International Journal of Adhesion & Adhesives 69 (2016) 110–114

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Development of a simplified etch-and-rinse adhesive containing niobiophosphate bioactive glass

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ARTICLE INFO

Available online 19 March 2016

Keywords:
Novel adhesives
Dentine
Micro-tensile
Radiopacity
Bioactive glass

ABSTRACT

Purpose: The aim of this study was to evaluate radiopacity, degree of conversion (DC), Knoop hardness (KHN), ultimate tensile strength (UTS) and microtensile bond strength (μTBS) to dentin of an experimental adhesive containing micro-filler of niobium–phosphate bioactive glass (NPG).
Materials and methods: The NPG glass was produced by fusion of NbO_5, Na_2CO_3, CaO, $(NH_4)_2HPO_4$ at 1400 °C. After cooling, the glass was ground to a mean particle size < 25 μm, and either added (40 wt%) to an experimental adhesive resin mix containing monomers and solvent, or not. The DC of the adhesives was evaluated by Fourier transform infrared spectroscopy. Flat dentin surfaces were obtained from 16 molar teeth, and prepared for use to evaluate μTBS ($n=8$). An hourglass-shaped matrix (UTS and KHN) or disk-shaped matrix (radiopacity) was filled with adhesive and light-polymerized. The data from each test were analyzed by appropriate statistical methods.
Results: The presence of glass particles made the adhesive system radiopaque. Addition of bioactive NPG glass particles to the adhesive system prevented decreases in bond strength; reduced the UTS and increased DC and KHN. All groups showed predominance of adhesive failure mode.
Conclusion: Addition of 40% NPG glass may be an alternative to obtain an adhesive system with adequate mechanical and bond strength to dentin properties.

1. Introduction

Recent studies have shown that adhesive-dentine interfaces degrade after relatively short periods of time (e.g., 6 months) caused by hydrolysis of the adhesive and collagen fibrils [1]. During the last decade, we have been developing biologically active restorative materials that may stimulate the repair of tooth structure through the release of cavity fighting components including calcium and phosphate; these materials are often referred to as “smart materials” [2].

A preventive alternative would be to produce a material that could be capable of inducing remineralization of the interfibrillar spaces not infiltrated by adhesive, thus protecting the collagen fibrils. Efflandt et al. [3] suggested that the demineralization of the dentin produced by acid etching may produce ideal sites at which apatite can nucleate, grow, and form a layer of hydroxyl-carbonate apatite close the entrances to the dentinal tubules [4,5].

Recently, some researchers have used bioactive glasses (45S5) to induce deposition of hydroxyl-carbonate apatite for osseointegration, thus indicating bioglass is capable of inducing natural mineralization of surfaces and tissues [6–8]. Sauro et al. [9] has shown the incorporation of bioglass into experimental adhesive systems did not prevent the reduction in bond strength values after 3 months of storage.

While most of the bioactive glasses are made of a mixture of calcium, phosphate and silica, recently it was proposed that addition of niobium to the composition of the bioglass could be advantageous [10,11]. The presence of niobium results in higher

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http://dx.doi.org/10.1016/j.ijadhadh.2016.03.015
0143-7496/

chemical durability of phosphate glasses; improved biocompatibility; mechanical properties and increased radiopacity. This new bioactive glass has shown promising results in the process of guided bone formation and bioactive layer [10–13].

In addition to biocompatibility due to the incorporation of bioactive particles, this new composition could act as a filler to improve the mechanical properties of the material. Some manufactures have reinforced adhesives systems by adding fillers as a component [14]. This material could therefore act as a stress absorbing layer, because of its lower elastic modulus, by allowing deflection between composite/dentine and improving marginal seal [15]. Furthermore, adhesives with fillers may have radiopacity, and prevent clinicians from being misled into interpreting adhesive radiotransparency as gap formation or recurrent caries at the restoration margin [16].

On the other hand, there is no etch-and-rinse and self-etch adhesive capable of completely replacing water in the extrafibrillar and intrafibrillar collagen compartments with resin monomers [17,18]. The objective of adding bioactive particles is to stimulate remineralization in areas where the collagen is unprotected, and to compensate degradation of the polymer matrix.

