International Journal of Adhesion and Adhesives 80 (2018) 122–127

Contents lists available at ScienceDirect

International Journal of Adhesion and Adhesives

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

Addition of nanoparticles for development of radiopaque dental adhesives

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ARTICLE INFO

Keywords:
Nanoparticles
Etch-and-rinse
Radiopacity
Mechanical properties

ABSTRACT

This study evaluate the effect of nanoparticles (Bi_2O_3 - bismuth oxide; YbF_3 - ytterbium trifluoride; SiO_2 - silicon dioxide) on radiopacity (R), translucency parameter (TP), degree of conversion (DC), bond strength to dentin (μTBS), and quality of the adhesive interface of experimental two-step, etch-and-rinse adhesive systems. The R was evaluated using an x-ray equipment. TP was verified in five replications and DC was performed in triplicate. The μTBS was evaluated in specimens stored in distilled water after 24 h, 6, 12 and 24 months. The bonded interfaces were qualitatively examined by scanning electron microscopy (SEM), and using x-ray energy dispersive spectroscopy (EDS) for elemental analysis. Data were statistically analyzed at $\alpha = 0.05$. YbF_3 resulted in statistically greater R when compared with all the other groups ($p = 0.024$), which did not differ from each other. Bi_2O_3 was the adhesive with lowest TP. For DC, the YbF_3 and C showed similar results ($p = 0.627$). Similar μTBS was obtained between groups. The addition of nanoparticles affected the chemical-mechanical properties. The incorporation of YbF_3 could be considered a promising approach for the development of radiopaque dental adhesives.

1. Introduction

With the purpose of improving the chemical and mechanical properties of dental resin-based materials, particles have been incorporated to reinforce the mechanisms in crystalline, semi-crystalline and amorphous materials [1]. Among these strategies, reducing the particle size down to the nanoscale level has been widely used [2–4].

Nanoparticles closer in size to those of the polymer chain have led to good interaction between the chain/polymer due to the increased surface to volume ratio of the fillers [5]. In adhesive systems, nanoparticles may increase mechanical properties such as strength, and viscosity [5,6]. Moreover, the incorporation of particles containing chemical elements with high atomic number may provide adhesive systems with radiopacity, which would be interesting, because the adhesive layer would typically be radiolucent. These radiolucent radiographic images may be similar to those of secondary caries or defective restorations. Consequently, clinical misdiagnosis and/or unnecessary replacement of restorations may occur [7], with additional costs, chair time, and discomfort to the patient.

To avoid this problem, the incorporation of the oxides such as silicon dioxide (SiO_2), barium oxide, barium sulfate, titanium dioxide, strontium oxide, zirconia dioxide have been used as radiopacifiers [2,8]. In addition, ytterbium trifluoride (YbF_3) has been shown to be a satisfactory source of radiopacity [9,10]; while the use of SiO_2 nanoparticles was more interesting to increase the cohesive strength of adhesive resins [2]. Unfortunately, all the additives mentioned above also may bring some unwanted problems. For example, incorporation of great quantity fillers into dental resin may have some adverse effects on the mechanical properties of materials because this leads to significantly reduced inter-particle spacing, increasing the number of particle collisions and suspension viscosity. Moreover, excessive amounts of fillers could cause loss of dimensional stability of the composite materials or deterioration in bond strength, decrease in flexural strength and elastic modulus, diametral tensile strength, and fracture toughness. One study showed that increase in nanoparticle radiopacifier concentration was associated with exponential growth in viscosity and exponential decay in the translucency parameter [10,11]. Furthermore, excessive amounts of fillers could cause loss of dimensional stability of the composite materials or deterioration in bond strength [12–14].

