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Physicochemical Effects of Niobic Acid Addition Into Dental Adhesives

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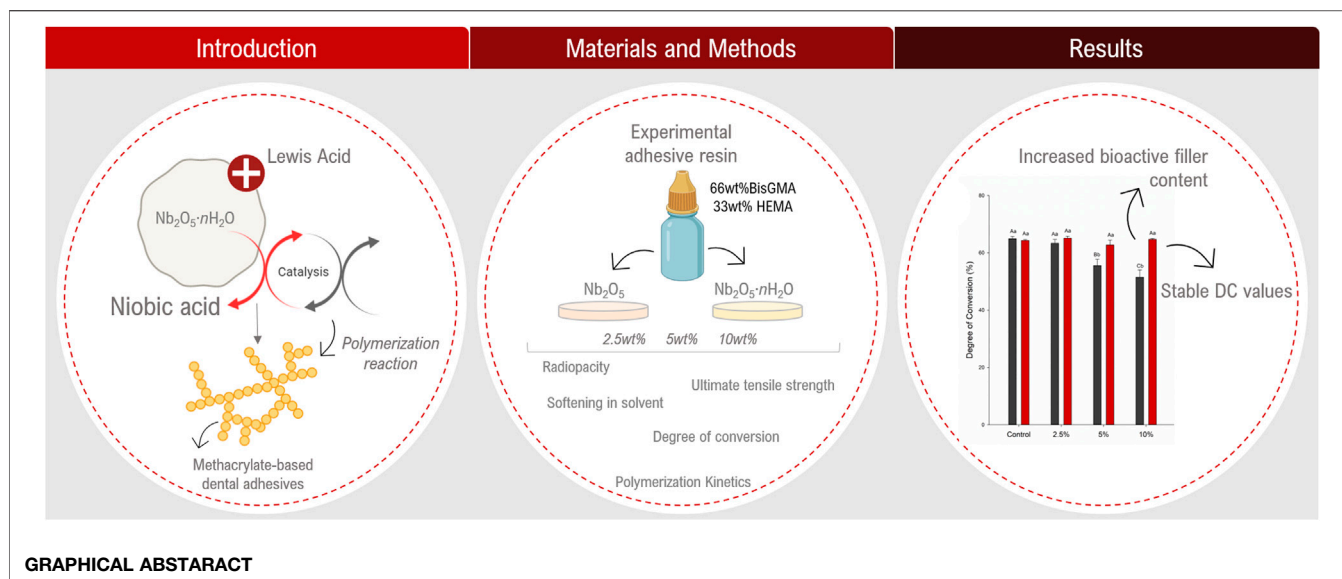
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The incorporation of metallic oxides in dental adhesives has been a strategy to confer improved radiopacity and physicochemical properties for polymers. Tailoring the structure of these fillers could contribute to their application in therapeutic strategies for dental restorations. The aim of this study was to evaluate the incorporation of niobic acid into experimental dental adhesives, and compare these adhesives to niobium pentoxide containing adhesives. A control group without Nb₂O₅·n H₂O or Nb₂O₅ was also used for comparison. Niobium-based particles have been used as a feasible approach, mainly because of their bioactivity. In this study, hydrated niobium pentoxide, also called niobic acid (Nb₂O₅·n H₂O), was incorporated into an experimental dental adhesive as a potential catalyst for monomer conversion. A base resin for dental adhesive was formulated with methacrylate monomers and photoinitiators. Two types of oxides were tested as filler for this adhesive: Nb₂O₅·n H₂O or niobium pentoxide (Nb₂O₅). Both fillers were added separately into the experimental adhesive at 0, 2.5, 5, and 10 wt.%. One group without Nb₂O₅·n H₂O or Nb₂O₅ (0 wt.% of filler addition) was used as a control group. The formulated materials were analyzed for radiopacity according to the ISO 4049 and used FTIR analysis to assess the degree of conversion (DC) and the maximum polymerization rate (RP_{max}). Mechanical properties were analyzed by ultimate tensile strength (UTS) in a testing machine. Softening in solvent was conducted by measuring Knoop microhardness before and after immersion of samples in ethanol. Normality of data was assessed with Shapiro-Wilk, and comparisons between factors were conducted with two-way ANOVA and Tukey at 5% of significance. Both fillers, Nb₂O₅ or Nb₂O₅·n H₂O, increased the radiopacity of dental adhesives in comparison to the unfilled adhesive (*p* < 0.05). There were no differences among groups for the ultimate tensile strength (*p* > 0.05), and all groups containing Nb₂O₅ or Nb₂O₅·n H₂O improved the resistance against softening in solvent (*p* < 0.05). The groups with 5 and 10 wt% addition of Nb₂O₅ showed decreased DC compared to the control group (*p* < 0.05), while the addition of Nb₂O₅·n H₂O up to 10 wt% did not alter the DC (*p* > 0.05). The polymerization rate did not change among groups (*p* > 0.05). In conclusion, Nb₂O₅·n H₂O is a promising filler to be incorporated into dental adhesives providing proper mechanical properties, improved resistance against solvents, and increased radiopacity, without changing the DC.

