UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

ERNESTO BYRON BENALCÁZAR JALKH

**Experimental 70% Al_2O_3 - 30% ZrO_2 composites: structural, topographical
and mechanical characterization before and after aging**

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Experimental 70% Al₂O₃ - 30% ZrO₂ composites: structural, topographical and mechanical characterization before and after aging

Compósitos experimentais 70%Al₂O₃-30%ZrO₂: caracterização estrutural, topográfica e mecânica antes e após envelhecimento

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RESUMO

Compósitos experimentais 70%Al₂O₃-30%ZrO₂: caracterização estrutural, topográfica e mecânica antes e após envelhecimento

Objetivo: Avaliar o efeito do envelhecimento na estrutura cristalina, topografia de superfície e propriedades mecânicas de um compósito experimental de alumina reforçada com zircônia (ZTA) composto por 70% de Al₂O₃ e 30% de uma zirconia de segunda geração, em comparação com os seus materiais individuais.

Materiais e métodos: Espécimes em formato de discos foram divididos em quatro grupos (n = 10 / material): 1) 3YSB-E (3Y-TZP de primeira geração), 2) Zpex (3Y-TZP de segunda geração), 3) Alumina e 4) ZTA-Zpex 70/30. Difração de raios X (DRX) e microscopia eletrônica de varredura (MEV) foram usados para caracterizar o conteúdo cristalino e a microestrutura dos materiais. Testes de refletância foram realizados para determinar a razão de contraste (RC) e o parâmetro de translucidez (PT). As propriedades mecânicas foram avaliadas pelo teste de resistência à flexão biaxial (RFB) para determinar os parâmetros de Weibull. ZTA, Zpex e Alumina foram adicionalmente testados sob nanoindentação para obter módulo de elasticidade (E) e dureza (H); e por Interferometria para avaliar parâmetros de rugosidade superficial 3D (Sa, Sq). Todas as análises foram realizadas antes e após o envelhecimento artificial (20h, 134°C, 2,2 bar). Os dados de propriedades ópticas foram avaliados por meio da análise de variância de medidas repetidas e testes de Tukey (p < 0,05); os dados da RFB foram analisados pela estatística de Weibull (IC95%); e dados de nanoindentação e resultados topográficos foram analisados usando modelos lineares mistos e testes pos-hoc de diferença de mínimos quadrados ($\alpha = 5\%$).

Resultados: Valores de alta densidade foram encontrados para todos os materiais e as imagens de MEV exibiram uma microestrutura densa. Os padrões de XRD revelaram a preservação do conteúdo cristalino no compósito ZTA, enquanto um aumento nos picos monoclinicos foi observado para zircônias puras após envelhecimento. Maior RC e menor PT foram observados para o compósito ZTA, seguido por alumina, 3YSB-E e Zpex. O maior estresse característico foi registrado para 3YSB-E, seguido por valores intermediários entre Zpex e ZTA, e o menor para Alumina. Al₂O₃ apresentou os maiores valores de H e E, seguido por ZTA-70/30 e Zpex, todos significativamente diferentes. O envelhecimento afetou as propriedades ópticas e mecânicas de ambas as zircônias, enquanto se manteve estável para o compósito ZTA e

alumina. O envelhecimento não afetou os parâmetros de rugosidade da superfície de ZTA-70/30 e Al_2O_3 , embora um aumento significativo de S_a tenha sido registrado para Zpex após o envelhecimento.

Conclusão: A síntese experimental do compósito ZTA 70-30% foi bem-sucedida e sua relevância para aplicações odontológicas está em sua maior capacidade de mascaramento, resistência ao envelhecimento em todos os parâmetros testados e resistência semelhante à zircônia. O envelhecimento aumentou significativamente o conteúdo monoclinico das zircônias puras e afetou as suas propriedades ópticas e mecânicas, bem como sua rugosidade superficial.

Palavras Chave: Compósitos; $\text{ZrO}_2\text{--Al}_2\text{O}_3$; Propriedades Mecânicas; Propriedades Ópticas; Nanoindentação; Topografia.

