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

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.

3.Statistical Analysys

The normality of the values obtained were tested using the Kolmogorov-Smirnov test. Since there was a normal distribution, the two-way ANOVA test was performed. If there were any differences between the groups, Tukey's multiple comparisons test were applied. All analysis were performed considering a significance level of 5%.

4.Results

The synthesis of SiNb particles through sol-gel route was successful. As shown in Figure 1A, the X-ray diffraction analysis of the SiNb powder showed the glassy structure obtained in the synthesis, as well as the amorphous structure of the powder. In the infrared spectroscopy (FTIR) graph, a peak was observed in $1078cm^{-1}$ regarding the chemical bonding between Silica, Oxygen and Niobium (Figure 1B). The mean particle size of SiNb was 2.054µm, and the surface area was 616,962 m^2/g (Table 1).

The refractive index range within the experimental resin cements is shown in Table 2. The SiNb group showed higher degree of conversion and polymerization rate in both concentrations. The Barium Glass groups showed higher radiopacity in both concentrations when compared to the SiNb groups. The film thickness values showed that the SiNb groups in both concentrations are thinner (Table 2).

The SiNb groups presented lower percentage of reduction of Knoop hardness after ethanol immersion (Table 3). In Table 4, it can be observed that the Barium Glass groups showed higher color change after 6 months in distilled water. Table 5 shows the results for flexural strength and micro shear bond strength tests, immediate and after 6 months.

The statistical analysis showed that after 6 months in distilled water, the resin cements formulated with Barium Glass obtained higher values for flexural strength, whereas the SiNb 65% group had the higher results for micro shear bond strength. All the failure modes between resin cement and ceramic analyzed after the micro shear bond strength test were mixed in all groups.

5.Discussion

A photopolymerizable resin cement with adequate color stability is still a clinical need in dental practice. The composition of dental resin cements consists of resin monomers, photoinitiators, inhibitors and inorganic fillers. In this present study, the experimental photopolymerized resin cements only differed by the inorganic filler particle and its' different concentrations within the groups, maintaining the same resin matrix. The use of SiNb as filler particle in a photopolimeryzable resin cement did not compromise the mechanical properties and improved optical properties.

The infrared spectroscopy finds the chemical composition of the SiNb powder, where it showed peaks related to O-Nb bonding (430cm^{-1}), Si-O-Si (800cm^{-1}) and Si-O-Nb (1078cm^{-1}) (Figure 2). This bond is previously shown in the synthesis of different particles with Si and Nb as components.[29] The analysis of surface area showed 616,92 m^2/g and the particle size, performed by laser diffraction had a medium size of 2.054 μm, which happens to be an adequate size for innorganic fillers in resin cements.[4,30] The refractive index range values are similar within all experimental groups, as shown in Table 2. This shows that the sol-gel synthesis allows the production of highly homogeneous particles with high specific surface area.

The values for degree of conversion and polymerization rate are directly related to the improvement of the properties of the polymer.[27,30] The photopolymerized resin cements formulated in the present study showed that the cements containing the SiNb filler had statistically significant difference when compared to the Barium Glass filler, showing better results for degree of conversion and polymerization rate (Table 2, Figure 2).

The x-ray diffraction analysis, showed amorphous structure (Figure 1), which may be more adequate to the application in photocured composites as it may allow better light transmission through the material.[31] This adequate formation of the polymeric structure could also explain why the results for film thickness (Table 2), softening in solvent (Table 3) and color stability (Table 4) were significantly better within the SiNb groups.

Also, the silanization process, as well as improving mechanical properties, affects the degradation of the polymeric matrix. The SiNb particles did not affect the formation of the polymeric matrix and its degradation as shown for softening in solvent results (Table 3). Taking into account that the particles of Barium Glass are smaller, it makes sense to associate this to a greater degradation, by allowing a greater penetration of the solvent in the resin matrix.

All the resin cements formulated in this study showed radiopacity when compared to the aluminum step wedge and the radiolucent background of the radiographic image (Table 2). However, the Barium Glass filler showed statistically significant higher values, and the control group with 65% Barium Glass was the most radiopaque between the formulations. The radiopacity of a substance is a function of its atomic number and it increases as the atomic number increases. Niobium has an atomic number of 41, and Barium 56, which is why many commercial composite resins contain Barium Glass filler to obtain radiopacity.