Keywords: niobium, dentin-bonding agents, polymerization, mechanical phenomena, dental materials



INTRODUCTION

Adhesive systems for dental restoration have undergone several modifications so that their physical and chemical properties could be improved, supporting long-lasting restorative treatments. Inorganic fillers have been incorporated into dental adhesives aiming to reduce polymeric degradation via increasing hydrolytic stability (Münchow and Bottino, 2017). Furthermore, these particles have been tuning in adhesives formulation to improve polymers' radiopacity (Garcia et al., 2020a) and mechanical properties (Lohbauer et al., 2010; Belli et al., 2014). Inorganic fillers have also been proposed to improve the therapeutic activity of resin-based materials. Bioactive particles have been used to assist in tooth remineralization (Balhaddad et al., 2019; Braga and Fronza, 2020), making bioactive resin-based dental materials to be feasible approaches to prevent dental demineralization and to provide the recovery of hard dental tissues affected by caries (Garcia et al., 2017; Ibrahim et al., 2020a; Ibrahim et al., 2020b). Calcium phosphates (Garcia et al., 2017; Braga and Fronza, 2020), calcium silicates (Profeta, 2014), bioactive glasses (Balbinot et al., 2020a; Yao et al., 2020), and zinc-based particles (Toledano et al., 2016) were already tested and showed mineral deposition or remineralization effect on dental hard tissues. Recently, niobium-based particles have been highlighted due to their interesting properties for dentistry, such as high radiopacity and bioactivity (Marins et al., 2018).

Niobium pentoxide (Nb_2O_5) has been proposed as a stable bioactive inorganic compound that has been used in different biomaterials in the biomedical field (Obata et al., 2012; Balbinot et al., 2018). The ability to promote deposition and growth of hydroxyapatite crystals on its surface when in contact with simulated body fluid (Karlinsey and Yi, 2008), artificial or natural saliva (Karlinsey et al., 2006) was explored in different materials in dentistry (Mazur et al., 2015) (Lopes et al., 2014; Altmann et al., 2017; Balbinot et al., 2018; Balbinot et al., 2019; Marins et al., 2019; Balbinot et al., 2020a; Balbinot et al., 2020b;

Marins et al., 2020). Nb_2O_5 was studied in experimental adhesives (Leitune et al., 2013a; Collares et al., 2014; Marins et al., 2018), endodontic sealer (Leitune et al., 2013b), and glass ionomer cements (Garcia et al., 2016), improving their radiopacity (Leitune et al., 2013a; Leitune et al., 2013b; Garcia et al., 2016; Marins et al., 2018), physical properties (Leitune et al., 2013a; Leitune et al., 2013b) and inducing mineral deposition on adhesives surfaces (Collares et al., 2014). Increasing the Nb_2O_5 content into the polymeric matrix may lead to modifications to the properties of the material. The higher concentration is related to the reduction in the conversion of carbon-carbon double bonds (C=C) into single carbon-bonds (C-C) of methacrylate groups (Leitune et al., 2013a; Leitune et al., 2013b). This ineffective polymerization results in more residual monomers are available in the resin matrix, which may lead to higher cytotoxic effects (Salehi et al., 2015), greater sorption and solubility (Collares et al., 2011), lower bonding effectiveness to dentin (Hass et al., 2013), and lower mechanical properties (Ferracane, 1985). Balancing the potential bioactivity of Nb_2O_5 with adequate physicochemical and mechanical properties is essential for the application of these materials in a clinical scenario.

Among the oxides of niobium (Nb), Nb_2O_5 is the most stable. Nb can present a wide range of oxidation numbers from +5 to -3, with higher oxidation stated being more frequent to be found, mainly +5 states (Nowak and Ziolk, 1999). Due to the coordination numbers variability of Nb, this is a versatile element to develop novel materials, including organometallic structures. Among the different forms of niobium oxides, it is possible to synthesize hydrated niobium pentoxide, also called niobic acid ($Nb_2O_5 \cdot nH_2O$), through the hydrolysis of niobium pentachloride ($NbCl_5$) or niobium ethoxide ($Nb(OC_2H_5)_5$) (Nakajima et al., 2011) or chemical reaction with acetophenones (Skrodczky et al., 2019). Niobic acid has been used in industry as a heterogeneous catalyst for chemical reactions due to its behavior as Lewis acid (Tanabe, 2003; Nakajima et al., 2011).

TABLE 1 | Description of the components used to design the dental adhesives according to the addition of fillers by weight.

