MECHANICAL PROPERTIES, AGING STABILITY AND TRANSLUCENCY OF SPEED-SINTERED ZIRCONIA FOR CHAIRSIDE RESTORATIONS

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Key words: Monolithic zirconia; Speed sintering; Multilayer zirconia; Aging; Mechanical properties

Declarations of interest

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HIGHLIGHTS

- Speed – sintering of 5Y-PSZ and 3Y-TZP zirconia ceramics revealed a similar density, microstructure, hardness, fracture toughness and average biaxial flexural strength, and hydrothermal aging resistance compared to the conventionally sintered references.
- Speed sintering of 3Y-TZP caused a decrease in translucency, while the optical properties of 5Y-PSZ were not affected by the sintering method
- Speed – sintering lowered the mechanical reliability of both the 3Y-TZP and 5Y-PSZ zirconia ceramics.

ABSTRACT

Objectives: To evaluate the performance of zirconia ceramics sintered in a speed sintering induction furnace by comprehensive understanding of their optical and mechanical properties, microstructure, phase composition and aging stability, in comparison to ceramics sintered in a conventional furnace.

Methods: Speed sintered (SS) Katana STML_{SS} (Kuraray Noritake) (total thermal cycle/sintering time/dwell temperature: 30 min/16 min/1560 °C) and CEREC Zirconia (CEREC Zr_{SS}) (Dentsply Sirona) (15 min/2 min/1578 °C) were compared to conventionally sintered (CS) Katana STML_{CS} (6.8 h/2 h/1550 °C) and inCoris TZI_{CS} (4 h/2 h/1510 °C). The translucency Parameter (TP) and Contrast Ratio (CR) were measured with a spectrophotometer. The chemical composition of the materials was determined by XRF and phase composition was characterized using XRD. Hydrothermal aging behavior was evaluated by measuring the tetragonal-to-monoclinic ZrO₂ phase transformation after accelerated hydrothermal aging in steam at 134°C. The indentation fracture toughness, Vickers hardness and biaxial strength of the sintered ceramics were assessed.

Results: Speed and conventionally sintered zirconia revealed similar density, microstructure, average strength and hydrothermal aging stability. Both Katana STML_{SS/CS} 5Y-PSZ ceramics were characterized with a higher content of cubic phase (≈ 53 wt%), which resulted in a higher amount of Y₂O₃ in the remaining tetragonal ZrO₂ phases compared to the 3Y-TZP CEREC Zr_{SS} and inCoris TZI_{CS} (8 wt% and 20 wt%, respectively). The sintering program did not affect the hydrothermal aging behavior of Katana STML_{SS} and CEREC Zr_{SS}. TP of Katana STML_{SS} (TP ≈ 32) was not affected by speed sintering, while the translucency of CEREC Zr_{SS} (TP=14) was significantly reduced. Hardness, fracture toughness and Weibull characteristic strength of Katana STML_{SS} and CEREC Zr_{SS} also reached the optimal level, but speed sintering substantially lowered their mechanical reliability.

Significance: Speed sintering of 3Y-TZP and 5Y-PSZ in a speed sintering induction oven appeared suitable for clinical applications. However, further studies should focus on improving of translucency and mechanical reliability of the speed-sintered zirconia ceramics.

Key words: Monolithic zirconia; Speed sintering; Multilayer zirconia; Aging; Mechanical properties

1. INTRODUCTION

In the last decade, computer-aided design/computer-aided manufacturing (CAD/CAM) systems have transformed the fabrication of dental restorations in both dental laboratories and clinics [1]. Three different CAD/CAM approaches have been developed and introduced: (1) in office or so-called 'chairside', (2) in-lab systems and (3) centralized production in milling centers [2,3]. In contrast to in-lab systems, where the production of the restoration is to some extent related to the dental laboratory, chairside fabrication allows a dentist to complete all the phases of restoration production within one single appointment, completely independent from a dental technician. One of the most popular chairside systems is the CEREC (computer assisted CERamic REConstruction, Dentsply Sirona, Bensheim, Germany) CAD/CAM system, which was introduced to the market in 1985. Even though some researchers have expressed their concern regarding the precision of the CEREC restoration marginal fit in the past, recent studies confirmed that it is possible to produce clinically long lasting restorations after the latest technological CEREC improvements [4].

