

Adhesives Doped with Bioactive Niobophosphate Micro-Filler: Degree of Conversion and Microtensile Bond Strength

Karina Kato Carneiro¹, Marcia Margarete Meier², Clenilton Costa dos Santos³, Adeilton Pereira Maciel⁴, Ceci Nunes Carvalho⁵, José Bauer⁶

To evaluate the effect of incorporating niobium phosphate bioactive glass (NbG) into commercial etch-and-rinse adhesive systems, with and without silane, on their degree of conversion (DC) (%) and microtensile bond strength (μ TBS). The NbG micro-filler was added to two etch-and-rinse adhesive systems: One Step (OS) and Prime Et Bond (PB) at 40% concentration. The following groups were formed: control without glass addition OS; addition of unsilanized NbG (OSNbG); addition of silanized NbG (OSNbGS); control without glass PB; addition of unsilanized NbG (PBNbG); addition of silanized NbG (PBNbGS). The DC was determined using total Fourier spectroscopy reflection (FTIR/ATR). For μ TBS testing, 48 human third molars (n=8) were restored and sliced to obtain specimens (0.8 mm²) and they were tested at two different time intervals: immediately and after 6 months. The fracture mode was evaluated with a stereoscopic loupe (40x) and by scanning electron microscopy (SEM). The data were subjected to ANOVA and Tukey tests ($\alpha=0.05$). NbG addition did not compromise the adhesive system DC values ($p>0.05$). Furthermore, the NbG added to the adhesive systems did not affect μ TBS values ($p>0.05$). Fracture occurred predominantly at the dentin-adhesive interface. NbG bioactive glass did not affect the DC or microtensile bond strength results.

Introduction

Poor penetration of simplified adhesive systems within the collagen layer and a hydrolytic degradation of the monomers can make the collagen exposed to enzymatic degradation (1-4), which may cause margin discoloration, microleakage and secondary caries (3).

Various alternatives have been applied to improve the bonding interface longevity: insertion of multi-layered adhesive (5), a device that improves adhesive infiltration into the collagen layer (6); longer application and polymerization times (5), which modify application of the protocol, by introducing additional steps leading to possible mistakes and increasing chair time.

On the other hand, some researches advocate that an increase in the adhesive system mechanical properties improves the quality of bonded interfaces (7). Therefore, some studies added colloidal silica particles (7) and barium borosilicate to the adhesive matrix (3). In addition to encouraging such interfaces to act as filler reinforcement, it would also be interesting that these particles induce mineral deposits on the interfaces and protect exposed collagen (8). Therefore, there is growing interest in the development of experimental materials associated with bioactive glass (45S5) that induces adhesive interface re-mineralization by releasing phosphate and calcium ions (1, 9-13). An ion release leads to an increase in pH, which may would cause

inhibition of bacterial growth and action of enzymes that degrade collagen (8,14,15).

The silicate glass has low chemical stability, which leads to high ion release in short periods, which can be solved by replacing Si with Nb (16,17). In some materials, the presence of Nb increases the biocompatibility (16), radiopacity (2) and chemical stability of bioactive glass (18). Recent studies have shown promising results in the deposition of ions at the dentin interface (4) and the formation of 'bioactive smear layers' (17).

The incorporation of bioactive particles into experimental adhesives is reported to be a promising option to induce re-mineralization (10-12), since it would not require extra steps to insert the bioactive glass into adhesive layer. The formulation of a new adhesive seems to be another challenge, because factors, such as pH of the mixture and proportion of acid monomers is very problematic (12). No one could demonstrate a consensus for the best formulation, or ever used a commercial adhesive without inorganic particles to insert bioactive ones.

Besides, the literature advocates particle silanization because the presence of silane produces interaction between inorganic and organic matrixes and uniform stress distribution (19). Silanization prevents cluster formation in the adhesive layer and compromise of the cohesive strength

¹Department of Restorative Dentistry, Dental School, Universidade CEUMA, São Luís, MA, Brazil

²Department of Chemistry, CCT, UDESC - Universidade do Estado de Santa Catarina, Joinville, SC, Brazil

³Materials Research Group, Physics Department, UFMA - Universidade Federal do Maranhão, São Luís, MA, Brazil

⁴Department of Chemistry, CCET, UFMA - Universidade Federal do Maranhão, São Luís, MA, Brazil

⁵Department of Endodontics, Dental School, Universidade CEUMA, São Luís, MA, Brazil

⁶Discipline of Dental Materials, Dental School, UFMA - Universidade Federal do Maranhão, São Luís, MA, Brazil

Correspondence: José Bauer, Rua dos Portugueses, 1966, Campus Universitário do Bacanga, 65080-805 São Luís, MA, Brasil. Tel: +55-98-3272-9541. e-mail: bauer@ufma.br

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of adhesive systems (19). This is why this study included an experimental group with silanized NbG micro-filler.