ABSTRACT

Experimental 70% Al₂O₃ - 30% ZrO₂ composites: structural, topographical and mechanical characterization before and after aging

Objectives: To evaluate the effect of aging on the crystalline structure, surface topography and mechanical properties of an experimental zirconia-toughened-alumina (ZTA) composite comprised by 70% Al₂O₃ and 30% of a 2nd-generation 3mol% yttria tetragonal zirconia polycrystal (3Y-TZP), compared to its individual counterpart materials.

Materials and Methods: Disc-shaped ceramic specimens were divided in four groups (n=10/material): 1) 3YSB-E (1st-generation 3Y-TZP), 2) Zpex (2nd-generation 3Y-TZP), 3) Alumina, and 4) ZTA-Zpex 70/30. X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to characterize the crystalline content and microstructure. Reflectance tests were performed to determine the contrast-ratio (CR) and translucency-parameter (TP). Mechanical properties were assessed by biaxial-flexural-strength (BFS) test to determine Weibull parameters. ZTA and its isolated materials were tested under nanoindentation to record elastic modulus (E) and hardness (H); and Interferometry to assess 3D surface roughness parameters (S_a, S_q). All analyses were conducted before and after autoclave aging (20h, 134°C, 2.2bar). Optical parameters were evaluated through repeated-measures analysis of variance and Tukey tests (p<0.05), BFS data were analyzed using Weibull statistics (95% CI); and nanoindentation and topographic results were analyzed using linear mixed-model and least square difference pos-hoc tests (α=5%).

Results: High density values were found for all materials and SEM images exhibited a dense microstructure. While XRD patterns revealed the preservation of crystalline content in the ZTA composite, an increase in the monoclinic phase was observed for pure zirconias after aging. Higher CR and lower TP values were observed for ZTA, followed by Alumina, 3YSB-E, and Zpex. The highest characteristic stress was recorded for 3YSB-E, followed by intermediate values between ZTA and Zpex, and the lowest for Alumina. Conversely, Al₂O₃ yielded the highest H and E values, followed by ZTA-70/30 and Zpex. Aging affected the optical and mechanical properties of both zirconias, while remained stable for ZTA and alumina. Aging did not affect the surface roughness parameters of ZTA and Alumina, although a significant increase in S_a was recorded for Zpex following aging.

Conclusion: The synthesis of the experimental 70-30% ZTA composite was successful and its relevance for dental applications relies on its higher masking ability, aging resistance, and strength similar to zirconia.

Keywords: Composites; $\text{ZrO}_2\text{-Al}_2\text{O}_3$; Mechanical properties; Optical properties; Nanoindentation; Topography.

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1 INTRODUCTION

1 INTRODUCTION

Yttria stabilized tetragonal zirconia polycrystals (3mol%, 3Y-TZP) have been widely used in dentistry due to its high flexural strength (900 - 1,300 MPa), fracture toughness (6 - 9 MPa m^{1/2}) and excellent biocompatibility.(1) Zirconia occurs naturally in three distinct temperature-dependent crystalline structures: monoclinic (m) stable at room temperature up to 1170°C, tetragonal (t) stable up to 2370°C, and cubic (c) stable from 2370°C up to the melting point.(2) In order to keep the tetragonal phase stabilized at room temperature, it is necessary to add stabilizing oxides to pure zirconia, such as magnesium, calcium, cerium or yttrium oxide (3mol%), being the last one widely used in dentistry due to its extensive range of solubility in the tetragonal and cubic phases.(3, 4)

3Y-TZP's outstanding mechanical properties rely on the transformation toughening mechanism, which is determined by the capability of tetragonal zirconia grains to undergo a stress-mediated phase transformation to monoclinic phase, phenomenon known as R-curve behavior.(5) Thus, first generation 3Y-TZP have been used in prosthodontics and implant dentistry for the manufacture of infrastructures of dental and implant supported crowns and fixed dental prostheses (FDPs) in the anterior and posterior regions, implant supported fixed full-arch prostheses and implant abutments.(6-12) Nevertheless, 3Y-TZP metastability makes it susceptible to low temperature degradation (LTD), a steady and continued tetragonal to monoclinic (t-m) phase transformation due to stress and moist environment exposition.(13) LTD may be accompanied by the appearance of micro cracks resulting from stress accumulation within the material eventually leading to loss of mechanical properties. (14)