Group	Filler content
Control	No filler addition
2.5%	2.5 wt.% Nb ₂ O ₅
5%	2.5 wt.% Nb ₂ O ₅ .nH ₂ O 5 wt.% Nb ₂ O ₅
10%	2.5 wt.% Nb ₂ O ₅ .nH ₂ O 10 wt.% Nb ₂ O ₅ 10 wt.% Nb ₂ O ₅ .nH ₂ O

Nb₂O₅.nH₂O has a high acid strength (H_o -5.6~-8.2) and Lewis and Brønsted acid sites are available in the Nb₂O₅.nH₂O surface, making this oxide an efficient catalyst due to the reception of electrons (Lewis acid) or donation of protons (Brønsted acid) (Ziolek and Ziolek, 1999). As a heterogeneous catalyst, niobic acid may confer lower necessary energy to activate the chemical reactions (Nakajima et al., 2011). These differences in chemical structure may result in an optimized response of Nb₂O₅.nH₂O for dental applications. Although Nb₂O₅ was analyzed in dental adhesives previously (Leitune et al., 2013a; Marins et al., 2018), the potential effect of Nb₂O₅.nH₂O was not investigated so far. The aim of this study was to evaluate the incorporation of niobic acid into experimental dental adhesives and compare these adhesives to niobium pentoxide containing dental adhesives. A control group without Nb₂O₅.nH₂O or Nb₂O₅ was also used for comparison. The following physicochemical properties were analyzed: radiopacity, ultimate tensile strength, softening in solvent, degree of conversion, and polymerization rate.

MATERIALS AND METHODS

Dental Adhesives Formulation

The experimental dental adhesives were formulated by mixing 66.66 wt.% of bisphenol A glycerolate dimethacrylate (BisGMA) and 33.33 wt.% 2-hydroxyethyl methacrylate (HEMA). Camphorquinone and ethyl 4-dimethylaminobenzoate at 1 mol% and butylated hydroxytoluene at 0.01 wt.% were added to all groups as photoinitiator system. Niobium pentoxide (Nb₂O₅) and niobic acid (Nb₂O₅.nH₂O) were incorporated at three different concentrations into this base resin: 2.5; 5 and 10 wt.%. As a control group, this base resin was used without Nb₂O₅ or Nb₂O₅.nH₂O addition in all tests. Table 1 describes the components used to design the adhesives resin groups according to the addition of fillers by weight. The monomers and the photoinitiator materials were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) and used without further purification. The fillers were hand-mixed for 5 min, sonicated for 180 s, and hand-mixed again for 5 min. A light-emitting diode (LED) unit (Radii, SDI, Bayswater, VIC, Australia) with 1,200 mW/cm² was used to perform the photoactivation for all tests.

Dental Adhesives Evaluation Radiopacity

The radiopacity of the dental adhesives was evaluated according to ISO 4049 [(ISO), 2009], using five samples per

group (10.0 mm diameter and 1.0 mm thick, n = 5). The samples were prepared using a polyvinyl siloxane mold (ADSIL, Vigodent, Rio de Janeiro, RJ, Brazil), 20 s of photoactivation on each side, and stored in distilled water for 24 h at 37°C. An X-ray source (DabiAtlante model Spectro 70X) at 70 kV and 8 mA was used to expose the samples and acquire the X-ray images. Phosphorus plates (Digital System, VistaScan, Dürer Dental GmbH & Co. KG, Bietigheim-Bissingen, Baden-Württemberg, Germany) were used with 0.8 s of exposition and a focus-film distance of 400 mm. Each film was exposed with one sample per group together with an aluminum step-wedge (8 mm thick with 1 mm steps) in all images acquirement. The images were saved in TIFF format, and the mean and standard deviation values of gray for each sample and each aluminum millimeter were obtained (Photoshop software, Adobe Systems Incorporated, San Jose, CA, USA). The values were expressed as the equivalent thickness of aluminum in mm (Leitune et al., 2013a).

