Original Article

Niobium silicate as a filler for an experimental photopolymerizable luting agent

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Abstract

Purpose: To synthesize niobium silicate particles (SiNb) and incorporate into resin-based luting agents.

Methods: SiNb particles were synthesized and characterized by x-ray diffraction, FTIR spectroscopy, particle size, and specific surface area. Luting agents were formulated with 50 wt% BisGMA, 30 wt% TEGDMA and 20 wt% UDMA. BAPO was used as a photoinitiator in 1mol%. The SiNb particles were incorporated into the agents at concentrations of 50 wt% (SiNb50%) or 65% wt% (SiNb65%). Barium glass particles at the same concentrations were used as controls (SiBa50% and SiBa65%). Refractive index, degree of conversion (DC), polymerization kinetics, softening in solvent, radiopacity, film thickness, color stability, flexural strength (FS) and micro shear bond strength (μ SBS) were evaluated.

Results: SiNb particles were successfully synthesized with an adequate structure to be applied as inorganic fillers. SiNb groups had higher DC, lower Δ E00, greater film thickness and greater radiopacity than the SiBa groups. Color stability was greater for SiNb50% and SiNb65% after six months of storage, as demonstrated by Δ E00. Δ WID values were lower for the SiBa groups. FS results decreased over time, and lower values were found for SiNb. In μ SBS, the values of SiNb65% were higher at 24 h (45.22 MPa) and at six months (36.83 MPa), with statistically differences from values for the SiBa groups.

Conclusions: SiNb particles were successfully synthesized using the sol-gel method, and their incorporation into luting agents at a concentration of up to 65% improved the physicochemical characteristics and color stability of these agents.

Keywords: Resin cements, Niobium, Silicates

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1. Introduction

Ceramic laminate veneers, used as a conservative treatment for the aesthetic rehabilitation of teeth, have an up to 98% survival rate in longitudinal clinical analyses [1–4]. The aesthetics, durability and biocompatibility of ceramic laminate veneers make them an appropriate option to restore and rehabilitate anterior teeth [3]. The use of these thin ceramic pieces is only possible because of adhesive techniques, as the use of veneers cannot rely on micromechanical retention. Therefore, cementation strategies play an important role in the success of these treatments [4].

Photopolymerizable luting agents are used as one of the main cementation strategies for ceramic laminate veneers because the thickness of ceramic allows the passage of light during the cementation procedure [5,6]. The adequate polymerization of these agents is fundamental for the performance of this material in clinical

scenarios [7]. The formation of a high-quality polymeric structure is associated with greater stability of the material over time [8], better mechanical properties [9], less free-monomer leaching [10], less degradation and greater color stability [11]. Filler concentration and composition of the polymeric matrix of agents may affect the polymerization of the material under these ceramic restorations [12], and the improvement of filler chemical structures may be an alternative to increasing the conversion of monomers in these materials [7,12]. Silicate particles have been used as fillers for dental composites [13–15], and changes in silicate structure may improve their properties.

Niobium (Nb) is a metal that, even when used in small amounts, increases resistance, is highly biocompatible, and may improve the properties of different materials [16–19]. Little is known about the development of niobium silicate particles [20] and their use in dental composites, but the combination of niobium and silica may be an alternative to improve the mechanical properties of luting agents. The sol-gel method may be used to synthesize these particles, which, when added to a methacrylate-based matrix, change the physicochemical properties, color and bonding stability of particle-filled luting agents over time. This study synthesized niobium silicate particles using the sol-gel method and incorporated them into a resin-based luting agent.

The null hypothesis of this study was that the addition of SiNb would not significantly change the associated properties of the experimental resin cement used in the study.