Therefore, the aim of the present investigation was to evaluate the effect of adding micro-filler of niobium–phosphate bioactive glass (NPG) to experimental bonding agent, on the following properties of the adhesive: microtensile bond strength (μTBS) to dentin after storage (24 h or 6 months) and mechanical properties (UTS and KHN), DC and radiopacity.

The null hypotheses to be tested were that the inclusion of NPG fillers in the composition of the experimental bonding agents: (i) would not make the adhesive system radiopaque; (ii) would not change the degree of conversion of the material (iii) would not affect the mechanical properties, and (iv) would not affect the bond strength durability.

2. Materials and methods

2.1. Preparation of the experimental niobiophosphate bioactive glass

NPG was prepared by melting mixtures of diammonium phosphate (Reagent Grade, Casa Americana, São Paulo, SP, Brazil), niobium oxide (Optical Grade, Companhia Brasileira de Mineração e Metalurgia, Araxá, MG, Brazil), calcium oxide (Reagent Grade, Casa Americana, São Paulo, SP, Brazil) and sodium carbonate (Reagent Grade, Casa Americana, São Paulo, SP, Brazil). The chemical compounds were mixed in a shaker-mixer for 1 h, placed in an alumina crucible, and heated in an electric furnace (Lindberg/Blue M, Watertown WI, USA).

The heating rate was 10 °C/min up to 500 °C. The material was then kept in air at this temperature for 30 min to eliminate the volatile products. After this, the material was heated to 1400 °C to completely melt the precursors, and kept at this temperature for 20 min for homogenization and degassing to eliminate the bubbles. The liquid was poured into a stainless steel mold and cooled at room temperature. The glass was then crushed in a vibrating system with a tungsten ball (Pulverisette, Fristsch, Idar-Oberstein, Germany) for 30 min [10–12]. After grinding, the resultant glass powder was passed through a series of 150 μm–75 μm–53 μm–38 μm–25 μm sieves (Bertel, Caieiras, SP, Brazil). Only the powder that passed through the 25 μm sieve was used.

2.2. Preparation of the experimental bioactive resin-base bonding agents

The experimental adhesives evaluated in the study were formulated through an intensive mixture of the components described in Table 1. The components where homogenized in a magnetic stirrer for 30 min. The mixing procedure was performed in a yellow-lit environment to prevent polymerization of formulations.

Table 1
Material composition and application mode of adhesive systems used.

	Composition	Application mode
Adhesive control	PMGDM, GDMA-P, HEMA, Bis-GMA, GDMA, camphorquinone, diaminoethyl benzoate and ethanol	(1) H_3PO_4 (37%) (15 s) (2) Washing (30 s) (3) Air blow 10 s/20 cm (4) 1st layer applied gently for 10 s (5) Air blow 10 s/20 cm (6) 2nd layer applied gently for 10 s
Adhesive NPG	PMGDM, GDMA-P, HEMA, Bis-GMA, GDMA, camphorquinone, diaminoethyl benzoate, ethanol and NPG micro-filler	(7) Air blow 10 s/20 cm (8) Light cure 10 s – 600 mW/cm^2

PMGDM: pyromellitic glycerol dimethacrylate; GDMA-P: glycerol dimethacrylate phosphate; GDMA: glycerol dimethacrylate; Bis-GMA: bisphenol-A-glycidyl methacrylate; HEMA: 2-hydroxyethyl methacrylate; NPG: experimental niobiophosphate bioactive glass

NPG microfillers were silanized by gamma-methacryloxypropyltrimethoxysilane (γ-MPTS, Aldrich Chemical Co; Milwalkee, WI, USA). Microfillers were added to an ethanol solution (Labsynth, Diadema, SP, Brazil) containing 3 wt% of γ-MPTS [19]. The mixture was stored for 24 h at 50 °C to ensure complete solvent removal and condensation reaction of γ-MPTS on the filler surface. Silanized NPG (40 wt%) were added to the resin and mixed mechanically with a motorized mixer (stirring). In order to assure adequate filler dispersion, experimental resins were ultrasonicated for 1 h. After this, the resin solution was divided into two groups: Control adhesive (without NPG) and NPG adhesive (containing 40 wt% of silanized NPG). Both experimental adhesive were kept in black bottles in order to protect the material from contact with light.