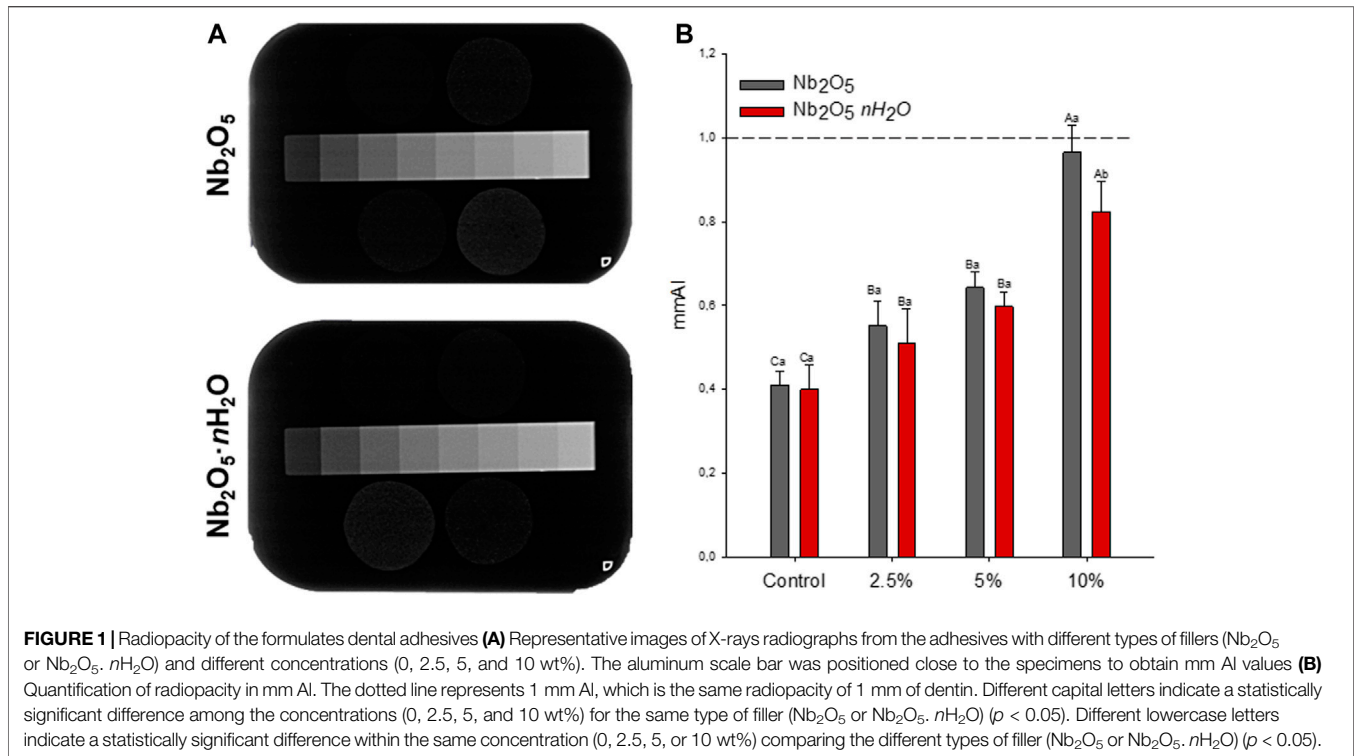
Ultimate Tensile Strength

Ten samples per group (n = 10) were prepared using a metallic mold with an hourglass shape (8 mm long, 2 mm wide, 1 mm thick, 1 mm² cross-sectional area). Each specimen was photoactivated for 20 s on each side, removed from the mold, and stored in distilled water at 37°C for 24 h. After this period, each sample had its constriction area measured with a digital caliper and fixed with a cyanoacrylate resin into metallic jigs. Each jig was positioned in a universal testing machine (EZ-SX Series, Shimadzu, Tokyo, Kantō, Japan). The upper part of the jig was tensile at a crosshead speed of 1 mm/min until the samples fracture. The values were recorded in Newtons (N), divided by the area of each sample (mm), and expressed in megapascals (MPa).

Softening in Solvent

Three samples per group (1 mm thick and 5 mm diameter, n = 3) (Garcia et al., 2019) were prepared with a polyvinyl siloxane (Express™ VPS Impression Material, 3 M ESPE, St. Paul, MN, USA) mold, 20 s of photoactivation on each side, and stored in distilled water for 24 h at 37°C. The samples were embedded in self-curing acrylic resin (Clássico, São Paulo, São Paulo, Brazil) and polished (Model 3v, Arotec, Cotia, SP, BR) with silicon carbide sandpapers (from 600 to 2000-grit, Klingspor, Pinhas, PR, Brazil) and felt disc sutured with alumina suspension (Alumina 1 μm, Fortel, São Paulo, SP, BR). The embedded samples were washed with running water and sonicated for 480 s (L100; Schuster, Santa Maria, RS, Brazil) with distilled water. After 24 h, the specimens were evaluated by three indentations at 10 g/5 s to obtain the initial Knoop hardness (KHN1) using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Kantō, Japan). The specimens were subjected to softening in ethanol for 2 h, and the hardness test was performed again (KHN2). The percentual hardness reduction was calculated for each sample and each group, according to Eq. 1:

