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PENTÓXIDO DE NÍÓBIO COMO CARGA PARA MATERIAIS DE BASE
POLIMÉRICA PARA USO ODONTOLÓGICO

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Orientadora

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“Os que se encantam com a prática sem a ciência são como os timoneiros que entram no navio sem timão nem bússola, nunca tendo certeza do seu destino.”

Leonardo da Vinci (1452 – 1519)

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RESUMO

O objetivo desta tese foi caracterizar o pentóxido de nióbio (Nb_2O_5), produzir materiais compósitos de matriz polimérica de uso odontológico e avalia-los. As partículas de Nb_2O_5 foram caracterizadas com difração de raios-X, microscopia eletrônica de varredura, granulometria a laser, método de Brunauer–Emmett–Teller e espectroscopia micro-Raman. Um adesivo experimental foi desenvolvido com a incorporação de diferentes concentrações de Nb_2O_5 (0, 5, 10 e 20 %, em peso). Este adesivo foi avaliado quanto à radiopacidade, grau e cinética de conversão, microdureza e a sua interface com a dentina. Um cimento endodôntico experimental de cura dual também foi desenvolvido com a incorporação de diferentes concentrações de Nb_2O_5 (0, 80, 100 e 120 %, em peso). Este cimento foi avaliado quanto à radiopacidade, escoamento, espessura de película, microdureza e grau de conversão (imediatamente, 7 dias e 14 dias após a fotoativação). A avaliação do Nb_2O_5 mostrou que as partículas utilizadas apresentavam estrutura monoclinica, com formato irregular, com tamanho médio de 38,16 μm , área de superfície de 3,86 m^2/g e estrutura química compatível com pentóxido de nióbio. A radiopacidade e dureza do adesivo aumentaram com a incorporação do Nb_2O_5 e ele pode ser detectado no interior da interface dentina/adesivo. No cimento endodôntico a incorporação do Nb_2O_5 também aumentou a radiopacidade e a dureza e reduziu o escoamento apenas no grupo com 120 %. O grau de conversão aumentou até 14 dias após a fotoativação, com exceção do grupo com 80%. Após a caracterização do Nb_2O_5 e da produção dos materiais experimentais, foi feito o depósito de pedido de patente de invenção. Conclui-se que o pentóxido de nióbio é uma nova e promissora partícula para uso em Odontologia como agente de carga.

Palavras-chave: Adesivos dentinários; Cimentos dentários; Nióbio

ABSTRACT

The aim of this thesis was to characterize the niobium pentoxide (Nb_2O_5), to produce resin-based composite for dental applications and evaluate them. Niobium pentoxide was characterised by X-ray diffraction, surface area, particle size, micro-Raman and scanning electron microscopy. An experimental adhesive resin was formulated with 0, 5, 10 and 20 wt% Nb_2O_5 . The formulated adhesive resins were evaluated based on microhardness, degree of conversion, radiopacity and interface (resin/dentin) characterisation by micro-Raman. An experimental dual-cured root canal sealer was produced with a methacrylate-based comonomer blend. Nb_2O_5 was added at four different concentrations: 0, 80, 100 and 120wt%. Radio-opacity, flow, film thickness, microhardness and degree of conversion (after 1, 7 and 14 days) were evaluated. The particles used in this study presented a monoclinic crystalline phase with typical chemical groups, mean size of 38.16 μm and 3.86 m^2/g of surface area. Microhardness and radiopacity increased with higher amounts of Nb_2O_5 , and the particles were able to penetrate into the hybrid layers. Microhardness and radiopacity increased with higher amounts of Nb_2O_5 in the adhesive resin, and the particles were able to penetrate into the hybrid layers. For the endodontic cement, the radiopacity and microhardness increased with the Nb_2O_5 addition. The flow was significantly smaller for the 120% group. All groups except those with 80wt% had higher values for degree of conversion after 14 days than immediately after photocuring. After the Nb_2O_5 characterization and the production of experimental materials, an application for patent was done. Niobium pentoxide is a new and promising filler for dental materials production.

Key-words: Dental cements; Dentin-Bonding agents; Niobium

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INTRODUÇÃO

O desenvolvimento de materiais de uso odontológico com melhores propriedades físicas e mecânicas ao longo do tempo e com características clínicas melhores vem sendo objeto de diversos estudos. Sendo assim, a busca pela melhora das características destes materiais, como maior radiopacidade (COLLARES et al., 2010), maior resistência à degradação hidrolítica (FERRACANE, 2006) e enzimática (PASHLEY et al., 2004) e a capacidade do material de interagir com as estruturas biológicas (TAY; PASHLEY, 2009), entre outras, vem sendo alvo de interesse da comunidade científica (TAY; PASHLEY, 2009; COLLARES et al., 2010) e da indústria (MICHL et al, 1986).

As propriedades dos materiais de base polimérica dependem da qualidade da rede polimérica formada (FERRACANE, 1985; MURCHISON; CHARLTON; MOORE, 1999; FERRACANE, 2006). A adição de partículas inorgânicas a um polímero pode interferir nas propriedades mecânicas e características do material, uma vez que altera o índice de refração do mesmo. Assim a disponibilidade de energia luminosa no interior do polímero pode ser modificada (SHORTALL; PALIN; BURTSCHER, 2008) e dificultar a mobilidade das cadeias durante a propagação da polimerização (ANDRZEJEWSKA, 2001). Entretanto, esta adição também pode melhorar as propriedades mecânicas, a radiopacidade e a longevidade do material (SCHULZ et al., 2008; COLLARES et al., 2010).

Quanto maior a quantidade de material inorgânico em um compósito, menor será a quantidade de matriz orgânica, em um mesmo volume. Essa redução da quantidade de matriz orgânica acarretará também em uma redução da contração e

do estresse de polimerização (GONCALVES; KAWANO; BRAGA) e um aumento na resistência mecânica (LI, J. et al., 2012). Diversas cargas inorgânicas vêm sendo utilizadas para o desenvolvimento de materiais de uso odontológico. Dentre essas cargas podemos destacar o fluoreto de itérbio, sulfato de bário, sílica, quartzo, entre outras (COLLARES et al., 2010; KARABELA; SIDERIDOU, 2011). Entretanto, a busca por novas cargas que apresentem melhores características continua sendo alvo de estudos (COLLARES et al., 2009; COLLARES et al., 2010).

As cargas inorgânicas podem ser empregadas em compósitos de base polimérica para uso odontológico com diversos propósitos. Essas cargas podem ser empregadas com a intenção de reduzir a degradação do material (SIDERIDOU, I. et al., 2004), como agente radiopacificante (COLLARES et al., 2010), com propriedades antimicrobianas (STOPIGLIA et al., 2012), com propriedades bioativas (WEIR; CHOW; XU, 2012), entre outras. Essas cargas podem ser óxidos metálicos (TOLEDANO et al., 2012), apatitas sintéticas (COLLARES et al., 2012), entre outros (COLLARES et al., 2010).

O Nióbio é um metal de transição de número atômico 41 e o seu óxido pode ter diversas aplicações (FICARRO et al., 2008). O pentóxido de nióbio (Nb_2O_5) vem sendo empregado em diversas áreas da ciência dos materiais (FICARRO et al., 2008) e algumas aplicações em biomateriais (COVANI et al., 2007). O Nb_2O_5 apresenta-se como um material biocompatível quando aplicado sobre a superfície de implantes de titânio, em íntimo contato com o tecido conjuntivo, aumentando a proliferação celular quando comparado ao titânio comercialmente puro (VELTEN et al., 2004). Quando associado a ligas metálicas de titânio, o nióbio mostrou-se não citotóxico, melhorando as propriedades da liga (LI, Y. et al., 2010). Quando aplicado em materiais em contato com saliva natural e artificial, apresentou a capacidade de

estimular a deposição de material mineral, caracterizando assim a sua bioatividade (KARLINSEY et al., 2006). Entretanto, até onde se saiba, o Nb_2O_5 ainda não foi empregado no desenvolvimento de materiais de base polimérica de uso odontológico.

OBJETIVO

Com base no exposto, o objetivo do presente estudo foi desenvolver compósitos de matriz resinosa de uso odontológico com a incorporação de pentóxido de nióbio de alta pureza e a posterior caracterização das propriedades dos materiais resultantes.

Objetivou-se ainda:

- Caracterizar o pentóxido de nióbio utilizado;
- Desenvolver um adesivo a base de metacrilato com a incorporação de pentóxido de nióbio;
- Avaliar o adesivo desenvolvido;
- Desenvolver um cimento endodôntico de polimerização dual a base de metacrilato com a incorporação de pentóxido de nióbio;
- Avaliar o cimento endodôntico desenvolvido.
- Proteger o conhecimento gerado por meio de depósito de pedido de patente.

MANUSCRITOS E PATENTE

A presente tese é composta por dois manuscritos e um depósito de pedido de patente de invenção. O Manuscrito I foi submetido para a Journal of Dentistry e encontra-se publicado (<http://dx.doi.org/10.1016/j.jdent.2012.04.022>) (LEITUNE et al., 2012b). O Manuscrito II foi submetido para a International Endodontic Journal e encontra-se publicado (<http://dx.doi.org/10.1111/j.1365-2591.2012.02107.x>) (LEITUNE et al., 2012a).

