

UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
FACULDADE DE ODONTOLOGIA

TIAGO LUÍS HERPICH

RESINA ADESIVA EXPERIMENTAL COM ADIÇÃO DE VIDRO BIOATIVO

Porto Alegre

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Trabalho de Conclusão de Curso apresentado ao Curso de Graduação em Odontologia da Faculdade de Odontologia da Universidade Federal do Rio Grande do Sul, como requisito parcial para obtenção do título de Cirurgião-Dentista.

Orientadora: Prof^a Dra. Susana Maria Werner Samuel

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RESUMO

O objetivo deste estudo foi avaliar a influência da adição de dois tipos de vidros bioativos nas propriedades de uma resina adesiva experimental. Foram produzidos dois vidros bioativos pelo método sol-gel, sendo um deles convencional e o outro com a incorporação de 2%, em peso, de Nb_2O_5 . Foram formuladas três resinas adesivas com 66,6% de BisGMA e 33,3% de HEMA: GC- Grupo Controle (resina sem vidro bioativo); BAG – resina contendo 2% em peso de vidro bioativo convencional; e BAGNb - resina contendo 2% em peso de vidro bioativo com nióbio. Avaliou-se radiopacidade (n=3), degradação em solvente (n=3), grau de conversão (n=3), resistência à flexão (n=5), resistência de união imediata e longitudinal de 1 ano (n=12) e deposição mineral das resinas adesivas. A análise estatística foi realizada utilizando ANOVA 1-via e Tukey para radiopacidade, degradação em solvente, grau de conversão e resistência à flexão; ANOVA 2-vias para resistência de união e teste t pareado para os valores de dureza inicial e final. Foi adotado um nível de significância de 5%. Não houve diferença estatisticamente significativa entre os grupos na análise de radiopacidade e grau de conversão. BAG teve maior degradação em solvente do que BAGNb, que, por sua vez não mostrou diferença em relação ao GC. A adição de vidro bioativo causou diminuição da resistência à flexão dos grupos BAG e BAGNb sem diferença entre ambos. BAG apresentou menor resistência de união imediata comparado ao BAGNb, que, por sua vez não mostrou diferença em relação ao GC. Após 1 ano, os grupos não apresentaram diferença estatisticamente significativa na resistência de união. BAGNb apresentou maior deposição mineral do que os grupos GC e BAG. Pode-se concluir que foi possível a produção de uma resina adesiva com a adição de vidro bioativo. A adição de um vidro bioativo com nióbio na resina adesiva mostrou melhores resultados que a incorporação do vidro bioativo Sol-gel convencional, como melhor resistência de união imediata e maior deposição mineral.

Palavras-chave: Adesivos dentinários. Materiais biocompatíveis. Vidros bioativos.

Nióbio.

ABSTRACT

The aim of this study was to evaluate the influence of the addition of two types of bioactive glasses in an experimental dental adhesive resin. Two bioactive glasses were produced by the sol-gel method (conventional and 2wt% of Nb₂O₅). Three adhesive resins were formulated with 66.6wt% BisGMA and 33.3wt% HEMA: CG-Control (resin without bioactive glass); BAG - with 2wt% bioactive glass; and BAGNb - with 2wt% bioactive glass with niobium. Radiopacity (n=3), softening in solvent (n=3), degree of conversion (n=3), flexural strength (n=5), immediate and longitudinal microtensile bond strength (n = 12) and mineral deposition were evaluated. Statistical analysis was performed using one-way ANOVA and Tukey for radiopacity, softening in solvent, degree of conversion and flexural strength; two-way ANOVA for bond strength and Paired t-test for hardness values before and after immersion, with a significance level of 5%. There was no statistical significant difference in the radiopacity and degree of conversion analysis. BAG had more softening in solvent compared to CG, which does not occur with BAGNb. The addition of both types of bioactive glasses caused a decrease in flexural strength, without difference between BAG and BAGNb. BAGNb presented higher immediate bond strength compared to BAG. There was no statistically significant difference between BAGNb and CG. After 1 year storage, groups presented no statistically significant difference in bond strength. BAGNb showed higher mineral deposition than CG and BAG. In conclusion, it was possible to produce an adhesive resin containing bioactive glass. The addition of bioactive glass with niobium showed better results compared to the addition of a conventional sol-gel bioactive glass, as better immediate bond strength and more mineral deposition.