The objective of this study was to characterize the bioactive glass (NbG) and evaluate the impact of adding NbG microfiller particles, with and without silane, on the degrees of conversion and microtensile bond strength, by using two different etch-and-rinse adhesive systems. The tested null hypothesis was that the inclusion of NbG in the composition of the commercial adhesives would induce: (i) no effect on the degrees of conversion and (ii) no effect on microtensile bond strength.

Material and Methods

Preparation and Characterization of NbG

NbG powder was prepared in accordance with previous studies (16,17,20). The micro-filler size distribution was determined using a particle analyzer with laser diffraction (CILAS Model 1064, Compagnie Industrielle des Lasers, Orleans, France).

Incorporation of NbG Glass into Commercial Adhesive Systems

Two commercial adhesive systems were used: One Step (Bisco, Schaumburg, IL, USA) and Prime Et Bond 2.1 (Dentsply, Rio de Janeiro, RJ, Brazil). NbG glass weight (unsilanized and silanized) was added to the unfilled commercial adhesives (3). NbG microfiller particles were silanized by gamma-methacryloxypropyltri-methoxysilane (γ -MPTS; Aldrich Chemical Co, Milwaukee, WI, USA). Micro-fillers were added to an ethanol solution (Labsynth, Diadema, SP, Brazil) containing γ -MPTS. The mixture was stored for 24 h at 50 °C to ensure complete solvent removal. NbG micro-filler concentration was determined by an analytical scale (Marte AL500, São Paulo, SP, Brazil). Micro-fillers were added to the adhesive and mixed (stirred) mechanically with a motorized mixer (magnetic stirring, model Q261M; Quimis, Diadema, SP, Brazil). To assure adequate micro-filler dispersion, experimental resins were ultrasonicated for 1 h. The mixing procedure was performed under yellow light to prevent polymerization.

Experimental Design

The groups were: OS: One Step control; OSNbG: with 40% weight of micro-filler NbG (40 wt%); OSNbGS: with 40 wt% of previously silanized NbG; PB: Prime Et Bond 2.1 control; PBNbG: with 40 wt% NBG; and PBNbGS: with 40 wt% of previously silanized NbG. Parameters evaluated were as follows: immediate degree of conversion (DC) (n=4) and bond

strength, immediately and after a period of six months (n=8).

Degree of Conversion

The DC was evaluated with infrared attenuated by total Fourier spectroscopy reflection (FTIR/ATR, Nexus 470, Nicolet, Thermo Scientific, Waltham, MA, USA). Two drops of each adhesive were applied on the spectrum reader. The first spectrum reading obtained by the transmission method (32 scans with a 4 cm⁻¹ resolution) was taken 10 s later. A new readout was taken after 20 s of specimen polymerization (Optilux 501, Kerr Dental, Kerr Corp., Orange, CA, USA) at 600 mW/cm².

The ratio between unpolymerized adhesive absorption bands of carbon double bonds - aliphatic (1639 cm⁻¹) and aromatic (1609 cm⁻¹) - is used to calculate degrees of conversion.

Percentage calculation formula (3):

$$DC(\%) = \left(1 - \frac{R_{(cured)}}{R_{(uncured)}} \right) \times 100$$

Microtensile Bond Strength

Forty eight freshly extracted human third molars were studied in accordance with the local Research Ethics Committee rules (No. 27 777/CAE 13264413.9.0000.5086). The exposed dentin surface was obtained from horizontal sections of the occlusal enamel layer, by using a constantly cooled cutting machine (Isomet 1000, Buehler, Lake Bluff, IL, USA). Next, the surface was sanded for 60 s with #120 silicon paper. Dentin surfaces were magnified 40x with an optical microscope to assess the absence of enamel.