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2. Materials and methods

2.1. Synthesis of niobium Silicate

The niobium silicate particles were synthesized using the sol-gel method, with tetraethyl orthosilicate (TEOS - Sigma Aldrich, St. Louis, MO, USA) as the silica precursor, and niobium pentachloride (NbCl₅- CBMM, Araxá, Minas Gerais, Brazil) as the niobium precursor. The sol was produced using a silica:niobium ratio of 9:1, and hydrolysis was catalyzed using 1M chloridric acid (HCl - Dinâmica, Indaiatuba, São Paulo, Brazil). The sol was kept at room temperature for 7 days for gelification, and the gel was dried and calcinated at 100° C and 500° C for 24 h each time. The particles synthesized were ground and sieved using a 500-mesh sieve before characterization and use as a filler for luting agents.

2.2 Particle characterization

2.2.1 X-ray diffraction

To assess the atom arrangement of the synthesized particles, x-ray diffraction was performed with a diffractometer (X'PertPRO, PANalytical MPD, Netherlands) using CuK α radiation at 40 kV – 40 mA, an angular range between 5° and 100°, and a step size of 0.02° for 2 s.

2.2.2 Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to analyze the chemical structure of the synthesized particles using an infrared spectrometer (VERTEX 70, Bruker Optics, Ettlingen, Germany) equipped with an attenuated total reflectance (ATR) device (Platinum ATR-QL; Bruker Optics, Ettlingen, Germany). The range of the analysis was 400–3000 cm⁻¹.

2.2.3 Surface area and particle size

The particles were dispersed in isopropyl alcohol (Sigma Aldrich, St. Louis, MO, USA), and particle size was measured by laser diffraction (CILAS 1180, Orleans, France). Based on data dispersion, median and 10%/90% quartile values were determined. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, based on nitrogen adsorption isotherm data. Nitrogen adsorption measurements were made using an Autosorb Quantachrome Nova 1200 instrument (Quantachrome Instruments Corporate Headquarters, USA).

2.2.4 Scanning electron microscopy

Scanning electron microscopy was used to analyze particle morphology. Samples were gold coated, placed in an aluminum sample holder and analyzed with a scanning electron microscope (JSM-6060; JEOL, Freising, Germany) at a 10 kV acceleration voltage.

2.3 Luting agent formulation

To formulate the experimental photopolymerizable luting agents, bisphenol a-glycidyl dimethacrylate (BisGMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) were used at concentrations of 50%, 30% and 20% by weight. The bis-alkyl phosphinic oxide (BAPO) was used for photoinitiation at a concentration of 1 wt%, and 0.01 wt% butylated hydroxytoluene (BHT) was added as a polymerization inhibitor.

The niobium silicate particles were added to the resin matrix at 50 wt% and 65 wt% concentrations, resulting in the SiNb50% and SiNb65% groups. Barium glass particles (Esstech, Essington, PA, USA) at the same concentrations were also added to prepare SiBa50% and SiBa65%. Before addition to the polymer, all particles were silanized with an acetone solution of 3-(trimethoxysilyl)propyl methacrylate (Merck KGaA, Darmstadt, Germany) at a 95 wt% acetone concentration. The fillers were

mixed manually and ultrasonicated for 480 s (L100; Schuster, Santa Maria, Brazil) before use. All samples were polymerized using a LED unit (Radii; SDI, Bayswater, Australia) at 1200 w/cm³ for 60s.

2.4 Luting agent characterization

2.4.1 Refractive index

The refractive index values of the luting agents were determined using a spectral ellipsometer (SOPRA GES-5E PUV, Semilab, Budapest, Hungary) adjusted for the wavelength range of 380 – 450 μ m. The measurements were made in the unpolymerized and polymerized samples of the particle-filled luting agents and in the filler-free material.

2.4.2 Degree of conversion and polymerization kinetics

The measurements were made by FTIR using a spectrometer (VERTEX 70, Bruker Optics, Ettlingen, Germany) equipped with an attenuated total reflectance (ATR) accessory composed of a horizontal diamond crystal at an angle of 45° with the mirror. Three samples (n = 3) measuring 1 mm high and 4 mm in diameter were tested for each group. All samples were photoactivated using a LED unit (Radii; SDI, Bayswater, Australia) for 60 s, at a standard distance of 1 mm from the unit tip. Data were processed using the Opus 6.5 software (Bruker Optics, Ettlingen, Germany), with a Blackman Harris 3-term apodization, 4 cm⁻¹ resolution and mirror speed of 2.8 mm/s. The degree of conversion (DC) 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. Polymerization kinetics was evaluated according to DC and polymerization rate over time [21].

