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Effects of Y-TZP blank manufacturing control and addition of TiO_2 nanotubes on structural reliability of dental materials

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ABSTRACT

Titanium dioxide (TiO_2) nanotubes have been applied to enhance the mechanical and biological properties of dental materials. Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) have been increasingly used in dentistry as a substructure for crowns and fixed partial prostheses. Aside from its optimal clinical results, Y-TZP is prone to failures due to microstructure-related defects introduced in the manufacturing process that may lower its structural and clinical reliability. The purpose of this study was to evaluate the role of the manufacturing process of blanks as well as their original composition modification by addition of TiO_2 nanotubes (0%, 1%, 2% and 5% in volume) while controlling all manufacturing steps. Materials were subjected to a biaxial flexural strength test, a fractographic qualitative analysis by scanning electron microscopy (SEM), a microstructure evaluation in field emission-SEM and X-ray diffraction. Values of flexural strength were subjected to ANOVA, Tukey ($\alpha = 0.05$) and Weibull statistics. Grain size values were subjected to Kruskal-Wallis and Dunn tests ($\alpha = 0.05$). Highlights of the results include that for experimental Y-TZP added 2% vol TiO_2 nanotube ceramics presented flexural strength values at 577 MPa and Weibull modulus (m) at 8.1. The addition of TiO_2 nanotubes in different blends influenced experimental Y-TZP properties, leading to lower flexural strength, although they presented higher m than the commercial Y-TZP. Nanotubes also led to bigger grain sizes, more pores and a slight increase in the monoclinic phase, influencing the microstructure of Y-TZP. Y-TZP blank manufacturing control as well as addition of TiO_2 nanotubes led to higher m values and, hence, greater structural reliability.

1. Introduction

Ceramics have been used in dentistry more in recent years, and their types and applications are constantly expanding. Ceramics generally are inorganic, nonmetallic solids synthesized by heat treatment and subsequent cooling [1,2]. Currently, the word “ceramic” refers to materials such as glass, advanced ceramics and cement systems [2], leading to a much broader meaning. High-strength oxide ceramic materials, such as zirconium dioxide (ZrO_2), have many different applications such as extrusion dyes, valves and port liners for combustion engines and low corrosion and thermal shock resistant refractory liners [3].

Zirconia stabilized with the addition of yttrium oxide, the so-called yttria-stabilized tetragonal zirconia polycrystal (Y-TZP), becomes a high-strength ceramic with enhanced mechanical properties and higher biological stability [2,4]. Y-TZP has been increasingly used in dentistry as a core material for dental crowns and fixed dental prostheses. Compared to other dental ceramics, zirconia-based ones generally present enhanced mechanical properties, such as a higher Young's modulus, flexural strength, fracture toughness and hardness [3,5],

Abbreviations: ANOVA, analysis of variance; cc, compression curls; EDX, Energy Dispersive X-Ray Spectroscopy; FE-SEM, Field Emission Scanning Electron Microscopy; hl, hackle lines; ISO, International Organization for Standardization; m, mirror region; m, Weibull modulus; p, pores; PMMA, Polymethyl methacrylate; SD, standard deviation; SEM, Scanning Electron Microscope; TEM, Transmission Electron Microscopy; wh, wake hackle lines; XRD, X-ray diffraction; Y-TZP, Yttria-stabilized tetragonal zirconia polycrystal; σ_0, characteristic strength

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while also presenting optimal clinical results [6,7].

However, Y-TZP has low fracture strength and is more prone to failures related to insufficient thickness of the fixed prostheses connector [8,9]. Also, each Y-TZP blank behaves as a single piece, and higher fracture strength does not always correspond to higher Y-TZP reliability [10,11]. Y-TZP is a very rigid, hard and brittle material whose strength is reduced by the presence of surface irregularities, internal voids and porosity [12,13]. Small surface scratches caused by finishing and polishing can initiate fractures [12]. Many characteristics may help prevent the formation and propagation of these flaws: fine-grained powders give more uniform surfaces, and reinforcement materials may act as break-off propagation. Particle or fiber reinforcement can create a toughening mechanism that is associated with cracks' bridging, but due to the chemical inertness of ceramics, the enhancement in fracture toughness obtained may be low [5]. Microcracks and defects that develop due to the thermal and mechanical processing of ceramics may significantly influence strength values [13] and especially structural reliability. The management of all manufacturing and machining steps involved is important to control the formation and distribution of defects and to lead to more predictable clinical behavior of the Y-TZP ceramic.

TiO_2 has been employed as nanoparticles or coatings in medical devices to improve mechanical properties and chemical stability [14,15]. In particular, nanotubes, like nanofibers, have a high surface area-to-volume ratio, which may lead to significant enhancements in physical and mechanical material properties [16,17]. Moreover, the hollow structure of the nanotube provides additional interlocking with the matrix through both the interior and exterior surfaces of the tubes, and the high aspect ratio provides higher interfacial interaction [17,18].

In the specialized literature, a number of studies have reported the successful association of TiO_2 nanotubes with PMMA bone cement [17] and flowable dental composites [16]. Also, the incorporation of TiO_2 nanoparticles in dental resins [19,20] and glass-ionomer cements [21] has resulted in enhanced mechanical properties. However, some studies have suggested that using nanoparticles to enhance the mechanical properties of materials may not be successful due to nanoparticle agglomeration [16,19,22], and, also, so far there are no studies reporting TiO_2 nanostructures' incorporation in ceramic materials.

