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Effect of titania content and biomimetic coating on the mechanical properties of the Y-TZP/TiO_2 composite

Ranulfo Benedito de Paula Miranda[a], Walter Gomes Miranda Junior[a], Dolores Ribeiro Ricci Lazar[c], Valter Ussui[c], Juliana Marchi[b], Paulo Francisco Cesar[a,*]

[a] Departamento de Biomateriais e Biologia Oral, Faculdade de Odontologia, Universidade de São Paulo, São Paulo, SP, Brazil
[b] Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil
[c] Centro de Ciência e Tecnologia de Materiais, Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, Brazil

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ABSTRACT

Objective. To investigate the effect of titania addition (0, 10 and 30 mol%) on the microstructure, relative density, Young's modulus (E), Poisson's ratio (υ), mechanical properties (flexural strength, σ_f, and Weibull modulus, m) of a Y-TZP/TiO_2 composite. The effect of the presence of a biomimetic coating on the microstructure and mechanical properties was also evaluated.

Methods. Y-TZP (3 mol% of yttria) and Y-TZP/TiO_2 composite (10 or 30 mol% of titania) were synthesized by co-precipitation. The powders were pressed and sintered at 1400°C/2 h. The surfaces, with and without biomimetic coating, were characterized by X-ray diffraction analysis and scanning electron microscopy. The relative density was measured by the Archimedes' principle. E and υ were measured by ultrasonic pulse-echo method. For the mechanical properties the specimens (n = 30 for each group) were tested in a universal testing machine.

Results. Titania addition increased the grain size of the composite and caused a significant decrease in the flexural strength (in MPa, control 815.4[a]; T10 455.7[b] and T30 336.0[c]), E (in GPa, control 213.4[a]; T10 155.8[b] and T30 134.0[c]) and relative density (control 99.0%[a]; T10 94.4%[c] and T30 96.3%[b]) of the Y-TZP/TiO_2 composite. The presence of 30% titania caused substantial increase in m and υ. Biomimetic coating did not affect the mechanical properties of the composite.

Significance. The Y-TZP/TiO_2 composite coated with a layer of CaP has great potential to be used as implant material. Although addition of titania affected the properties of the composite, the application of a biomimetic coating did not jeopardize its reliability.

* *Corresponding author at*: Departamento de Biomateriais e Biologia Oral, Faculdade de Odontologia, Universidade de São Paulo. Av. Professor Lineu Prestes, 2227, Cidade Universitária, 05508-000, São Paulo, SP, Brazil.
E-mail address: paulofc@usp.br (P.F. Cesar).

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1. Introduction

Dental treatments involving implant-supported prostheses not only result in the complete oral rehabilitation of edentulous patients, but also cause an improvement of their psychosocial characteristics [1]. The success of an implant can be affected by several factors, such as diameter, length, surgical technique, patient health and habits [2]. The most commonly used biomaterial to replace the dental root is titanium (commercially pure titanium or titanium alloy, Ti–6Al–4V), which has excellent biocompatibility and high mechanical properties [3]. Clinical studies showed that this material has success rate of 96% after six years [4] and 90% after eight years [5].

A significant disadvantage of titanium as a biomaterial is its grayish color, which may compromise the final aesthetic result of the oral rehabilitation in different manners: (a) when titanium becomes exposed over time due to gingival recessions and (b) when a grayish area appears near the gingival margin due to light transmission through the peri-implant tissues in patients with thin gingival biotype. In both cases, the most critical scenario occurs when the anterior dentition is affected [6]. An important alternative material to overcome these problems is yttria stabilized tetragonal zirconia polycrystal (Y-TZP), as it has a whitish shade and therefore results in better outcomes for treatments involving implants with great aesthetic requirement [7].

The use of Y-TZP has increased considerably in the dental field due to its outstanding mechanical properties and good aesthetics. Y-TZP is most commonly processed via CAD–CAM systems and is indicated for the construction of single crowns, fixed partial dentures (FPDs), orthodontic brackets, abutments and dental implants [8–10]. This diversity of dental applications is related to the high fracture toughness (K_{Ic}) of Y-TZP, which is greater than those observed for other ceramics [11]. The excellent mechanical behavior of this biomaterial is explained by the toughening mechanism known as martensitic transformation. After phase transformation is triggered by localized stresses, there is a volumetric expansion of zirconia grains ranging from 3 to 5%, resulting in the creation of significant compressive stresses in the wake of the propagating crack. Such stresses hinder further crack propagation and increase the material fracture toughness [12–14].