So far, different ceramic and non-ceramic materials have become available for chairside CEREC CAD/CAM systems. In particular, esthetic ceramics (feldspatic and leucite reinforced ceramics), polymer-infiltrated ceramics and high-strength ceramics (lithium (di)silicate glass ceramics) or composite resins can be milled efficiently (usually in less than 20 min) in their final structure without any major mechanical damage. This is crucial as only minimal post-milling processing is needed in order to complete the restoration. The fabrication process has thus been substantially shortened, so the final restoration can be fabricated and cemented in only one appointment. However, zirconia ceramics have always been a chairside CAD/CAM issue. Zirconia restorations could be CAM fabricated either by hard machining of a fully sintered zirconia block or by soft machining of a partially sintered zirconia block [5]. Hard milling of fully sintered zirconia is rather difficult and expensive due to its high strength and hardness, and longer milling times, which cause a significantly faster wear of the milling tools. For this reason, zirconia blocks are normally milled in the pre-sintered porous form by so-called soft machining. The milled restorations have to be additionally sintered to achieve full density, which usually takes 6-8 h including heating, cooling and dwell time; this thermal process normally takes place overnight.

The recent introduction of speed-sintering furnaces and the development of novel speed-sintering protocols have substantially shortened the sintering time of zirconia ceramics (from 6 h up to 10 min) allowing the fabrication of zirconia restorations in only one visit. Such speed-sintering furnace (SpeedFire, Dentsply Sirona) was introduced to the market 2 years ago and has gained a high popularity among dentists in a short period. In comparison with conventional sintering furnaces, where heat is generated by electrical resistive heating elements, a SpeedFire furnace generates heat by electromagnetic induction [6]. In brief, an induction heating coil surrounds a susceptor body, which in

turn surrounds the pre-sintered zirconia ceramics. The induction coil emanates a fluctuating induced magnetic field, which generates heat in the electroconductive susceptor body, usually composed of zirconium or graphite. More information is provided elsewhere [7]. This induction sintering method is considered to be beneficial compared to conventional sintering as high temperatures can be achieved extremely fast. The most advanced conventional sintering furnaces in air can achieve maximum heating rates of 40-70 °C/min up to maximum 1800 °C using MoSi₂ heating elements [7].

At the same time, the popularity of zirconia-based restorations have been rapidly increased among dentists due to their superior biocompatibility, favorable mechanical properties and promising esthetic potential [8]. Specifically, biomedical grade 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP) is used in dentistry for fabricating dental crowns and fixed partial dentures. Since it is characterized by a high strength (≈ 1000 MPa), it is considered a material of choice for the fabrication of long-span fixed dental prosthesis (FDP). However, the main drawback of 3Y-TZP ceramics is its high opacity, especially when placing anterior restorations next to natural teeth. One way to improve the esthetic appearance of zirconia ceramics and to mimic optical properties of natural tooth enamel is to cover the opaque zirconia with high-translucent porcelain veneering. The brittle nature of porcelain however frequently caused chipping or delamination from the zirconia framework [9]. For that reason, there is a clear trend towards monolithic zirconia restorations that could solve the problem of chipping and additionally avoid excessive tooth preparation inevitable for placement of bi-layered zirconia ceramics. Different approaches were proposed to improve the translucency. Zirconia materials with a higher Y₂O₃ content (> 4 mol%) successfully increased the translucency but lowered the mechanical properties due to a reduction or absence of transformation toughening, restricting the usage of these materials to low stress-bearing areas.

Sintering of zirconia is considered to be a critical step in ceramic processing and has been a focus of interest of many researchers [10–12]. Previous research has already shown that changes in the sintering procedure directly influence the density and microstructure, including grain size and phase composition, which that can reflect on the mechanical and optical properties of zirconia ceramics [13]. Conventional sintering of Y-TZP ceramics usually includes slow and stable heating and cooling rates (up to 20 °C/min) to a sintering temperature of 1400-1500 °C which lasts for a couple of hours of dwell time [14]. On the other hand, speed sintering has been proposed as a potential strategy to obtain a finer microstructure by preventing grain growth by applying a fast heating rate while maintaining a high material density [15]. A recent study reported that an increased sintering temperature in combination with a decreased sintering time indeed yielded a smaller grain size and higher translucency [14]. In a different study where the samples were fast sintered by putting them in a pre-heated furnace at 1580°C for 10 min, the flexural strength of zirconia ceramics was significantly improved [16]. So far, the main reported drawbacks of conventional rapid sintering are correlated with

inhomogeneous densification or so-called shell densification of 3Y-TZP, which can have a negative impact on the microstructure of ceramics, consequently causing mechanical defects and lowering its mechanical and optical properties [17,18].