Considering the high biological reactivity of TiO_2 nanotubes and the inertness of Y-TZP, and also the lack of studies on the interaction between these two materials and its consequences for ceramic material properties, the purpose of this study was to evaluate the mechanical behavior and microstructure of experimental Y-TZP ceramics with different blends (0%, 1%, 2% and 5% in volume) of TiO_2 nanotubes, controlling all manufacturing steps. The study investigated whether there would be differences in structural reliability between controlled Y-TZP blank manufacturing compared to commercial Y-TZP.

2. Material and methods

2.1. Synthesis of the TiO_2 nanotubes

The nanotubes used in this study were obtained using a method described elsewhere [15]. In summary, the specimens were prepared by mixing 12 g anatase TiO_2 (Aldrich, 99%) in 200 ml of 10 M NaOH, kept at 120 °C for 24 h in a Teflon open container, which was placed in a glycerin bath, using a mantle heater for heating. The syntheses were carried out at ambient pressure, where only precursor reagents were subjected to alkaline treatment. After the alkaline treatment, the mixture was washed with 0.1 M hydrochloric acid (HCl) and deionized water repeatedly to remove the sodium ions. Finally, the materials obtained were dried in a conventional oven at 200 °C for 24 h in open air to obtain TiO_2 nanotube powder.

Fig. 1 shows an image of the TiO_2 nanotubes obtained by TEM (CM 200, Phillips, Netherlands) with electron acceleration of 200 kV. A single sheet of spiral-wound TiO_2 results in nanotubes with, on average, 200 nm length, 20 nm thickness and 10 nm of inner diameter, each.

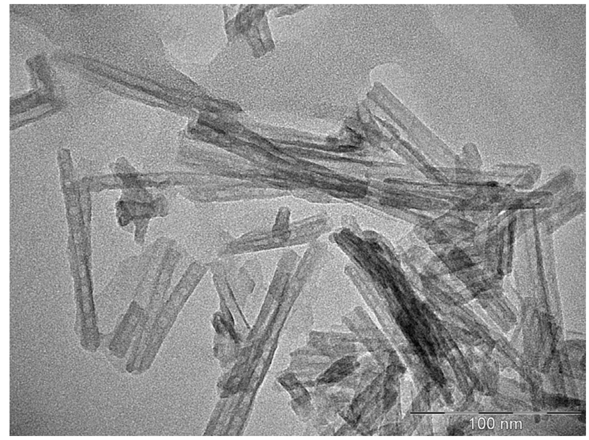

Fig. 1. TEM image of TiO_2 nanotubes obtained with average dimensions: 200 nm length, 20 nm thickness and 10 nm of inner diameter.

2.2. Specimen preparation

The Y-TZPs evaluated are described in Table 1. All zirconia-based ceramics used presented a tetragonal crystal phase stabilized with 3% mol of yttria (Y_2O_3). Only group 1 was composed of a commercially available ceramic. The other groups' ceramics were prepared from powder to sintering, controlling every step.

The experimental Y-TZP manufacturing was carried out using a process summarized in Fig. 2. The tetragonal crystal phase stabilized with 3% mol of yttria (Y_2O_3) powder (Tosoh Corporation, Tokyo, Japan; Lot. Z306234P) had grains with a surface area of 15.1 m^2/g. The solvent, binder and deflocculant agents were added to the Y-TZP powder. The powder (zirconia + nanotubes)/liquid (isopropyl alcohol) proportion was 30/70% in volume. The proportion of TiO_2 nanotubes added was calculated considering the total volume of the mixture, and the proportion of each component is presented in Table 2. Each of the components was weighed on a digital precision scale AUW220D (0.00000) (Shimadzu Corporation, Tokyo, Japan).

The jar containing zirconia balls and the mixture, except the nanotubes, was taken to a vibratory mill for 2 h for homogenization. Nanotubes were added to the appropriate groups after this mixture and were again taken to the vibratory mill with only 10% of the zirconia balls for 10 min.

Then, the mixture was poured into a glass container and dried with a heat gun at 60 °C with manual stirring until all solvent was eliminated in order to isolate the ceramic powder. The zirconia balls used in the mixture were discarded, and the powder was granulated in stainless steel sieves, meshes #50 (300 µm) and #80 (180 µm), in order to obtain dimensional homogeneity with the agglomerates and ease the weighing step.

Conformation of the ceramic discs was carried out in two steps: uniaxial and isostatic pressing. For the uniaxial pressing, the granulated powder was manually inserted in a hardened steel mold 16 mm in diameter, previously oiled with oleic oil ($C_{18}H_{34}O_2$) (Labsynth, Diadema, Brazil) and slightly vibrated for powder accommodation. To have a final thickness of 1.2 mm, considering an average sintering shrinkage of 20%, 0.75 g of ceramic powder was used for each disc. Uniaxial pressing was done in a hydraulic press at 100 MPa for 30 s maximum. In sequence, for the isostatic pressing, specimens were inserted in elastomeric balloons. The air was evacuated by a vacuum pump, and the balloons were tied tight. The balloon with the Y-TZP discs was inserted into the isostatic pressing machine and remained there for 30 s at approximately 206 MPa (30,000 psi) pressure to