O Depósito de Pedido de Patente, apresentado ao Instituto Nacional de Propriedade Industrial (INPI) pela UFRGS, tendo como inventores Vicente Castelo Branco Leitune, Susana Maria Werner Samuel, Fabrício Mezzomo Collares, Antonio Takimi e Carlos Perez Bergmann em 08 de maio de 2012, sob o título "Material compósito, Processo de produção de material compósito e Uso do material compósito de matriz polimérica com incorporação de carga inorgânica de pentóxido de nióbio", foi cadastrado sob o nº PI BR 1020120108887.

MANUSCRITO I**Niobium Pentoxide as a novel filler for dental adhesive resin**

Short Title: **Nb₂O₅ for adhesive resin**

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Niobium Pentoxide as a novel filler for dental adhesive resin

Abstract

Objectives: The purpose of this study was to develop an adhesive resin with incorporation of niobium pentoxide and evaluate the its properties. **Methods:** Niobium pentoxide was characterised by X-ray diffraction, surface area, particle size, micro-Raman, scanning electron microscopy and the effectiveness of silanisation process by Fourier Transform Infrared (FTIR). An experimental adhesive resin was formulated with 0, 5, 10 and 20 wt% Nb₂O₅. The formulated adhesive resins were evaluated based on microhardness, degree of conversion, radiopacity and interface (resin/dentin) characterisation by micro-Raman. **Results:** The particles used in this study presented a monoclinic crystalline phase with typical chemical groups and micrometer mean size. Microhardness and radiopacity increased with higher amounts of Nb₂O₅, and the particles were able to penetrate into the hybrid layers. **Conclusions:** Therefore, Nb₂O₅ may be an alternative for polymer-based biomaterials.

Clinical Significance: Niobium pentoxide could be used to produce adhesive resins with enhanced properties.

Keywords: Niobium pentoxide, Dentin bonding agents, Composite resins

Niobium Pentoxide as a novel filler for dental adhesive resin

Introduction

In dentistry, the effectiveness of adhesion of resin to a tooth is directly related to several factors like demineralization of substrate, resin infiltration and polymer setting¹. This adhesion is vital for the success of long-term resin composites used to restore tooth cavities¹. Poor adhesion to tooth substrates may produce postoperative hypersensitivity, marginal discoloration and less retention of restoration²⁻⁴. The following efforts have been made to increase bond strength to dental tissues: reducing the hydrophilicity of polymer^{5, 6}, adding fillers⁷, controlling the enzymatic activity⁸⁻¹¹ and changing other factors¹.

Attempts to incorporate filler particles into adhesive resin to improve the resin/tooth bond strength were made in several previous studies and commercial products. Colloidal silica, hydroxyapatite, ytterbium trifluoride, tantalum oxide, glass and zirconia are among the filler particles that have been tested^{5, 7, 12-16}. A hybrid layer that is less prone to degradation could be created by incorporating filler in adhesive resin¹⁷, thereby decreasing the water sorption and increasing the material properties. The reliable bonding of dental materials to tooth substrates depends on the mechanical and chemical features of the polymer. Therefore, improving the material's properties will lead to a more durable restorative treatment¹⁸.

Niobium is a transition metal and has the atomic number 41. This metal is widely used to enhance mechanical properties in the development of metal alloys¹⁹. Its application in the biomedical area was started recently and is due to the titanium and steel alloys that are used in the biomedical field^{20, 21}. Niobium pentoxide (Nb_2O_5) has shown bioactive properties, like hydroxyapatite crystal growth when in contact

with human saliva ²² and has been used as an anti-allergic coating in endoprostheses with favourable results ²³. Therefore, it appears to be an alternative for composite development.

However, to the best of our knowledge, there are no reports on the use of niobium pentoxide in resin matrix production for biomedical use. The purpose of this study was to develop an adhesive resin, with niobium pentoxide, and evaluate the properties for using to restore tooth cavities.

Materials and Methods

The monomers used in this study were bisphenol A glycol dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA), camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDAB) and were provided by Esstech Inc., USA. These materials were used without further processing. Niobium pentoxide (Nb_2O_5) was provided by Companhia Brasileira de Metalurgia e Mineração (CBMM, Araxá, MG, Brazil). The organic phase of the adhesive was produced by mixing 50 wt.% Bis-GMA, 25 wt.% TEGDMA and 25 wt.% HEMA. CQ and EDAB were added at 1 mol% to all groups, according to the monomer moles. Nb_2O_5 was added at the following four different concentrations: 0, 5, 10 and 20 wt%. No radical scavenger was added. To improve the adhesion interface between filler particles and the matrix, Nb_2O_5 was subjected to a silanisation process with 5% of silane (γ -methacryloxypropyltrimethoxysilane, Aldrich Chemical Co., Milwaukee, WI, USA) and 95% of solvent (acetone), in weight ²⁴. After the silanisation process, the particles were stored for 24 hours at 37°C to allow the solvent to evaporate. All components were weighed using an analytical balance (AUW220D, Shimadzu, Japan), mixed and ultrasonicated for 1 hour. To perform monomer photo-activation, a light-emitting diode unit (Radii Cal, SDI LTD., Australia) was used. An irradiation value of 1200 mW/cm² was confirmed with a digital power meter (Ophir Optronics, USA).

Characterisation of Nb_2O_5

X-Ray diffraction

To identify the crystalline phases in the powder, a Philips diffractometer (X'Pert MPD model) operating at 40 kV and 40 mA, using CuK α radiation was used. The scanning rate was 0.05°/min, and the time-step was 1 s. Analyses were performed within a 5–60° range.

Micro-Raman spectroscopy

The typical chemical groups of Nb₂O₅ compounds were identified by micro-Raman spectroscopy using Bruker Optics (SENTERRA model) equipment. The range of the analysis was 80 to 2700 cm⁻¹.

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to evaluate the morphology of the Nb₂O₅ powder using Hitachi (TM3000 model) equipment.

Surface area and particle size

Using a Quantachrome NOVA1000 Autosorb Automated Gas Sorption System (Boynton Beach, FL, USA), the specific surface area of the Nb₂O₅ powder was determined through the Brunauer–Emmett–Teller (BET) method. Before the analysis, the sample was outgassed for 3 hours at 300°C in vacuum. The particle size distribution was assessed using a laser diffraction particle size analyser (CILAS 1180, Orleans, France).

Evaluation of the silanisation process

Fourier transform infrared (FTIR) spectroscopy was used to evaluate the attachment of silane to the Nb₂O₅ surface. The FTIR measurements were performed

in the Vertex 70 FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany). Nb_2O_5 powder was dispensed over a diamond crystal of Attenuate Total Reflectance (ATR) accessory. A total of 16 scans were collected from 400 cm^{-1} to 4000 cm^{-1} at a 4 cm^{-1} resolution. The C=C signal at 1636 cm^{-1} in the FTIR spectrum of Nb_2O_5 was used to verify the existence of the double bond following the surface treatment.

Refractive Index

The refractive index values of co-monomer blend, before and after polymerization, were evaluated by spectral ellipsometry. The sample was analyzed using an ellipsometer SOPRA GES-5E (SEMILAB-SOPRALAB, Courbevoie, France) adjusted for wavelength range of 0.30 to $0.75\ \mu\text{m}$, at $\theta = 68^\circ$ ^{25, 26}.

Radiopacity

The radiopacity of model adhesive resins was evaluated according to ISO 4049 ²⁷ standards. Five specimens per group ($n=5$), 10.0 mm ($\pm 0.5\text{ mm}$) in diameter and 1.0 mm ($\pm 0.1\text{ mm}$) in thickness, were produced. X-ray images were obtained with the phosphorous plates Digital System (VistaScan, Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Germany) using an exposure time of 0.4 s and a focus-film distance of 400 mm . The X-ray source (DabiAtlante model Spectro 70X) operated with a tungsten anode at 70 kV and 8 mA . Each of the five films contained one specimen of each of the four experimental groups. An aluminium step-wedge was exposed with the specimens in all images. The aluminium step-wedge thickness ranged from 0.5 mm to 5.0 mm in increments of 0.5 mm . The images were saved in TIFF format for less compressed files. Digital images were handled with Photoshop

software (Adobe Systems Incorporated, CA, USA). The means and standard deviations of the grey levels (density of pixels) of the aluminium step-wedge, and the specimens were obtained in a standardised area.

Degree of conversion

The degree of the conversion and polymerisation kinetics of the dental adhesive resin were evaluated using differential scanning calorimetry (DSC-Q2000, TA Instrument Co., Delaware, USA) with a photo-calorimetric accessory (PCA). PCA emits light from a high-pressure mercury lamp (250-650 nm) with an intensity of 2000 mW/cm². The intensity and wavelength were adjusted to 100 mW/cm² and 350-500 nm, respectively. The formulations (approximately 14 mg) were polymerised in open aluminium DSC pans with 6.8-mm diameters. An additional empty aluminium pan was used as the control. The sample was kept at 37°C for 30 seconds. Then, the lamp was switched on for 5 minutes, and the energy (heat flow) was recorded. The analysis was performed with a nitrogen flow of 50 mL/min. Assuming that the value of the heat involved is proportional to the reacted molar amount, the degree of conversion was determined according to equation 1:

$$\alpha(\text{mol}\%) = 100 \frac{[M]_0 - [M]}{[M]_0} = \frac{100Q}{(\Delta H_{p,0}/\Delta H_p)Q_{\text{tot}}} \quad (1)$$

where $\Delta H_{p,0}$ (kJ.mol⁻¹) corresponds to the heat of polymerisation for a total conversion; ΔH_p (kJ.mol⁻¹) is the heat of polymerisation obtained by the apparent area of the curve that corresponds to the total heat of reaction Q_{tot} (J.g⁻¹); and Q corresponds to the heat released as partial area under the curve for a time t . The $\Delta H_{p,0}$ found in the literature of a double bond of the methacrylates is -56 J.mol⁻¹.