2.3. Radiopacity

A stainless steel mold was used to prepare the specimens. Five specimens measuring 5.0 mm in diameter and 1.0 mm thick were prepared for each experimental adhesive system. The adhesive was dispensed directly into the mold until it was completely filled. Solvent was evaporated by gentle air blowing from a dental syringe for 40 s. A glass cover slip was placed on top of the adhesive. Each specimen was polymerized for 40 s with a visible-light curing unit (Optilux 501, Kerr, Orange, CA, USA). Enamel and dentin specimens were obtained from 1.0 mm thick longitudinal sections of human molars. Slices were prepared using a low-speed Isomet saw (Buehler, Lake Bluff, IL, USA). A total of three radiographs were taken. Each radiograph was taken with two experimental adhesive specimens and the enamel-dentin samples placed on the digital sensor. Intraoral digital radiographs (70 kV_p and 7 mA) were then taken with an exposure time of 0.2 s and a standardized radiographic position (the central x-ray beam focused at a 90° angle to the surface of the image receptor at a 30 cm focus/object distance, with parallelism between the sensor and the specimen) using a Sirone machine (Asahi Roentgen IND, Kyoto, Japan). The digital radiopacity (% white) was measured by counting pixels using the UTHSCSA ImageTool 3.0 software (Department of Dental Diagnostic Science, University of Texas Health Science Center, San Antonio, TX, USA).

2.4. Degree of conversion analysis

The degree of conversion was analyzed by Fourier transform infrared/attenuated total reflectance (Spectrum 100, PerkinElmer, Shelton, CT, USA) at 25 °C under 64% relative humidity. One drop of each adhesive system ($n=3$) was applied to the surface of a zinc selenide pellet (PerkinElmer). Before polymerization for 10 s with an LED light (FlashLite 1401, Discus Dental, Culver City, CA, USA; irradiance at 1100 mW/cm^2) positioned 3 mm from the pellet surface, the solvent of each adhesive resin was volatilized. The absorption spectra of nonpolymerized and polymerized adhesive resins were obtained from the region between 4000 and 650 cm^{-1} with 32 scans at 4 cm^{-1}. Aromatic vinyl bonds of bisphenol and aliphatic bonds of the methacrylate functional group, the aliphatic carbon-to-carbon double-bond absorbance peak intensity (located at 1638 cm^{-1}) and that of the aromatic component (located at 1608 cm^{-1}) were obtained.

2.5. Ultimate tensile strength (UTS) and Knoop microhardness (KHN)

An hourglass-shaped rubber matrix 10 mm long, 2 mm wide, and 1 mm deep was used to construct the adhesive system specimens [20]. After isolating the matrix, the adhesive system was added drop-wise to the mold, and gently air dried (40 s). Then a glass cover slip was placed on top of the adhesive and it was light polymerized at 600 mW/cm^2 for 60 s.

Five specimens were used for each experimental condition. After 24 h storage in distilled water at 37 °C, the specimens were attached to the device (Odeme, Joaçaba, SC, Brazil) and stressed to failure, by using a universal testing machine (Inston 3342, Cantom, MA, USA) at a crosshead speed of 1.0 mm/min. The UTS was expressed in MPa, calculated by dividing force (N) by the fracture area (mm^2).

The five halves of fractured specimens from the UTS test were placed in a HMV-2 microhardness tester (Shimadzu, Tokyo, Japan) equipped with a Knoop indenter. The measurements were performed on the exposed surface at three randomized points using a Knoop indenter with a load of 50 gf and 15 s dwell time. The KHN values obtained from the same specimen were averaged for statistical purposes.

