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Titanium dioxide nanotubes addition to self-adhesive resin cement: Effect on physical and biological properties

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ABSTRACT

Objectives. This study has investigated the influence of Titanium dioxide nanotubes (TiO_2-nt) addition to self-adhesive resin cement on the degree of conversion, water sorption, and water solubility, mechanical and biological properties.

Methods. A commercially available auto-adhesive resin cement (RelyX U200™, 3M ESPE) was reinforced with varying amounts of nanotubes (0.3, 0.6, 0.9 wt%) and evaluated at different curing modes (self- and dual cure). The DC in different times (3, 6, 9, 12 and 15 min), water sorption (Ws) and solubility (Sl), 3-point flexural strength (σf), elastic modulus (E), Knoop microhardness (H) and viability of NIH/3T3 fibroblasts were performed to characterize the resin cement.

Results. Reinforced self-adhesive resin cement, regardless of concentration, increased the DC for the self- and dual-curing modes at all times studied. The concentration of the TiO_2-nt and the curing mode did not influence the Ws and Sl. Regarding σf, concentrations of both 0.3 and 0.9 wt% for self-curing mode resulted in data similar to that of dual-curing unreinforced cement. The E increased with the addition of 0.9 wt% for self-cure mode and H increased with 0.6 and 0.9 wt% for both curing modes. Cytotoxicity assays revealed that reinforced cements were biocompatible.

Significance. TiO_2-nt reinforced self-adhesive resin cement are promising materials for use in indirect dental restorations. Taken together, self-adhesive resin cement reinforced with TiO_2-nt exhibited physicochemical and mechanical properties superior to those of unreinforced cements, without compromising their cellular viability.

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1. Introduction

Self-adhesive resin cements were developed to clinical time by simplifying cementation procedures due to the elimination of the acid etching and application of adhesive steps [1–3]. Its adhesive properties are attributed to the presence of the modified acidic group's methacrylate monomers that allows the infiltration and demineralization of the substrate, that result in micromechanical retention and chemical bonding with hydroxyapatite [3].

However, the presence of these acidic monomers in self-adhesive resin cements may adversely affect the degree of conversion (DC) because of its interference with the amine coinitiator, which results in changes in the curing [4] and the loss of some physical and mechanical properties [5–7]. Moreover, being dual-cured, not all cements present the same conversion rates of monomers when self- or/and light-activated. In general, light-activation promotes higher conversion of monomers [8].

To improve certain properties of resin materials, the addition of titanium dioxide nanostructures have demonstrated positive results in the behavior of polymeric materials such as resin composites [9,10], flowable resin composites [11], orthodontic resin cements [12] and glass ionomer cements [13]. The decrease in size of different oxides at the nanoscale promotes a wide range of applications in different materials because their behavior changes when compared to the bulk size [14], making it an effective functional material [15]. Nano-sized oxides such as TiO_2 can provide unique physical and chemical properties due to their small size and high density of surface sites, increasing their reactivity and interaction with the environment [16]. In particular, the nanotubes' shape provides a large surface area that can give rise to strong internal and external interactions with the matrix in which they are embedded, chemical stability and a high refractive index [17].

Whereas oxides at the nanoscale can be easily incorporated into the resin-based materials when manipulated, adding these to the self-adhesive resin cement can be an alternative to improve the overall performance of the indirect restoration. Therefore, the aim of the current investigation was to determine the physical–chemical, mechanical and biological properties of a self-adhesive resin cement (RelyX U200™—Seefeld, Germany) in the presence of TiO_2-nt at three different concentrations: 0.3%, 0.6% and 0.9% (w/w).

2. Materials and methods

2.1. Experimental design

The factor under study was the incorporation of different concentrations of TiO_2-nt (w/w) into self-adhesive resin cement RelyX U200™. For degree of conversion (DC), the study factors were as follows: (1) concentration of TiO_2-nt (0.3, 0.6 and 0.9 wt.%), (2) curing mode dual- and self-curing and (3) time (3, 6, 9, 12 and 15 min). For water sorption (WS) and solubility (SL), flexural strength (σf), modulus of elasticity (E) and hardness (H), the study factors were: (1) concentration of TiO_2-nt (0.3, 0.6 and 0.9 wt%) and (2) curing mode (dual- and self-curing). For cell viability study, the factors were as follows: (1) concentration of TiO_2-nt (0.3, 0.6 and 0.9 wt.%) and (2) time (24, 48 and 72 h). Two polymerization conditions were used: self- and dual-cured polymerization. For the self-curing condition, the cement handling and the specimens' preparation were performed in an environment with room light. Thirty minutes after cement handling, specimens were removed from the custom devices used in each test and stored in distilled water at 37 °C. For the dual-curing condition, the specimens were handled in an environment with room light, embedded in custom devices used in each test of the study. Nine minutes after handling of self-adhesive resin cement, the light source 780 mW/cm^3 DB LED 686 (Dabi Atlante, Ribeirão Preto, Brazil) was applied for 20 s in different areas of the specimens so that the whole specimen was reached by light. The 9 min time was used once delay in light activation had shown to improve properties of resin-based cements [18,19].

The specimens of the self-adhesive resin cement were randomly assigned into 8 groups: **SCT** = self-adhesive resin cement in self-cure condition, which has no TiO_2-nt; **S03** = self-adhesive resin cement in self-cure condition with the addition of 0.3 wt.% of TiO_2-nt; **S06** = self-adhesive resin cement in self-cure condition with the addition of 0.6 wt.% of TiO_2-nt; **S09** = self-adhesive resin cement in self-cure condition with the addition of 0.9 wt.% of TiO_2-nt; **DCT** = self-adhesive resin cement in dual-cure condition, which has no TiO_2-nt; **D03** = self-adhesive resin cement in dual-cure condition with the addition of 0.3 wt.% of TiO_2-nt, dual cure; **D06** = self-adhesive resin cement in dual-cure condition with the addition of 0.6 wt.% of TiO_2-nt; **D09** = self-adhesive resin cement in dual-cure condition with the addition of 0.9 wt.% of TiO_2-nt.

2.2. Specimen preparation

TiO_2-nt were obtained from a commercial mixture of anatase TiO_2 powder (Sigma–Aldrich, St. Louis, USA) mixed with an alkaline solution of sodium hydroxide (NaOH; 10 M), which remained for 24 h at 120 °C in an atmospheric pressure environment Teflon container. Then, the mixture was washed with deionized water and hydrochloric acid (HCl; 0.1 M) sequentially and repeatedly until reaching a pH of 4. After that, the mixture were placed in a furnace at 200 °C for 24 h to eliminate the liquid phase and to obtain the final powdered material [20]. The nanotubes were measured with open source Image J software and had an average diameter of 10 nm and were 200 nm in length, formed by a single sheet of spiral-wound TiO_2. The image was obtained by Transmission Electron Microscopy (TEM) (CM 200, Phillps, Netherlands) with electrons acceleration of 200 kV [20]. The resin cement that had the same portion of base and catalyst paste dispensed by packing clicker was dispensed on a mixing pad and weighed on a precision scale of 0.0001 g (Denver Instrument, São Paulo, Brazil). Then, the nanotubes were weighed with the value corresponding to the resin cement weigh. TiO_2-nt was manually added to the base paste and handled for 10 s. Then, the base paste and TiO_2-nt were mixed with the catalyst paste for another 10 s.