2.4.3 Softening in solvent

Softening in solvent was analyzed in specimens (n = 5) measuring 5 mm in diameter and 1 mm thick, embedded in acrylic resin and polished with a felt disc containing alumina suspension (Alumina, 6 μ m, Arotec, Cotia, Brazil). Five indentations (25 g/20 s) were made on each specimen using a digital Knoop hardness tester (HNV 2, Shimadzu, Tokyo, Japan), and mean Knoop microhardness was used as the initial measurement (KHN1). The specimens were immersed in 70% ethanol for 2 h, and KHN was measured again, under the same conditions (KHN2). The percentage difference between KHN1 and KHN2 in each sample and the mean reduction in KHN (% KHN) were calculated [22].

2.4.4 Radiopacity

Radiopacity was analyzed according to ISO 4049:2009 [23]. Radiographic images were obtained on phosphor plates (VistaScan, Dures plus GmbH & Co. KG, Bietigheim-Bissingen, Germany) after 0.4 s exposure at a focal length of 40 cm. The X-ray source was operated at 70 kV and 8 mA. The specimens from each group were positioned along an aluminum step wedge on each phosphor plate. The pixel density of each specimen and each step of the aluminum scale (standard 25 mm² central area) were measured using the ImageJ software (Wayne Rasband, National Institutes of Health, Bethesda, MD, USA). Pixel density values were converted to mmAl according to the pixel density in each image.

2.4.5 Film Thickness

Film thickness was tested in accordance with ISO 4049: 2009 [23]. Two glass plates with a contact surface area of 200 $\pm$ 25 mm² each and a thickness of at least 5 mm had their thicknesses measured with a digital caliper (M1). A standardized portion of the experimental luting agents was placed on the center of a plate. Another plate was placed on top of the material, and a 150-N force was applied for 180 s. After this time, the force was removed, and the sample was photopolymerized for 60 s. The thickness of the set was measured again (M2). The difference between the two measurements was the result of film thickness (M1-M2). For each

experimental group, the test was repeated three times, and the mean result values were used.

2.4.6 Color stability

The color of particle-filled luting agents was assessed with a spectrophotometer (Carry 500 UV-Vis-NIR, Agilent, Santa Clara, CA, USA) using the Commission Internationale de L'Eclairage method (CIELab, Vienna, Austria). Specimens, which measured 10 mm in diameter x 1 mm thick (n=5), were stored in distilled water at 37° C for the 24-h and the six-month analyses. The fractions corresponding to the red, green and blue wavelength fractions were used to determine L*, a* and b* values. Based on the relative intensity of each wavelength at the 24-h and in the six-month measurements, the L*, a* and b* values were used to calculate chroma (C*) and hue (h*). The average color difference was calculated using CIEDE2000 (ΔE_{00}) [24] and the whiteness index for dentistry (ΔWID) [25].

Three different color parameters were calculated using the values of each parameter. The color difference (E) between immediate and longitudinal measurements were calculated by the equation:

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

where: L = color changes; a = color changes over the red/green scale; and b = color changes over the yellow/blue scale.

2.4.7 Micro shear bond strength

Twenty lithium disilicate ceramic discs (IPS E.max, Ivoclar Vivadent, Schaan Liechtenstein) measuring 10 mm in diameter and 2 mm high were used for micro shear bond strength analysis. After sintering, the discs were embedded in acrylic resin and polished with alumina suspension (Alumina, 6 μ m, Arotec, Cotia, SP, Brazil) on a felt disc. Samples were randomly separated into the four experimental groups (n=5). Sample surfaces were sandblasted and ultrasonicated for 5 min. For ceramics preparation, 10% hydrofluoric acid gel (Condac porcelana 10%, FGM, Joinville, Brazil) was applied for 20 s, and the samples then were rinsed under running water and washed in an ultrasonic tank with distilled water for 5 min (L100; Schuster, Santa Maria, Brazil). Silane (RelyXTM Ceramic Primer, 3M ESPE, Sumaré, Brazil) and a layer of adhesive (AdperTM ScotchbondTM Multiuso, 3M ESPE, Sumaré, Brazil) were applied to the ceramic surfaces for 5 s. Six luting agent cylinders measuring 0.7 mm in diameter and 1.0 mm high were produced on each disc. The specimens were photopolymerized (Radii Cal; SDI, Bayswater, Australia) for 60 s. The samples were stored in distilled water at 37° C for 7 days for the immediate (24 h) and longitudinal (6 mo.) analyses.