Keywords: Dental adhesives. Biocompatible materials. Bioactive glasses. Niobium.

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1 INTRODUÇÃO

Os avanços na Odontologia adesiva vêm possibilitando a adoção de estratégias cada vez mais conservadoras. 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 (PASHLEY et al., 2004; FERRACANE, 2006; TAY; PASHLEY, 2009; COLLARES et al., 2010). Recentemente os materiais com potencial de interação com os tecidos adjacentes vêm ganhando espaço (DOROZHKIN, 2013).

A longevidade das restaurações dentárias está relacionada com o sucesso na formação do polímero (FERRACANE et al., 2006). Muitas pesquisas visam produzir adesivos com menor degradação (COLLARES et al., 2011), inibição da enzimas que degradam colágeno (PASHLEY et al., 2004), adição de carga (VAN LANDUYT et al., 2007) (KALACHANDRA, 1989) (KIM et al., 2005) e bioatividade (DEGRAZIA et al., 2017) (LEITUNE et al., 2013a) (LEITUNE et al., 2013b). A remineralização de dentina pode substituir e preencher áreas com água ou colágeno exposto na camada híbrida (TAY et al., 2008), além do fato de que a remineralização da dentina é importante para o controle de cáries dentinárias, melhoria da estabilidade da ligação adesiva à dentina (DEGRAZIA et al., 2016) (IMAZATO et al., 2014) (SAURO et al., 2015). A remineralização da interface adesiva pode até funcionar como proteção contra ácidos produzidos por bactérias orais (DEGRAZIA et al., 2017). Os vidros bioativos podem induzir a formação de apatita na dentina (FERNANDO et al., 2017), mesmo em dentina completamente desmineralizada (WANG et al., 2011), indicando que o processo não é dependente de pontos de cristalização na dentina. Além disso, os vidros bioativos podem ser eficientes para a oclusão dos túbulos dentinários (CURTIS et al., 2010).

Os vidros bioativos são compostos cerâmicos capazes de liberar íons em meio aquoso, interagindo com os tecidos circundantes. Esses íons são capazes de favorecer o processo de remineralização de tecidos duros. O vidro bioativo conhecido como 45S5® foi um dos primeiros vidros bioativos desenvolvidos na segunda metade do século 20, apresentando ótimos resultados para a remineralização (HENCH, 2006).

A bioatividade desses materiais depende de suas composições químicas e microestruturas, sendo o método de produção do vidro, determinante para o

estabelecimento das suas propriedades. A fundição é o método de produção dos vidros bioativos comerciais disponíveis atualmente, como o 45S5[®] (um vidro bioativo do sistema quaternário $\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5$). Como alternativa, se tem o método sol-gel que também pode ser utilizado na produção desses vidros, gerando materiais com maior solubilidade devido à sua menor cristalinidade e com maior porosidade e área superficial, favorecendo assim a interação do material com o meio (GROH; DÖHLER; BRAUER, 2014; JONES, 2013).

Além de um processo de produção mais fácil, vidros bioativos produzidos pelo método sol-gel permitem a incorporação de componentes a fim de melhorar as propriedades do material (JONES, 2013; PIRAYESH; NYCHKA, 2013; SIQUEIRA; PEITL; ZANOTTO, 2011), assim como outros métodos de produção (MIGUEZ-PACHECO et al., 2018). Dentre os componentes com potencial para utilização com esse fim está o Pentóxido de Nióbio (Nb_2O_5), que apresenta excelente biocompatibilidade (FOOLADI et al., 2013; LEITUNE et al., 2013) e está associado à redução da citotoxicidade, à indução de calcificação quando em contato com células humanas, e ao aumento da atividade da fosfatase alcalina (KUSHWAHA et al., 2012; LOPES et al., 2014).

Considerando que a interface adesiva fica exposta ao meio oral, ocorrendo ali grande parte das falhas restauradoras (SPENCER et al., 2010; BOHATY et al., 2013) e que muitas vezes, principalmente em lesões profundas de cárie há a presença de tecido desmineralizado no fundo da cavidade (SCHWENDICKE; GÖSTEMEYER, 2016), um material que favoreça a mineralização é desejável. Não foram encontrados na literatura estudos avaliando a adição de vidros bioativos com adição de nióbio a resinas adesivas, portanto, a incorporação desse vidro bioativo com nióbio a uma resina adesiva experimental merece ser estudada, podendo ser uma opção para promover avanços e melhorias ao material. Sendo assim, o objetivo deste trabalho foi desenvolver um adesivo experimental com a adição de dois tipos de vidros bioativos e avaliar suas propriedades.