$$\% \Delta KHN = 100 - ((KHN2 \times 100) / KHN1). \quad (1)$$

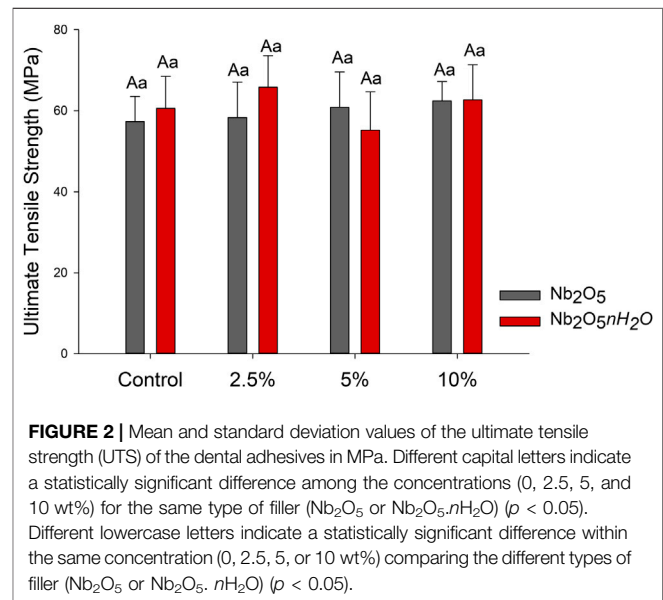


Degree of Conversion

Three samples per group ($n = 3$) were evaluated by Fourier Transform Infrared Spectroscopy (FTIR) with a spectrometer (Vertex 70, Bruker Optics, Ettlingen, Baden-Württemberg, Germany) equipped with an attenuated total reflectance device (ATR). The uncured adhesives were dispensed onto the crystal using a polyvinyl siloxane mold of 1 mm thick and 5 mm diameter. The spectra from each sample were acquired using Opus 6.5 software (Bruker Optics, Ettlingen, Baden-Württemberg, Germany) with Blackman Harris 3-Term apodization, in the range from 400 to $4,000\text{ cm}^{-1}$, with 64 scans and 4 cm^{-1} resolution. Then, the sample was light-cured for 20 s at a standardized distance of 1 mm between the tip of the LED unit and the top of the sample. Immediately after the light-curing process, the spectra of the cured adhesive samples were obtained. The degree of conversion (DC) was calculated according to previous studies using the peaks at $1,610\text{ cm}^{-1}$ (aromatic carbon-carbon double bonds) and $1,640\text{ cm}^{-1}$ (aliphatic carbon-carbon double bonds) (Collares et al., 2011; Collares et al., 2013; Garcia et al., 2018; Garcia et al., 2020b).

Polymerization Rate

The polymerization rate of three samples per group of dental adhesives ($n = 3$) were evaluated by differential scanning calorimetry (DSC, DSC-Q2000, TA Instrument Co., New Castle, DE, USA) with a photocalorimetric accessory (PCA) adjusted to 100 mW/cm^2 . The uncured adhesives were photoactivated with PCA under a nitrogen flow rate of 50 ml/min. The maximum polymerization rate was determined according to a previous study (Rodrigues et al., 2015).



Statistical Analysis

SigmaPlot software (version 12.0, Systat Software, San Jose, CA, USA) was used for the statistical analyses. Shapiro-Wilk test was used to analyze the data distribution. Radiopacity, DC, polymerization rate, UTS, and softening in solvent were evaluated using two-way ANOVA and Tukey post-hoc test considering the two factors: concentrations (0, 2.5, 5, or 10 wt.%) and filler (Nb_2O_5 or $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$). A significance level of 0.05 was used to analyze the data statistically.

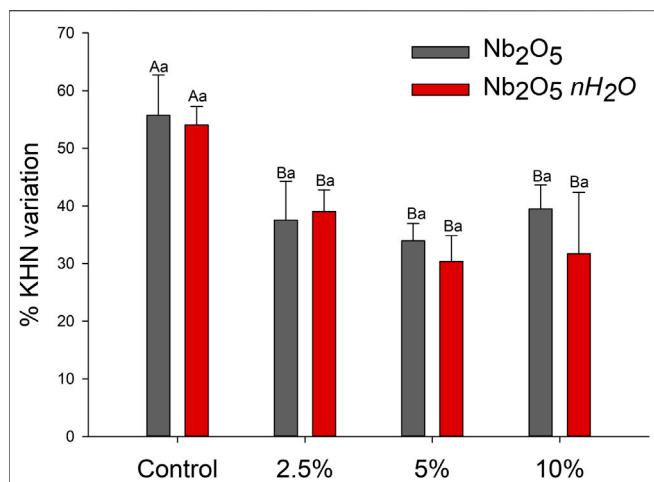


FIGURE 3 | Mean and standard deviation of softening in solvent after immersion in ethanolic solution in percentage of microhardness variation. Different capital letters indicate a statistically significant difference among the concentrations (0, 2.5, 5, and 10 wt%) for the same type of filler (Nb₂O₅ or Nb₂O₅.nH₂O) ($p < 0.05$). Different lowercase letters indicate a statistically significant difference within the same concentration (0, 2.5, 5, or 10 wt%) comparing the different types of filler (Nb₂O₅ or Nb₂O₅.nH₂O) ($p < 0.05$).

RESULTS

The results of the radiopacity evaluation of the dental adhesives are displayed in **Figure 1**. Representative x-ray images were shown in **Figure 1A** with an aluminum scale bar used as a comparison for mm Al calculation. With increasing the content of Nb₂O₅ or Nb₂O₅.nH₂O, the radiopacity increased in contrast to the

control group ($p < 0.05$). There were no differences between the groups with 2.5 or 5 wt.% of fillers regardless of its type (Nb₂O₅ or Nb₂O₅.nH₂O) ($p > 0.05$). The group with 10 wt.% of Nb₂O₅ showed higher radiopacity in comparison to 10 wt.% of Nb₂O₅.nH₂O ($p < 0.05$). However, within the same filler type, the incorporation of 10 wt.% of Nb₂O₅ or Nb₂O₅.nH₂O showed the highest radiopacity ($p < 0.05$), with values close to 1 mm of aluminum.

