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Physicochemical and bioactive properties of innovative resin-based materials containing functional halloysite-nanotubes fillers

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ABSTRACT

Objective. This study aimed to assess the degree of conversion, microhardness, solvent degradation, contact angle, surface free energy and bioactivity (e.g., mineral precipitation) of experimental resin-based materials containing, pure or triclosan-encapsulated, aluminosilicate-(halloysite) nanotubes.

Methods. An experimental resin blend was prepared using bis-GMA/TEGDMA, 75/25 wt% (control). Halloysite nanotubes (HNT) doped with or without triclosan (TCN) were first analyzed using transmission electron microscopy (TEM). HNT or HNT/TCN fillers were incorporated into the resin blend at different concentrations (5, 10, and 20 wt%). Seven experimental resins were created and the degree of conversion, microhardness, solvent degradation and contact angle were assessed. Bioactive mineral precipitation induced by the experimental resins was evaluated through Raman spectroscopy and SEM-EDX.

Results. TEM showed a clear presence of TCN particles inside the tubular lumen and along the outer surfaces of the halloysite nanotubes. The degree of conversion, surface free energy, microhardness, and mineral deposition of polymers increased with higher amount of HNTs. Conversely, the higher the amount (20 wt%) of TCN-loaded HNTs the lower the microhardness of the experimental resins.

Significance. The incorporation of pure or TCN-loaded aluminosilicate-(halloysite) nanotubes into resin-based materials increase the bioactivity of such experimental restorative materials and promotes mineral deposition. Therefore, innovative resin-based materials containing functional halloysite-nanotube fillers may represent a valuable alternative for therapeutic minimally invasive treatments.

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1. Introduction

Dental caries represents one of the main reasons for placement and replacement of resin composite restorations [1,2]. Minimally invasive treatment of carious lesions in dentin requires selective removal of infected tissue, leaving as much caries-affected dentin as possible for therapeutic remineralization [3].

The advent of the latest generation of adhesive systems have radically influenced modern operative management of dental caries [4,5] in minimally invasive dentistry (MID), in particular during atraumatic restorative treatments (ART) of deep carious lesions. Moreover, the application of adhesive systems on demineralized dentin (e.g. H_3PO_4-etched dentin), followed by placement of esthetic light-curing resin composites represents the main clinical procedure performed daily by many general dentists [6,7].

The main concern in MID/ART may be associated to the "poor" durability of the resin–dentin interface. The reason is that such esthetic restorations have no therapeutic antibacterial and/or remineralization effect on caries-affected dentin [8,9]. Hence, it is still necessary to generate new types of resin-based restorative materials with enhanced therapeutic properties at the resin–dentin interface, which can also prevent the recurrence of secondary caries [9,10].

Triclosan (TCN) is a typical agent used in several antibacterial products such as toothpastes, mouth-rinse solutions and detergents. TCN seems to be particularly active against gram-positive microorganisms, such as *Streptococcus mutans*; one of the main pathogens, along with *S. aureus*, *Lactobacillus* spp., and *Actinomyces* spp., involved in dental caries process [11]. Because of its antimicrobial effectiveness, small size and easy processing, the use of TCN has constantly increased over the last 30 years [12].

The development of polymer-based adhesives with advanced physicochemical and biological properties represents a key target for researchers and dental manufacturers in order to develop innovative restorative materials that can increase the durability of the resin–dentin interface and impede the formation of secondary caries [5,9]. It is well known that the inclusion of inorganic fillers into the polymeric matrix decreases the polymer ratio, leading to an improvement in the mechanical properties of resin composite materials and to the reduction of the polymerization stress and shrinkage in such restorative materials [13]. Nevertheless, the excessive incorporation of fillers into resin-based materials may result in an interference with the penetration of light energy during light-curing procedures, thus hindering chain mobility in the propagation phase and therefore jeopardizing their final degree of conversion (DC) [14].

Halloysite nanotubes (HNTs), aluminosilicate nanoclay ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) fillers, may be easily incorporated into different co-monomer resin blends [15]. This unique filler is characterized by an outer surface made of Si–O bonds along with few silanols at the crystal defect sites. The inner walls of HNTs are mainly characterized by aluminols. Unlike traditional silica fillers, HNTs are able to promote a better polymerization rate of methacrylates [16], due to a special coordination between the carbonyl groups of the monomers and the electron deficient atom of aluminum (Al) in the nanoclay [17].

HNTs have hollow tubules with an inner and outer diameter in the range of 10–40 and 40–70 nm, respectively [18]. Therefore, many chemically and biologically active substances such as tetracycline, khellin and nicotinamide adenine dinucleotide have been loaded into HNTs by soaking in a saturated drug solution under vacuum [19]. The drug released from the HNTs can last 30–100 times longer than the drug alone or in other carriers [20].

The objective of this study was to perform a series of tests to assess the physicochemical properties of seven experimental dental resin-based materials containing different concentrations of aluminosilicate-(halloysite) nanotubes doped with or without triclosan. Moreover, the bioactivity of such experimental materials was also assessed through Raman spectroscopy and SEM-EDX. The first hypothesis tested in this study was that the incorporation of different amounts (%wt) of HNT/TCN or HNT would confer bioactive properties to the experimental resin-based materials. The second hypothesis was that the incorporation of different amounts (%wt) of HNT/TCN or HNT would not alter the degree of conversion, microhardness, solvent degradation, contact angle and surface free energy of the experimental resin-based materials tested in this study.

2. Materials and methods

2.1. *Preparation of TCN-loaded HNTs and transmission electron microscopy (TEM)*

Halloysite nanoclay (HNT: $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$) was purchased (Sigma–Aldrich, St. Louis, MO, USA), sieved (<150 μm), and then immersed into a 95% acetone solution containing 5 wt% 3-metacryloxypropyltrimetoxysilane (FGM, Joinville, SC, Brazil) for 24 h at 110 °C. Subsequently, the silanized halloysite filler was mixed (ratio 1:1) with an antimicrobial 2,4,4-trichloro-2-hydroxydiphenyl ether (TCN: triclosan, Fagron, Rotterdam, SH, Netherlands). This treated filler was then dispersed (0.03 mg/mL) in absolute ethanol at 30 °C for 1 h under continuous sonication and subsequently dehydrated for 10 days in a desiccator at 30 °C.

The pure halloysite (HNT) and the TCN-loaded HNT (HNT/TCN) fillers were dispersed at 5% (0.03 mg/mL) in absolute ethanol for 24 h at 25 °C and finally stirred for 15 min. Three specimens were created by dispersing 20 μL and 10 μL of uranyl acetate on 400 mesh square copper grids (Electron Microscopy Sciences, Hatfield, PA, USA). These HNT and HNT/TCN specimens were imaged using the TEM (JEM 1200 EXll, JEOL, Tokyo, Japan) at 80–100 kV and a magnification ranged between 20,000× and 500,000×.

2.2. *Preparation of experimental resin-based materials*

A control resin blend was created by mixing 75 wt% bis-GMA (2,2-bis-[4-(hydroxyl-3-methacryloxy-propyloxy)phenyl] propane) and 25 wt% triethylene glycol dimethacrylate (TEGDMA) (Sigma–Aldrich, St. Louis, MO, USA) for 30 min under continuous sonication. Camphorquinone (CQ), ethyl