In this respect, it has also been reported that an uneven low radial density distribution caused by a combination of cold isostatic powder compaction and non-optimized sintering protocol, can increase the hydrothermal aging susceptibility of 3Y-TZP ceramics [19]. Namely, in between 1999 and 2001, hundreds of zirconia femoral heads suffered from a catastrophic failure which led to their sale suspension and withdrawal from the market [20]. Subsequently, the femoral heads were subjected to a thorough examination revealing that the applied thermal sintering cycle of the ball-heads resulted in the presence of residual stresses and an uneven radial core density. This consequently lead to the unexpected rapid aging rate and the growth of aging-induced defects in the region of maximum tensile loading [19].

To the best of the authors' knowledge, a detailed evaluation of zirconia ceramics sintered in a CEREC SpeedFire (Dentsply Sirona) furnace is still missing. Therefore, the main objective of this study was to evaluate the performance of speed-sintered commercially available monolithic zirconia. The null hypothesis to be tested was that speed sintering would not affect the mechanical properties, microstructure, optical properties and aging behavior of monolithic dental zirconia.

2. MATERIALS & METHODS

2.1. *Experimental materials and specimen preparation*

Four commercial pre-sintered zirconia ceramics, of which two grades were indicated to be sintered conventionally ("CS"; Katana STML, Kuraray Noritake, Tokyo, Japan and inCoris TZI, Dentsply Sirona, York, PA, USA) and two additional grades ("SS"; Katana STML, 12Z, Kuraray Noritake, Tokyo, Japan and CEREC Zirconia medi S, Dentsply Sirona, York, PA, USA) following a speed-sintering protocol, were cut into plates with dimensions of approximate 15 × 15 × 3.5 mm. Katana STML_{SS} and CEREC ZR_{SS} samples were subsequently sintered in a SpeedFire furnace (Dentsply Sirona, York, USA) following the sintering program provided by the furnace manufacturer (Fig. 2). The total sintering time for Katana STML_{SS} was 28 min and heating was done in 3-steps: (1) 350 °C/min up to 1300 °C; (2) 150 °C/min up to 1500 °C; (3) 10 °C/min up to 1560 °C. The dwell time at 1560 °C lasted for 16 min, after which the samples were cooled at 170 °C/min to 1200 °C in a closed furnace and at 480 °C/min to room temperature by opening the furnace. The sintering program for CEREC Zr_{SS} started with a heating rate of 330 °C/min up to 1050 °C and continued with the rate of 150 °C/min until the sintering temperature of 1580 °C. After 3 min dwell at 1580 °C, the samples were cooled down at 175 °C/min to 1200 °C and at 400 °C/min to room temperature. On the other hand, Katana STML_{CS} (total sintering time: 6.8h; dwell time: 2h at 1550 °C) and inCoris TZI_{CS} (total sintering time: 4h; dwell time: 2h at 1510 °C), indicated only for conventional sintering, were sintered in a conventional furnace (Nabertherm, Lilienthal, Germany), following the instructions of the respective material manufacturers. Details on the thermal cycles are provided in Fig. 2. Both Katana STML_{CS} and Katana STML_{SS} are multilayered, while CEREC Zr_{SS} and inCoris TZI_{CS} are monolayer materials with the same A2 color grade.

The sintered materials were ground parallel and gradually polished down to 1 µm with diamond suspensions and with colloidal silica until a mirror surface was achieved. The final sample size was 12 x 12 x 0.5 mm for evaluating density, microstructure, optical properties and hydrothermal aging, and 12 x 12 x 1.2 mm for analyzing biaxial flexural strength, hardness and toughness (Fig. 1).

2.2. *Chemical, phase and microstructural characterization*

The chemical composition of the zirconia grades was evaluated by wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF; Bruker S8 Tiger, Germany) using a 4 kW X-ray tube. The raw data of the chemical composition of the sample were automatically provided using Quant-Express software (Bruker, Karlsruhe, Germany).

The density of the sintered ceramics (n = 6) was determined according to the Archimedes principle in ethanol.