The results from the mechanical evaluation of the dental adhesives are shown in **Figure 2**. Among all groups, the values ranged from 55.17 (± 9.48) for 5 wt.% of Nb₂O₅.nH₂O to 65.80 (± 7.79) for 2.5 wt.% of Nb₂O₅.nH₂O. There were no statistically significant differences among groups regardless of the fillers' concentration or filler type ($p > 0.05$).

Figure 3 displays the results of softening in solvent. For Nb₂O₅ groups, the addition from 2.5 wt.% of this filler decreased the percentage of softening compared to the control group ($p < 0.05$), without statistically significant differences among 2.5, 5, and 10 wt.% ($p > 0.05$). The same behavior occurred for Nb₂O₅.nH₂O groups: the incorporation of any tested concentration of Nb₂O₅.nH₂O improved the resistance against softening in solvent in comparison to the unfilled adhesive ($p < 0.05$), and no changes were observed from 2.5 to 10 wt.% of Nb₂O₅.nH₂O ($p > 0.05$).

The DC and $R_{p_{max}}$ are presented in **Figure 4**. For Nb₂O₅ groups, the DC ranged from 64.93 (± 0.78) for the control to 51.49 (± 2.55) for 10 wt.% ($p < 0.05$). From 5 wt.% of Nb₂O₅ addition, the DC decreased in comparison to 0 and 2.5 wt.% ($p < 0.05$), with lower DC result for the 10 wt.% Nb₂O₅ addition ($p < 0.05$). For Nb₂O₅.nH₂O groups, the DC ranged from 65.13 (± 0.68) for 2.5 wt.% to 62.74 (± 1.71) for 5 wt.% (**Figure 4A**). There were no statistically significant differences among groups with different

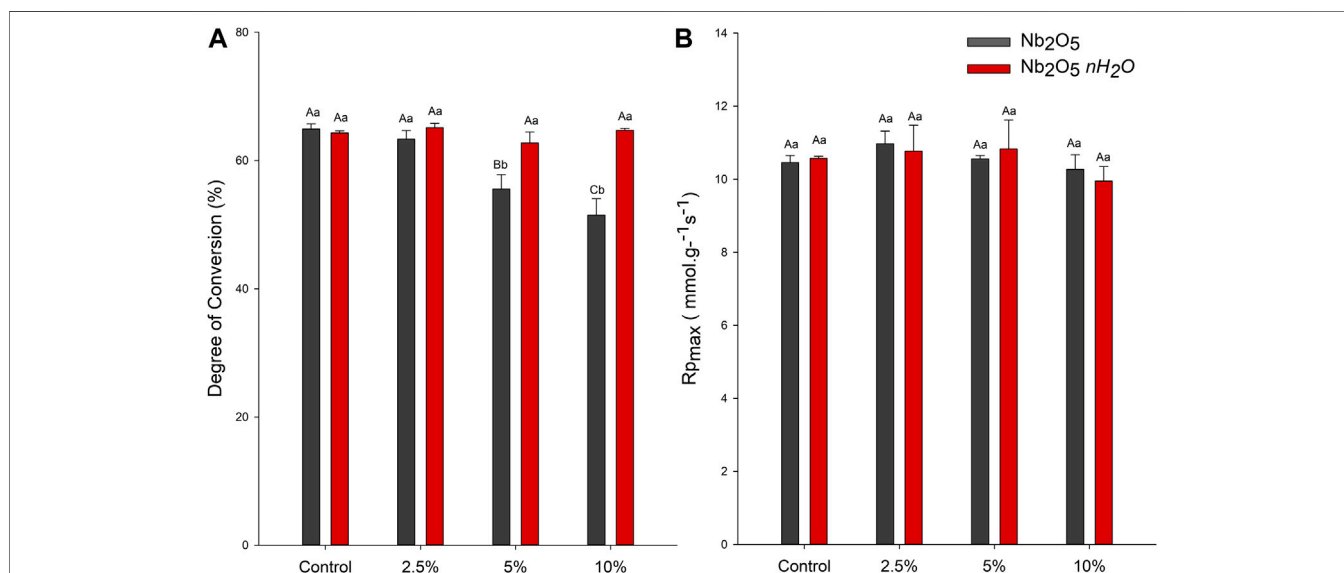


FIGURE 4 | Degree of conversion (DC) and maximum polymerization rate ($R_{p_{max}}$) of dental adhesives (A) Percentage of converted carbon-carbon double bonds of the dental adhesives after photoactivation via FTIR-ATR (B) $R_{p_{max}}$ of the dental adhesives via DSC-PCA. Different capital letters indicate a statistically significant difference among the concentrations (0, 2.5, 5, and 10 wt%) for the same type of filler (Nb₂O₅ or Nb₂O₅.nH₂O) for the DC or $R_{p_{max}}$ evaluation ($p < 0.05$). Different lowercase letters indicate a statistically significant difference within the same concentration (0, 2.5, 5, or 10 wt%) comparing the different types of filler (Nb₂O₅ or Nb₂O₅.nH₂O) for the DC or $R_{p_{max}}$ evaluation ($p < 0.05$).

concentrations of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($p > 0.05$). The addition of five or 10 wt.% of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ induced higher DC in comparison to five or 10 wt.% of Nb_2O_5 . The $R_{p_{\max}}$ via DSC showed no difference among groups, neither between the two types of filler, neither among fillers concentration (**Figure 4B**).