The binding between a silanizing agent and a base resin matrix may not occur at all silanized points. As it is shown in Table 5, all the experimental resin cements showed statistically significant decrease on the flexural strength values

after 6 months immersed in distilled water. However, the Barium Glass groups showed greater values after 6 months when compared to the SiNb. This decrease in flexural strength of SiNb in comparison to Barium Glass resin cement could be partially attributed to this smaller number of binding points in the resinous matrix, which is most likely to be caused by the greater particle size and surface area of the SiNb particles. The smaller the filler size is, the more amorphous the structure of the resin matrix becomes, and the number of micro cracks, which is the cause of fractures, is reduced.

In the micro shear bond strength test, however, the values in Table 5 showed the best result for the SiNb 65% group after 6 months, whereas the other groups had no statistically significant difference between them. Also, the SiNb 50% group showed no significant decrease after 6 months storage. This could be related to the film thickness values of the SiNb resin cements (Table 2), which was significantly thinner, allowing a greater penetration in the ceramic discs, guaranteeing greater adhesion and therefore, better results after 6 months storage.

Photopolimerizable resin cements are the first choice for cementing laminated veneers. Thus, color stability matters substantially, since the main reason to replace laminated veneers is due to the color change.[1] The experimental resin cements formulated in this study were submitted to the color stability test, where the spectophotometer calculates 3 different color parameters. ΔL represents tonality and luminosity changes, Δa the changes over the scale red-green and Δb over the yellow-blue scale. As shown in table 4, the control group exhibited color change after 6 months, due to the ΔL values. The specimens in that group showed little difference as far as the color

goes, but they were much more opaque after 6 months, whereas the SiNb groups remained stable. This could also have happened due to the smaller particle size and surface area of the Barium Glass, which allows water penetration and therefore, shows greater degradation.

The values of all tests obtained in this study, showed that the addition of SiNb particles in an experimental photopolymerized resin cement has no negative effects on the degradation and mechanical properties, sugesting that it could be a promising alternative for dental materials, since the experimental groups with SiNb as an inorganic filler presented better optical, mechanical and physical properties overall.

6.Conclusion

The results obtained in the present study showed that Niobium Silicate can be successfully synthesized and used as an inorganic filler particle in photopolymerizable resin cements, with satisfactory mechanical, physical and optical properties.

7.Clinical Relevance

Since the main reason for the need of replacement of ceramic laminates is due to the color change of the resin cement, a light-cured resin cement that exhibits color stability over time is of great importance in clinical practice. The addition of SiNb to an experimental photopolymerizable resin cement showed not only improvement of the optical properties, but also of mechanical properties.

Compliance with Ethical Standards

Ethical approval: This article does not contain any tests or experiments that involve human or animals as participants in the study. Therefore, there is no need of ethical approval or informed consent.