A problem related to the use of Y-TZP for dental implants is the fact that this material is bioinert, i.e., it has weak interaction with the surrounding tissues [15]. In implantology, low bioactivity adversely affects the osseointegration process and can lead to implant failure [16]. One clinical trial followed 831 Y-TZP implants for a period of five years, observing a success rate of 95% [17]. Another study followed 170 Y-TZP implants for three years and reported a success rate of 82% [18]. A clinical trial followed 20 Y-TZP implants involving esthetic areas for a period of four years and showed a success rate of 100% [19].

A way to overcome the low bioactivity of Y-TZP is to add other bioactive ceramics to this material in order to form a ceramic composite [20]. Titania (TiO_2) has been investigated as a potential biomaterial, as the presence of Ti–OH groups on its surface has been associated to high bioactive response [15]. These chemical groups induce apatite nucleation when in contact with fluids containing the same ionic composition of blood plasma (SBF, simulated body fluid) [21]. The formation of apatite on the surface of titania after immersion in SBF has been fully described in the literature [22]. The addition of 11 mol% of titania to a bioactive glass improved its bioactivity and accelerated the formation of apatite [23]. Better cell adhesion, spreading, proliferation and differentiation have also been associated with titania [24,25]. A study using pigs reported that pure titanium implants coated with titania nanotubes showed increased bone formation and more expression of genes related to bone remodeling and formation compared to implants without surface modification [26].

Another approach that can be used to enhance bone growth around implants is to deposit a calcium phosphate layer on the implant surface [27]. Calcium phosphate ceramics are bioactive and/or bioabsorbable, depending on their Ca/P molar ratio. This biomaterial is also biocompatible and osteoconductive, as it can successfully stimulate migration, division and growth of cells associated with osteogenesis and therefore establish a direct connection between bone and implant. However, due to the relatively low mechanical properties, the applications of calcium phosphate are in general limited to cements, scaffolds and thin films [28,29].

The first study of our research group regarding TiO_2–ZrO_2 composites was performed with a high content of titania (40, 50 and 60 wt%) and assessed density, roughness, microstructure, hardness and in vitro cell behavior of this biomaterial. The TiO_2–ZrO_2 specimens showed significantly more cell adhesion and growth compared to pure TiO_2 and pure ZrO_2 specimens [30]. In order to improve the mechanical properties of the developed ceramic composite, a second study was published using Y-TZP instead of ZrO_2, and adding lower amounts of TiO_2 (maximum of 30 mol%) [20]. This second investigation also evaluated the effect of the presence of a biomimetic calcium phosphate layer on the physical and chemical properties of the Y-TZP/TiO_2 composites. It was demonstrated that the calcium phosphate layer was crystalline for specimens with 30% of TiO_2 and amorphous for specimens with 0 and 10% of TiO_2. Chemical analysis indicated that this layer was composed of type A carbonate apatite, which is expected to deliver good bioactivity since it is also found in bone mineral. However, no characterization of the mechanical properties of the composites coated with a biomimetic film has been performed so far. Therefore, the first objective of the present work was to evaluate the effect of titania content (0, 10 or 30 mol%) on the microstructure, relative density, Young's modulus (E), Poisson's ratio, mechanical properties (flexural strength, σ_f, and Weibull modulus, m) of a Y-TZP/TiO_2 composite. The second objective was to evaluate the presence of a biomimetic coating on microstructure and mechanical properties of the composite. The tested hypothesis was that both the titania content and the presence of a biomimetic layer would affect the studied properties of the ceramic composite.

Table 1 – Composition of Y-TZP/TiO_2 ceramic powder.