DISCUSSION

Dental adhesives have been modified to present superior therapeutic and physicochemical properties (Profeta, 2014; Balbinot et al., 2020a; Bendary et al., 2020; Garcia et al., 2020b; Yao et al., 2020). In this context, bioactive fillers have been incorporated into dental adhesives (Profeta, 2014; Balbinot et al., 2020a; Bendary et al., 2020; Braga and Fronza, 2020; Yao et al., 2020). However, the effect of these fillers in the physicochemical properties of resin-based materials must be addressed to guarantee the proper behavior for dental adhesives. In the present study, niobic acid was studied as a potential catalyst bioactive inorganic filler into dental adhesives. The radiopacity, the resistance against softening in solvents, and the mechanical properties were maintained for niobic acid-containing adhesives when compared to niobium pentoxide filled materials. The highest concentrations of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ supported a high DC in comparison to the unfilled adhesive, with an increased percentage of conversion when compared to Nb_2O_5 in the same concentrations.

The life span of resin composite restorations is importantly affected by the recurrence of caries and the identification of marginal gaps, leading to the premature replacement of composites (Brouwer et al., 2016). Adhesives must be distinguishable from the adjacent tissues in the radiographic examination to assist in the proper diagnose of carious affected tissues (Brouwer et al., 2016; Mjor, 2005). The low radiopacity of adhesives hampers their distinguish from adjacent tissues and pathological processes, and as shown in **Figure 1A**, unfilled adhesives are difficult to be observed on X-ray radiographs. The International Organization for Standardization (ISO) established that polymer-based restorative materials must present radiopacity equal or superior to dentin (International Organisation for Standardization, 2009) and it is known that 1 mm of dentin has a radiopacity similar to 1 mmAl in the aluminum step-wedge (Mjor, 2005). Thus, reaching this value is the goal of the development of radiopaque materials. Neither particle reached a radiopacity average with this value, as shown in **Figure 1B**. However, both types of filler, Nb_2O_5 , and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, provided dental adhesives with higher radiopacity than the unfilled material, which has a similar composition to a commercial widely used adhesive (Ogliari et al., 2006). Our results indicated that Nb_2O_5 or $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ at 10 wt.% reached ~0.8–0.95 mm Al for the groups suggesting that, despite the potential bioactivity, these fillers could provide suitable radiopacity for the developed dental adhesives.

The main responsibility for the increased radiopacity is the higher atomic number of Nb (41) in comparison to the other components of the dental adhesive [carbon (6), hydrogen (1), nitrogen (7), oxygen (8)]. At 10 wt.% concentration, higher values

were observed for Nb_2O_5 when compared to $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ (**Figure 1**; $p < 0.05$). Differences in chemical composition between both particles may have led to the higher radiopacity of adhesives doped with Nb_2O_5 when 10 wt.% was added. The particles of $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ are commonly derived from the hydrolysis of niobium pentachloride, forming $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. In contrast, the particles of Nb_2O_5 are mostly composed of Nb, and O. Differences in the particle densities and, consequently, in the volume of filler incorporated, maybe was responsible for the radiopacity variation between the groups of adhesives with 10 wt.% of Nb_2O_5 or $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$.

The formulated dental adhesives were also analyzed for their mechanical properties via UTS and softening in solvent. The UTS shows the intrinsic resistance of materials against fractures when they are tensioned. Inorganic particles may act via toughening behavior such as crack deflection and increased elastic modulus (Lohbauer et al., 2010). In this study, we did not observe differences in the UTS (**Figure 2**; $p > 0.05$), while the softening in solvent for all groups containing a filler, regardless of its type, decreased in comparison to the control group (**Figure 3**). This test evaluates the ability of polymers to resist solvents. Therefore, the hydrophilicity and the crosslinking density of the polymers are involved in this process outcome.

When exposed to solvents, polymers are prone to swell because the forces among the polymer chains are surpassed by the attraction between polymer chains and molecule solvents (Schneider et al., 2008). Then, depending on the polymer network formation, the time of immersion, and the solubility parameter of the solution used, polymer chains maybe degrade via hydrolysis (Ferracane, 2006; Schneider et al., 2008). In this study, after the immersion in solvent, all groups presented lower Knoop hardness, corroborating with previous analyses (Schneider et al., 2008; Garcia et al., 2020b). Resins with inorganic fillers, such as the metallic oxides here tested, are less susceptible to suffer chemical degradation mainly because ionic bonding between atoms in oxides is more stable than covalent bonding within the organic matrix. Therefore, adhesives doped with inorganic fillers can present lower softening in solvent compared to unfilled adhesives (Stürmer et al., 2020). Irrespective of the concentration of Nb_2O_5 or $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, both materials provided successful decreased softening for the dental adhesives. Therefore, the crosslinking density of the filled materials was superior to the control group, or the fillers were able to increase stability by reducing the amount of organic content.

