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Nanotube-modified dentin adhesive—Physicochemical and dentin bonding characterizations

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ABSTRACT

Objective. The aim of this study was to investigate the effect of aluminosilicate clay nanotubes (Halloysite, HNT) incorporated into the adhesive resin of a commercially available three-step etch and rinse bonding system (Adper Scotchbond Multi-Purpose/SBMP) on dentin bond strength, as well as the effect on several key physicochemical properties of the modified adhesive.

Methods. Experimental adhesives were prepared by adding five distinct HNT amounts (5–30 wt.%) into the adhesive resin (w/v) of the SBMP dentin bonding system. Bond strength to human dentin, microhardness, and degree of conversion (DC) of the modified adhesives were assessed.

Results. From the shear bond strength data, it was determined that HNT incorporation at a concentration of 30 wt.% resulted in the highest bond strength to dentin that was statistically significant ($p = 0.025$) when compared to the control. Even though a significant increase in microhardness ($p < 0.001$) was seen for the 30 wt.% HNT-incorporated group, a significantly lower DC ($p < 0.001$) was recorded when compared to the control.

Significance. It was concluded that HNT can be incorporated up to 20 wt.% without jeopardizing important physicochemical properties of the adhesive. The modification of the SBMP dentin bonding agent with 20 wt.% HNT appears to hold great potential toward contributing to a durable dentin bond; not only from the possibility of strengthening the bond interface, but also due to HNT intrinsic capability of encapsulating therapeutic agents such as matrix metalloproteinase (MMP) inhibitors.

1. Introduction

Adhesive dentistry has advanced tremendously over the past twenty years [1–5]. Needless to say, bonding of resin composite restorations to enamel using the acid-etch technique advocated by Buonocore [6] has been considered a safe and predictable restorative procedure [1,3,5,7]. Regrettably, the achievement of a reliable and durable bond to dentin still poses a great challenge to the field, in part due to the high

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organic content levels existing in dentin (e.g., collagen) when compared to enamel [2,4,5,7]. Nevertheless, another major contributor to resin–dentin bond degradation relates to the well-known hydrolytic process experienced by underpolymerized hydrophilic resins and the deterioration of water-rich, resin–sparse collagen matrices by matrix metalloproteinases (MMPs) and cysteine cathepsins [3–5,8,9].

In order to hinder resin–dentin bond degradation and therefore improve the longevity of resin-based restorations, numerous adhesive chemistries and bonding strategies have been proposed [3–5,8,9]. Among them, recent advances in nanoscience and nanomaterials processing have supported the use of an ample variety of fillers in the form of nanorods, nanoparticles, whiskers and nanotubes as reinforcing agents in adhesive systems targeting not only improved material properties (i.e., adhesive) but also the enhancement of bonding to dentin [2,10–14]. Noteworthy, the size scale of these fillers and the concomitant increased surface area yield a unique combination of mechanical properties through the reinforcement of the polymer matrix via localized plastic deformation around the fillers and crack deflection [15,16]. Furthermore, it has been suggested that these nanofillers can infiltrate into the dentinal tubules, decreasing polymerization shrinkage, stiffening the adhesive layer, and ultimately strengthening the adhesive interface via micromechanical bonding [12,13].

A series of studies investigating the mechanical properties enhancement of engineered resins incorporated with aluminosilicate ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) clay nanotubes (Halloysite, HNT) have been reported [17–20]. Overall, the results from those studies led to the present work for two major reasons. First, aluminosilicate clay nanotubes [21–24] have many advantages (e.g., biocompatibility, hydrophilicity, and high mechanical strength) that make them a good candidate to be used as a reinforcing agent for improving resin-based dental adhesive properties. Second, these clay nanotubes have been demonstrated to act as biologically safe reservoirs for encapsulation and controlled delivery of a wide variety of therapeutic drugs [23,25], which in adhesive dentistry could potentially serve as a carrier of MMP inhibitors, that could in turn positively contribute to minimizing and/or eliminating resin–dentin bond degradation [4,8,9]. Currently, there appears to be no reports on the use of Halloysite in adhesive dental resins. The purpose of this study was to investigate the effect of incorporating Halloysite in the adhesive resin of a commercially available three-step etch and rinse bonding system on dentin bond strength. Physical properties of the HNT-incorporated adhesives such as microhardness and degree of conversion were also evaluated. The null hypotheses tested were that HNT incorporation would neither increase bond strength to dentin nor negatively impact adhesive properties such as degree of conversion and microhardness.

