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

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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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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).