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FIGURES

Figure 1: Characterization of SiNb particles. The crystalline structure (A) and chemical composition (B) are observed.
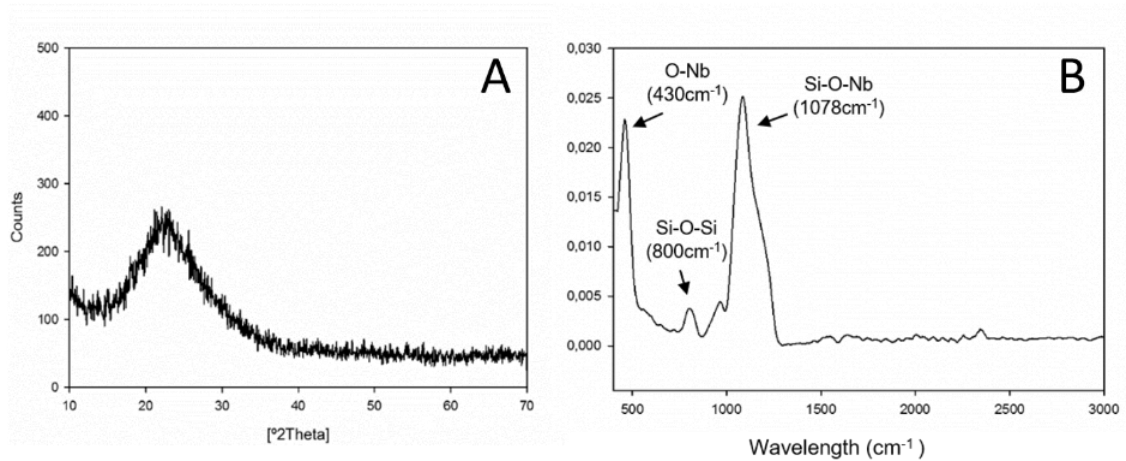
Figure 2: Polymerization kinetics of each experimental photopolymerizable resin cement. Degree of conversion (%) **(A)** and polymerization rate (Rp.[s^{-1}]) **(B)** are shown over the time. The relationship between polymerization rate and degree of conversion is plotted in **(C)**.
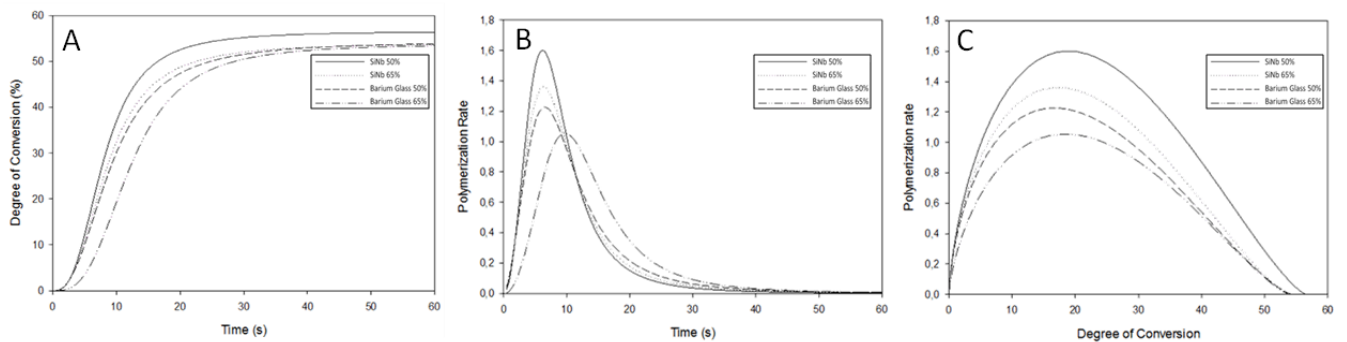
TABLES

Table 1: Surface Area in m²/g and Particle Size in µm d50% (d10% - d90%) of the filler particles.

	SiNb	Barium Glass
Surface Area	616.96 m^2/g	454 m^2/g*
Particle Size	2.054 µm (0.66µm – 4.22µm)	1.3 µm*

Information provided by the manufacturer

Table 2: Results obtained for refractive index range, degree of conversion, polymerization rate, radiopacity and film thickness between the photopolymerizable resin cements

	Refractive Index	Degree of conversion (%)	Polymerization Rate (mmol.g^{-1}.s^{-1})	Radiopacity (mmAl)	Film Thickness (μm)
SiNb 50%	1.52 - 1.48	65,07 (±1,5)^A	1,60 (±0,4)^A	1.13 (±0.1)^C	16.66 (±5.7)^A
SiNb 65%	1.54 - 1.51	66,58 (±7,9)^A	1,36 (±0,3)^B	1.23 (±0.1)^C	20.00 (±6.9)^A
Barium Glass 50%	1.50 - 1.45	55,30 (±0,9)^B	1,23 (±0,3)^B	2.08 (±0.2)^B	36.33 (±5.6)^B
Barium Glass 65%	1.52 - 1.47	56,8 (±1,7)^B	1,04 (±0,3)^C	2.98 (±0.1)^A	36.33 (±5.6)^B

Different capital letters indicate statistically significant difference in the same column within each group. (P<.05).