2.6. Restoration procedure

Sixteen recently extracted sound human third molars were collected after obtaining informed consent from the patients. The Local University Review Board reviewed and approved this study. Sixteen teeth were divided into two groups according to combinations of the main factors Adhesive at two levels (Control and NPG) and Time of storage at two levels (Immediate and 6 months).

Flat superficial dentin surfaces were created after removing the occlusal enamel with a low speed diamond saw (Isomet 1000, Buheler, Illinois, USA) under water-cooling. The exposed enamel-free dentin surfaces were polished on wet #600-grit SiC paper for 60 s to standardize the smear layer. Both adhesive systems were classified as the two-step etch-and-rinse type. One experimental adhesive system without bioactive glass (control) and one experimental adhesive system with bioactive glass (NPG) was applied as described in Table 1. Resin composite build-ups (Opallis, FGM, Joinville, SC, Brazil) were constructed on the bonded surface (3 increments of 1.5 mm each) each increment was light-activated with a halogen light appliance (Optilux 501, Kerr, Orange, CA, USA) at an intensity of 600 mW/cm^2 (Radiometer, Kerr) for 40 s. Next, the specimens were stored in distilled water at 37 °C for 24 h.

After this, teeth were serially sectioned using a diamond saw (Isomet 1000, Buheler, Illinois, USA) to obtain resin-dentin bonded sticks. The cross-sectional area of each stick was measured to the nearest 0.01 mm using a digital caliper and recorded (Absolute Digimatic, Mitutoyo, Tokyo, Japan). All sticks from each tooth were randomly divided according to the test time interval: half were tested immediately after cutting, and the other half after 6 months.

For testing, the individual bonded sticks were glued onto the Geraldeli device (Odeme, Joaçaba, SC, Brazil) with a cyanoacrylate adhesive (Pegamil Bond Gel, Buenos Aires, Argentina). Each stick was stressed to failure by means of a universal testing machine (Instron 3342, Canton, MA, USA) at a crosshead speed of 1.0 mm/min. The maximum tensile load was divided by the specimen cross-sectional area to express the results in MPa.

2.7. Failure pattern analysis

The fractured surface of each test specimen was evaluated under a stereoscopic loupe (Kozo Optical and Electronic Instrumental, Nanjing, Jiangsu, China) at 40X magnification and classified as adhesive (A); failure at the resin-dentin interface, mixed (M); failure at the resin-dentin interface, which included cohesive failure of the neighboring substrates, cohesive resin (CR); failure exclusive within resin composite dentin, or cohesive dentin (CD); failure exclusive within dentin. The failure modes were expressed as percentages (%).

2.8. Statistical analysis

Statistical analysis was performed using the SigmaPlot 12 software (SigmaPlot v. 12.3, Systat Software Inc., San Jose, USA). Before submitting the data to analysis using the appropriate statistical test, the Kolmogorov–Smirnov and Levene's tests were performed. After observing the normality of the data distribution and the equality of the variances, the statistical analysis was performed.

The radiopacity data were submitted to a one-way ANOVA. Degree conversion, KHN and UTS were analyzed by the Student's-t test ($P<0.001$), and the Student–Newman–Keuls test ($P<0.05$) was used for post hoc comparisons.

The experimental unit in this study was the specimen (tooth). The microtensile bond strength (μTBS) of all sticks from the same specimen (tooth) was averaged for statistical purposes. The μTBS (MPa) means for every test group were expressed as the mean of the eight specimens used per group.

The number of prematurely debonded sticks (D) per tooth during specimen preparation was recorded but not included in the statistical analysis. The μTBS means were analyzed with two-way ANOVA (Adhesive vs. Storage) and Tukey tests for pairwise comparisons ($\alpha=0.05$).

3. Results

3.1. Radiopacity

One-way ANOVA detected statistically significant difference between groups (Table 2; $p<0.0001$). The experimental adhesive with NPG showed higher radiopacity than the control adhesive.

3.2. DC, UTS and KHN

The DC, UTS and KNH values of the adhesive systems tested presented statistically significant difference ($p<0.001$). The NPG adhesive system showed the highest DC and KNH values, and lowest UTS values when compared with the control adhesive system (Table 3).