Groups	Composition (mol%)		
	ZrO_2	Y_2O_3	TiO_2
T0	97	3	0
T10	87.3	2.7	10
T30	67.9	2.1	30

2. Materials and methods

2.1. *Power synthesis*

Y-TZP/TiO_2 composites with varied TiO_2 content (0, 10 and 30 mol%, Table 1) were synthesized from precursors (zirconium oxychloride, titanium chloride and yttrium chloride) using a co-precipitation route. The suspensions were filtered, washed with water, ethanol and n-butanol. After azeotropic distillation, the ceramic powders were dried at 100°C in an incubator, calcined (800°C/1 h, Fornitec, Brazil) and milled in a high energy attrition mill for 24 h using zirconia ball media in ethyl alcohol. This procedure was described in more detail in a previous paper [31].

2.2. *Specimens processing*

The synthesized Y-TZP/TiO_2 powders were uniaxially pressed at 50 MPa into cylindrical metallic dies and sintered at 1400 °C for 2 h in a furnace (Lindberg Blue, USA). The specimens (n = 180) had their surfaces rectified in a semi-automatic polishing machine (Ecomet II, Buehler, USA) with diamond suspension of 45 μm. The final dimensions of the specimens were ~12.0 mm in diameter and 1.0 mm in thickness.

2.3. *Biomimetic coating*

Half of specimens of each group (n = 30) were coated with a calcium phosphate layer using the biomimetic method, as described in an earlier work [32]. Briefly, specimens were immersed in sodium silicate solution for seven days, washed in deionized water, dried at room temperature, and immersed in 1.5 SBF for seven days. The solution was changed every two days. After the coating procedure, the Y-TZP/TiO_2 specimens were washed and dried. All coating procedures were performed in a shaker at 40 rpm at 36.5°C (TE-420, Tecnal, Brazil). Groups submitted to this procedure were named as T0-CaP, T10-CaP and T30-CaP depending on the titania content into Y-TZP.

2.4. *Specimens characterization*

The final density after sintering of the specimens (ρ) were determined by a method based in Archimedes' principle, using water as immersion liquid. These values were estimated according to percentage of the theoretical density of the material, using the law of mixtures [33] and the expected theoretical density of each component. The values of Young's modulus (E) were determined by the ultrasonic pulse-echo method using a 200 MHz ultra-sonic pulser-receiver (5900PR, Panametrics, Waltham, USA), 20 MHz longitudinal and shear transducers with a delay material, and a coupling paste applied between the specimen and the transducer [34].

Microstructural analysis was performed by scanning electron microscopy (SEM, XL30, Phillips, USA) before and after the biomimetic coating. The ceramic specimens of the control group (without biomimetic coating) were polished and subjected to thermal etching (1350°C for 30 min) in a microwave oven (EF-1700 Fortelab, Brazil) to reveal the inter granular boundaries. The grain size of the sintered ceramics was numerically estimated by the linear intercept method using SEM micrographs. The crystalline phases were identified by X-ray powder diffraction analysis, which was performed in a diffractometer (Rigaku, DMAX 3000, USA), using Cukα_1 radiation. The diffraction peaks were compared with the International Centre for Diffraction Data (ICDD) powder diffraction patterns.

The specimens were fractured in a biaxial flexural setup using a piston-on-3-balls fixture in a universal testing machine (EMIC DL 2000, Brazil). During the test, the specimens were immersed in artificial saliva at 37°C. For each group, 30 specimens were tested at a loading rate of 0.5 mm/min. The flexural strength was calculated by Eq. (1), according to ASTM F 394-78 [35].

$$\sigma_f = \frac{-0,2387\ F(X-Y)}{w^2} \quad (1)$$

where F is the fracture load, w is the specimen thickness and X and Y were determined by Eqs. (2) and (3).

$$X = (1+\upsilon).\ln\left(\frac{B}{C}\right)^2 + \left(\frac{1-\upsilon}{2}\right).\left(\frac{B}{C}\right)^2 \quad (2)$$

$$Y = (1+\upsilon)\left[1+\ln\left(\frac{A}{C}\right)^2\right] + (1-\upsilon).\left(\frac{A}{C}\right)^2 \quad (3)$$

where υ is the Poisson's ratio, A is the radius of the support circle (4 mm), B is the radius of the tip of the piston (0.85 mm) and C is the radius of the specimen (~6 mm). The Poisson's ratio was determined for each material using the pulse-echo method.