2 ARTIGO CIENTÍFICO

EXPERIMENTAL ADHESIVE RESIN WITH ADDICTION OF BIOACTIVE GLASSES

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ABSTRACT

The aim of this study was to evaluate the influence of the addition of two types of bioactive glasses in an experimental dental adhesive resin. Two bioactive glasses were produced by the sol-gel method (conventional and 2wt% of Nb₂O₅). Three adhesive resins were formulated with 66.6wt% BisGMA and 33.3wt% HEMA: CG-Control (resin without bioactive glass); BAG - with 2wt% bioactive glass; and BAGNb - with 2wt% bioactive glass with niobium. Radiopacity (n=3), softening in solvent (n=3), degree of conversion (n=3), flexural strength (n=5), immediate and longitudinal microtensile bond strength (n = 12) and mineral deposition were evaluated. Statistical analysis was performed using one-way ANOVA and Tukey for radiopacity, softening in solvent, degree of conversion and flexural strength; two-way ANOVA for bond strength and Paired t-test for hardness values before and after immersion, with a significance level of 5%. There was no statistical significant difference in the radiopacity and degree of conversion analysis. BAG had more softening in solvent compared to CG, which does not occur with BAGNb. The addition of both types of bioactive glasses caused a decrease in flexural strength, without difference between BAG and BAGNb. BAGNb presented higher immediate bond strength compared to BAG. There was no statistically significant difference between BAGNb and CG. After 1 year storage, groups presented no statistically significant difference in bond strength. BAGNb showed higher mineral deposition than CG and BAG. In conclusion, it was possible to produce an adhesive resin containing bioactive glass. The addition of bioactive glass with niobium showed better results compared to the addition of a conventional sol-gel bioactive glass, as better immediate bond strength and more mineral deposition.

Keywords: Dental adhesives. Biocompatible materials. Bioactive glasses. Niobium.

INTRODUCTION

Advances in adhesive dentistry promoted the increase of conservative strategies. The development of materials for dental use with better physical and mechanical properties over time and with better clinical characteristics has been the subject of several studies (PASHLEY et al. 2004; FERRACANE, 2006; TAY,

PASHLEY, 2009; COLLARES et al., 2010). Recently materials with potential for interaction with adjacent tissues have been more studied (DOROZHUKIN 2013).

Dental restorations longevity is related with a successfully polymer formation (FERRACANE et al., 2006). Many researches aim to produce adhesives with lower degradation (COLLARES et al., 2011), inhibition of enzyme collagen degradation (PASHLEY et al., 2004), filler addition (VAN LANDUYT et al., 2007) (KALACHANDRA S., 1989) (KIM et al., 2005) and bioactivity (DEGRAZIA et al., 2017) (LEITUNE et al., 2013a) (LEITUNE et al., 2013b). Dentin mineralization can replace and fill up areas with water or exposed collagen on hybrid layer (TAY et al., 2008), besides the fact that dentin remineralization is important to dentinal caries control, improvement of dentin bonding stability (DEGRAZIA et al., 2016) (IMAZATO et al., 2014) (SAURO et al., 2015). Resin-dentin interface mineralization can even work as protection from acids produced by oral bacteria (DEGRAZIA et al., 2017). Bioactive glasses can induce apatite formation in dentin (FERNANDO et al., 2017), even in completely demineralized dentin (WANG et al., 2011), indicating that the process is not dependent on seed crystalites in dentin. Furthermore, BAGs can be efficient for tubule occlusion, with the formation of plugs in those or apatite layer in its surface (CURTIS et al., 2010).

Bioactive glasses are ceramic compounds capable of releasing ions in aqueous medium, interacting with the surrounding tissues. These ions are capable of favoring the process of remineralization of hard tissues. The bioactive glass known as 45S5[®] was one of the first bioactive glasses developed in the second half of the 20th century, presenting excellent results for remineralization (HENCH, 2006).