For the micro shear bond strength tests, the specimens were positioned in a universal test machine (EZ-SX; Shimadzu, Japan), and a shear force was applied at 1 mm/min by a steel cable measuring 0.2 mm in diameter and positioned as close as possible to the cement interface. The force was applied until fracture, and bond strength was calculated in mega pascals (MPa). Failure modes, analyzed visually using a stereomicroscope at a magnification of 40x, were classified as: (1) adhesive failure between the luting agent and the ceramic; (2) cohesive failure inside the ceramic; (3) cohesive failure inside the luting agent; and (4) mixed.

2.4.8 Flexural strength

For the flexural strength tests, a metallic matrix measuring 25 ± 0.1 mm x 2.0 ± 0.1 mm x 2.0 ± 0.1 mm was used to produce rectangular specimens (n=10). Specimens were photoactivated for 30s in two windows on each side and stored in distilled water for 24 h and six months for immediate and longitudinal analyses. At each time point, specimens were submitted to a three-point flexural strength test in a universal mechanical testing machine (EZ-SX Series, Shimadzu, Tokyo, Japan) at a crosshead speed of 1 mm/min. The values were recorded in newtons (N) and transformed into mega pascal (MPa) by the formula prescribed in ISO 4049:2009 [23].

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

where σ is the flexural strength in MPa, F is the maximum load in N, L is the distance in mm between the holders, B is the width in mm at the center of the specimen measured just before the test, and H is the length in the center of the specimen measured just before the test.

3. Statistical Analysis

Descriptive analysis was performed for the characterization of niobium silicate particles and for refractive index. Data normality was assessed with the Kolmogorov-Smirnov test. As data distribution was normal, one-way ANOVA and the Tukey test were used to analyze the differences in DC, KHN 1, % KHN, radiopacity, ΔE_{00} , ΔWID and film thickness between groups. The comparison of colorimetric parameters, micro shear bond strength and flexural strength between groups and time points was performed with two-way ANOVA and the Tukey test. The difference between KHN1 and KHN2 in solvent softening was analyzed using a paired Student t test. The level of significance was set at 5% for all tests and analyses.

4. Results

Niobium silicate particles were successfully synthesized using the sol-gel method. As shown in Figure 1A, the X-ray diffraction analysis of the SiNb powder demonstrated the glassy structure resulting from the synthesis. Chemical bonding was observed in FTIR (Fig. 1B). The Si-O-Nb bonding was found in the 1078cm⁻¹ band. Mean particle size of SiNb particles was 2.054 μ m, and the surface area was 616.962 m²/g (Table 1).

The refractive index range in the particle-filled luting agents and in the filler-free monomers is shown in Table 2. The higher the amount of filler in the specimens in the SiNb and in the SiBa groups, the greater the mismatch between IR in the filler-containing and filler-free materials. Polymerization kinetics is shown in Figure 2. Rate of polymerization increased faster in luting agents with a 50% concentration of filler and was higher in the SiBa than in the SiNb groups. No statistically significant differences were found in DC between groups. The SiBa groups had greater radiopacity than the SiNb groups at both concentrations. Reduced film thickness was observed in the SiNb groups (Table 2), and all groups had values in the range of 40 μ m, which is required by ISO 4049:2009.