Phase identification was performed by X-ray diffraction (XRD; 3003 T/T, Seifert, Ahrensburg, Germany). Mirror-polished surfaces of each material were scanned using Cu K_α (40 kV, 40 mA) from 20

to 90° (2θ) with the step size of 0.01° for 3s. Rietveld analysis was used to assess the phase composition and lattice parameters using TOPAS academic V5 software (BRUKER AXS, Karlsruhe, Germany). The Y₂O₃ content in the tetragonal ZrO₂ phase was calculated based on the *a* and *c* unit cell parameter of the tetragonal ZrO₂ phase, as explained by Yamashita *et al.* and Gibson *et al.* [21,22].

The microstructure of the ceramics zirconia was characterized using scanning electron microscopy (SEM; Philips XL-30 FEG, Eindhoven, The Netherlands). Prior to analysis, the samples were mirror polished and thermally etched (1250 °C) to reveal the grain boundary network and Pt coated. Secondary electron (SE) images were acquired at 10⁻⁵ mbar pressure, an acceleration voltage of 10 kV and 144 μA beam current. The zirconia grain size of at least 1000 grains was measured on SE micrographs using Image-Pro PLUS 6.0 software (Media Cybernetics, Rockville Pike, USA) according to the linear intercept method [23]. The average grain size with standard deviation and grain-size distributions were reported without any corrections.

2.3. Low-temperature degradation

In vitro hydrothermal aging was performed following ISO standard 13356. Double-sided mirror-polished specimens were autoclaved at 134 °C and 2 bar in water vapor up to 60 h. The autoclave with specimens was placed in an oil bath in order to obtain an internal temperature of 134 °C. The amount of monoclinic ZrO₂ phase was determined using XRD (Seifert 3003 T/T, Seifert) at 40 kV and 40 mA of Cu-K_α radiation. XRD patterns were recorded in the range of 27-33° (2θ) in the θ–2θ mode with a scan speed of 2 s/step and a scan step of 0.02° (the maximum X-ray penetration depth was calculated to be 7.5 μm (Cu K_α with 98% absorption)). The surface monoclinic phase (*V_m*) content was calculated using the formula of Garvie *et al.* [24] and Toraya [25]:

$$V_m = \frac{1.311 \times (I_m^{-111} + I_m^{111})}{1.311 \times (I_m^{-111} + I_m^{111}) + I_t^{101}} \quad (1)$$

with *I* representing the intensity of monoclinic (-111 and 111) and tetragonal (101) phase peaks indicated by the subscripts *m* and *t*. For each curve, two specimens (four exposed surfaces) were evaluated and the average value was reported.

2.4. Optical property characterization

The translucency of the ceramics was measured on a double-sided mirror-polished plate specimens (*n* = 7, thickness = 0.5 mm) using a spectrophotometer (SpectroShadeTM MICRO, MHT Optic Research, Niederhasli, Switzerland) before and after 60 h of hydrothermal aging. Lithium-(di)silicate glass-ceramic (LS₂) samples (*n* = 7, thickness = 0.5 mm) were fabricated from IPS e.max CAD HT block (Ivoclar

Vivadent, Schaan, Liechtenstein; “HT” = high translucency) as translucency reference control. The spectrometer was used to record the CIELAB coordinates (L^* , a^* and b^*) from the specimens positioned on a black and white background. A thin layer of vaseline was put in-between specimen and background for better optical contact. The translucency parameter (TP) was calculated according to:

$$TP = \sqrt{(L_B^* - L_W^*)^2 + (a_B^* - a_W^*)^2 + (b_B^* - b_W^*)^2} \quad (2)$$

with subscripts B and W representing the coordinates over a black and white background, respectively.

The spectral reflectance (Y), obtained from the L^* values, over black and white backgrounds were additionally used to calculate the contrast ratio (CR) following equation [26]:

$$CR = \frac{Y_b}{Y_w} \quad (3)$$

CR linearly correlates with TP [27]. A high TP represents high translucency and low CR, and vice versa. More specifically, CR is 0.0 for a transparent material and 1 for a completely opaque material.

2.5. Mechanical property characterization

The micro-hardness and fracture toughness of the mirror-polished samples were measured by the indentation method using a Vickers micro-hardness tester (Model FV-700, Future-Tech, Tokyo, Japan) with a load of 98 N applied for 10 sec. The indentation toughness was calculated according to the Anstis equation with an E-modulus of 210 GPa [28]. For each ceramic grade, 10 indentations were made.