The bioactivity of these materials depends on their chemical compositions and microstructures, being the method of production of the glass determinant for the establishment of its properties. Melt-quench is the production method of commercially available bioactive glasses, such as 45S5[®] (a bioactive glass of the SiO₂-Na₂O-CaO-P₂O₅ quaternary system). As an alternative, there is the sol-gel method that can also be used for the production of these glasses, generating materials with greater solubility due to their lower crystallinity and with greater porosity and surface area, favoring the interaction of the material with the medium (GROH; DÖHLER; BRAUER, 2014; JONES, 2013).

Besides an easier production process, bioactive glasses produced by sol-gel method allow the incorporation of components in order to improve the properties of

the material (JONES, 2013, PIRAYESH; NYCHKA, 2013; SIQUEIRA; PEITL; ZANOTTO, 2011), as well as other methods (MIGUEZ-PACHECO et al., 2018). Among the components with potential for this purpose are niobium compounds, as niobium pentoxide (Nb_2O_5), which has excellent biocompatibility (FOOLADI et al., 2013) and is associated with the reduction of cytotoxicity, the induction of calcification and the increase of alkaline phosphatase activity (KUSHWAHA et al., 2012; LOPES et al., 2014).

Most of the restorative failures occur in the adhesive interface (tooth-restoration interface), an area exposed to the oral medium (SPENCER et al., 2010; BOHATY et al., 2013). Besides, often there is the presence of demineralized tissue at the bottom of the cavity, especially in deep caries lesions (SCHWENDICKE; GÖSTEMEYER, 2016). Considering those facts, a material favoring mineralization is desirable, and the incorporation of bioactive glasses with niobium to an experimental adhesive resin should be studied. The aim of this study was to develop an experimental dental adhesive resin with the addition of two types of bioactive glasses and evaluate its properties.

MATERIAL AND METHODS

In this study were used the monomers bisphenol A glycol dimethacrylate (BisGMA) and hydroxyl-2-ethyl methacrylate (HEMA), purchased from Sigma-Aldrich (St. Louis, MO, USA). The photo-initiators camphorquinone (CQ), ethyl dimethyl-4-aminobenzoate (EDAB) and hydroxytoluene butylated (BHT) were purchased from Aldrich Chemical (Milwaukee, MI, USA). Niobium chloride (NbCl_5 - CBMM, Araxá, MG, Brazil), nitric acid (HNO_3 – Merck, Darmstadt, Germany), tetraethyl orthosilicate (TEOS– Sigma Aldrich, St. Louis, Missouri, EUA), triethyl phosphate (TEP Sigma Aldrich, St. Louis, Missouri, EUA), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$ - Química Moderna, Barueri, São Paulo, Brazil) and sodium nitrate (NaNO_3 – Química Moderna, Barueri, São Paulo, Brazil) were used in the synthesis of bioactive glasses.

PRODUCTION OF BIOACTIVE GLASSES

Glasses are result of a mixture of precursors and mineral modifiers. TEOS [Si(OCH₂H₅)₄] and TEP [C₂H₅)₃PO₄] were used as precursor while calcium nitrate [Ca(NO₃)₂] and sodium nitrate [NaNO₃] were the mineral modifiers. Precursors were hydrolyzed in 250ml of HNO₃ 1M solution under stirring for 20min. Thereafter, 0.015 mol of TEOS were mixed during 60min and the other reagents were sequentially added in 45min intervals as following: 0.017mol of TEP, 0.085 mol of Ca(NO₃)₂ and 0.16 mol of NaNO₃. The obtained sol was stored during 5 days in room temperature. Gel was submitted to ageing in 70°C/24 hours, drying in 120°C/24 hour and calcinated in 700°C/24h.

For bioactive glasses with niobium (BAGNb) synthesis, 0.4g of niobium chloride (NbCl₅) was mixed to 8.3ml ethanol and 0.17ml distilled water. Niobium was added to bioactive glasses during mixture of precursors.

FORMULATION OF EXPERIMENTAL ADHESIVE RESINS

Experimental adhesive resins were obtained by mixing 66.6 wt% BisGMA and 33.3 wt% HEMA. CQ and EDAB were added at 1 mol% as photoinitiator system, according to the mols of used monomers. There was also added 0.1 wt% of BHT to the resin. Three experimental adhesive resins were formulated: CG (Control group, without addition of bioactive glasses), BAG (with 2 wt% of conventional bioactive glass) and BAGNb (with 2 wt% of bioactive glass with niobium). Reagents were handmixed and sonicated for 180 s. The light source device used for photoactivation for all tests was Radium Cal (1200 mW/ cm², SDI, Bayswater, Victoria, Australia).