While first generation 3Y-TZP, presents high success rate as framework for bilayered dental supported single crowns,(11) its clinical performance as infrastructure for FDP have revealed a high rate of mechanical complications, where cohesive fractures of the veneered porcelain emerged as the main finding.(8) Such complication seems to be crucial in implant supported prostheses, where fracture rates of up to 22.8 and 34.8% in 5 years (for partial and full-arch FDP, respectively) led to the latest European Academy for Osseointegration (EAO) consensus of 2018 to consider veneered zirconia prostheses as clinically unacceptable for implant supported reconstructions. (7)

In an effort to eliminate chipping of the veneered porcelain, modifications in the Alumina content and grain size of first generation 3Y-TZP, led to the development of the

translucent second generation 3Y-TZP, intended to be used as monolithic restorative material. (15) While a modest increase in translucency was achieved, the optical properties of second generation 3Y-TZP were reported to be insufficient for esthetic treatments in the anterior region, especially compared with highly esthetic glass ceramics.(16, 17) Furthermore, the reduction of alumina content, a metallic oxide used as a stabilizer of the tetragonal phase, leave the material more susceptible to the effects of phase transformation in the oral environment. Therefore, the limited light transmission and the potential hydrothermal instability of second generation 3Y-TZPs, led to the development of a third generation of dental zirconias, classified as “ultra-translucent” systems (18).

The third generation of dental zirconias is characterized by a predominant presence of optically isotropic cubic phase in its composition (more than 50%), where the partial stabilization of zirconia (Y-PSZ) is achieved by increasing yttria content to ~4-5 mol%. While the presence of cubic phase in Y-PSZ improved significantly the optical behavior of the material, a notable reduction on its mechanical properties was also observed.(16) The partial stabilization of zirconia limits the stress-induced transformation toughening of tetragonal 3Y-TZP, which compromise its mechanical properties.(15) Therefore, the indications for ultra-translucent systems are limited to anterior and posterior single crowns, similar to several glass-ceramics, (15, 19) that present additional advantages for its clinical application, including well-established bonding protocols,(20, 21) favorable esthetic outcomes,(22, 23) and high success rates in the long term.(11, 24)

In light of the well documented limitations of 3Y-TZP systems currently used in dentistry, innovation in the synthesis of polycrystalline ceramic composites of zirconia and alumina for dental applications has been proposed.(25-28) Such composites intend to improve the mechanical performance of pure alumina and provide high hydrothermal stability when compared to stabilized zirconia.(13) In the orthopedic field, composites of alumina reinforced with zirconia particles, (Zirconia-toughened-Alumina or ZTA) have been describe since early 2000s due to the dramatic failure of over 800 zirconia femoral head prostheses, associated with an accelerated process of low-temperature degradation.(29, 30) Since then, ZTA composites have been widely used in orthopedics, and are the current standard for orthopedic prostheses. (31)

ZTA composites are comprised by an Al_2O_3 matrix and a secondary phase of disperse 3Y-TZP grains, combining the advantageous properties of both materials through a trade-off

between enhanced toughening by crack-shielding, favorable tribochemical properties, and LTD resistance. (32-37) While it has been suggested that the maximum 3Y-TZP fraction to limit the spread of transformation may be related to the interconnectedness of the zirconia phase,(38) studies have suggested favorable mechanical properties when 15-30% of 3Y-TZP particles were uniformly dispersed within an Al_2O_3 matrix, (39-41) as well as favorable resistance to t-m phase transformation after hydrothermal aging. (40, 42) Furthermore, it has been reported that the mechanical properties of ZTA composites tend to proportionally vary as the weight percentage of 3Y-TZP increase, as postulated by the rule of mixtures (33).