The dentin surface was etched with 37% H₃PO₄ (15 s), rinsed for 15 s, and kept the dentin slightly moist, so that all adhesives were applied on the moist substrate (21); two layers of the adhesive system were applied, and soft air jets were blown on the samples for 10 s, followed by polymerization (Optilux 501, Kerr, Orange, CA, USA) at 600 mW/cm² for 20 s. Table 1 shows the application

Table 1. Material, manufacturer, composition and application mode of adhesive systems*

Adhesiv	Composition	Application Mode
One Step (Bisco)	Bis-GMA, BPDm, HEMA, photoinitiator and acetone	(1) H ₃ PO ₄ (37%) (15s) (2) Washing (15s) (3) Air blowing 10s / 20cm
Prime Et Bond 2.1 (Dentsply)	PENTA, elastomeric dimethacrylate, photoinitiator, stabilizer, cetilamine hydrofluoride and acetone	(4) 1 st layer applied gently for 10 seconds (5) Air blowing 10 s/20 cm (6) 2 nd layer applied gently for 10 s (7) Air blowing 10 s/20 cm (8) Light polymerization 20 s - 600 mW/cm ²

*Composition provided by the manufacturers. Bis-GMA: Bisphenol A-glycidyl methacrylate; BPDm: biphenyldicarboxylic-acid dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; PENTA: Dipentaerythritol penta acrylate monophosphate.

mode, composition, manufacturer and lot number of the used materials.

After the adhesive procedure, a 6.0 mm high composite resin restoration (Lis, FGM, Joinville, SC, Brazil) was performed in three 2-mm increments of and light polymerized for 40 s.

After mounting the tooth in the cutting machine device (Isomet 1000), the bond interface was placed perpendicularly to the blade. Two sequences of longitudinal and perpendicular cross sections were cut to obtain specimens of approximately 0.8 mm². The cross-sectional area was measured and recorded using digital calipers (Absolute Digimatic, Mitutoyo, Tokyo, Japan). After this, the specimens were randomly divided into two groups that were tested at different time intervals: immediately after preparation (24 h) and after 6 months of storage at 37 °C.

Each specimen was fixed with cyanoacrylate gel glue to a Geraldeli testing jig (Odeme, Joaçaba, SC, Brazil), and then coupled to a universal testing machine (Instron 3342, Norwood, MA, USA). Tests were performed at 1.0 mm/min and the results were expressed in MPa.

Failure Pattern Analysis

Fractured specimen analysis was performed with a stereomicroscope at 40× magnification (Kozo Optical and Electronic Instrumental, Nanjing, Jiangsu, China) and fracture mode was classified as follows: (01) cohesive in dentin (CD); (02) cohesive in composite resin (CR); (03) adhesive-mixed at the interface (AM). Two specimens of each molar were randomly selected for interface evaluation by SEM (ProX Phenom, Phenom-World, Dillenburgstraat,

Eindhoven, Netherlands).

Statistical Analysis

The adhesives systems' data were analyzed separately. Each control was compared only with its corresponding experimental groups. Statistical analysis was performed using the SigmaPlot software 12 (SigmaPlot 12.3; Systat Software Inc., San Jose, CA, USA). All evaluations used 80% test power to calculate the sample sizes. After confirming normality of the distribution by the Shapiro-Wilk test, a one-way analysis of variance (ANOVA) was used to analyze the DC data. Two-way ANOVA was used to analyze the microtensile bond strength (μ TBS), considering the adhesive and storage period as the main factors. The Tukey's significant difference test was used to compare individual data and the level of significance was set at $\alpha=0.05$. The cohesive in dentin or resin and the pre-failure specimens were excluded from statistical analysis.

Results

Characterization of NbG

Particle size analyses indicated that most obtained micro-fillers were between 0.1 and 100 μ m (Fig. 1). The average size obtained was 10.42 μ m (Fig. 1A). Figure 1B shows a different size of filler, some smaller than 10 μ m and nanometric size.

Degree of Conversion

The DC results for all adhesive systems are presented in Table 2. There was no significant difference between the control groups and the experimental groups ($p>0.05$).