The biaxial flexural strength was determined by performing piston-on-3-balls (P3B) testing on mirror-polished ceramic samples (12 x 12 x 1.2 mm) according to the ISO standard 6872 (n=20) [29]. All tests were conducted using a universal machine (Instron 4467, Norwood, MA, USA) at a crosshead speed of 0.5 mm/min. After fracture, all fragments were carefully collected and their amount was registered. The biaxial flexural strength of square samples was calculated as indicated in the ISO standard 6872 for disks, with the specimen radius replaced by half of the sample side length [30]. Therefore, the biaxial flexural strength was calculated following the equations:

$$\sigma = -0.2387P(X - Y)/b^2 \quad (4)$$

$$X = (1 + \nu) \ln \left(\frac{r_2}{l} \right)^2 + \left[\frac{(1 - \nu)}{2} \right] \left(\frac{r_2}{l} \right)^2 \quad (5)$$

$$Y = (1 + \nu) \left[1 + \ln \left(\frac{r_1}{l} \right)^2 \right] + (1 - \nu) \left(\frac{r_1}{l} \right)^2 \quad (6)$$

where σ is the maximum center tensile stress, P is the total load causing fracture (in N), ν is the Poisson's ratio, r_1 is the radius of the support circle, r_2 is the radius of the loaded area, l is half of the sample side length and b is the specimen thickness.

2.6. Statistical analysis

Grain size, translucency and biaxial strength of different materials were analyzed using one way analysis of variance (ANOVA) followed by post-hoc Tukey or Games-Howell test for multiple comparisons. Differences were considered statistically significant if $p < 0.05$. All statistical analysis were performed using SPSS statistical software (SPSS, Version 20, Chicago, IL, USA).

3. RESULTS

3.1. Density measurements

The density of the tested materials is reported in Table 1. The zirconia ceramics Katana STML_{SS} and CEREC Zr_{SS} revealed a density of $6.03 \pm 0.01 \text{ g/cm}^3$ and $6.06 \pm 0.02 \text{ g/cm}^3$ respectively which was statistically similar as that of the conventionally sintered Katana STML_{CS} ($6.03 \pm 0.01 \text{ g/cm}^3$) and inCoris TZI_{CS} ($6.09 \pm 0.02 \text{ g/cm}^3$).

3.2. Chemical, phase and microstructural characterization

The chemical characterization of the tested materials is presented in Table 2. Katana STML_{SS} had a similar composition as its conventionally sintered control Katana STML_{CS}. The amount of Y₂O₃ in both Katana materials was between 8.9 and 9.04 wt% ($\approx 5 \text{ mol\%}$), characterizing them as a 5 mol% yttria-stabilized zirconia (5Y-PSZ). Apart from the HfO₂ impurity in all ZrO₂ grades, a small amount of MgO (0.15 wt%) was found in the conventionally sintered Katana STML_{CS}. On the other hand, CEREC Zr_{SS} and inCoris TZI_{CS} contained 4.89 wt% and 5.5 wt% of Y₂O₃, respectively, which corresponds to a 3 mol% yttria-stabilized tetragonal zirconia polycrystalline ceramic (3Y-TZP). Er₂O₃ was found as coloring agent in both 3Y-TZP materials, whereas CEREC Zr_{SS}, also contained a small amount of Fe₂O₃.

XRD patterns reflecting the zirconia phase composition in each zirconia ceramic are shown in Fig. 3. Katana STML_{SS} and Katana STML_{CS} as well as CEREC Zr_{SS} and inCoris TZI_{CS} displayed similar XRD patterns, proving that Katana STML_{CS} and inCoris TZI_{CS} were suitable references for the tested materials. Monoclinic ZrO₂ phase peaks were not present in any of the XRD patterns. Rietveld analysis (Table 3) revealed the same amount of cubic zirconia (*c*-ZrO₂) for Katana STML_{SS} ($53 \pm 4 \text{ wt\%}$) and its reference Katana STML_{CS} ($53 \pm 2 \text{ wt\%}$). CEREC Zr_{SS} and inCoris TZI_{CS} showed lower amounts of *c*-ZrO₂ ($8 \pm 0.5 \text{ wt\%}$ and $20 \pm 1 \text{ wt\%}$, respectively). The Y₂O₃ content in the residual tetragonal ZrO₂ phase was comparable and highest in Katana STML_{SS} ($4.5 \pm 0.02 \text{ mol\%}$) and Katana STML_{CS} ($4.2 \pm 0.1 \text{ mol\%}$). A substantially lower amount of Y₂O₃ was measured for CEREC Zr_{SS} and inCoris TZI_{CS} ($3.2 \pm 0.04 \text{ mol\%}$ and $2.7 \pm 0.01 \text{ mol\%}$, respectively). The tetragonality ($c/a\sqrt{2}$) in the remaining tetragonal phase was lower in speed-sintered Katana STML_{SS} and CEREC Zr_{SS} (1.0104 ± 0.0001 and 1.0139 ± 0.0001 , respectively) compared to the conventionally sintered Katana STML_{CS} and inCoris TZI_{CS} (1.0112 ± 0.0002 and 1.0530 ± 0.0000 , respectively).