The rate of polymerisation (R_p) is proportional to the flow of heat released in the isotherm as a function of irradiation time (t). Thus, R_p ($\text{mol}\cdot\text{s}^{-1}$) at any point during the reaction can be derived from the heat flow using the $\Delta H_{p,o}$ of the monomer from the equation 2:

$$R_p = (dH/dt) \cdot (M/ \Delta H_o.n) \quad (2)$$

where dH/dt is the heat flow in $\text{J}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$; M is the concentration of the monomer; and n is the number of double bonds per molecule of monomer.

Knoop microhardness

To determine the Knoop microhardness (KHN), the specimens produced for radiopacity evaluation were used. Five specimens for each experimental adhesive resin were embedded in acrylic resin and polished in a polisher (Model 3v, Arotec, Cotia, SP, Brazil) with a felt disc embedded in aluminium suspension (Alumina 1.0 μm , Arotec, Cotia, SP, Brazil). The specimens were dried and stored at 37°C for 24 hours. The specimens were subjected to a microhardness test in which 5 indentations (50 g/15 s), 100 μm apart, were assessed using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Japan). The calculation of the hardness value was performed using equation 3:

$$\text{KHN} = (14228.c)/d^2 \quad (3)$$

where **14228** is a constant, c is the load in grams and

d is the length of the longer diagonal in μm .

Interface characterisation by micro-Raman

Four lower incisor bovine teeth were cleaned of organic debris and stored in distilled water at 4°C. The labial enamel was removed using a water-cooled, low-speed diamond saw (Low Speed Saw; Buehler, Lake Bluff, IL, USA) to expose the superficial dentin. A smear layer was produced by grinding the flat surface with a 600-grit silicon carbide (SiC) disc under water for 30 s. The dentin was etched with phosphoric acid for 15 s and washed for an additional 15 s. A commercial primer (Primer Scotch bond multi-purpose, 3M ESPE, St Paul, MN, USA) was applied, and the solvent was dried for 5 s with an air spray. Adhesive resin was applied according to the experimental group and photocured for 20 seconds. A commercial composite resin (Z350, 3M ESPE, St Paul, MN, USA) was inserted in two increments of 2 mm and photocured for 40 seconds each to simulate tooth restoration.

The bonded specimens were stored in distilled water in a light-proof container at 37°C for 24 h. Sections (1 mm in thickness) were prepared by sectioning perpendicular to the flat adhesive-dentine surface. Four samples were obtained from each tooth.

Micro-Raman spectroscopy was performed using a SENTERRA Raman Microscope (Bruker Optics, Ettlingen, Germany). The samples were analysed using the following micro-Raman parameters: a 100 mW diode laser with 785 nm wavelength and spectral resolution of $\sim 3.5 \text{ cm}^{-1}$. One-dimensional mapping was performed over a 70 μm line across the adhesive-dentine interface at 1 μm intervals using a computerised XYZ stage. These areas covered the composite resin, adhesive layer, hybrid layer, partially demineralised and un-affected dentine and

were visualised and focused at x500 magnification. Accumulation time per spectrum was 5 seconds with 2 co-additions. Two mappings were performed per sample at random sites. The samples were kept moist throughout the experimental procedure. Post-processing was performed in Opus6.5 (Baker Optics) and consisted of analysis with modelling, which distinguished spectral components of the adhesive and dentine. One correspondent peak of each substance was used for integration. For the hydroxyapatite, 960 cm^{-1} was used, and for Nb_2O_5 , 685 cm^{-1} was used.

Statistical Analysis

The normality of data was evaluated using the Kolmogorov-Smirnov test. Statistical analysis was performed using one-way ANOVA (Nb_2O_5 concentration) and Tukey's post hoc test at the 0.05 level of significance.

Results

X-ray diffraction of the analysed sample is shown in Figure 1. It was possible to observe that the monoclinic Nb₂O₅ (ICDD 37-1468) was the only crystalline phase found in the sample. Morphology of Nb₂O₅ powder is shown in the SEM micrographs in Figure 2. also observed that the powder was composed of irregular particles. However, some spherical particles could be detected. The specific surface area of the Nb₂O₅ powder was 3.86 m²/g, and the mean particle size was 38.16 μm. The presence of silane in the particles was confirmed by the presence of the 1636 cm⁻¹ peak (Figure 3) at FTIR spectrum. Raman analysis presented typical chemical groups of niobium pentoxide compounds. The refractive index of co-monomer blend used ranged from 1.47 to 1.59 for monomer and from 1.50 to 1.62 for polymer.

The radiodensity values of the dental adhesive resins are presented in Figure 4. The values were expressed in millimetres of aluminium. The group with 20 wt% Nb₂O₅ presented the highest value of radiopacity, whereas the groups with 10 wt% and 5 wt% Nb₂O₅ showed lower levels of radiopacity than 20 wt% group (p<0.05). The control group presents lower levels than both the 10 wt% and 20 wt% groups (p<0.05).

All groups showed degrees of conversion that were higher than 55%. The highest value was 64.93% in the group without Nb₂O₅. The values of degree of conversion and the kinetic of conversion are shown in Figure 5. The addition of niobium pentoxide influenced the kinetics of conversion during the time of experimental adhesive resins. The groups with Nb₂O₅ exhibited a small increase in the reaction rate.

The values of Knoop microhardness of the model dental adhesive resins are presented in Figure 6, indicating that higher amounts (20 wt%) of Nb_2O_5 led to increased microhardness values.

A representative image from the interface characterisation is shown in Figure 7. The presence of niobium can be observed across the hybrid layer, and it is possible to observe the penetration of Nb_2O_5 at almost the same extension of dentin demineralisation. All groups with filler addition exhibited the same behaviour across the hybrid layer.

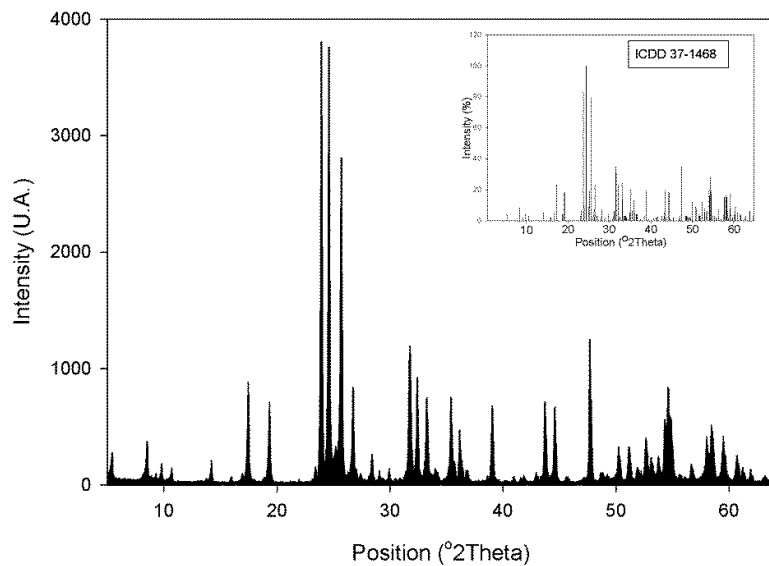


Figure 1. XRD analysis of the niobium pentoxide and the ICCD 37-1468 (inset).