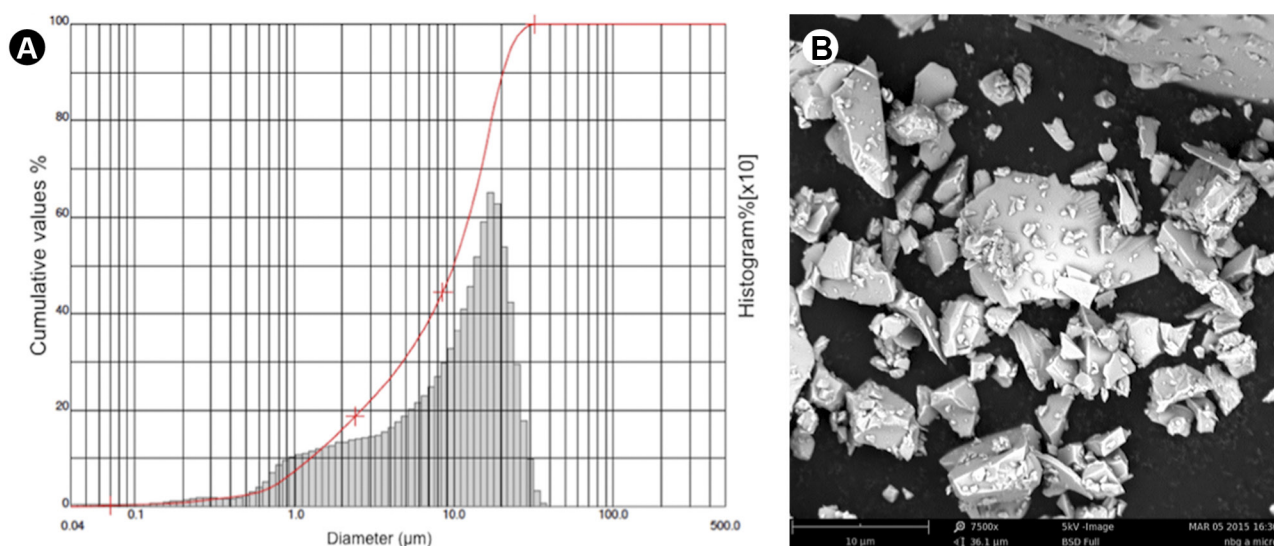


Figure 1. (A) NbG particle size analysis. The Silas device found micro-filler between 0.1 to 100 μ m and average size was 10.42 μ m. (B) SEM showed images of NbG micro-filler smaller than 10 μ m.

Table 2. Mean and standard deviations of degree conversion (%) and microtensile bond strength values (MPa) obtained for the different experimental groups

Adhesive (Degree of conversion)	Microtensile bond strength (MPa) (N of tested/pre-failure) [Failure % AM/CD/CR]	
	Immediately	After 6 months
OS (33.0±2.16 ^a)	43.25±9.0 A (49/1) [91.83/0/8.16]	32.77±17.1 B (52/1) [98.0/0/2.0]
OSNbG (32.0±1.41 ^a)	35.29±3.89 A (68/2) [100/0/0]	28.43±6.0 B (54/3) [100/0/0]
OSNbGS (30.3±3.4 ^a)	33.65±8.7 A (67/0) [100/0/0]	23.58±9.0 B (59/1) [100/0/0]
PB (28.36±5.53 ^a)	24.42±8.6 a (50/13) [98/0/2]	13.25±6.1 b (20/19) [100/0/0]
PBNbG (23.70±6.0 ^a)	26.82±8.8 a (47/15) [100/0/0]	15.87±7.1 b (34/6) [100/0/0]
PBNbGS (30.00±0.81 ^a)	28.06±12.2 a (68/17) [98.5/1.5/0]	17.35±7.2 b (51/11) [100/0/0]

Total number of beams (tested stick/pre-load failure) and percentage distribution of failure mode after microtensile bond strength testing [Failure % AM/CD/CR]. Different letters after mean values represent statistically significant differences between groups (p<0.05).

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Microtensile Bond Strength

The average cross-sectional area of specimens ranged from 0.79 to 0.83 mm². The statistical analysis found no interaction between the main factors (p=0.988). Table 2 shows microtensile bond strength values of adhesive systems tested in the different time intervals (immediately and after 6 months). The addition of NbG micro-fillers did not affect bond strength of the tested adhesives (p<0.05). Bond strength values were reduced in all the tested adhesives (p<0.05) over six months.