RADIOPACITY

For radiopacity (RP) assay, three specimens for group (n=3), 6mm in diameter and 1mm thickness, were produced. X-ray images were taken with 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) was operated with a tungsten anode at 70 kV and 8 mA. Each of the three films contained one specimen of each of the three 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. Images obtained were analysed with software Image J.

DEGREE OF CONVERSION

The degree of conversion (DC) was evaluated by Fourier transform infrared spectroscopy (FTIR) with a Vertex 70 (Bruker Optics, Ettlingen, Germany) spectrometer equipped with an attenuated total reflectance device (Platinum ATR-QL; Bruker Optics) composed of a horizontal Diamond crystal with a 45° mirror angle. A support was used for leaving a 1 mm distance between Light curing unit and samples. The Opus software (Bruker Optics, Ettlingen, Germany) used a Blackman-Harris 3-Term apodization function in a range of 4000 to 400 cm^{-1} and 64 scans with a 4 cm^{-1} resolution. Samples (n=3) were directly dispensed onto the diamond crystal into a polyvinylsiloxane matrix for standardization (5 mm in diameter and 1 mm in height) and one spectrum was obtained prior photoactivation and another one immediately after photoactivation for 20 s. DC was calculated according to a previous study (LEITUNE et al., 2013a).

MICROHARDNESS AND SOFTENING IN SOLVENT

Specimens as used for radiopacity assay were used for Knoop microhardness (KHN) and softening in solvent (n=3). Those resin specimens were embedded in acrylic resin and polished with carbide sandpapers (# 600, 1000, 1200, 2000, under distilled water irrigation) and felt discs with alumina suspension (Alumina 1.0 mm, Arotec, Cotia, SP, Brazil). The specimens were dried and stored at 37°C for 24h and then subjected to a initial microhardness test (KHN1) with three indentations (10g/5s) using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Japan). Specimens were then subjected to softening in absolute ethanol for 2 h at 37 °C and the microhardness values were measured again (KHN2). The percent difference was calculated as a preview study (LEITUNE et al. 2013b).

FLEXURAL STRENGTH

Five samples of each group measuring 10 mm long, 2 mm wide, 2 mm thick were subjected to flexural strength test. The adhesive resins were inserted into a metallic matrix and a polyester strip was placed on them before 30s light curing at the bottom and at the top of the specimens. The samples were stored for 24h at 37°C and submitted to flexural strength test using a mechanical testing machine

(Shimadzu EZ-SX, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/min until rupture of the specimen.

MICROTENSILE BOND STRENGTH

Seventy-two bovine incisors, free of cracks and caries, were obtained at a slaughterhouse and stored for a maximum period of 3 months. Buccal surface of the teeth was worn out until dentin was exposed. Lingual face was worn out too in order to let both faces plane. Before restoration, buccal face was polished with a #600 carbide sandpaper to simulate the smear layer. Dentin surface was etched with acid gel for 15s and rinsed with water for 30s. A thin film of Scotchbond™ Primer (Primer Scotch bond multi-purpose, 3 M ESPE, St Paul, MN, USA) was applied for 20s. Then, experimental adhesive resin was applied, light cured for 30s and two layers of composite (FILTEK™ Z350) were applied, one by one, and light cured for 30s. After 24 h of storage in distilled water at 37 ° C, teeth were sectioned by a precision cutter (IsoMet; Buehler, Lake Bluff, IL, USA), under constant irrigation of distilled water, to obtain sticks with 0.7 mm² of cross-section. For immediate bond strength (n = 12), restored teeth were stored in distilled water for 24h and analyzed using a mechanical testing machine (Shimadzu EZ-SX, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 1mm/min until fracture of the specimen. For longitudinal analysis, restored teeth were stored in distilled water, at 37°C, for 1 year and then were analyzed.

MINERAL DEPOSITION

Specimens as used for degree of conversion were used for mineral deposition. Samples were polished using a #1200 grit silicon-carbide paper under constant irrigation. Then, 3 samples of each group were immersed in 15ml of simulated body fluid (SBF) prepared according to Kokubo et al.(2006) for 7, 14 and 28 days. A sample that was not immersed in SBF was also analyzed (0 days).