Lower %KHN was observed in the SiNb group, but there were no statistical differences in the KHN1 analysis (Table 3). KHN values decreased in the SiBa groups after sample immersion in ethanol. Greater color stability was observed for SiNb50% and SiNb65% after six months of storage, as confirmed by ΔE_{00} . The ΔWID values were lower for SiBa groups (Table 4). All luting agents had perceptible and nonacceptable changes in color after six months of storage according to ΔE_{00} and ΔWID . Changes in L* values in the SiBa groups and in C* values in the SiNb groups over time were significant.

Table 5 shows the results of the flexural strength and micro shear bond strength tests at 24 h and six months. Immediate flexural strength analysis revealed no statistical differences between groups, whereas SiBa50% and SiBa65% had higher MPa values after six months of storage. In the SBS immediate analysis, the SiNb65% group had higher bond strength values. After six months, a decrease was observed in the SiNb65% group, whereas the other groups had no statistical differences. The type of failure mode was mixed after SBS in all specimens.

5. Discussion

Filler type and concentration in photopolymerizable luting agents affect their physicomechanical properties [15], color stability [26] and adhesive properties [27]. The stability of luting agents in cemented ceramic

Fig. 1. Characterization of SiNb particles. (A) Crystalline structure, analyzed using XRD, showed amorphous structure of synthesized particles; (B) Chemical composition, according to FTIR findings, confirmed Si-O-Nb bonding; (C) Scanning electron microscopy characterized details of particle morphology.

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

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

* Information provided by the manufacturer

Table 3. Mean and standard deviation values of the hardness of the experimental luting agents 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
SiBa 50%	32.15 (±9.2) ^{Aa}	19.42 (±2.5) ^b	37.31 (±14.4) ^B
SiBa 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).

laminate veneers is associated with reduced debonding failure, color change and marginal discoloration [1,4]. In this study, niobium silicate was synthesized as a novel filler for luting agents, and its properties were evaluated. An increased degree of conversion, reduced film thickness, reduced softening and increased color stability was observed for luting agents with niobium silicate addition. Thus, the null hypothesis should be partially rejected. The incorporation of 65% of niobium silicate particles resulted in increased μSBS in the immediate and longitudinal analyses.

The sol-gel method was used to produce niobium silicate particles, and their synthesis resulted in amorphous particles with Si-O-Nb bonding, as observed in particle characterization (Fig. 1). This structure has been previously found in the synthesis of different particles that have Si and Nb as components [28], but no previous study has described the synthesis and the characterization of niobium silicate particles as this study. The sol-gel method is a simple and low-cost [29] alternative to produce homogeneous particles with a high specific surface area [30]. The synthesized particles in this study had a specific surface area of 616.92 m²/g, which is greater than the values observed for particles with a similar size [13]. The sol-gel method produced particles with a high surface porosity, and, therefore, a high surface area is observed in the synthesized particles [31]. Particle size was adjusted by sieving, so that particle structure was adequate for the use as a filler in luting agents [32].

The incorporation of fillers into a polymeric matrix affects monomer conversion in composites [33]. Figure 2 shows that both filler type and concentration, in addition to DC, affect polymerization initiation, according

Table 2. Results obtained for refractive index range, degree of conversion, radiopacity and film thickness between the photopolymerizable luting agents.

	Refractive Index	Degree of conversion (%)	Radiopacity (mmAl)	Film Thickness (mm)
SiNb 50%	1.52 - 1.48	48.68 (±2.15) ^A	1.13 (±0.1) ^C	16.66 (±5.7) ^A
SiNb 65%	1.54 - 1.51	47.34 (±1.45) ^A	1.23 (±0.1) ^C	20.00 (±6.9) ^A
SiBa 50%	1.50 - 1.45	48.35 (±3.54) ^A	2.08 (±0.2) ^B	36.33 (±5.6) ^B
SiBa 65%	1.52 - 1.47	48.47 (±0.83) ^A	2.98 (±0.1) ^A	36.33 (±5.6) ^B
Filler-Free luting agent	1.50 - 1.48	-	-	-