The fracture pattern shows a prevalence of adhesive-mixed fractures for all groups that were tested (Table 2). Figures 2A and 2B reveal adhesive-joint fractures for OS and PB control groups where exposure of dentinal tubules and adhesive layer area is seen.

Figure 3 (A, B and C) shows fractures between the adhesive and composite resin of the OSNbG group, where considerable particle dispersal in the resin matrix of the adhesive material was identified. There were some larger micro-filler particles (white arrow 3C) and in some areas, free spaces revealed the NbG pull-out load (white arrow 3B).

Figure 4 (A, B and C) depicts micro-fillers dispersed in the resin matrix of the PBNbGS group adhesive layer; the lower amount of micro-filler dispersed in both the matrix and at the entrance of the dentinal tubules.

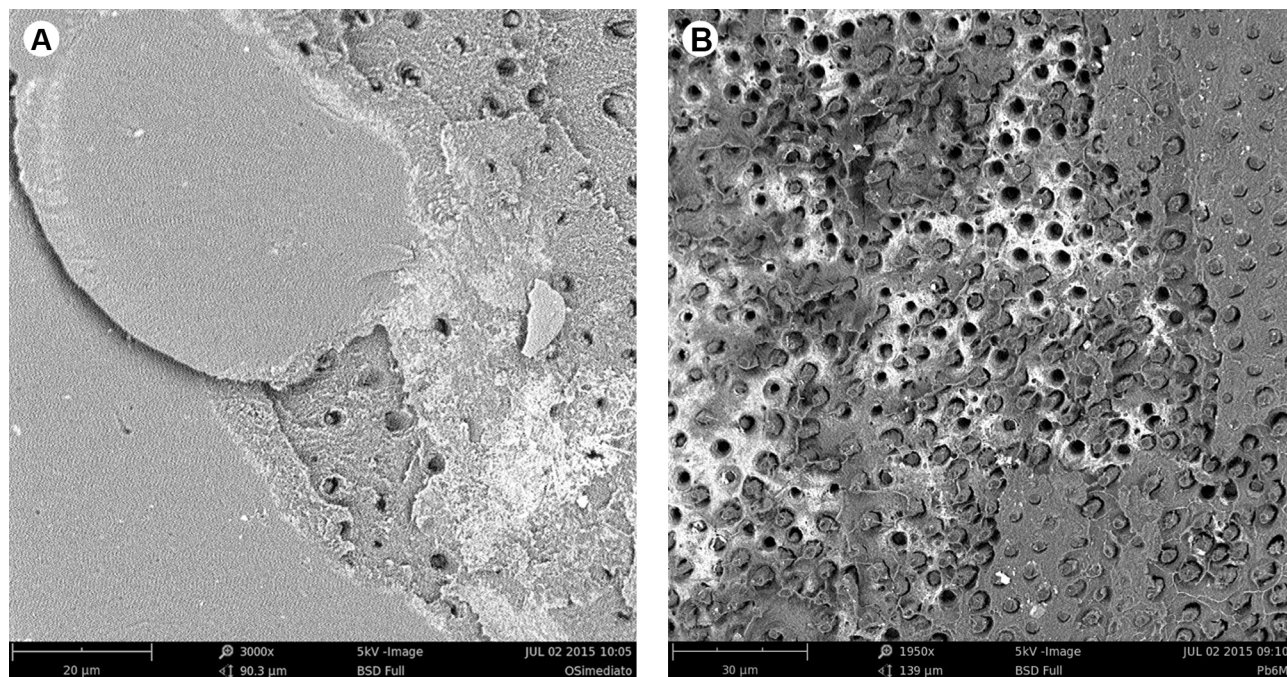


Figure 2. Representative specimen of control group: SEM evaluation of adhesive/mixed fracture of commercial adhesive systems (A) One Step (Immediate) (B) Prime Et Bond 2.1 (Six months). Both had extensive areas of exposed dentinal tubules.

Discussion

The addition of bioactive glass micro-filler in the adhesives may contribute to release of Ca^{2+} and PO_4^{-3} ions, and provide the re-mineralization of unprotected collagen (11,12). The presence of bioactive glass in an adhesive systems may contribute to increase the pH (2), thus inhibiting bacterial growth and blocking MMP action (3,15).