The properties of Nb_2O_5 and $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ particles, such as density, size, and volume, as well as their chemical composition, may affect the loading of these fillers into the dental adhesives. The ability to convert carbon-carbon double bonds into carbon-carbon single bonds highly depends on the availability of light through the polymer thickness since these materials are photoactivated (Par et al., 2020). By increasing metallic oxides content into adhesives, it is likely to observe a decreased DC (Leitune et al., 2013a; Garcia et al., 2018; Garcia et al., 2020a). This effect may be related to the higher opacity that filled adhesives may present in comparison to unfilled adhesives (Shortall, 2005). Moreover, it was suggested that the presence of oxides into the composition of unsilanized glasses could also jeopardize the

degree of conversion, depth of cure, and polymerization rate *via* “premature termination of free-radical-mediated polymerization” (Par et al., 2020). The results of the present study were in accordance with previous analyses when the addition of Nb₂O₅ decreased the DC of dental adhesives (Leitune et al., 2013a). While the addition of 5 wt.% of Nb₂O₅ was enough to reduce the DC in comparison to the control group, the use of Nb₂O₅·nH₂O did not change this property up to 10 wt.% (Figure 2A). The high DC, even with 10 wt.% of Nb₂O₅·nH₂O, could be a result of the activity of this oxide within the resin during the polymerization reaction. The presence of Lewis and Brønsted acid sites in these particles may increase the reaction during the polymerization (Tanabe, 2003; Nakajima et al., 2011). In this way, even with possible lower light penetration through the filled adhesives, the catalyst activity of Nb₂O₅·nH₂O could minimize this effect and support the DC. Interestingly, there were no differences in the R_{p,max} to indicate the adhesive with Nb₂O₅·nH₂O decreased the energy required for the polymerization reaction (Figure 2B). However, the catalytic effect may also have shifted the chain mobility without altering the R_{p,max} and maintaining DC.

While the catalysis effect could explain the DC values, during the manipulation and polymerization process, differences in the optical properties between groups were observed. Nb₂O₅ is known to have a high refractive index (Leitune et al., 2013a), and the adhesives in this group presented an opaque white color, while Nb₂O₅·nH₂O containing materials were more translucent and yellowish. These differences could be observed in both uncured and cured adhesives, and this finding may be endorsed in the precursors of Nb₂O₅·nH₂O synthesis since NbCl₅ is a yellowish material. However, other features such as the refractive index difference between Nb₂O₅·nH₂O and Nb₂O₅, the density of the fillers, and the volume incorporated may lead to these color variations. Although color and translucency were not investigated in this study, with this exploratory tuning of both fillers was already possible to identify some interesting differences between Nb₂O₅·nH₂O and Nb₂O₅.

The balance between the bioactivity and the physicochemical properties is a demand in the study of bioactive dental materials. Niobium pentoxide was shown to induce mineral deposition by the formation of a phosphate-rich layer on 2.5 wt.% and 5 wt.% loaded dental adhesives (Collares et al., 2014). Increasing the quantity of bioactive fillers into the adhesives could lead to a higher release of niobium compounds that may induce higher mineral formation in the adhesive layer as the availability of ions could cause deposition of mineral as described previously (Obata et al., 2012). Nb₂O₅·nH₂O doped adhesives showed improved outcomes, such as higher radiopacity, maintenance of mechanical strength, and lower softening in solvent. With the incorporation of Nb₂O₅·nH₂O up to 10 wt.%, the DC was sustained, suggesting that the control of particle properties may be an alternative for the development of dental adhesives doped with metallic oxides. It is a limitation of the present study to not have tested the mineral

deposition capacity of the formulated adhesives. Future studies are encouraged to evaluate the possible bioactivity of Nb₂O₅·nH₂O doped adhesives.

CONCLUSION

In this study, we explored two niobium-based fillers for dental adhesives: niobium pentoxide (Nb₂O₅) and niobic acid (Nb₂O₅·HY). These fillers were tested at 0, 2.5, 5, and 10 wt.%. Overall, Nb₂O₅ and Nb₂O₅·HY doped adhesives showed improved outcomes, such as higher radiopacity, maintenance of mechanical strength, and lower softening in solvent. Through of addition of Nb₂O₅·HY up to 10 wt.%, the DC was sustained as presented the unfilled adhesive. In conclusion, Nb₂O₅·HY is a promising filler to be incorporated into dental adhesives providing proper mechanical properties, improved resistance against solvents, and increased radiopacity, without changing the DC.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

IG: Investigation, Formal Analysis, Data Curation, Visualization, Writing—Original Draft. VL: Conceptualization, Formal Analysis, Resources, Writing—Review & Editing. GB: Visualization, Writing—Review & Editing. AB: Writing—Original Draft. MM: Writing—Original Draft. SS: Resources, Writing—Review & Editing. FC: Conceptualization, Resources, Writing—Review & Editing, Supervision, Funding acquisition.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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