The results of the SEM microstructural analysis are presented in Fig. 4. Katana STML_{SS} was characterized with substantially larger grains ($0.96 \pm 0.55 \text{ }\mu\text{m}$) as compared with its reference Katana STML_{CS} ($0.36 \pm 0.19 \text{ }\mu\text{m}$). The average grain size of CEREC Zr_{SS} ($0.29 \pm 0.12 \text{ }\mu\text{m}$) was similar to that of inCoris TZI_{CS} ($0.31 \pm 0.13 \text{ }\mu\text{m}$). Moreover, the particle size distribution histogram of Katana STML_{SS}

revealed wide distribution tendency resulting in a bimodal grain-size distribution, while a unimodal grain-size distribution was observed in Katana STML_{CS}, CEREC Zr_{SS} and inCoris TZI_{CS}.

3.3. Low-temperature degradation

The monoclinic ZrO₂ phase content in function of the increased hydrothermal aging time is presented in Fig. 5. Both speed-sintered zirconia ceramics showed the same transformation curves as their conventionally sintered references. Katana STML_{SS} and conventionally sintered Katana STML_{CS} revealed no transformation up to 60 h of hydrothermal aging at 134 °C. Cerec Zr_{SS} and inCoris TZI_{CS} revealed a significant phase transformation already starting after a short aging period of 2 h. The saturation value for Cerec Zr_{SS} is higher than for inCoris TZI_{CS}, which in perfect agreement with the lower c-ZrO₂ phase content in Cerec Zr_{SS} (see Table 3).

3.4. Optical properties characterization

TP of the zirconia ceramics before and after hydrothermal aging is presented in Fig. 6. Katana STML_{SS} and Katana STML_{CS} revealed a higher TP compared with the 3Y-TZP ceramics CEREC Zr_{SS} and inCoris TZI_{CS}. Moreover, the speed-sintered CEREC Zr_{SS} (TP=15) had a lower TP than the conventionally sintered inCoris TZI_{CS}, while the TP of the Katana zirconia ceramics were not influenced by the type of sintering process employed. Nonetheless, the TP of lithium (di)silicate glass ceramics was still significantly higher compared to the investigated zirconia ceramics. The low-temperature degradation during 60 h significantly decreased the TP of the tested 3Y-TZP (CEREC Zr_{SS} and inCoris TZI_{CS}) ceramics while it had no effect on the TP of the 5Y-PSZ (Katana STML_{SS} and Katana STML_{CS}) ceramics.

3.5. Mechanical property characterization

Vickers hardness of all groups ranged between 1330 – 1350 kg/mm² (Fig. 7). Katana STML_{SS} showed a statistically lower Vickers hardness compared to Katana STML_{CS}. On the other hand, CEREC Zr_{SS} showed a significantly higher hardness compared to its conventionally sintered reference inCoris TZI_{CS}. The fracture toughness was higher for Cerec Zr_{SS} and inCoris TZI_{CS} compared to both Katana zirconia ceramics. Moreover, the fracture toughness was significantly higher for Katana STML_{SS} compared to its conventionally sintered control Katana STML_{CS} while there was no difference between speed-sintered CEREC Zr_{SS} and conventionally sintered inCoris TZI_{CS}.