Seeking innovation, the aim of this work was to evaluate the effect of aging on the crystalline structure, surface topography and mechanical properties of an experimental zirconia-toughened alumina (ZTA) composite comprised by 70% Al_2O_3 and 30% of a second-generation 3Y-TZP, compared to its individual counterpart materials. The mechanical behavior of ZTA composites was analyzed before and after aging and compared to a first- and second-generation dental zirconia to further elucidate potential applications of polycrystalline composites for oral rehabilitation. A crucial stage of the innovation process comprises the extensive structural and mechanical characterization by systematic methods that may provide tools for exploring the properties of innovative biomaterials and potentially compare them with other experimental or commercially available products. Based on structural, topographical, and mechanical characterizations, this doctoral thesis presents the validation of a synthesis method of ZTA composites as well as a discussion on the effects of aging in zirconia-based dental materials and its potential implications in the performance of dental reconstructions.

2 ARTICLES

2 ARTICLES

2.1 ARTICLE 1

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2.2 ARTICLE 2

Nanoscale physico-mechanical properties of an aging resistant ZTA composite

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3 DISCUSSION

3 DISCUSSION

Long-term stability of the physical-mechanical properties of biomedical materials plays a crucial role in the clinical success. For this reason, it is important not only to develop materials with high strength but also with high degradation stability. In the orthopedic field, the development of stable materials to replace LTD susceptible 3Y-TZP started in the early 2000s, due to the dramatic failure of several zirconia femoral head prostheses. However, first and second generation 3Y-TZP are still broadly used in dentistry, probably because of the limited understanding of the LTD process among clinicians, and to the lower criticality of a dental device failure when compared to hip replacement failures. The manuscripts presented in this thesis propose a method for the synthesis of an aging resistant zirconia-toughened alumina (ZTA) composite in a weight ratio of 70% alumina and 30% zirconia intended for dental applications. The microstructural, topographical and mechanical characterization, as well as the effect of accelerated laboratory aging in autoclave were analyzed for all materials and discussed in light of its relevance to the field.

Overall, the synthesis of the experimental composite was successful, providing a dense microstructure and homogeneous distribution of zirconia particles within the alumina matrix, which was a consistent finding in the presented manuscripts. SEM imaging of ZTA depicted spherical and dense zirconia and alumina particles with few microstructural pores and defects distributed along the ceramic surface, commonly related to the ceramic processing. Such microstructure was similar to previous findings of our research group for ZTA composites synthesized with similar protocols but comprised by 85 and 80% of Al_2O_3 , reinforced with 15 and 20% of 3Y-TZP, respectively. (26, 28) Grain measurements presented in Article 2 depict a similar grain size of zirconia particles in both, the ZTA composite and the pure formulation ($\sim 0.44 \mu\text{m}$). Conversely, Al_2O_3 showed a smaller particle size in the composite ($\sim 0.95 \mu\text{m}$) when compared with the pure formulation ($3.96 \mu\text{m}$). This finding may be explained due to the interaction of the matrix with the zirconia particles during the densification process, where the different sintering temperatures of both phases, along with the homogeneous distribution of the secondary phase within the matrix may have contributed to effectively control the grain growth of the alumina particles during sintering. (43)

The x-ray diffraction spectra and monoclinic phase percentage calculation in both studies confirmed the hydrothermal stability of ZTA composites formulated with 70% of Al_2O_3 and 30% 3Y-TZP. Our findings demonstrated a significant lower transformation after aging for

ZTA (~3.45%), compared to first and second generation 3Y-TZPs (~8.5 and ~22.36%, respectively). The hydrothermal stability of ZTA was expected through the limited interconnectivity of tetragonal 3Y-TZP grains provided by the Al_2O_3 matrix. Furthermore, as discussed in Article 2, the high hardness and stiffness of the Al_2O_3 particles compared to the secondary phase, may also be responsible for the high hydrothermal stability of the composite. In this scenario, it has been suggested that the constraint that the matrix exerts on the Y-TZP particles may maintain them in the metastable tetragonal state, acting as a mechanical stabilizer,(43, 44) and enhancing the energy threshold for *t-m* transformation in the vicinity of zirconia grains. (36) Thereby, the accumulation of higher tensile stresses is necessary to trigger the transformation in ZTA composites.(44) Previous studies have reported a broad variation in the phase transformation susceptibility and its detrimental effects among 3Y-TZP systems. This variation has been related with differences in the composition, microstructure, grain size, manufacturing, processing methods, and different aging protocols (26, 29, 45-52). In Article 1, first and second generation 3Y-TZP presented a significant tetragonal to monoclinic phase transformation (8.53% and 23.66%, respectively). The monoclinic percentage difference between both materials was expected due to the reduced Aluminum oxide content in second generation 3Y-TZP, that have demonstrated higher susceptibility to LTD,(53) where phase transformation was almost threefold higher than first generation 3Y-TZPs, altering optical and mechanical properties after laboratory aging.