Table 3: Mean and standard deviation values of the hardness of the experimental resin cements before (KHN1) and after the immersion in solvent (KHN2) and the percentage reduction of Knoop hardness after ethanol immersion (ΔKHN).

Groups	KHN1	KHN2	ΔKHN (%)
SiNb 50%	26.04 (±1.8)^{Aa}	24.12 (±1.7)^{a}	7.32 (± 3.6)^{A}
SiNb 65%	40.7 (±7.6)^{Aa}	35.58 (±4.7)^{a}	11.98 (± 5.1)^{A}
Barium Glass 50%	32.15 (±9.2)^{Aa}	19.42 (±2.5)^{b}	37.31(±14.4)^{B}
Barium Glass 65%	37.27(±10.4)^{Aa}	18.15 (±0.2)^{b}	48.02 (±17.4)^{B}

Different capital letters indicate statistically significant difference in the same column. Different small letters indicate statistically significant difference in the same line. ($P<.05$).

Table 4: Mean values of ΔL*, Δa*, Δb* and ΔE of the resin cements evaluated after 6 months in distilled water.

Groups	ΔL*	Δa*	Δb*	ΔE
SiNb 50%	1	0.6	- 2.7	4.3^A
SiNb 65%	2	0.1	- 2	4.005^A
Barium Glass 50%	- 7	1	0.7	25.24^B
Barium Glass 65%	- 6	0.5	- 0.4	18.2^B

Different capital letters indicate statistically significant difference in the same column.

Table 5: Mean and standard deviation values of the Flexural Strength (FS) and Micro Shear Bond Strength tests, immediate and after 6 months (MPa).

Groups	FS (24h)	FS (6m)	μSBS (1w)	μSBS (6m)
SiNb 50%	57.06 (±6.2)^{Aa}	41.04 (±5.9)^{Bb}	21.01 (±6.1)^{Ca}	18.34 (±4.7)^{Ba}
SiNb 65%	54.29 (±3.2)^{Aa}	39.04 (±3.2)^{Bb}	45.22 (±5.8)^{Aa}	36.83 (±5.3)^{Ab}
Barium Glass 50%	59.96 (±5.1)^{Aa}	51.02 (±6.5)^{Ab}	24.19 (±6.4)^{Ca}	21.08 (±6.2)^{Ba}
Barium Glass 65%	57.65 (±6.8)^{Aa}	48.57 (±3.7)^{Ab}	31.14 (±6.1)^{Ba}	24.79 (±4.8)^{Bb}

Different capital letters indicate statistically significant difference in the same column. Different small letters indicate statistically significant difference in the same line. ($P<.05$).

4. Considerações Finais

Os silicatos têm sido usados como partículas de carga em materiais dentários [46], mostrando interação adequada com a matriz polimérica, bem como mantendo as propriedades mecânicas e ópticas dos materiais.[47-49] Materiais com alto teor de sílica e modificados com componentes bioativos, tendo em vista melhorar as propriedades biológicas dessas partículas, parecem ser uma nova e promissora alternativa no desenvolvimento de novos materiais.

Um dos principais motivos para a troca de restaurações cerâmicas delgadas é a mudança de coloração dos cimentos resinosos. A adição de silicato de nióbio em cimento resinoso fotopolimerizável experimental apresentou resultados motivadores, pois mostrou estabilidade de cor satisfatória, sendo expressivamente melhor do que a carga dos grupos controle, que é a mais comumente utilizada pelas marcas comerciais disponíveis atualmente no mercado. Além das propriedades ópticas favoráveis, a carga sintetizada no presente estudo também apresentou resultados satisfatórios no que diz respeito às propriedades mecânicas, mostrando que o silicato de nióbio pode ser uma alternativa viável no estudo de agentes bioativos incorporados aos materiais odontológicos.

Apesar das limitações do presente estudo, pode-se considerar que o objetivo proposto foi alcançado, sugerindo que a incorporação de silicato de nióbio em cimentos resinosos é uma alternativa promissora. Futuramente, pode também ser incorporado a outros materiais odontológicos e em novos

estudos, podendo ser submetida a diferentes testes metodológicos in vitro e in vivo.

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