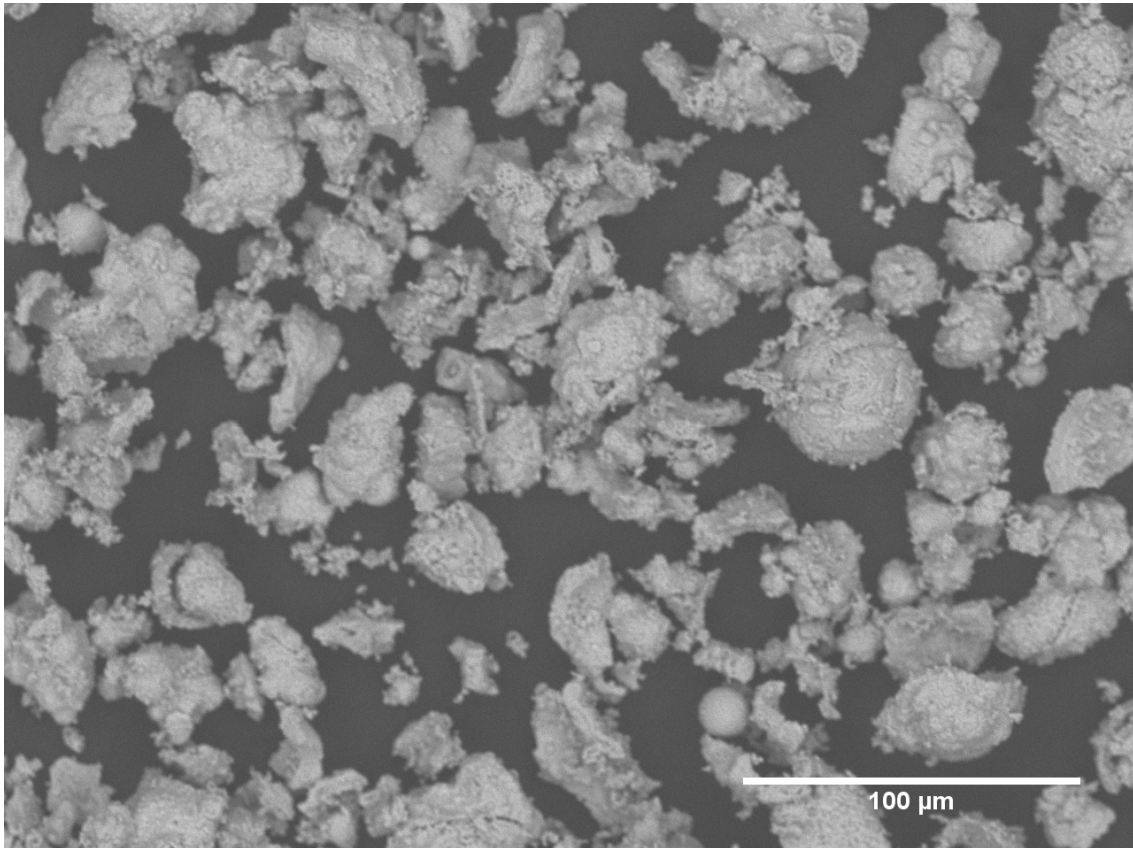


Figure 2. Microstructure of Nb₂O₅ powder (SEM – 500x).

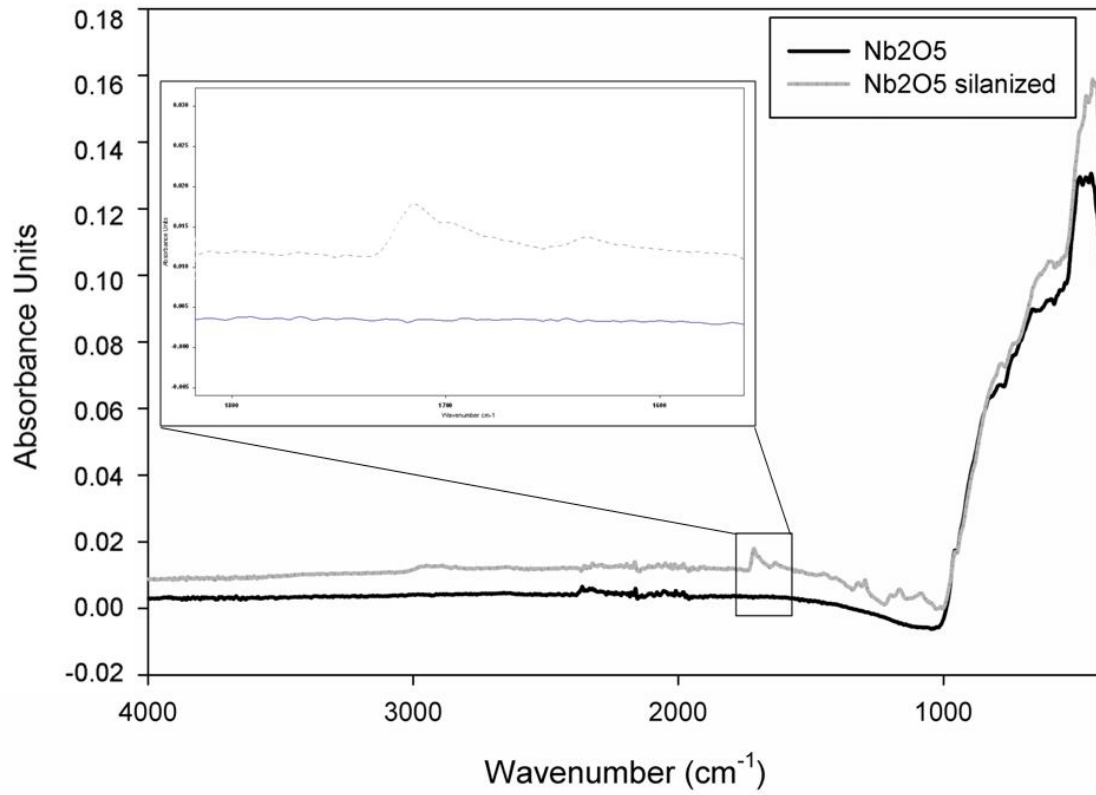


Figure 3. FTIR analysis of Nb₂O₅ with and without silane. The region of the peak at 1640 cm⁻¹ is enlarged.

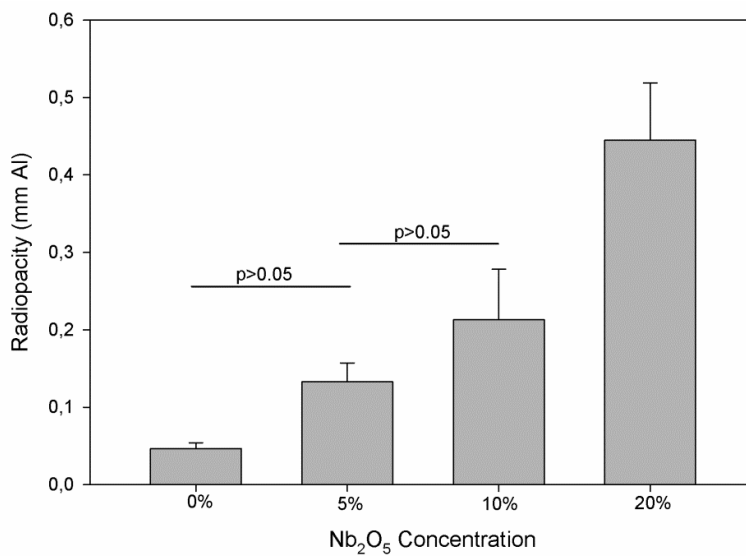


Figure 4. Means and standard deviations of radiopacity values for experimental adhesive resins. Adhesive resins in which the radiopacity was not significantly different are connected by a horizontal line ($p>0.05$).

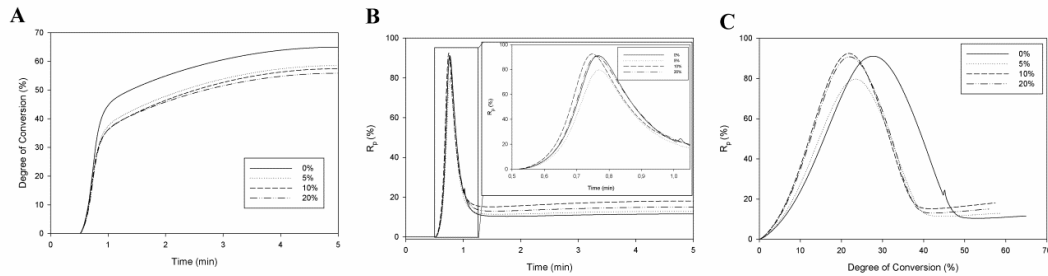


Figure 5. Degree of conversion and reaction kinetics of experimental adhesive resins. (A) Degree of conversion during the time, (B) polymerisation rate as a function of the curing time, and (C) polymerisation rate as function of the degree of conversion.

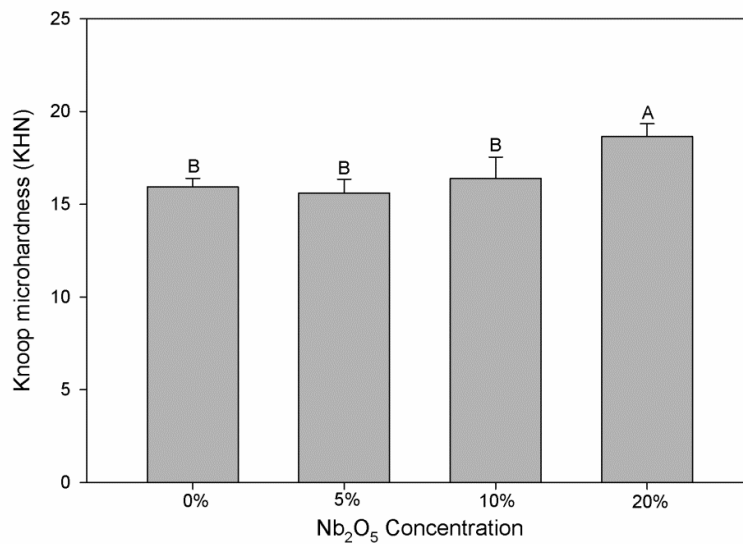


Figure 6. Means and standard deviations of Knoop microhardness values (KHN) for experimental adhesive resins. Different capital letters indicate significant differences ($p<0.05$).