The biaxial strength results, including the average flexural strength, characteristic strength (σ_0) [95% C.I.] and Weibull plots are presented in Table 4 and Fig. 8. The average strength of CEREC Zr_{SS} and inCoris TZI_{CS} ceramics ranged between 918 ± 135 MPa and 823 ± 95 MPa, respectively. Speed-sintered Katana STML_{SS} and conventionally sintered Katana STML_{CS} ceramics showed lower values between 619 ± 135 MPa and 702 ± 127 MPa, respectively (Table 4). Importantly, there was no statistical difference

between the strength of conventionally and speed-sintered zirconia ceramics for both the 3Y-TZP (Katana STML_{SS} and Katana STML_{CS}) and 5Y-PSZ (CEREC Zr_{SS} and inCoris TZI_{CS}) grades. However, speed-sintering decreased the Weibull modulus of the tested zirconia ceramics. More specifically, the shape values (m) for Katana STML_{SS} and CEREC Zr_{SS} were 5.4 and 6.8, respectively, compared to their conventionally sintered references, revealing an m value of 6.3 for Katana STML_{CS} and 9.7 for inCoris TZI_{CS}.

4. DISCUSSION

The present results demonstrate that speed-sintering of zirconia ceramics in a SpeedFire furnace (Dentsply Sirona) did not affect density, phase composition, hardness, toughness and hydrothermal aging stability of both the 3Y-TZP (CEREC Zr_{SS} versus InCoris TZI_{CS}) and 5Y-PSZ (Katana STML_{SS} versus Katana STML_{CS}) zirconia grades, but it had a negative impact on the translucency and mechanical reliability. For this reason, the null hypothesis, stating that speed sintering does not affect mechanical properties, the microstructure, optical properties and aging behavior of monolithic dental zirconia can only be partially accepted.

In agreement with previous studies [31,32], the chemical composition of the tested zirconia ceramics revealed that both conventionally sintered Katana STML_{CS} and speed-sintered Katana STML_{SS} contained the same amount of Y₂O₃, which is characteristic for 5 mol% yttria partially stabilized zirconia (5Y-PSZ). On the other hand, the amount of Y₂O₃ in InCoris TZI_{CS} and CEREC Zr_{SS} were lower, and comparable to a biomedical grade 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP). Moreover, this finding was in part confirmed by the phase characterization, which revealed, as expected, both 5Y-PSZ speed-sintered Katana STML_{SS} and conventionally sintered Katana STML_{CS} contained a significant amount of *c*-ZrO₂ compared to the *t*-ZrO₂ rich 3Y-TZP (Cerec Zr_{SS} and InCoris TZI_{CS}). Speed sintering did not have any influence on the phase composition of 5Y-PSZ and on the amount of Y₂O₃ in the tetragonal phase and its tetragonality, most likely due to the higher yttria content enabling faster diffusion. On the other hand, the phase composition of the 3Y-TZP zirconia ceramics was affected by speed sintering, as the CEREC Zr_{SS} contained a higher amount of *t*-ZrO₂ (92.1%) compared to the conventionally sintered InCoris TZI_{CS} (80%). Nevertheless, both zirconia compositions remained were in the range of typical 3Y-TZP zirconia ceramics [33].

The impact of the sintering conditions on the microstructural development of zirconia ceramics has already extensively been studied [34]. It is well known that sintering factors such as high temperatures (1400 – 1600 °C), sufficient dwell time and the steady heating and cooling period are crucial for obtaining optimal density and microstructure of zirconia ceramics [34,35]. In our study, both speed-sintered 3Y-TZP and 5Y-PSZ showed similar full density values compared to their conventionally sintered references. This implies that high heating and cooling rates can be employed to obtain full density dental zirconia starting from pre-sintered blocks. Besides, in agreement with previous studies, 3Y-TZP zirconia showed higher density values compared to 5Y-PSZ, which could be attributed to the higher amount of higher density *t*-ZrO₂ compared to the lower density *c*-ZrO₂ [36]. According to earlier studies where the reported density values of zirconia ceramic was above 6.00 g/cm³ [37,38], both speed-sintered Katana STML_{SS} and CEREC Zr_{SS} can be considered fully dense [39]. Density measurements represent the first indicator of optimum sintering, as they indicate the presence of

various structural defects such as pores or voids. In this context, it is important to understand that even though minimizing the presence of pores is highly beneficial, their complete avoidance is practically impossible to be achieved by conventional (pressureless) sintering [40]. During sintering, the green body will go through different sintering stages, where the continuous irregular porosity would gradually decrease by atomic diffusion until only small isolated spherical bubble pores are left inside the sintered body [41]. The elimination of this final 5% of closed pores during pressureless sintering requires a dwell time of several hours at the sintering temperature [42]. Incomplete sintering can leave a large amount of porosities and large pores in the sintered body, which could behave as critical flaws diminishing the strength of the material [40]. Thus, the main goal of achieving good mechanical properties of ceramic materials has always been to aim for maximum densification combined with minimal grain growth.