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

to the analysis of polymerization over time. When 65% of SiNb filler was incorporated into the matrix, the increase in DC in the first 5 s was slower than in the groups with 50%. This behavior, found in different composites, may be explained by the reduction of light transmittance during polymerization [34,35] when a high filler content is added to the matrix. A similar behavior was observed for SiBa at 65% and 50% concentrations, but the comparison of SiNb and SiBa groups revealed that the first had a faster DC increase. This may be explained by the higher light transmittance, found in SiBa groups as a result of the mismatch between RI values, which were lower than those of the filler-free resin. The maximum polymerization rate was greater in the SiBa groups (Fig. 2), which may also explain the effect of filler composition on polymerization. The lower polymerization rate and the delayed gel phase found in SiNb groups may be associated with a lower shrinkage rate [34] and, consequently, a lower polymerization stress of particle-filled luting agents [36]. Polymerization kinetics of SiNb groups may be associated with the high greater light scattering promoted by the morphological characteristics of synthesized SiNb particles. Particle size and surface area affect the passage of light through the matrix [37] and the high specific surface area found in SiNb particles (Table 1) raises the hypothesis that light scattering in the matrix/particle interface may affect the polymerization kinetics of particle-filled luting agents. [34,37]. Despite the differences in polymerization kinetics, no statistical differences were found in DC values between the different filler compositions and concentrations (Table 2).

Adequate polymer formation and composite stability are necessary for luting agents that are prone to degradation in the exposed portion of the cementation line. The solvent softening test revealed a low percentage reduction of KHN in the SiNb groups (Table 3). This result may be associated with the adequate formation of a polymeric structure (Table 2) and the stability of the Si-O-Nb bonding found in SiNb particles (Fig. 1). Moreover, the Si groups in the glassy structure of synthesized particles

Table 4. Mean values of L*, a*, b*, C* and h* for luting agents in 24h and 6-month analysis. ΔE_{00} and ΔWID calculated based on the CIELab color coordinates.

	24h					6m					ΔE_{00}	WI_D
	L*	a*	b*	C*	h*	L*	a*	b*	C*	h*		
SiNb50%	55.18 (± 2.70) ^{Ba}	-2.59 (± 0.38) ^{Ba}	6.17 (± 0.56) ^{ABa}	7.29 (± 0.72) ^{Aa}	122 (± 2.59) ^{Ba}	56.13 (± 0.90) ^{Aa}	-2.41 (± 0.39) ^{Ba}	3.36 (± 0.82) ^{Aa}	4.94 (± 0.96) ^{Ab}	137.36 (± 3.90) ^{Ab}	2.53 (± 0.93) ^A	3.16 (± 1.61) ^A
SiNb65%	56.79 (± 2.18) ^{Ba}	-2.76 (± 0.79) ^{Ba}	6.57 (± 0.79) ^{Aa}	7.77 (± 1.57) ^{Aa}	123.21 (± 4.96) ^{Ba}	59.17 (± 2.35) ^{Aa}	-2.46 (± 0.72) ^{Ba}	4.5 (± 1.95) ^{Aa}	5.84 (± 2.14) ^{Ab}	130.58 (± 5.72) ^{Ab}	2.28 (± 0.56) ^A	2.82 (± 1.41) ^A
SiBa50%	61.57 (± 4.10) ^{Aa}	-1.62 (± 0.14) ^{Aa}	2.08 (± 0.14) ^{Ca}	3.22 (± 0.33) ^{Ca}	139.86 (± 7.87) ^{Aa}	47.18 (± 3.02) ^{Bb}	-2 (± 0.31) ^{Aa}	2.76 (± 0.57) ^{Ba}	4.08 (± 0.72) ^{Aa}	137.52 (± 2.44) ^{Aa}	6.93 (± 2.21) ^B	-7.22 (± 2.72) ^B
SiBa65%	55.05 (± 2.92) ^{Ba}	-2.77 (± 0.33) ^{Ba}	4.12 (± 0.33) ^{Ba}	5.85 (± 0.96) ^{Ba}	135.51 (3.48) ^{Aa}	42.73 (± 1.63) ^{Bb}	-2.29 (± 0.19) ^{Aa}	3.78 (± 0.45) ^{Ba}	5.1 (± 0.52) ^{Aa}	132.34 (± 1.56) ^{Aa}	6.16 (± 1.05) ^B	-7.02 (± 0.83) ^B

Different capital letters indicate a statistically significant difference in the same column. Different small letters indicate a statistically significant difference between 24h and 6m analysis.