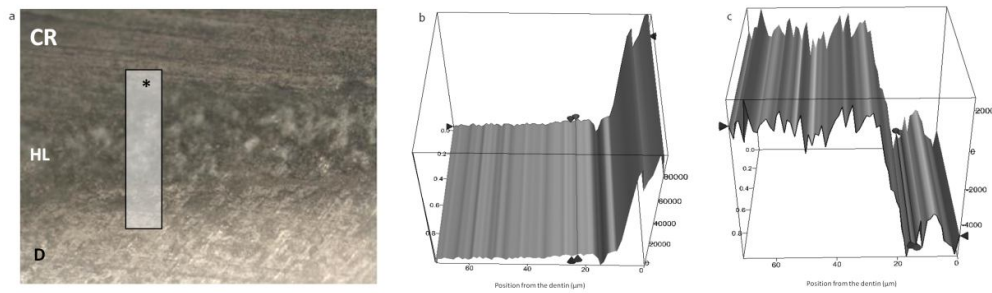


Figure 7. Interface analysis by micro-Raman. (a) Picture of the interface where CR is the composite resin, HL is the hybrid layer, D is the dentin and the rectangle marked by * is the representation of the analysed area. (b) Graph representing the integration of the hydroxyapatite corresponding peak (960 cm^{-1}) of the analysed area (*). (c) Graph representing the integration of the corresponding niobium pentoxide peak (638 cm^{-1}) of the analysed area (*)

Discussion

The incorporation of niobium pentoxide (Nb_2O_5) increased the radiopacity, microhardness and rate of polymerisation of the experimental adhesive resin. The degree of conversion presented values in accordance with the literature ²⁸, even with the addition of higher amounts of Nb_2O_5 . The particles of the oxide presented desirable characteristics, such as only one crystalline phase, a small surface area, a mean particle size on the micrometre scale, an effective silanisation process and a penetration into the hybrid layer, even without the incorporation of Nb_2O_5 at the primer step. These characteristics indicate that Nb_2O_5 may be a promising filler in dentistry.

Regarding the chemical stability of the filler in the oral environment, the filler contains no detectable impurity and the monoclinic phase appears to be less prone to degradation ²⁹. In addition, the filler is only present in one crystalline phase, and Raman analysis showed characteristics of pure niobium pentoxide ³⁰.

Many methods have been used to treat the filler particles with a silane-coupling agent; however, there is no consensus regarding the best method of silanisation ³¹. In this study, the presence of silane was confirmed on the surfaces of the particles (Figure 3), which could indicate a composite less prone to leach filler particles. An adhesive resin with less leaching of particles results in a stable and durable adhesion of restoration to tooth substrate ³².

Restorative dental materials should be radiopaque. In this study, a radiopaque adhesive resin was produced with Nb_2O_5 filler particles. Although the experimental adhesives did not meet the ISO requirements (1 mmAl), groups with 10 and 20 wt% showed higher values of radiopacity than control group ($p < 0.05$). The increase in

radiopacity of a restorative material improves the diagnosis accuracy of recurrent caries^{33, 34}. Furthermore, a large number of false positive diagnoses can be explained by low radiopacity materials used for restorations³⁵, leading to erroneous re-intervention because the commonly used radiographic images in dental practice are two-dimensional.

The addition of inorganic particles to the polymeric matrix could change its properties, including the degree of conversion and microhardness, considering that the refractive index of substances may decrease the availability of light energy within the polymer³⁶. The refractive index increases after polymerization of the blend and is lower than Nb₂O₅ refractive index (2.21 - 2.85)³⁷. In this study, the addition of the filler particles to the adhesive resin led to increased microhardness of the group with 20% wt of Nb₂O₅ (4.8% vol) and the values for degree of conversion were in accordance with the literature²⁸. Although the increase of microhardness was expected with the increase of filler content was expected, considering the relatively low filler content in the evaluated composite resin (max 4.8%vol), a small increase in microhardness value are showed. This could be explained because the hard particles are pressed into the soft matrix during the indentation and result in plastic deformation of the matrix³⁸.

However, with the increased filler content, an alteration in the kinetics of reaction was observed, leading to increased conversion rates. The increased kinetics is associated with the increase of viscosity of the reacting system. As filler content increases and viscosity rises, radical mobility is reduced which significantly decreases the probability of bi-radical termination and therefore autoacceleration occurs more quickly and at a higher rate³⁹⁻⁴¹. Transition metals and their oxides are known catalysts. Nb₂O₅ has been extensively studied as a heterogeneous catalyst in

numerous reactions. Nb_2O_5 has a band gap energy of 3.4 eV, presenting photocatalytic properties⁴². In the present study, the addition of Nb_2O_5 in the polymeric matrix may have increased the reactivity of the system and reduced the necessary energy to produce free radicals, thereby resulting in an increased polymerisation rate. The role of photocatalytic of Nb_2O_5 in the used co-monomer blend may be confirmed in further studies. Earlier maximum conversion rates could have led to a higher contraction stress of a polymeric material⁴³. However, when applied as adhesive resin, this polymeric material could release the contraction stress⁴⁴ and is applied as a thin film⁴⁵. Considering the hydrophilic behaviour of dentin, the passage of water into the adhesive layer and composite resin could decrease the *in situ* polymer network formation and increase the degradation of these polymeric materials⁴⁶. A hydrophobic layer of adhesive resin over the hydrophilic primer increases the bond strength to dentin and decreases the degradation over time¹. The addition of a filler could result in an adhesive resin that is less prone to degradation and undergoes faster polymerisation reactions.

In the present study, the Raman spectra revealed information about niobium pentoxide penetration and mineral content (hydroxyapatite) in the hybrid layer. A band in close proximity to $\sim 960\text{ cm}^{-1}$ was observed in the spectrum of the hybrid layer. This band is associated with ν_1 PO_4 of calcium phosphate complexes⁴⁷. A band close to $\sim 685\text{ cm}^{-1}$ was observed in the spectrum of the hybrid layer as well. The relatively higher intensity of doublets at approximately 685 cm^{-1} (ν_2) could be due to extensive edge sharing of the octahedra of Nb_2O_5 ^{30, 48} and could be observed at the same extension of absence of hydroxyapatite in the hybrid layer. These results indicate a penetration of filler present in the adhesive resin into hybrid layer, allowing the interaction between Nb_2O_5 and dentin tissue. Although the mean particle size

(38.16 μm) difficult tubules penetration, the presence of inorganic filler into hybrid layer could increase the stability of adhesive interface.

In the present study, the incorporation of Nb_2O_5 promoted desired properties, such as radiopacity, increase of hardness of the composite and the ability to infiltrate through the hybrid layer. The infiltration of niobium pentoxide into a collagen matrix exposed by acid etching could promote a hybrid layer that is less prone to degradation and has better biological properties. Most commercially available dentin adhesives do not contain a filler; therefore, some amount of monomers could be released from the adhesive layer, leading to cytotoxic effects of adjacent tissues^{49, 50}. Increasing the filler content leads to a decrease in the relative amount of resin matrix. Considering the relatively small surface area (3.86 m^2/g) and relatively large size (38.16 μm) of the used particles, higher amounts of filler could be incorporated⁵¹. Filler particles may leach from the composite⁵²; therefore, a bioactive filler, such as niobium pentoxide²², could promote a more biocompatible adhesive resin. Therefore, niobium pentoxide may be a promising alternative for polymer-based biomaterials.

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MANUSCRITO II**Niobium pentoxide as a new filler for methacrylate-based root canal sealers**VCB Leitune ^{1*}A Takimi ²FM Collares ¹PD Santos ¹C Provenzi ¹CP Bergmann ²SMW Samuel ¹

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Running title: **Nb₂O₅ for root canal sealers**

Niobium pentoxide as a new filler for methacrylate-based root canal sealers

Abstract

Aim To evaluate the influence of several niobium pentoxide (Nb_2O_5) concentrations on the radio-opacity, flow, film thickness, microhardness and degree of conversion of an experimental root canal sealer.

Methodology An experimental dual-cured root canal sealer was produced with a methacrylate-based comonomer blend. Nb_2O_5 was added at four different concentrations: 0, 80, 100 and 120wt%. Radio-opacity was evaluated according to ISO 6876 using a digital system (n=5). Flow and film thickness were determined in accordance with ISO 6876 (n=3). Microhardness was evaluated with 50 g for 15 s (n=5). Degree of conversion was evaluated with FTIR immediately after photocuring and after 1, 7 and 14 days. The data were analysed using ANOVA and Tukey's test. The degree of conversion over time was evaluated using RM-ANOVA ($\alpha=0.05$).

Results The groups with 80wt% and 100wt% of filler showed no significant difference in radio-opacity from that of equivalent 2mmAl ($p>0.05$). The addition of 120wt% resulted in radio-opacity values higher than 2mmAl ($p<0.05$). The flow was significantly smaller for the 120% group ($p<0.05$). All groups had a film thickness of less than 50 μm (ISO 6876). All groups with Nb_2O_5 showed higher values of microhardness than the control group. The group with 0wt% was associated with a higher degree of conversion at all times. All groups except those with 80wt% had higher values for degree of conversion after 14 days than immediately after photocuring.

Conclusion The addition of Nb_2O_5 increases radio-opacity and microhardness; this material may be a promising filler for the production of a new endodontic sealer.

Keywords: degree of conversion, niobium pentoxide, root canal sealer

Introduction

The search for a root canal sealer that has optimal sealing ability, radio-opacity, flow, film thickness, and biological properties is ongoing (Camilleri 2009, Desai & Chandler 2009, Duarte et al. 2010, Kim et al. 2010). The main function of a root canal sealer is to fill the interface between the core material and the dentine wall, the voids inside the core material and the accessory canals (i.e. gutta-percha, polycaprolactone cones) and to obtain an apical seal. Resin-based root sealers have been developed because they possess a lower solubility than conventional cements (e.g. zinc oxide) (McMichen et al. 2003). However, few studies have focussed on the development of materials that stimulate the repair process through biomimetic remineralisation.