3. Results

3.1. *Density and elastic constants*

Table 2 shows the density (ρ), relative density ($\rho_{relative}$), Poisson's ratio (υ) and Young's modulus (E) of the sintered composites. The addition of titania significantly decreased the density of the composite. The control group (without titania) showed the highest relative density (99.0%), which was significantly higher than that obtained for the group with 30% of titania (96.3%). The material with addition of 10% of titania showed significantly lower density (94.4%) compared to the other two groups. With respect to the Poisson's ratio, the group containing 30% titania showed the highest mean value of υ. Groups containing 0% and 10% titania showed similar υ values, which were significantly lower than the value obtained for the group with 30% of titania. Regarding Young's modulus,

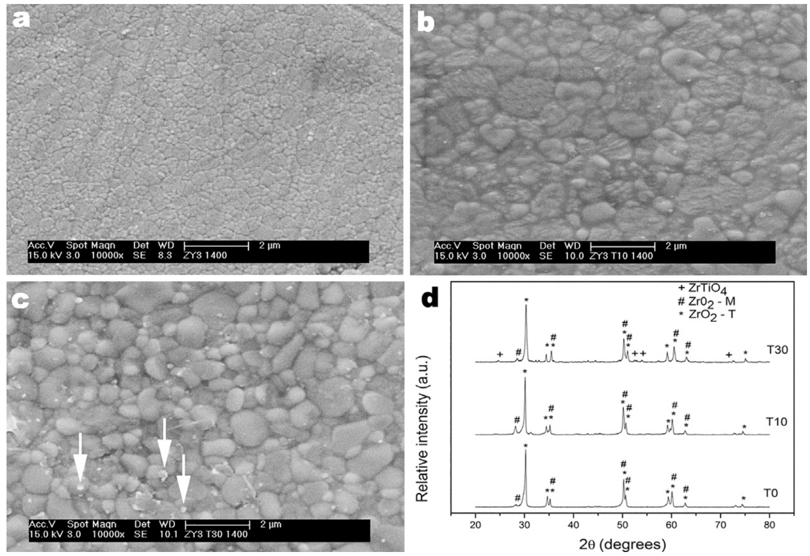

Fig. 1 – Scanning electron micrographs of Y-TZP/TiO_2 pellets after sintering at 1400 °C/2 h (polished and thermally etched) before coating (a) T0; (b) T10; (c) T30 and X-ray diffraction patterns (d) before coating. White arrows (1c) indicate zirconium titanate crystalline phase.