One different sample per time (n=1) was analyzed with Raman spectroscopy (Senterra, Bruker Optics, Ettlingen, Germany) to check the amount of mineral phase precipitated on the specimens after different periods of storage in SBF.

A standard area was analyzed (100 equidistant points) for each specimen. The integral of the 962 cm⁻¹ peak absorbance was calculated using the spectroscopy software (Opus 7.5, Bruker Optics, Ettlingen, Germany). Absorbance increase of the peaks at 962 cm⁻¹ indicated the deposition of phosphate on the

sample surfaces, and the results were processed to obtain digitalized images of the phosphate deposition using Sigma Plot version 12.0 for Windows (Systat Software Inc, San Jose, CA, USA).

STATISTICAL ANALYSIS

Statistical analysis was performed using one-way ANOVA and Tukey for radiopacity, softening in solvent, degree of conversion and flexural strength; two-way ANOVA for bond strength and Paired t-test for hardness values before and after immersion, with a significance level of 5%. Descriptive analysis was used for mineral deposition.

RESULTS

Radiopacity results are shown in Table 1, in pixel density. There was no statistical significant difference between the groups tested ($p > 0.05$). Radiopacity values were lower than 1mm aluminium (55.09) ($p < 0.05$). There was no statistical significant difference in degree of conversion among the groups, but all groups presented results higher than 55%.

Table 1- Mean and standard deviation of the radiopacity values, in pixel density and Degree of conversion

Groups	Radiopacity	Degree of conversion (%)
Control	26.66 (2.41) A	56.89 (1.35)A
BAG	28.38 (2.90) A	56.05 (0.51)A
BAGNb	28.54 (2.74) A	56.77 (1.11)A

Different capital letters in the same column indicate statistical difference ($p < 0.05$).

Control group presented higher initial hardness than BAG, and there was no statistical significant difference between the other groups. BAG and BAGNb decreased hardness after immersion in ethanol. BAG presented higher softening in solvent than CG and BAGNb. (Table 2).

Table 2 - Mean and standard deviation of Knoop hardness values and percentage of degradation (%).

Groups	Inicial hardness	Final hardness	Softening in solvent (%)
Control	24.83 (0.42)Aa	21.22 (2.62)Aa	14.20 (1.72)A
BAG	19.29 (0.45)Ba	14.68 (0.40)Bb	23.85 (2.78)B
BAGNb	22.41 (0.97)ABa	19.55 (0.28)Ab	12.53 (4.25)A

Different capital letters in the same column indicate statistical difference ($p < 0.05$). Different lower-case letters indicate statistical difference in the same row ($p < 0.05$).

Flexural and bond strength results are presented in Table 3. The addition of both types of bioactive glasses decreased the flexural strength values, compared to CG ($p < 0.05$). Regarding to bond strength, BAGNb presented higher immediate values compared to BAG ($p < 0.05$). There was no statistically significant difference between the other groups ($p > 0.05$). BAG and BAGNb presented decreased bond strength along 1 year, compared to immediate. However, after 1 year, the three groups showed no statistically significant difference in bond strength.

Table 3 - Mean and standard deviation of Flexural Strength and Bond Strength

Groups	Flexural strength (Mpa)	Bond strength (Mpa)	Bond strength (1 year) (Mpa)
Control	138.63 (9.65) A	56.77 (11.89)ABa	46.68 (11.45)Aa
BAG	104.61 (22.55)B	53.16 (14.48)Ba	41.54 (10.63)Ab
BAGNb	101.37 (23.71)B	66.68 (15.49)Aa	40.40 (10.24)Ab

Different capital letters in the same column indicate statistical difference ($p < 0.05$). Different lower-case letters indicate statistical difference in the same row ($p < 0.05$).

Figure 1 shows the Raman map of phosphate deposition. Red areas indicate more phosphate content. After 7 days BAG and BAGNb present very low amount of phosphate in its surface. After 14 and 28 days the intensity of the phosphate peaks increased in BAG and BAGNb. BAGNb at 28 days showed higher phosphate peaks than other samples tested.