The materials used for a root canal come in direct contact with dentine and periapical tissues. Therefore, the materials should not be cytotoxic and would ideally be biological stimulators. Root canal materials that are capable of ionic delivery have been proposed to produce increased sealing in the apical region (Alani et al. 2009). However, these materials have high solubility and degrade over time. Some inorganic fillers with a monoclinic phase (e.g. niobium pentoxide) appear to be less prone to degradation (Khan et al. 1992) and could possess bioactive properties (Karlinsky et al. 2006). Niobium pentoxide (Nb_2O_5) is an oxide of a transition metal (atomic number of 41) with desired properties for biomedical uses (Khan et al. 1992, Karlinsky et al. 2006). This oxide has never been used as filler for polymeric-based root canal sealers.

The purpose of this study was to evaluate the effects of several Nb_2O_5 concentrations on the radio-opacity, flow, film thickness, microhardness and degree

of conversion of an experimental dual-cured methacrylate-based root canal sealer. The null hypothesis was that the addition of niobium pentoxide will not influence the properties of the experimental methacrylate-based root canal sealer.

Materials and Methods

The monomers used to produce an experimental root canal sealer were urethane dimethacrylate (UDMA), glycerol 1,3-dimethacrylate (GDMA), ethoxylated bisphenol A glycol dimethacrylate (BISEMA6), camphorquinone (CQ), N,N-dihydroxyethyl-para-toluidine (DHEPT), and benzoyl peroxide (BP), which were supplied by Esstech Inc (Essington, PA, USA). These materials were used without further processing. Nb_2O_5 , with a mean particle size of 38.16 μm (Leitune et al. 2012), was obtained from Companhia Brasileira de Mineração e Metalurgia (CBMM, Araxá, MG, Brazil). The filler was silanised using gamma-methacryloxypropyltrimethoxysilane (γ -MPTS, Aldrich Chemical Co., Milwaukee, WI, USA). The filler was added to an acetone (Labsynth Ltda., Diadema, SP, Brazil) solution containing γ -MPTS (5% of the filler wt) to form a slurry. The mixture was stored for 24 h at 37°C to ensure complete solvent removal (Sideridou & Karabela 2009).

The experimental root canal sealers were made by mixing 70 wt.% UDMA, 15 wt.% BISEMA6 and 15 wt.% GDMA. CQ, DHEPT, and BP were added to produce a dual-cure root canal sealer (Collares et al. 2012). The filler particles were used in four different concentrations (0, 80, 100 and 120 wt%). Considering the weight of the comonomer blend, a relative amount of filler was added (e.g. to 1 g of resin 1.2 g of Nb_2O_5 was added in the group with 120 wt%). The density of niobium pentoxide is 4.6 g/cm^3 , of UDMA is 1.12 g/cm^3 , of GDMA is 1.12 g/cm^3 and of BisEMA6 is 1.10 g/cm^3 . Consequently, the volumetric concentrations of the experimental groups were 0, 19.44, 24.25 and 29.16 vol%. The mixture (resin/particles) was hand-mixed for 120 s, sonicated for 480 s and hand-mixed for another 120 s. To perform sealer photo-activation, a light-emitting diode activation unit (Radii Cal, SDI, Bayswater, Victoria,

Australia) was used. An irradiation value of 1200 mW/cm² was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA). Radio-opacity, flow and film thickness were tested according to ISO 6876 (Standardization 2001).

Radio-opacity

The radio-opacity of the experimental sealers was evaluated using five specimens per group. The specimens were 6.0 mm (± 0.5 mm) in diameter and 1.0 mm (± 0.2 mm) in thickness. X-ray images were obtained by a digital system with phosphorous plates (VistaScan, Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Germany) with an exposure time of 0.4 s and a focus-film distance of 400 mm. The X-ray source (DabiAtlante model Spectro 70X) was operated with a tungsten anode at 70 kV and 8 mA. For each film, one specimen from each group with the same concentration was used, resulting in a total of five films per concentration. For all images, an aluminium step-wedge was exposed simultaneously with the specimens. The thickness of the aluminium step-wedge ranged from 0.5 to 5.0 mm in increments of 0.5 mm. The aluminium alloy used contained Al 99.12, Fe 0.47, Mg 0.41, and <0.1 of Cu (mass %), and met ISO 6876 standards (Standardization 2001). The images were saved in TIFF format and analysed using Photoshop software (Adobe Systems Incorporated, San Jose, CA, USA). The means and standard deviations of the grey levels (pixel density) of the aluminium step-wedge and the specimens were measured in a standardised area of 1.5 mm² (Collares et al. 2010).

Flow test

The flow test was conducted according to ISO 6876 (Standardization 2001). A total of 0.5 mL of each experimental sealer was placed on a glass plate (40 x 40 x 5

mm) with a graduated 1.5 mL syringe. At 180 ± 5 s after mixing was started, another plate with a mass of 20 ± 2 g and a load of 100 g was placed on top of the material. Ten minutes after mixing had been started, the load was removed, and the major and minor diameters of the compressed material were measured using a digital calliper. If both measurements were within 1 mm of each other, the results were recorded. If the major and minor diameter discs were not uniformly circular or did not fall within 1 mm of each other, the test was repeated. The test was conducted three times for each experimental group, and the mean value was recorded.

Film thickness

The film thickness was evaluated according to ISO 6876 (Standardization 2001). Two glass plates that measured 5 mm in thickness and 10 mm in length were placed together, and their combined thickness was measured. The centre of one of the plates was covered with 0.5 mL of experimental sealer, and a second plate was placed on top of the material. At 180 ± 5 s after the start of mixing, a load of 150 N was applied vertically on top of the glass plate. Ten minutes after the mixing had been started, the thickness of the two glass plates and the interposed sealer film was measured using a digital calliper. The difference in the thickness of the two glass plates, with and without sealer, was recorded as the film thickness of the experimental sealer material. The mean value of three measurements for each sealer was recorded as the film thickness of the material.

Knoop microhardness

The specimens used for the evaluation of radio-opacity were also used to determine the Knoop microhardness. For each experimental sealer, five specimens

were embedded in acrylic resin and polished using a manual polisher (Model 3v, Arotec, Cotia, SP, Brazil) with a felt disc saturated with in an alumina suspension (Alumina 1.0 μm , Arotec, Cotia, SP, Brazil). The samples were then dried at 37°C and stored for 24 h. The specimens were subjected to a microhardness test in which 5 indentations (50 g/15 s), which were placed 100 μm apart from each other, were assessed using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Japan). The calculation of the hardness value was carried out using equation 3:

$$\text{Knoop microhardness} = \frac{14228 \cdot c}{d^2} \quad (3)$$

Where

14228 is a constant

c is the load in grams

d is the length of the larger diagonal, in μm .

The Knoop microhardness number (KHN) was the mean of the five indentations for each specimen.

Degree of conversion

The degree of conversion of the experimental root canal sealers was evaluated using real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) with a Vetrex 70 (Bruker Optics, Ettlingen, Germany) spectrometer equipped with an attenuated total reflectance device composed of a horizontal diamond crystal with a mirror angle of 45 degrees. A support was coupled to the spectrometer to fix the light-curing unit and standardise the distance between the fibre tip and sample at 5 mm. Opus software (Bruker Optics, Ettlingen, Germany) was used in the monitoring scan mode, with Blackman-Harris 3-Term apodisation in a range of 4000 to 400 cm^{-1}

and resolution of 4 cm^{-1} . With this setup, one spectrum was obtained prior to photocuring and one immediately after photocuring. The same samples were analysed on days 1, 7 and 14. The samples ($3\ \mu\text{l}$) were directly dispensed onto the diamond crystal and light-activated for 40 s ($n=3$). The degree of conversion was calculated as described in a previous study (Collares et al. 2011), considering the intensity of carbon-carbon double bond stretching vibration (peak height) at 1635 cm^{-1} , and using the carbonyl group at 1720 cm^{-1} from the polymerised and unpolymerised samples as an internal standard (Stansbury & Dickens 2001).

Statistical analysis

The normality of the data was evaluated using the Kolmogorov-Smirnov test. Statistical analysis was performed using one-way ANOVA (Nb_2O_5 concentration) and Tukey's post-hoc test. The degree of conversion over time was evaluated using repeated measures ANOVA at the 0.05 level of significance.

Results

The radio-opacity data, measured in pixels, are shown in Table 1. The group with a ratio of 80wt% and 100wt% showed no significant difference from that of equivalent 2 mm of Al ($p>0.05$). The addition of 120wt% increased the radio-opacity, resulting in values greater than 2 mmAl ($p<0.05$), but less than 3 mmAl ($p<0.05$). The flow and film thickness values are shown in Table 1. The flow of experimental sealers ranged from 19.09 mm to 21.90 mm with significant differences among the different groups ($p<0.05$). The group with 120 wt% niobium pentoxide was associated with lower flow values than groups with 100% and 80% filler. The measurement of flow of the group with 0 wt% niobium pentoxide was not possible since the material flowed more than the size of glass plate. According to ISO 6876, all groups had a film thickness of less than 50 μm , and no significant difference ($p=0.729$) was found. The microhardness of experimental root canal sealers increased with increasing amounts of filler (Table 1). All groups containing Nb_2O_5 had higher values of microhardness than the control group (without filler addition). However, no difference was found among the groups containing Nb_2O_5 (80, 100 and 120 wt%). The degree of conversion results are presented in Figure 1. The group without added filler had a higher degree of conversion at all times (immediate, 1, 7 and 14 days). All groups, except for the group with 80 wt% filler, had higher degrees of conversion after 14 days compared with immediately after photocuring. No significant difference between different times of evaluation was noted.