Table 2
Means and standard deviations of the radiopacity of enamel, dentin and adhesive systems by pixel intensity.

Groups	Enamel	Dentin	Adhesive NPG	Adhesive control
Pixel intensity	68.7 ± 2.4^{a}	31.6 ± 2.0^{b}	19.0 ± 2.4^{c}	7.5 ± 0.6^{d}

Means identified with the same superscript letters indicate statistically similar means ($p > 0.05$).

Table 3
Means and standard deviations of the ultimate tensile strength (MPa), Knoop microhardness (KNH), and degree of conversion (%) as well as the statistical significance for each method (*).

Groups	Adhesive control	Adhesive NPG
Degree of conversion (%)	50.4 ± 3.2^{b}	65.6 ± 1.2^{a}
UTS	7.4 ± 1.7^{a}	3.4 ± 0.4^{b}
KNH	6.7 ± 0.5^{b}	9.9 ± 1.6^{a}

To standardize, the highest values must be accompanied by the letter (a) and lower values with the letter (b).

* On the same line, different letters indicate the presence of significant statistical difference ($P < 0.05$).

Table 4
Mean and standard deviation (SD) of microtensile bond strength values (MPa), total number of beams (tested stick/pre-load failure) and distribution of failure mode after microtensile bond strength testing [Failure A/M/CD/CR].

Adhesive	**Microtensile bond strength values (MPa)** (N of tested/pre-failure) [Failure A/M/CD/CR]	
	24 h test	**6 month test**
Adhesive control	56.0 ± 13.4A (77/0) [66/10/0/1]	40.9 ± 5.7B (79/0) [70/9/0/0]
Adhesive NPG	43.8 ± 5.7A (80/0) [77/13/0/0]	34.8 ± 4.2A (81/0) [71/10/0/0]

Different letter indicates statistical difference in same line ($p > 0.05$).

3.3. Microtensile bond strength

There were statistically significant effects of adhesives ($F=8.50$; $p=0.07$) and storage ($F=14.79$; $p < 0.001$), but there was no statistically significant interaction between the factors ($F=0.95$; $p=0.33$). Differences between adhesives were found only at the immediate testing time when the experimental adhesive containing NPG presented significantly lower bond strength than the control, NPG-free adhesive ($p=0.011$). Such differences were not observed at the 6 months test period ($p=0.18$). Storage caused significant reduction in bond strength values for the control, NPG-free adhesive ($p=0.002$), whereas there were no detectable differences between the 24 h vs. 6 months bond strength for the NPG-containing adhesive ($p=0.06$).

The percentage of specimens with premature failure and the frequency of each fracture pattern mode are shown in Table 4. Most of the specimens showed adhesive failures.

4. Discussion

Radiopacity is one of the essential prerequisites of dental materials, and this may be obtained by incorporating different radiopaque elements [2,16,18,21]. Although, International Organization for Standardization recommend the use an Al bar with a 8-stepwedge with 1 mm per step to radiopacity evaluation [22], there are different studies that use, a 1 mm tooth slice to evaluate the radiopacity, mainly in adhesive systems [20,23–25]. Recently, de Moraes Porto et al. [24] evaluated the radiopacity of adhesive evaluate with a Al bar and with 1 mm tooth slice, as well as, used in the present study. The results showed that, no statistical difference in radiopacity was observed between 1 mm of Al and 1 mm of dentin and between 2 mm of Al and 1 mm of enamel. This means that the use of tooth slice can be considered as option to evaluate radiopacity in adhesive systems [24].

Some recent studies have obtained radiopaque adhesive systems with the inclusion of barium–borosilicate glass [20], or niobium pentoxide [26]. However, these inorganic filler particles do not have the ionic release capacity that could contribute to bioactivity. Thus, it would be very important to add microparticulate fillers that may have the ability to provide the materials with radiopacity and bioactive potential, thus developing new innovative and smart therapeutic resin adhesive systems.