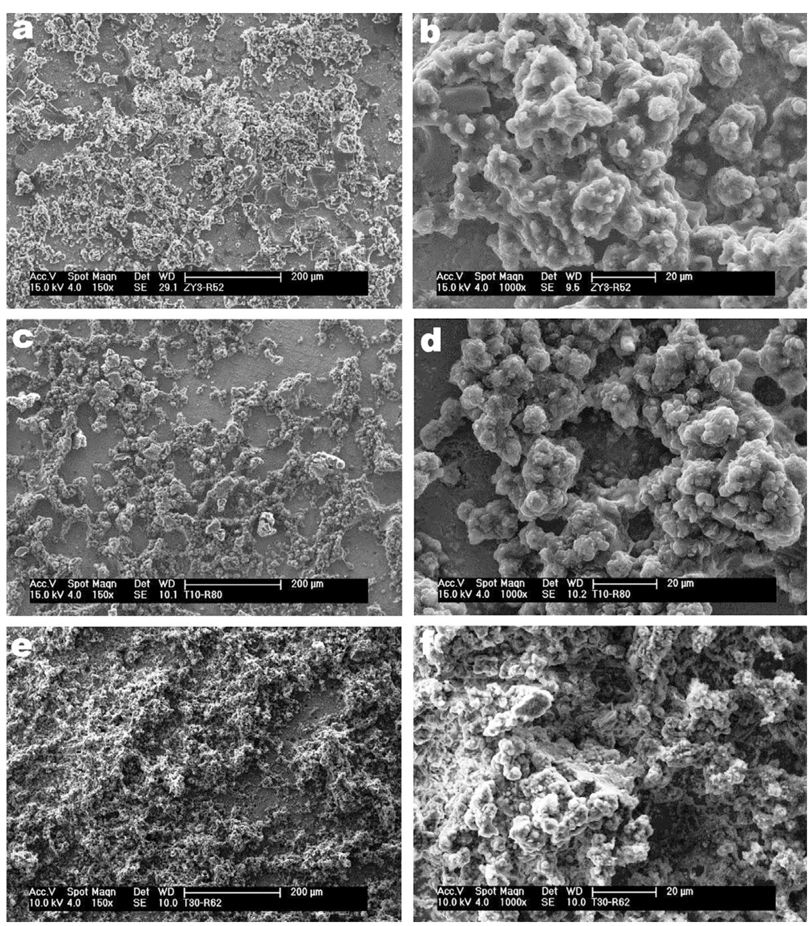

Fig. 2 – Scanning electron micrographs of Y-TZP/TiO_2 pellets after sintering at 1400 °C/2 h after coating, showing different magnitudes (a) and (b) T0-CaP; (c) and (d) T10-CaP; (e) and (f) T30-CaP.

Table 2 – Theoretical density ($\rho_{theorical}$), grain size (gs) and mean ± standard deviation (coefficient of variation) of density (ρ), relative density ($\rho_{relative}$), Poisson's ratio (υ) and Young's modulus (E). Values followed by the same letter are statistically similar (p > 0.05).

Parameter	Titania content (mol%)		
	0	10	30
$\rho_{theoretical}$	6.10	5.77	5.34
Gs (μm)	0.21	0.47	0.53
ρ (g/cm³)	6.05 ± 0.05ᵃ (1%)	5.45 ± 0.06ᵇ (1%)	5.15 ± 0.07ᶜ (1%)
$\rho_{relative}$ (%)	99.0 ± 1.0ᵃ (1%)	94.4 ± 1.0ᶜ (1%)	96.3 ± 1.3ᵇ (1%)
υ	0.31 ± 0.01ᵇ (3%)	0.31 ± 0.01ᵇ (3%)	0.33 ± 0.01ᵃ (5%)
E (GPa)	213.4 ± 4.1ᵃ (2%)	155.8 ± 5.3ᵇ (3%)	134.0 ± 4.2ᶜ (3%)

the addition of titania significantly decreased this property in comparison to the control group.

3.2. *Microstructure*

3.2.1. *Before apatite coating*

Fig. 1a–c shows typical scanning electron micrographs of the surfaces of the sintered specimens that were polished and thermally etched. Groups containing titania (Fig. 1b and c) showed larger zirconia grains (0.47 μm for T10 e 0.53 μm for T30) than those observed for the control group (0.21 μm) (Fig. 1a and Table 2). Group T30 (Fig. 1c) showed grains protruding out of the material surface (indicated by white arrows). Fig. 1d shows the X-ray diffraction pattern of the sintered specimens. Tetragonal zirconia (ICDD 89-9068) and monoclinic zirconia (ICDD 37-1484) crystalline phases were identified in all specimens. Group T30 also showed zirconium titanate ($ZrTiO_4$, ICDD 07-0290) as a secondary crystalline phase.

3.2.2. *After apatite coating*

Fig. 2a–f shows typical scanning electron micrographs of the specimens after apatite coating. All specimens showed a thin superficial layer of sub-micrometric globules forming agglomerates. These globular formations containing multiple layers covered the surface of the discs in a heterogeneous manner. The T30-CaP group apparently showed denser apatite layer compared to the other two groups. The X-ray diffraction patterns of the coated specimens are shown in Fig. 3. Tetragonal zirconia (ICDD 89-9068), monoclinic zirconia (ICDD 37-1484) and hydroxyapatite as secondary phase (HAp, ICDD 09-0432) were identified in all surfaces.

3.3. *Biaxial flexure strength and Weibull analysis*

Two-way analysis of variances was performed for flexural strength data (σ_f). The main factor "titania content" was statistically significant (p = 0.0001), whereas the factor "biomimetic coating" was not significant (p = 0.152). The interaction between the two factors was not statistically significant as well (p = 0.267).

Table 3 shows the mean flexural strength values as a function of the titania content and the presence of biomimetic coating. The addition of titania significantly decreased the flexural strength values of the composite and the presence of the biomimetic coating did not significantly alter the mean flexural strength values, regardless of the titania content. The T0 group (815.4 MPa) and T0-CaP (763.6 MPa) showed statistically higher strength compared to all other groups. Groups T10 (455.7 MPa) and T10-CaP (439.4 MPa) showed intermediate strength values, which were significantly higher the mean values obtained for both groups containing 30% of titania.