Table 1. Mean (\pm standard deviation) of radio-opacity, flow, film thickness and Knoop microhardness of experimental root canal sealers.

	Radio-opacity (pixels)	Flow (mm)	Film Thickness (μm)	Knoop Microhardness (KHN)
0%	28.81 (± 1.76) ^C	*	26.70 (± 5.00) ^A	17.38 (± 0.74) ^B
80%	115.97 (± 8.78) ^B	21.90 (± 0.64) ^A	26.67 (± 5.77) ^A	25.78 (± 2.65) ^A
100%	126.26 (± 5.02) ^A	21.13 (± 0.25) ^A	26.67 (± 5.77) ^A	25.48 (± 2.81) ^A
120%	133.98 (± 1.62) ^A	19.09 (± 0.16) ^B	23.33 (± 5.77) ^A	28.48 (± 5.95) ^A

Same capital letter indicate no significant difference in the same column ($p > 0.05$). * indicates that was not possible to perform the flow test for group with 0% of Nb_2O_5 .

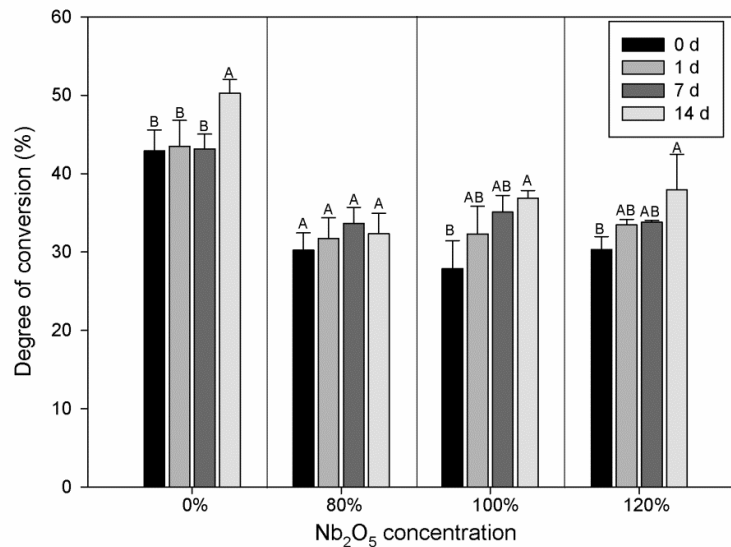


Figure 1. Degree of conversion of sealers as a function of Nb_2O_5 concentration over time. Different letters indicate significant differences between different times at the same concentration ($p < 0.05$).

Discussion

The addition of a filler to methacrylate-based materials improves the properties of the polymer network by increasing radio-opacity (Collares et al. 2009, Collares et al. 2010), adjusting the rheological behaviour (Hanemann 2008), and decreasing the stress of contraction (Goncalves et al. 2010). In this study, a novel filler particle (Nb_2O_5) was added to experimental methacrylate-based cement and led to increased radio-opacity and Knoop microhardness, no alteration in the film thickness and a small reduction in flow (120 wt% of Nb_2O_5). The degree of conversion of experimental root canal sealers decreases with the addition of filler material; however, the values are still in accord with those of the commercially available sealers used in the literature (Lee et al. 2011). Therefore the null hypothesis must be rejected.

Small amounts of filler could promote high viscosity in the resin-based composite due to an increase in the superficial area (Hanemann 2008). In the present study, microsized particles of Nb_2O_5 , with a diameter of 38.26 μm and a superficial area of 3.86 m^2/g , were used. However, even with the addition of 100% (in weight) of Nb_2O_5 , there were no significant differences in viscosity and film thickness between this group and the group without added filler. Regarding film thickness, the group with 120 wt% filler was not significantly different from the group without added filler. The film thickness evaluation of all groups showed results in accordance with the commercial sealers evaluated elsewhere (Versiani et al. 2006, Salz et al. 2009). These results represents an important physical property of experimental root canal sealer, since the ability to create a thin film of sealer could promote a better seal (De Deus et al. 2003). Although the group containing 120 wt% of Nb_2O_5 had flow values that were not in accordance with ISO 6876 (Standardization 2001), a commercially

available and widely used resin-based root canal sealer has lower values than established by standardisation (Almeida et al. 2007). The flow property could determine the filling efficiency of accessory canals and voids between core materials (McMichen et al. 2003).

The radio-opacity of root canal sealer is necessary for clinical use (Collares et al. 2010); the clinician has to be able to distinguish the filling material from hard and soft tissues that surround the root (Krejci et al. 1991). For this purpose, the ISO standardisation (Standardization 2001) established the reference value of 3 mm Al. In this study, all groups had values that were significantly different from 3 mm Al. The groups contained large weight-based amounts of filler material; however, when considering the volumetric fraction of Nb₂O₅ relative to resin, there was a relatively low volumetric concentration of Nb₂O₅ (max 29.16 vol%). However, higher amounts of Nb₂O₅ could not be used without compromising the flow of the sealer (Table 1). A viable alternative could be the addition of a second filler with the goal to increase radio-opacity without losing the biological properties provided by Nb₂O₅ (Karlinsky et al. 2006).

The addition of inorganic particles to the polymeric matrix could change its properties, including the degree of conversion and microhardness, because the refractive index of a given substance may decrease the availability of light energy within the polymer (Shortall et al. 2008). In this study, the addition of the filler particles to the root canal sealer led to an increase in microhardness in all groups. The degree of conversion in groups containing Nb₂O₅ was lower than that in groups without added filler. However, considering the methacrylate-based sealers, the values for degree of conversion are similar to those found in the literature (Lee et al. 2011). The evaluation of degree of conversion of the experimental root canal sealers

within a specific time is very important because chemical initiators (e.g. benzoyl peroxide) were used in these formulations and could increase the degree of conversion of the sealer. The group containing 80 wt% filler was less influenced than groups with 100 wt% and 120 wt% because the initial value of degree of conversion showed no significant difference compared with days 1, 7 and 14. The presence of less filler (80wt%) could lead a more availability of light and consequently promote a higher initial degree of conversion than groups with 100 wt% and 120 wt%.

Niobium pentoxide was added to improve the properties of methacrylate-based sealers and introduces a new filler with bioactive properties (Karlinsky et al. 2006). In the oral environment, methacrylate resins degrade over time (Ferracane 2006). This degradation is thought to be a limiting factor because it could lead to gap formation, fluid infiltration (Kim et al. 2010) and leaching of monomers, resulting in undesirable tissue reactions (Yamanaka et al. 2011). Theoretically, Nb_2O_5 could be deposited at the root canal surface during the degradation process, thereby increasing the biocompatibility of the sealer. Furthermore, some substances are known to have the capacity to induce crystal growth on material surfaces, such as octacalcium phosphate (Barrere et al. 2001), amorphous calcium phosphate (Johns et al. 2010), bioglass (Hashimoto et al. 2010), and ionomer cement (Hashimoto et al. 2010). In the present study, Nb_2O_5 was shown to be a novel filler material, considering that the literature reveals that this oxide could promote crystal growth and biomimetic mineralisation of the surrounding tissues because of its known bioactive properties (Karlinsky et al. 2006).

Conclusion

On the basis of the results of this study, the addition of Nb_2O_5 increases radio-opacity and microhardness and may be a promising filler for the production of new endodontic sealers.

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DEPÓSITO DE PEDIDO DE PATENTE

Após a caracterização do pentóxido de nióbio (Nb_2O_5) e a sua utilização para a produção de materiais de base polimérica para uso em Odontologia (adesivo e cimento endodôntico) com sucesso, iniciou-se o processo para a proteção do conhecimento gerado por meio de depósito de pedido de patente. Inicialmente procedeu-se uma busca em bases de patentes utilizando as palavras-chave nióbio, pentóxido de nióbio, compósito, adesivo dentinário, cimento e Nb_2O_5 para as bases em língua portuguesa. As palavras-chave em inglês utilizadas foram *niobium*, *niobium pentoxide*, *composite*, *dentin adhesive*, *cement* e Nb_2O_5 . Como resultado da busca, obteve-se seis patentes. Dentre essas patentes, apenas uma apresentava material que apresentava potencial similaridade com a presente invenção. Entretanto a patente utilizava carbetos, nitretos e carbonitretos, materiais esses bastante diferentes do utilizado na presente invenção. As demais patentes aplicaram o nióbio em ligas metálicas ou materiais cerâmicos.

Concluída a etapa de busca de patentes existentes, procedeu-se a redação do Relatório Descritivo de Patente de Invenção com auxílio da Secretaria de Desenvolvimento Tecnológico da UFRGS (SEDETEC) e de um escritório especializado em proteção de propriedade intelectual. Após todas as revisões e correções necessárias em todas as seções do relatório (Campo da Invenção, Antecedentes da Invenção, Sumário da Invenção, Descrição Detalhada da Invenção, Reivindicações e Resumo), o Depósito de Pedido de Patente (Figura 1) foi registrado no Instituto Nacional de Propriedade Industrial (INPI), tendo como depositante a Universidade Federal do Rio Grande do Sul e como inventores Vicente

Castelo Branco Leitune, Susana Maria Werner Samuel, Fabrício Mezzomo Collares, Antonio Takimi e Carlos Perez Bergmann, sob o título " Material compósito, Processo de produção de material compósito e Uso do material compósito de matriz polimérica com incorporação de carga inorgânica de pentóxido de nióbio".