Fig. 2. Polymerization kinetics of each experimental photopolymerizable resin cement. Degree of conversion (%) (A) and polymerization rate (Rp.[s⁻¹]) (B) over time. Association of polymerization rate and degree of conversion is plotted in (C).**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)	mSBS (1w)	mSBS (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}
SiBa 50%	59.96 (± 5.1) ^{Aa}	51.02 (± 6.5) ^{Ab}	24.19 (± 6.4) ^{Ca}	21.08 (± 6.2) ^{Ba}
SiBa 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 a statistically significant difference in the same column. Different small letters indicate a statistically significant difference in the same line. ($P < 0.05$).

may promote an effective interaction between the polymeric matrix, the coupling agent and the fillers [14]. The interaction of particles with the polymeric matrix is also affected by particle stability, and the low solubility of the Si-O-Nb bonds [38] leads to a lower particle leaching. Thickness should also be addressed when studying the cementation line stability. Reduced film thickness was observed in the SiNb groups, and this may contribute to a reduction in luting agent degradation and to the maintenance of bonding stability over time, as marginal defects in ceramic veneers are some of the main reasons of failure in this type of treatment [1,2]. Binding between a silanizing agent and the resin matrix may not occur at all silanized points, and stress is most probably concentrated in these areas [39]. All the experimental luting agents had a statistically significant decrease of flexural strength values from 24 h to six months of storage (Table 5). The SiBa groups showed greater values than the SiNb groups at six months. This decrease in the flexural strength of SiNb in comparison to SiBa materials may be partially attributed to this smaller number of binding points between the coupling agent and the resinous matrix, which is most likely to result of the fact that the surface area of the SiNb particles is larger. This, however, seemed to have a smaller effect on μ SBS results

(Table 5). The SiNb65% group had significantly higher MPa values in the immediate and longitudinal analyses, with no cohesive failure in the cementation line. The μ SBS values are in accordance with the characteristics of commercial luting agents [40], indicating that the synthesized particles may be added to luting agents to produce a reliable adhesive interface.

Photopolymerizable luting agents are the first choice for cementing laminate veneers, and color maintenance over time is important for clinical success [41]. The experimental luting agents formulated in this study were submitted to a color stability test by measuring the color parameters of the specimens after 24 h of preparation and after six months of storage in distilled water. The SiBa groups had a significantly higher ΔE_{00} after six months (Table 4). The ΔE_{00} analysis revealed that all luting agents had unsatisfactory results in the analysis of both acceptable and perceptible thresholds [42,43]. This difference resulted from the decrease in the ΔL of the SiBa groups and the decrease in ΔC of the SiNb groups. The ΔWID values confirmed the ΔE_{00} analysis, as a negative difference was found in the SiBa groups, which indicates that samples became darker over time [44,45]. The color stability observed in the SiNb-containing luting agents is of major importance, as these materials are frequently used in ceramic laminate veneers in aesthetic areas [41], and changes in the visual perception in these areas may affect the clinical performance of treatments.

The synthesis of novel fillers for dental composites should tailor these materials to their clinical applications. The requirements for the cementation of ceramic laminate veneers include aesthetics, and the adhesive properties of these materials should ensure the success of the rehabilitation procedure [3]. The addition of niobium silicate particles, synthesized in this study, to methacrylate-based photopolymerizable luting agents may be an alternative to the development of more stable materials with adequate adhesive properties and color stability.

6. Conclusion

This study found that:

- Niobium Silicate was successfully synthesized using the sol-gel method;
- SiNb addition to luting agents in an up to 65% concentration resulted in reliable physicomechanical properties;
- SiNb addition resulted in color stability of the particle-filled materials.

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