2. Materials and methods

2.1. Materials and experimental adhesive formulation

Halloysite aluminosilicate clay nanotubes (HNTs, Dragonite-1415JM®) were donated by Applied Minerals (New York, NY, USA). Previous to dentin bonding agent modification (i.e., the adhesive resin of Adper Scotchbond Multi-Purpose/SBMP), an aqueous dispersion of HNTs was prepared to confirm the surface morphology as well as the hollow structure of the nanotubes by scanning (FE-SEM, JEOL, JSM6701-F, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan), respectively [26]. On an Al stub for HNT imaging, a predetermined approximate 0.5 mL volume of the HNT aqueous dispersion was added, allowed to dry and then sputter-coated with Au before SEM evaluation. Similarly, one 10 μL drop of the dispersion was added to a holey carbon TEM grid (Cu 200 mesh, SPI Supplies, West Chester, PA, USA), allowed to air-dry and imaged at 100 kV [26]. Representative FE-SEM and TEM images of the HNTs are shown in Fig. 1. HNTs displayed an overall uniform rod-like tubular structure with an estimated mean length in the submicron range (Fig. 1A). The HNT hollow structure was confirmed by TEM (Fig. 1B).

As previously mentioned, the experimental adhesives were prepared by adding five distinct HNT amounts (5, 10, 15, 20 and 30 wt.%) accurately (five-decimal-places) weighed using an analytical balance (Mettler Toledo, Ohio, OH, USA) into the adhesive resin (w/v) of the SBMP dentin bonding system. Briefly, HNTs were incorporated into a predetermined adhesive resin volume (w/v), mixed with a motorized mechanical stirrer using the companion conical micro pestle adapter (Roti-Speed, Roth, Karlsruhe, Germany) and then sonicated (Ultrasonic cleaning L&R 2014, Mfg Co., Kearney, NJ, USA) for 1 h to further enhance the dispersion [12] of HNTs within the adhesive resin. Detailed information of the commercial dentin bonding system (SBMP) used is given in Table 1.

2.2. Dentin bonding, shear testing, failure mode and resin–dentin interface evaluation

Shear bond testing has been considered one of the most simple methods for testing adhesives bond strength in vitro [27]. Here, we used this test to screen for significant deleterious impact on the dentin bond strength achieved through HNT incorporation into the adhesive resin of a commercially available three-step etch and rinse bonding system (SBMP).

Seventy two caries-free human third molars were immersed in 0.5% chloramine solution after soft tissue removal and then stored in distilled water in a refrigerator at 4 °C. Teeth within six months of extraction were used under an approved IRB (Institutional Review Board, Indiana University-Purdue University Indianapolis) protocol (NS1004-03). Each tooth's occlusal third was removed with a low-speed diamond saw (Buehler Ltd., Lake Bluff, IL, USA) mounted on a precision cutting machine (Isomet 1000, Buehler Ltd., Lake Bluff, IL). Teeth were individually embedded in Teflon molds using acrylic resin (Bosworth Fastray, powder lot# D681092139209, liquid lot# D68109213950C, Bosworth Company, Skokie, IL, USA). Following that, a flat mid-coronal dentin surface was obtained using a finishing procedure with SiC abrasive papers 240–600 grit under running water to ensure a standardized and uniform smear layer. The teeth were then randomly distributed into six groups ($n = 12$), namely the control (G1-0 wt.%, no HNT incorporation) and five experimental groups (G2-5 wt.%, G3-10 wt.%, G4-15 wt.%, G5-20 wt.% and G6-30 wt.%).