< Uso exclusivo do INPI >	
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Espaço para etiqueta	

DEPÓSITO DE PEDIDO DE PATENTE OU DE CERTIFICADO DE ADIÇÃO

Ao Instituto Nacional da Propriedade Industrial:

O requerente solicita a concessão de um privilégio na natureza e nas condições abaixo indicadas

1. Depositante (71):

- 1.1 Nome: UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
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continua em folha anexa

2. Natureza: Invenção Modelo de Utilidade Certificado de Adição

Escreva, obrigatoriamente, e por extenso, a Natureza desejada: Patente de Invenção

3. Título da Invenção ou Modelo de Utilidade ou Certificado de Adição(54):

MATERIAL COMPÓSITO, PROCESSO DE PRODUÇÃO DE MATERIAL COMPÓSITO E USO DO MATERIAL COMPÓSITO DE MATRIZ POLIMÉRICA COM INCORPORAÇÃO DE CARGA INORGÂNICA DE PENTÓXIDO DE NÍOBIO

continua em folha anexa

4. Pedido de Divisão: do pedido N° Data de Depósito:

5. Prioridade: interna unionista

O depositante reivindica a(s) seguinte(s):

Pais ou organização de origem	Número de depósito	Data do depósito

6. Inventor (72):

Assinale aqui se o(s) mesmo(s) requer(em) a não divulgação de seu(s) nome(s)

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continua em folha anexa

INPI Formulário 1.01 – Depósito de Pedido de Patente ou de Certificado de Adição (folha 1/2)

Figura 1. Depósito de Pedido de Patente no Instituto Nacional de Propriedade Industrial.

7. Declaração na forma do item 3.2 do Ato Normativo nº 127/97:

7.1 Declaro que os dados fornecidos no presente formulário são idênticos ao da certidão de depósito ou documento equivalente do pedido cuja prioridade está sendo reivindicada.

em anexo

8. Declaração de divulgação anterior não prejudicial: (Período de Graça):
(art. 12 da LPI e item 2 do AN nº 127/97)

em anexo

9. Procurador (74)

9.1 Nome:

9.2 CNPJ/CPF:

9.3 API/OAB:

9.4 Endereço completo:

9.5 CEP:

9.6 Telefone:

9.7 Fax:

9.8 E-Mail:

10. Listagem de sequências Biológicas (documentos anexados) (se houver):

- Listagem de sequências em arquivo eletrônico: n° de CDs ou DVDs (original e cópia).
- Código de controle alfanumérico no formato de código de barras: fl.
- Listagem de sequências em formato impresso: fls.
- Declaração de acordo com o artigo da Resolução INPI nº 228/09: fls.

11. Documentos anexados (assinale e indique também o número de folhas):
(Deverá ser indicado o n° total de somente uma das vias de cada documento)

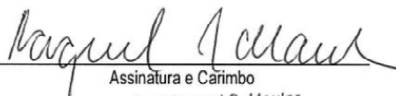
<input checked="" type="checkbox"/>	11.1 Guia de Recolhimento	1 fls.	<input checked="" type="checkbox"/>	11.5 Relatório descritivo	9 fls.
<input type="checkbox"/>	11.2 Procuração	fls.	<input checked="" type="checkbox"/>	11.6 Reivindicações	2 fls.
<input type="checkbox"/>	11.3 Documentos de Prioridade	fls.	<input type="checkbox"/>	11.7 Desenhos	fls.
<input type="checkbox"/>	11.4 Doc. de contrato de trabalho	fls.	<input checked="" type="checkbox"/>	11.8 Resumo	1 fls.
<input checked="" type="checkbox"/>	11.9 Outros que não aqueles definidos no campo 11 (especificar) Autorizações de cessão de invenção; Portaria de Competência; cópia Diário Oficial da União.				9 fls.

12. Total de folhas anexadas (referentes aos campos 10 e 11): 22 fls.

13. Declaro, sob penas da Lei, que todas as informações acima prestadas são completas e verdadeiras.

Porto Alegre, 07/05/2012

Local e Data



Assinatura e Carimbo

Profª Raquel S. Mauler
Secretária de Desenvolvimento
Tecnológico
UFRGS

ANEXO DE INVENTORES

Título: MATERIAL COMPÓSITO, PROCESSO DE PRODUÇÃO DE MATERIAL COMPÓSITO
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Figura 1 (continuação). Depósito de Pedido de Patente no Instituto Nacional de Propriedade Industrial.

CONSIDERAÇÕES FINAIS

No presente estudo foi possível desenvolver um cimento endodôntico e um adesivo odontológico a base de metacrilato com a incorporação de partículas de pentóxido de nióbio (Nb_2O_5). A busca por melhores propriedades dos materiais para uso odontológico tem resultado na incorporação de novas cargas a esses materiais (COLLARES et al., 2010; TOLEDANO et al., 2012). desta forma têm sido estudadas cargas que promovam melhores propriedades mecânicas (RASTELLI et al., 2012), maior dureza (KRUMOVA et al., 2001), maior resistência ao desgaste (TAMURA; KAKUTA; OGURA, 2012), maior radiopacidade (COLLARES et al., 2010) e maior interação do material com o ambiente que o circunda (COLLARES et al., 2012).

O pentóxido de nióbio pode se apresentar com diversas formas polimórficas (LE VIET et al. 2010). A análise do Nb_2O_5 utilizado nesse estudo mostrou que a partícula apresenta estrutura monoclinica. Um estudo mostrou que o Nb_2O_5 com estrutura monoclinica é menos susceptível à degradação do que as outras formas (pseudo-hexagonal, ortorrômbica e tetragonal), sendo a forma pseudo-hexagonal a menos estável (LE VIET et al. 2010). A maior estabilidade da partícula de carga dentro de um compósito pode reduzir a degradação e a alteração de cor do material ao longo do tempo e aumentar a longevidade do tratamento restaurador. As partículas utilizadas no presente estudo apresentaram tamanho médio de de 38,16 μm e área de superfície de 3,86 m^2/g .

Os adesivos desenvolvidos apresentaram maior radiopacidade e maior dureza do que o adesivo controle, sem adição de Nb_2O_5 . A radiopacidade é uma importante característica dos materiais usados na odontologia restauradora. Mais

especialmente dos adesivos em que uma radiopacidade adequada permite ao cirurgião-dentista distinguir entre o material restaurador e o tecido dentário desmineralizado ou não (GOSHIMA; GOSHIMA, 1990). Os adesivos desenvolvidos com incorporação de 10% e 20% de Nb_2O_5 apresentaram radiopacidade superior a do grupo sem carga. O grau de conversão ficou acima de 55% para todos os grupos. Esse valor de grau de conversão é compatível com adesivos comerciais (FARIA-E-SILVA et al., 2010). O Nb_2O_5 presente nos adesivos experimentais foi capaz de penetrar na interface com a dentina, sendo sua presença detectada por meio de espectroscopia Raman.

Os cimentos endodônticos experimentais também apresentaram maior radiopacidade e maior dureza do que o grupo controle. Apesar de o grupo com 120%, em peso, de Nb_2O_5 ter apresentado radiopacidade superior a 2mm de alumínio, não conseguiu atingir os 3 mmAl preconizados pela ISO 6876. Entretanto essa limitação pode ser solucionada com a adição de outra carga radiopacificante como sulfato de bário ou trifluoreto de itérbio (COLLARES et al., 2010). Tendo em vista que no presente estudo pretendeu-se avaliar somente a influência do pentóxido de nióbio, nenhuma outra carga foi adicionada em combinação com o Nb_2O_5 .

O Brasil é o maior exportador de Nióbio do mundo. Entretanto o desenvolvimento de produtos manufaturados com a utilização desse minério no país ainda é pequena. Na presente tese obteve-se sucesso na incorporação da pentóxido de nióbio em blendas comonoméricas. Os resultados foram publicados em dois artigos em periódicos indexados internacionalmente (LEITUNE et al., 2012b; LEITUNE et al., 2012a). Tendo como objetivo a proteção do conhecimento gerado, fez-se o pedido de depósito de patente de invenção sob o título "Material compósito,

Processo de produção de material compósito e Uso do material compósito de matriz polimérica com incorporação de carga inorgânica de pentóxido de nióbio".

A incorporação do pentóxido de nióbio em materiais de base polimérica para uso odontológico mostrou-se uma interessante alternativa para a produção de materiais inovadores. Com a presente tese buscou-se a geração de conhecimento científico com a produção de artigos baseados na introdução de pentóxido de nióbio para a produção de compósitos de matriz polimérica. Foi possível também proteger o conhecimento gerado por meio de um pedido de depósito de patente e com isso pretende-se apresentar um nova aplicação para um produto produzido no Brasil e exportado na forma de matéria prima, o pentóxido de nióbio, transformando-o em um produto manufaturado. Buscando-se alcançar, portanto, um dos objetivos do Plano de Desenvolvimento Institucional da Universidade Federal do Rio Grande do Sul que é promover o progresso social por meio da formação, geração de conhecimento e inovação (UFRGS, 2010) e eventualmente produzir produtos nacionais que possam substituir competitivamente os materiais atualmente importados.

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