The optical properties presented in Article 1 were described in a previous Master's dissertation (54) and are consistent with the findings reported by our research group for other ZTA compositions. (26, 28) The optical behavior of these composites may be explained due to the refractive index mismatch between the two polycrystalline phases that hampers light transmission, along with the presence of pores and defects associated with ceramic processing. (53, 55) First and second generation 3Y-TZP presented intermediate and higher values of translucency regarding the ZTA composite. However, aging significantly affected the optical behavior of both pure 3Y-TZP compositions, where a notable increase in translucency was observed. The improved light transmission as a consequence of the crystalline morphology rearrangement, and the possible sealing of defects as a result of the volumetric expansion associated with tetragonal-to-monoclinic phase transformation,(53, 56) may be critical in the clinical performance of esthetic restorations for both monolithic and bilayered prostheses. While it has been suggested that the optical changes in aged 3Y-TZP monolithic restorations may not be clinically perceptible during the clinical life of dental restorations (57), more recent

in and *ex-vivo* studies have demonstrated aging kinetics to be remarkably faster than commonly observed in *in-vitro* studies. (47, 58, 59) Therefore, the stability of the optical behavior of ZTA composites is desirable to assure the results of esthetic treatments in the long term.

The mechanical characterization through biaxial flexural strength test presented in Article 1 evidenced a favorable characteristic stress and Weibull modulus for ZTA composites. The high flexural strength reported in Article 1 is compatible with published literature in the orthopedic field, (41) and with our previous work (26, 28) where advantageous flexural strength for ZTA composites with reinforcements ranging from 15 to 30% of zirconia particles has been reported. The characteristic stress reported for the formulation with 30% of zirconia evaluated in the present work (914 MPa) was slightly higher to the results reported by Lopes et al (2020) for a ZTA reinforced with 20% of zirconia particles (860 MPa).(28) Moreover, it has been reported that the mechanical properties of ZTA composites tends to vary proportionally to the modifications in weight percentage of 3Y-TZP, as postulated by the rule of mixtures. (33) Therefore, as the zirconia ratio increase in the composition, the flexural strength of the ZTA composite is expected to raise.

The probability of survival calculated for ZTA composites at 300 and 500 MPa, makes it an interesting alternative for anterior and posterior three-unit FDP frameworks according to ISO 6872:2015 biaxial flexural strength recommendation for fixed dental prostheses. Promising advantages for ZTA composites as infrastructure material include higher strength regarding pure alumina, remarkable hydrothermal stability when compared to first and second generation 3Y-TZPs, and a less challenging scenario from an esthetic perspective when compared to metallic frameworks. Nevertheless, further research towards the optimization of the processing parameters with the aim to obtain a finer microstructure are encouraged in order to improve the mechanical performance of ZTA composites under higher loads, aiming the indication as larger span fixed dental prostheses frameworks. Among recent innovations regarding aging-resistant zirconia based composites, it is noteworthy the development of ceria-stabilized zirconia containing two second phases, α -alumina and strontium hexa-aluminate proposed by Reveron et al (2017)(60). This composite primarily composed by zirconia has resulted in high strength (~ 1100 MPa), fracture toughness (>10 MPa $\sqrt{\text{m}}$) and remarkably high Weibull modulus (60). Although initial characterizations evidenced promising results for such materials, further characterizations for specific dental applications and clinical evaluations are warranted.