In this study, an experimental bioactive glass with Nb was used (16). Tamai et al. (13) showed that Nb-based bioactive glass is able to increase the activity of alkaline phosphatase and promote osseointegration. The amount of calcified tissue was directly proportional to the concentration of dissolved Nb ions (13). The NbG stimulated bone growth in the tibia of rabbits demonstrating high bioactivity (16). Carvalho et al. (4) recently demonstrated that experimental gutta-percha containing NbG micro-

fillers was able to deposit precipitates along the root dentin interface that increased bond strength of 'bioactive gutta', showing the bioactivity of this new material (4). Another important clinical advantage of NbG added to adhesive systems is the possibility of obtaining a radiopaque material. A similar study demonstrated that with this concentration (40%w/w), it was possible to obtain radiopacity, making it possible to distinguish the restorative material from enamel and dentin, in addition to allowing the diagnosis of caries lesions (22).

In this study, the DC values found for the two control groups (PB and OS) were in agreement with values in the literature (21,23). Leitune et al. (2) found no difference in the DC when incorporating Nb_2O_3 micro-filler into an experimental adhesive system. Similarly, the addition of bioglass (45S5) did not affect the DC of composite



Figure 3. Representative specimen of OSNbG group: Immediately debonded specimens. (A) SEM evaluation of mixed fracture between composite resin and adhesive system. (B) Same image denotes NbG micro-filler size diversity: some $>\pm 10 \mu\text{m}$ distributed in the adhesive layer with particles pulled out of the resin matrix (white arrow). (C) Aggregates formed by possibly smaller particles incorporated into the resin matrix (black arrow); larger particles loose in the adhesive layer (white arrow).

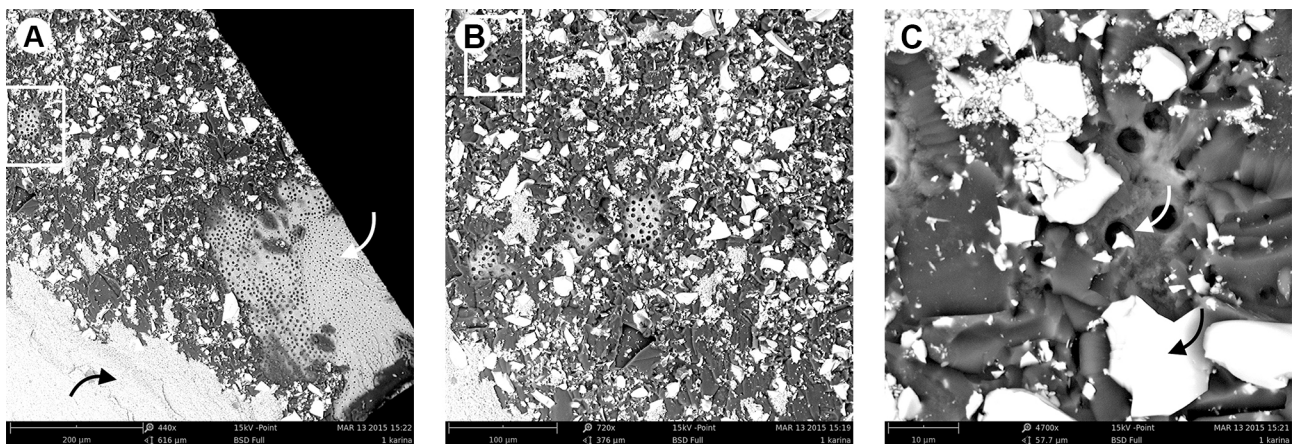


Figure 4. Representative specimen of PBNbGS group after six months: (A) SEM evaluation of mixed fracture with silanized NbG, exposure of dentinal tubules (white arrow) and composite resin (black arrow). (B) Large volume of micro-filler distributed in the adhesive layer. (C) Micro-filler at the dentinal tubule entrances.

material (15).

On the other hand, a high ionic release of NbG may somehow neutralize the action of acidic monomers (BPDM and PENTA) and decrease the conversion of monomers. Reduced DCs make adhesive layers more permeable and susceptible to degradation (7). However, the addition of NbG did not affect the DCs of PB and OS adhesive systems, which is a favorable result, as it could compromise mechanical properties. Leitune et al. relate that when niobium pentoxide was incorporated to experimental adhesives, a slight increase in the reaction rate of the DC was observed (2), which suggests that the presence of NbG could compensate any decrease of DC. Thus, the null hypothesis of this study was accepted (i).