The incorporation of NPG particles was capable of producing a radiopaque adhesive system. Thus, the (i) null hypothesis of the study was rejected. According to these results, it is possible to distinguish the restorative material, enamel and dentin, in addition to allowing a more precise diagnosis of caries lesions [27], by means of radiographs.

Another advantage of the incorporation of bioactive glass particles, observed in the present study, was the increase in the degree of conversion of the adhesive system with the presence of NPG. However, innumerable studies have demonstrated the incorporation of filler particles that do not present bioactivity (radiopacifying filler agents: La_2O_3, BaO, $BaSO_4$, SrO and ZrO_2), diminished the degree of conversion of resin materials [28–31]. This may occur because the mobility of monomer-chain may be restricted by the incorporation of the fillers, leading to decreasing the mobility of monomers and radicals, thus resulting in lower conversion [31]. This reduction in the degree of conversion may, in some cases, occur due to the particle size being close to the curing unit wavelength [32]. In the present study, irregular filler particles of a size below 25 μm were used, therefore, a value much higher than that of the wavelength of the light polymerizing unit (0.468 μm).

Some studies have shown that the addition of filler particle does not change the degree of conversion of adhesive systems, because of the uniform distribution of the filler particles within the material [20,33]. However, increased filler content (Nb_2O_5), can change the reaction kinetics, leading to increased conversion rates of the adhesive system [26].

In this study, incorporation of the NPG increased the degree of conversion of the adhesive system. Thus, (ii) null hypothesis of the study was rejected. We speculated that light of the curing device is reflected in the bioactive glass and this may lead to improvements in the degree of conversion and polymerization efficacy [34].

Recently, Tauböck et al. [35] found an increase in the degree of conversion of a composite with the addition of 20% ultrafine bioactive particles (SiO_2–Na_2O–CaO–P_2O_5–Bi_2O_3). In this study, and in several others, the addition of fillers was found to increase the microhardness [20,26,35] in agreement with our findings.

On the other hand, the incorporation of 40% bioactive fillers into NPG reduced the UTS of adhesive system. The addition of particles has been well established as a reinforcing mechanism of polymer materials [36]. However, this is only observed when high concentrations of filler particles are added, around 60% [20]. On the other hand, the impact of the addition of filler particles on the mechanical properties of commercial adhesives does not seem to bring benefits to the material [37].

The results indicated that there was an initial negative effect of adding NPG to the adhesive system since the immediate bond strengths were significantly reduced. This could somehow be associated with the fact that the UTS of the adhesive was also

reduced when NPG were incorporated (see our results, Table 3). By assuming the immediate bond strengths observed for each adhesive as the maximum value, storage for 6 months caused a 27% reduction in the bond strength of the control adhesive and a 20.5% reduction for the NPG-containing adhesive. Such reductions were statistically significant for the control, but there were no differences for the NPG-adhesive. The exact reason why the presence of NPG could have helped to preserve the bond strength is unclear.

However, one could speculate the increased degree of conversion in the NPG adhesive could have made the adhesive less prone to hydrolytic degradation during storage. From our findings, it is unclear at this point and impossible to determine whether NPG would have any protective effect on the degradation of the collagen fibrils. The effects of NPG on enzymes such as MMPs and cathepsins have not yet been determined, although it is known that NPG glass has some anti-biofilm activity [38]. The null hypothesis should, therefore, be rejected.

5. Conclusion

The present outcomes showed that the inclusion of micro-filler of niobium phosphate bioactive glass could produce an adhesive system with higher radiopacity, degree of conversion and Knoop hardness when compare to control (without bioglass) and mainly with no significant decreasing of the bond strength after 6-month of water storage. Therefore, NPG glass may be a promising development alternative for dental biomaterials.

Acknowledgments

This study was supported by the Foundation for the Support of Scientific and Technological Research of Maranhão (FAPEMA – 2107/12 and 02225/13) and by the National Council for Scientific and Technological Development Grant (CNPq - 237066/2012-2). The CBMM (Companhia Brasileira de Metalurgia e Mineração) for providing the niobium pentoxide and Esstech Inc. for monomer and initiators.

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