Table 3 indicates that, considering the groups without the biomimetic coating, the addition of titania resulted in a significant increase in the Weibull modulus only for the group containing 30% titania. For groups containing biomimetic coating, no statistical differences were found among the Weibull moduli. Table 3 also indicates that there was no effect of the biomimetic coating on the Weibull modulus regardless of the titania content. The relationship between the probability of fracture and fracture stress (Weibull plot) is shown in Fig. 4. The higher slope of the regression curve obtained for group T30 in relation to that obtained for group T0-CaP is related to the significantly higher Weibull modulus of the first, as seen in Table 3.

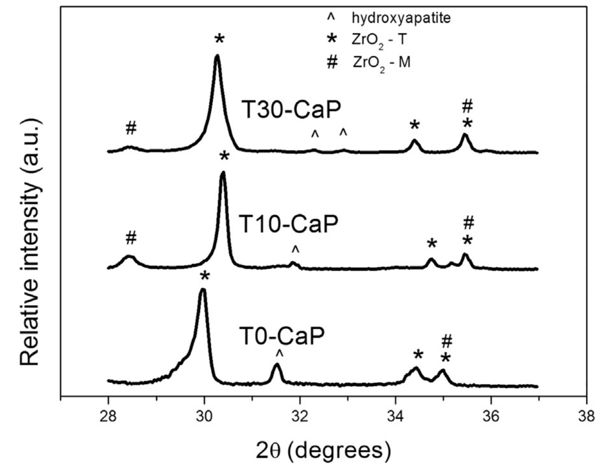

Fig. 3 – X-ray diffraction patterns of Y-TZP/TiO_2 samples after coating.

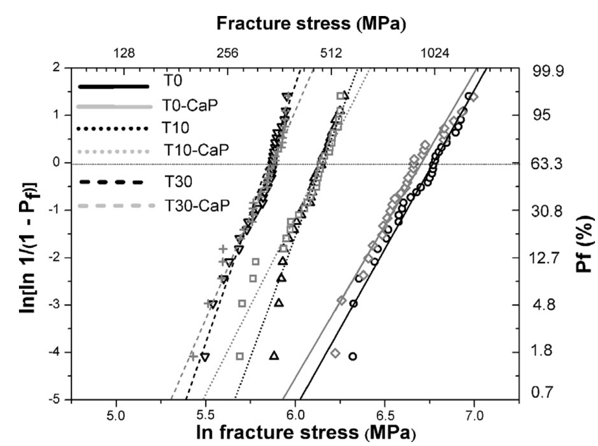

Fig. 4 – Weibull plot showing the fracture stress as a function of the failure probability (P_f).

Table 3 – Mean ± standard deviation (coefficient of variation) of flexural strength (σ_f) and Weibull modulus (95% confidence interval) (m). Values followed by the same letter are statistically similar ($p > 0.05$).

Titania content (mol%)	Flexural strength (σ_f) (MPa)		Weibull modulus (m)	
	Biomimetic coating		Biomimetic coating	
	No	Yes	No	Yes
0	815.4 ± 145.1^{a} (18%)	763.6 ± 144.2^{a} (19%)	6.4^{b,c} (4.7–8.6)	5.4^{c} (3.9–7.4)
10	455.7 ± 48.4^{b} (11%)	439.4 ± 65.4^{b} (15%)	10.5^{a,b} (7.7–14.1)	8.7^{a,b,c} (6.3–11.7)
30	336.0 ± 38.7^{c} (11%)	334.2 ± 43.6^{c} (13%)	11.7^{a} (8.6–15.8)	9.9^{a,b,c} (7.3–13.4)

4. Discussion

The relative density values obtained in this study for Y-TZP specimens synthetized via co-precipitation route [31] are in agreement with the values commonly found in the literature [13]. It is difficult to make a direct comparison of the flexural strength values obtained in the current investigation with those reported in the literature for Y-TZP, as a wide range of values has been reported, ranging from 680 to 1200 MPa [11,36–38]. This disparity in strength values is related to various factors, such as surface state of the specimens, processing methods, grain size, porosity level and flaw population.