Although nanomechanical testing in Article 2 did not evidence significant alterations either in the hardness or elastic modulus of aged 3Y-TZP, the increase in surface roughness is alarming considering the clinical indication of second generation 3Y-TZPs as a monolithic restorative material, (18) where an increase in surface roughness may have a potential impact on antagonist wear (61, 62), biofilm adhesion (63, 64) as well as the potential effects on the long-term performance of these rehabilitations.

In a nutshell, the findings of the presented manuscripts demonstrated that aging significantly affected the crystalline structure, optical, mechanical and topographical properties of stabilized zirconia, which raise concerns about the integrity of 3Y-TZP microstructure, increasing defect population, and its effects on the esthetic, biological and mechanical performance of monolithic prostheses. The laboratory simulation of hydrothermal degradation using autoclave has been effective to promote zirconia tetragonal-to-monoclinic (t-m) phase transformation (51) and is considered a standard method according to ISO 13356:2015 requirements.(65)

The ISO protocol, comprised by autoclave aging at 134°C, 2.2 bar, for five hours has been reported in orthopedic literature to be roughly equivalent to 2–4 years *in vivo* aging (37 °C). (29) However, recent evidence concerning the *in vivo* effects of LTD on 3Y-TZP systems have suggested that aging kinetics can be almost three times faster than the conventionally accepted *in vitro-in vivo* extrapolations.(58) Furthermore, in a prospective clinical study with *ex vivo* monitoring of monolithic 3Y-TZP dental prostheses, Koenig, Bekaert et al. (2021) demonstrated that along with the effects of LTD, the tribological stresses generated in the occlusal surface of the prostheses produce surface crushing and grain pull-out, which suggest an underestimation of the aging process when characterization tests are limited to monoclinic phase quantification.(59) Based on the current evidence that *in vivo* aging kinetics can be remarkably faster than *in vitro* studies, aging resistant materials, such as ZTA composites, are highly desirable, especially when considering the range of stresses levels required for dental prostheses' applications.

Single load-to-failure tests, as the ones presented in this work, have been frequently used in dental research to compare and characterize the mechanical properties of restorative materials. However, during function, dental prostheses are subjected to repetitive lower-intensity stresses that lead to cumulative damage and slowly compromise the integrity of the restoration.(66) Such mechanisms seem critical in yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) based restorative materials, where the metastability of the tetragonal

phase may be affected by mechanical stress, humidity and relatively low temperature, including body temperature.(58, 67) Therefore, studies including fatigue characterization and/or clinical evaluation are warranted to further assess the effects of cyclic loading and LTD in the mechanical and hydrothermal degradation of 3Y-TZP and ZTA composites.

4 CONCLUSIONS

4 CONCLUSIONS

The synthesis of experimental 70-30% ZTA composite was successful and its relevance for dental applications relies on its higher masking ability, aging resistance in all tested parameters, and strength similar to zirconia. Aging significantly increased the monoclinic content of first and second generation zirconias and affected their optical and mechanical properties as well as surface roughness. Further investigations including fatigue characterization and clinical evaluations are warranted, as well as continued innovations in the development of aging-resistant polycrystalline ceramics for large-span dental applications.

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6 APPENDIX

DECLARATION OF EXCLUSIVE USE OF THE ARTICLE IN THESIS

As co-authors, we hereby declare that we are aware that the article "**Aging resistant ZTA composite for dental applications: Microstructural, optical and mechanical characterization**" published in Dental Materials, will be included in the thesis of the PhD candidate **Ernesto Byron Benalcázar Jalkh**. We also declare that this manuscript was not used and may not be used in other graduation or postgraduation works for any Program in or out the Bauru School of Dentistry, University of São Paulo.

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DECLARATION OF EXCLUSIVE USE OF THE ARTICLE IN THESIS

As co-authors, we hereby declare that we are aware that the article "**Nanoscale physico-mechanical properties of an aging resistant ZTA composite**" published in the Journal of the Mechanical Behavior of Biomedical Materials, will be included in the thesis of the PhD candidate **Ernesto Byron Benalcázar Jalkh**. We also declare that this manuscript was not used and may not be used in other graduation or postgraduation works for any other Program in or out the Bauru School of Dentistry, University of São Paulo.

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