Moreover, only few studies have evaluated the radiological, chemical and mechanical properties of experimental adhesives containing nanoparticles. In other words, there are other particles that may contribute to increasing the performance of these modified adhesives, but

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http://dx.doi.org/10.1016/j.ijadhadh.2017.10.009
Accepted 17 October 2017
Available online 07 November 2017

they have not yet been evaluated. For example, bismuth oxide (Bi_2O_3) is an agent commonly used for radiopacity purposes in dental materials, including but not limited to mineral trioxide aggregate (MTA) materials [15].

Therefore, the aim of this study was to investigate the effect of nanoparticles (Bi_2O_3, YbF_3, and SiO_2) on radiopacity, translucency parameter degree of conversion, immediate and long-term bond strength to dentin, and on the quality of the bonded interfaces. The null hypothesis to be tested was that the incorporation of nanoparticles would provide radiopacity without compromising the properties and bonding performance of the adhesive systems.

2. Materials and methods

2.1. Adhesive resin formulations

A stock methacrylate-based resin was formulated by mixing 35 wt% of 2-hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, St. Louis, MO, USA), 15 wt% of urethane dimethacrylate (UDMA, Esstech, Essington, PA, USA), 10 wt% of triethyleneglycol dimethacrylate (TEGDMA, Esstech), 10 wt% of bisphenol-A glycidyl dimethacrylate (Bis-GMA, Esstech, and 10 wt% of glycerol dimethacrylate (GDMA, Esstech). A 20 wt% fraction of ethanol (Labsynth Ltda., Diadema, SP, Brazil) was used as solvent. A ternary photoinitiator system consisting of 0.4 M% of camphorquinone (CQ, Esstech), 1 M% of ethyl 4-dimethylaminobenzoate (EDAB, Fluka, Milwalkee, WI, USA), and 1 M% of diphenyliodonium hexafluorophosphate (DPI, Sigma-Aldrich) was used.

YbF_3 (40–80 nm average particle size, Nanostructured & Amorphous Materials, TX, USA) and Bi_2O_3 nanoparticles (90–210 nm average particle size, Nanostructured & Amorphous Materials) were superficially treated with a 10 wt% phosphate monomer/ethanol solution, whereas SiO_2 nanoparticles (7 nm average particle size, Aerosil 380, Degussa, Germany) were silanized with a 10 wt% solution of organosilane (γ-methacryloxypropyltrimethoxysilane, Sigma-Aldrich) in acetone (Labsynth Ltda.) The slurry was stored at 37 °C for 24 h to assure complete solvent removal (acetone). The SiO_2 particles were then sonicated and filtered using sieves with 150 μm openings to avoid agglomeration.

Next, the stock resin was divided into four groups, according to the type of nanoparticle incorporated: 10 wt%): Bi_2O_3, YbF_3, SiO_2, control (without particles). The nanoparticles were mechanically mixed with the resin, first with the help of a spatula and subsequently by using a motorized mixer (stirring process). After this, the resin adhesives were ultrasonicated for 1 h.

2.2. Radiopacity

The radiographic test was performed in accordance with ISO 4049 [16]. Radiographic images of five cylindrical specimens (5 mm in diameter, 1 mm thick) per adhesive were distributed on periapical film (Insight; Kodak, Rochester, NY, USA) and the images were captured by means of an X-ray device (Spectro 70X Seletronic; Dabi Atlante, Ribeirão Preto, SP, Brazil) using 70 kV, 8 mA; a 40 cm focus-film distance; and exposure to irradiation for 0.4 s. An aluminum step-wedge (aluminum purity range > 99.0%) with thickness ranging from 0.5 to 5 mm; 0.5 mm for every increasing step was exposed simultaneously to the radiation (control). The gray levels (pixel density) of the digital images were analyzed by image software, and the aluminum equivalence values (mm) of each specimen were recorded. The data were statistically analyzed using one-way ANOVA and the Tukey test (α = 5%).