Addition of titania to the Y-TZP matrix significantly reduced the density of the resulting Y-TZP/TiO_2 composite. Such reduction is related to the lower theoretical density of titania compared to Y-TZP. While titania (rutile phase) has theoretical density of 4,24 g/cm^3, Y-TZP (tetragonal phase) has density of 6.10 g/cm^3 [39]. The addition of titania to the Y-TZP also decreased the relative density of the composite Y-TZP/TiO_2. While the group without titania (T0) showed a relatively high relative density of 99.0%, groups T10 and T30 showed relative densities of respectively 94.4% and 96.3%, indicating that the addition of titania favors the formation of pores within the material. A study had already shown that addition of titania could result in the formation of pores in this type of composite [40]. One possible way to decrease the porosity level of the composite is to optimize the time and/or sintering temperatures [40,41].

Zirconium titanate ($ZrTiO_4$) secondary phase was identified in specimens containing 30% of titania. This phase has been associated with a decrease in the mechanical properties of Y-TZP/TiO_2 [40]. It is important to note that zirconium titanate was not identified in the group containing 10% of titania, at least at levels that could be detected by the X-ray diffraction technique used herein. Probably the titania concentration of 10% forms a solid solution within the zirconia crystal lattice, hindering the formation of zirconium titanate [42]. Another important microstructural change was the increase in grain size observed for both groups containing titania. It has been demonstrated that dopants such as Ti, with smaller ionic radius and lower effective charge, increase the grain mobility, resulting in larger grain size [43].

The elastic modulus and the flexural strength of the composite decreased with the increase in titania content. This fact can be explained by the lower mechanical properties of titania in relation to Y-TZP; and also by the greater degree of porosity observed for groups containing titania in comparison to the control group. It is well known that the mechanical properties ceramic materials are negatively affected by the presence of pores in the microstructure, since these defects act as stress concentrators and reduce the cross-sectional area of the material [44,45].

The greater reliability calculated for group T30, expressed by the higher Weibull modulus and the lower slope of its regression curve in Fig. 4, is related to the low variability in size and geometry of pores and other intrinsic defects. From a practical standpoint, it is important to note that a higher Weibull modulus translates into a more predictable mechanical behavior [46]. Unfortunately, the high reliability of group T30 was not combined with high strength values, indicating that further developments should focus in improving the mechanical strength of this material in order to make it as strong as pure titanium or titanium alloys normally used of implants.

Several studies in the literature applied biomimetic coatings in order to increase the bioactivity of different biomaterials, but none of them determined the effect of this surface alteration on the mechanical properties of the substrate material [20,47,48]. One important issue regarding the applicability of the biomimetic coating is related to the interaction of this layer rich in Ca^{2+} and PO_4^{3-} with the composite surface, which may result in the nucleation of defects that could compromise the mechanical strength of the specimen. The results of this study showed that the biomimetic coating did not significantly alter the existing defect population of the composite, as there was no statistical difference between the values of flexural strength and Weibull modulus obtained before and after the biomimetic coating. This finding has not been previously demonstrated in the literature and is considered relevant as it corroborates the application of biomimetic coating on the composite surface without jeopardizing its reliability [49–51].

The presence of apatite globules on the composite surface indicated that the hydroxyapatite layer was relatively heterogeneous. This layer has great bioactive potential and therefore may result in faster osseointegration for implant purposes. The association of this biomimetic coating with a composite containing low concentrations of titania, which is also bioactive, may further improve the final osseointegration in dental implants [20,47,51]. A previous work had already applied a biomimetic coating containing calcium phosphate to the surface of Y-TZP/TiO_2, however this investigation used different titania contents, crystal structures, surface characteristics and SBF immersion time [20,44].

5. Conclusion

The Y-TZP/TiO_2 composite coated with a layer of CaP has great potential to be used as implant material. Addition of titania to Y-TZP caused an increase in grain size, a significant decrease in flexural strength, modulus of elasticity, density and relative density. The addition of 30% of titania caused substantial increase in the Weibull modulus and Poisson's ratio. The presence of biomimetic coating did not significantly affect the flexural strength and Weibull modulus of the Y-TZP/TiO_2 composite.

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