The incorporation of glass into the tested adhesive systems was unable to prevent the reduction in bond strength after 6 months of storage. A reduction in μ TBS values was observed in all groups, thus the null hypothesis was rejected (ii).

However, comparing the microtensile values in the groups in which the particles were silanized, it is possible to observe that the values were not changed. This could be confirmed by the fracture mode, from which it was possible to observe that adhesive-mixed layer prevailed in all groups.

The SEM images revealed that NbG-added glass groups clearly showed cohesive cracks in the adhesive system layer (Fig. 3). An ultimate tensile strength test should have been performed to evaluate the effect of the addition of bioactive filler particles on the cohesive strength of adhesive systems, however with the PB adhesive system, it was impossible to obtain specimens for this test, because after polymerization, the hour-glass shaped specimens showed moisture and softness.

Other studies have also not been successful with the incorporation of bioglass (45S5) into adhesive systems, as the presence of a bioactive glass in dental adhesives did not prevent the decrease in bond strength after 3 months (11,12). Profeta (10) et al. observed maintenance of μ TBS values after 6 months, but this was found in the group that used an adhesive and added 45S5 associated with the application of 45S5 solution to rewet the dentine (10). It was also hypothesized that bioactive micro-filler particles may have reacted with water to release calcium hydroxide that increased the alkalinity of the surrounding environment and the alkaline pH may have slowed the activity of MMPs.

Moreover, adhesive systems containing 45S5 glass are capable of increasing nanohardness and the modulus of elasticity of the adhesive interface, suggesting dentin remineralization (12). Some studies detected mineral crystals deposited in the adhesive interface layer, which reduced nanoleakage (10,12).

In this study, it was possible to detect bioactive NbG nano-fillers in the dentinal tubule entrances (Fig. 4). However, further studies are still required to confirm the influence of NbG nano-filler deposition within the hybrid layer by another test.

At this time, many researchers are looking for adhesive material able to re-mineralize hybrid layers and completely restore the mechanical properties of mineral-depleted dental collagen structures within resin-bonded interfaces by biomimetic apatite formation. The greatest challenge of these researchers is to insert demineralized bioactive glasses smaller than 40 nm between collagen fibrils, since this is the size required to fit into this network (24). However, the presence of the NbG micro-filler next to the collagen network may provide ions (Ca^{2+} and PO_4^{-3}) to inhibit enzymatic degradation, bacterial growth and re-mineralize collagen.

The incorporation of experimental NbG into commercial adhesives at 40% concentration maintained the DC values unaltered. However, it was unable to prevent a reduction in bonding strength after 6 months.

Resumo

Avaliar o efeito da incorporação de vidro niobofosfato bioativo (NbG, 40% em peso) em dois sistemas adesivos simplificados convencionais (One Step [OS] e Prime Et Bond [PB]) com e sem silano, no grau de conversão (%) e resistência de união (RU) após 6 meses. Os seguintes grupos foram testados: Controle OS: sem adição de partículas; OS e adição de NbG sem silano (OSNbG); OS e adição de partículas silanizadas NbG (OSNbGS); Controle PB: sem adição de partículas; PB e adição de partículas de NbG sem silano (PBNbG); PB e adição de partículas silanizadas NbG (PBNbGS). O grau de conversão (GC) foi determinado utilizando espectroscopia de Fourier (FTIR/ATR). Para RU, 48 terceiros molares humanos ($n=8$) foram restaurados e cortados para obter corpos-de-prova ($0,8 \text{ mm}^2$) e, em seguida, testados em dois momentos: imediato e após seis meses. O padrão de fratura foi avaliado com lupa estereoscópica (40x) e microscópio eletrônico de varredura (MEV). Os dados foram submetidos à análise de variância e Tukey ($\alpha=0,05$). NbG não comprometeu valores de GC dos sistemas adesivos ($p>0,05$). Além disso, a adição de NbG aos sistemas adesivos não afetou os valores de RU ($p>0,05$). O padrão de fratura ocorreu predominantemente na interface dentina-adesivo. NbG não afetou os resultados de GC e RU.

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