2.3. Translucency parameter (TP)

The TP of cylindrical specimens of each adhesive (7 mm in diameter, 1 mm thick) was measured. The adhesives were placed in silicone molds, polyester strips were placed on the top and bottom surfaces, which were then photoactivated for 60 s. The specimens were stored in distilled water at 37 °C. The CIEL*a*b* color coordinates were measured after 24 h using a spectrophotometer (SP60; X-Rite, Grand Rapids, MI, USA). Color readouts were taken against white (L* = 93.07, a* = 1.28, b* = 5.25) and black (L* = 27.94, a* = 0.01, b* = 0.03) Munsell-like neutral value scale sheet backgrounds (AG-5330; BYK-Chemie, Wesel, Germany). The TP for each specimen was calculated using the formula: $TP = [(L^*_W - L^*_B)^2 + (a^*_W - a^*_B)^2 + (b^*_W - b^*_B)^2]^{1/2}$, where W and B referred to the color coordinates measured against the white and black backgrounds. Five specimens were tested for each material. The data were statistically analyzed using one-way ANOVA and the Tukey test (α = 5%).

2.4. Degree of conversion (DC)

The degree of conversion of the adhesives was evaluated using real-time Fourier Transform infrared spectroscopy (FTIR, Prestige21, Shimadzu, Tokyo, Japan) with an attenuated total reflectance device. A micropipette was used to drop a controlled amount of each material onto the total reflectance accessory (10 μl), and a preliminary readout for the uncured material (monomer) was taken using 24 co-added scans and 4-cm^{-1} resolutions. Data was taken from readouts in triplicate (n = 3). The adhesive was photoactivated for 20 s using a light-emitting diode (LED) curing unit (Radii, SDI, Bayswater, Victoria, Australia) with 1400 mW/cm^2 irradiance, and readouts were taken again for the polymer. DC was calculated (%) as previously described [17]. The data were statistically analyzed using one-way ANOVA and the Tukey test (α = 5%).

2.5. Microtensile bond strength (μTBS) test

Forty bovine incisors were used in this study. The middle dentin layer was exposed and wet-polished with 600-grit SiC papers for 60 s under water-cooling. The dentin was etched with 37% phosphoric acid gel for 15 s and cleansed with air-water spray for 15 s. Two coats of the experimental adhesives were applied; the solvent was evaporated for 10 s using an air stream; and the samples were photoactivated for 20 s using the LED unit. Composite resin restorations (Filtek Z250, 3 M ESPE, St Paul, MN, USA) were built up on the surfaces in 2 mm increments. The samples were stored in distilled water at 37 °C.

After 24 h, the bonded samples were sectioned into beam-shaped specimens with an area of ~ 0.7 mm^2. The specimens were randomly divided into four time intervals (24 h, and 6, 12, or 24 months). The specimens were stored in distilled water at 37 °C (n = 20). After this, μTBS test was performed with a universal testing machine (DL500, EMIC, São José dos Pinhais, PR, Brazil) at a crosshead speed of 1 mm/min. μTBS values were recorded in MPa, and the data were subjected to two-way ANOVA (adhesive × storage period as factors) and the Tukey test (α = 5%). The fractured specimens were observed at 500X magnification, and the failure modes were classified as adhesive, cohesive within resin, cohesive within dentin, or mixed.

2.6. SEM and EDS analyses

The different adhesives with nanoparticles were analyzed by scanning electron microscopy at 15 kV (Jeol, JSM - 6610LV, USA). Six bovine teeth were obtained and the adhesive system was applied as described earlier (n = 2). The dentin discs were bonded to each other using a thin layer of photo-activated composite resin, generating a dentin-composite resin-dentin sandwich specimen. The specimens were embedded cross-sectionally in epoxy resin so that the dentin-resin composite-interface was visible. After 24 h, the specimens were wet polished with 600, 1200, 1500 and 2000-grit SiC papers and polished with 3-, 1- and 0.5-μm diamond suspensions. The surfaces were etched with 50% phosphoric acid solution for 5 s and deproteinized by