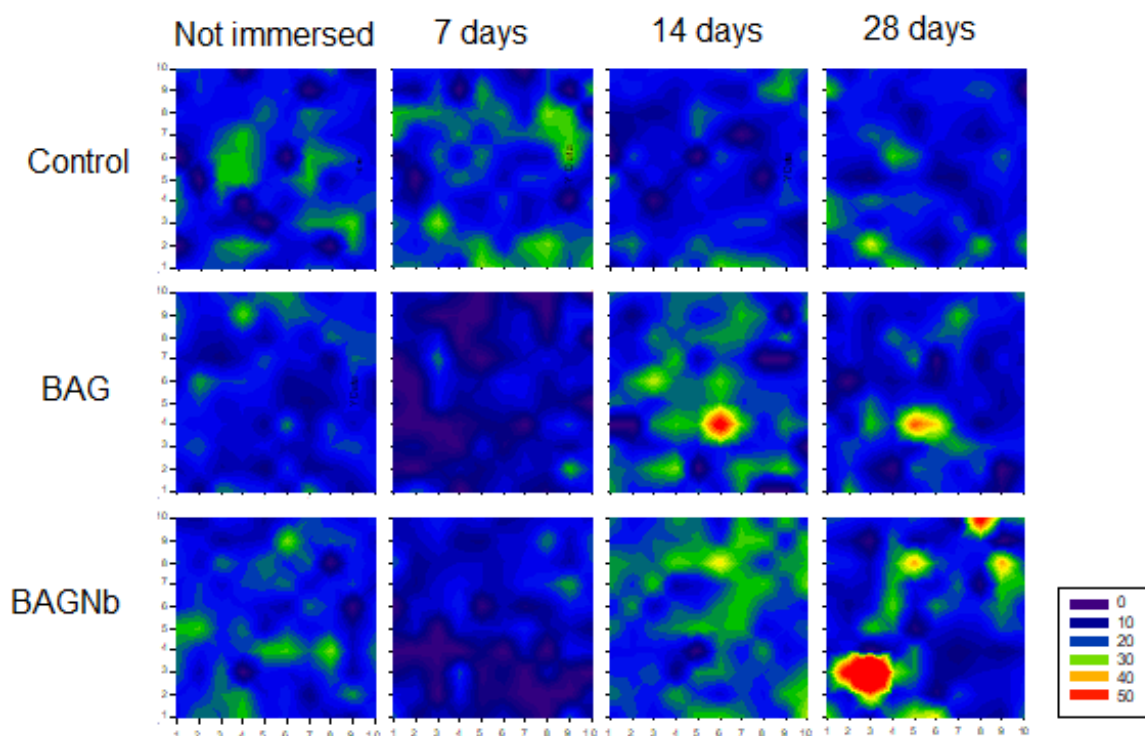


Figure 1 - Raman map of phosphate deposition. The intensity is given by the integration of 960 cm^{-1} peaks.

DISCUSSION

Bioactive glasses and niobium pentoxide have been studied in dental adhesives because of the potential to enhance these materials properties, such as bring bioactivity to promote mineral deposition (FERNANDO et al., 2017) (SAURO et al., 2012) (COLLARES et al., 2014) (LEITUNE et al., 2013a). Bioactive glasses can induce mineral formation on dentin, reduce nanoleakage in the hybrid layer (FERNANDO et al., 2017) (SAURO et al., 2012). As well as bioactive glasses, niobium pentoxide can induce mineral formation (COLLARES et al., 2014), infiltrate on hybrid layer, and increase hardness and radiopacity (LEITUNE et al., 2013a). In this study, two kinds of bioactive glasses, one conventional and one with Nb_2O_5 , were produced by sol-gel method and were successfully incorporated as fillers into a BISGMA/HEMA adhesive resin. The bioactive glasses produced present high porosity, superficial area and predominance of amorphous phase (BALBINOT et al., 2015), what favor the interaction of these materials with the medium, with a more reactive bioactive glass, and can promote even more bioactivity to the adhesive resin. As far as we know, this is the first study about incorporation of bioactive glasses with niobium (BAGNb) in an adhesive resin, and the addition of BAGNb

presented good results as a filler into an adhesive resin and showing higher mineral deposition in 28 days than other groups.

After 7 days of immersion in SBF, BAG and BAGNb did not present mineral deposition, what is probably because the high solubility of phosphate in these glasses. After 14 and 28 days of immersion, therefore, BAG and BAGNb demonstrated bioactivity by mineral deposition in BAG, what corroborate with bioactive glasses capability of apatite formation described in literature (FERNANDO et al., 2017) (SAURO et al., 2012). BAGNb, after 28 of immersion, presented higher mineral deposition than BAG and CG, probably allying bioactive glasses (FERNANDO et al., 2017) (SAURO et al., 2012) and niobium (COLLARES et al., 2014) capability of mineral formation described and presenting the best results.

Continuous influx of calcium and phosphate may induce remineralization and even mechanical recovery of mineral deficient dentin, due to association of minerals and organic matrix (FERNANDO et al., 2017). Bioactive glasses are been widely studied aiming to promote remineralization of dentin (FERNANDO et al., 2017) (SAURO et al., 2012). This mineralization occurs due to the constant influx of these ions, leached from the bioactive glasses, what supersaturate the medium and promote the formation of apatite content (FERNANDO et al., 2017). Reseaches show increase in mineral content of dentin after use of bioactive glasses, but without match the mechanical properties of normal dentin, due to the lack of intrafibrillar collagen remineralization (FERNANDO et al., 2017). Sauro et al. (2012), for example, show decrease in bond strength of adhesives with bioactive glasses after 3 months of storage compared to control. In this study BAGNb showed higher immediate values than BAG. After 1 year, BAG and BAGNb presented decrease in bond strength compared to its immediate results, in agreement with those obtained by Sauro et al. (2012) and probably are due to bioactive glasses leach, whereas this is a soluble material. But, after 1 year storage, BAG and BAGNb presented no statistical difference to CG for bond strength, instead other results in literature (SAURO et al., 2012) showing the stability of these adhesives. Also, in this study, the addition of BAG and BAGNb did not influence the degree of conversion and BAGNb did not influence hardness and softening in solvent. Therefore, there was a successfully polymer formation and stability in its formation, what is related in literature with a durable restorative treatment (VAN LANDUYT et al., 2010)

An important characteristic a filler could bring to an adhesive resin is the radiopacity, due to the possibility of decreasing failure of diagnosis of recurrent caries and overhang restorations (MURCHISON, CHARLTON, MOORE, 1999) (GOSHIMA, GOSHIMA, 1990). This clinical application is because of possible false-positives diagnosis of demineralized tissue caused by adhesives with no radiopaque characteristics (KREJCI et al., 1991). In this study, nor the addition of BAG or BAGNb were able to promote radiopacity properties to the experimental adhesive resin, although Nb_2O_5 radiopacity capability described in literature (LEITUNE et al., 2013a), probably because of the low content of niobium in the adhesive. Flexural strength was decreased in both bioactive glasses groups, probably because of the creation of concentration points. However, values presented are higher than what literature considers suitable for this analysis (YAP; TEOH, 2003).

Adhesive resins degrade over time and fillers can be leached with this process (SODERHOLM; YANG; GARCEA, 2000). So, it is important to the filler the absence of cytotoxicity effects. Hench L.L., 2006 has already described bioactive glasses high biocompatibility properties in the early 60's years. Niobium pentoxide also is described as having excellent biocompatibility (FOOLADI et al., 2013). Furthermore, bioactive glasses seem to be a promising filler for adhesive resins because of the material characteristics, such as bioactivity, the fact that can be in close proximity to the pulp tissue and the possibility to enhance dentin apatite content. In this study, the addition of niobium to the bioactive glass to an adhesive resin showed better results than a conventional BAG.

CONCLUSIONS

The incorporation of 2% of bioactive glass with niobium (BAGNb) into an adhesive resin presented favorable results. The addition of BAGNb to the experimental adhesive increased immediate bond strength compared to BAG and mineral deposition, without prejudice mechanical properties of the adhesive. Therefore, BAGNb may be a promising filler for adhesive resin.

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3 CONCLUSÃO

Os resultados deste estudo permitem concluir que é possível a produção de uma resina adesiva com a adição de vidro bioativo. A adição de 2% de um vidro bioativo com nióbio (BAGNb) apresentou resultados favoráveis, como o aumento da resistência de união imediata comparado com BAG e deposição mineral, sem prejudicar as propriedades mecânicas do adesivo. Sendo assim, BAGNb pode ser uma carga promissora para uma resina adesiva.

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