In order to control the grain size of zirconia ceramics, various approaches have been proposed. Apart from doping zirconia powder with dopants that suppress grain growth by segregation at the grain boundaries [43], the grain size can also be suppressed by modifying the heating rates during sintering [44]. Some researchers have reported speed sintering as a promising strategy for preserving a fine microstructure and preventing grain growth in the final stage of sintering [45]. In another study, conventional sintering yielded larger grains compared to so-called “super-speed” sintering, when the samples were inserted in a preheated furnace (10 min dwell time at 1580 °C) and speed sintering (99 °C/min, 30 min dwell time at 1540 °C) [16]. Of course, it should be bared in mind that the formation of a fine microstructure can also be problematic for zirconia ceramics, as smaller t-ZrO₂ grains generally result in a higher phase stability with a lower transformation toughening effect, which can diminish the fracture toughness of zirconia [46]. However, speed sintering of all ceramics in general, including zirconia, could be problematic as the rapid temperature changes could cause a thermal shock, which could lead to surface-crack formation and subsequent material fracture.

Additionally, Chen and Mayo (1993) have also described the formation of a non-homogeneous but gradually dense outer shell structure due to rapid heating and low thermal conductivity of zirconia [47]. This rapid consolidation would cause the formation of a so-called core-shell structure characterized by a fully dense surface layer and high inner porosity [48]. Our SEM micrographs, on the other hand, did not reveal the presence of pores, voids or other structural defects regardless the type of sintering method, which might be regarded notably for the investigated speed sintering.

Additionally, the SEM micrographs showed the difference in grain size between conventionally and speed-sintered zirconia ceramics. While the mean grain size of the 3Y-TZP grades (CEREC Zr_{SS} and inCoris TZI_{CS}) was rather similar regardless of the way of sintering, the 5Y-PSZ grades (Katana STML_{SS}) had significantly larger grains when the material was speed-sintered. The impact of sintering temperature on the growth of grains has already been vastly recognized, as the higher sintering

temperature and longer dwell time yielded larger grains [10]. Accordingly, it is still not clear why Katana STML_{SS} had substantially larger grains compared to its conventionally sintered reference Katana STML_{CS} since both materials were sintered at rather similar temperatures. A possible explanation might lie in the difference in density of the pre-sintered blocks, as both materials intended for speed sintering were approximately 3% denser compared to their conventionally sintered references.

The results of our study show that speed sintering did not influence the hydrothermal aging of both 3Y-TZP and 5Y-PSZ ceramic grades in regards of the subtle differences in hardness, phase content and microstructure. Moreover, these results agree with the previous studies, in which it was already well established that 3Y-TZP is prone to hydrothermal aging in contrast to 5Y-PSZ, which is known to be aging resistant [49]. The hydrothermal stability of 5Y-PSZ can be explained by the high amount of yttria content and non-transformable cubic phase present in both tested 5Y-PSZ, which agrees with previous studies [33,50]. Moreover, CEREC Zr_{SS} reached a higher monoclinic saturation level compared to inCoris TZI_{CS} after 60 h of hydrothermal aging. These findings are consistent with our phase composition results, as CEREC Zr_{SS} contains a higher amount of transformable tetragonal phase than its conventionally sintered reference inCoris TZI_{CS}.

5Y-PSZ showed higher translucency values compared to 3Y-TZP. However, speed sintering lowered the translucency of the 3Y-TZP zirconia grade CEREC Zr_{SS} compared with its reference, while it did not have any effect on the translucency of the 5Y-PSZ ceramics. The low translucency is still considered to be one of the major drawbacks of conventional 3Y-TZP zirconia. The low ability of Y-TZP to transmit light does not allow to mimic a natural enamel appearance, especially if the thickness of the material exceeds 1 mm. So far, the impact of various factors influencing the translucency of zirconia ceramics have extensively been studied [51,52]. In particular, the most significant factor that diminishes the translucency of 3Y-TZP (which is characterized with predominately tetragonal crystallography), is light scattering by birefringence at the grain boundaries or at residual pores or secondary phases like Al₂O₃ [53]. Fortunately, the dental industry succeeded to improve zirconia translucency by substantial reduction (even down to 0.05 wt%) or complete elimination of light scattering of the alumina additive, by minimizing residual porosity by sintering zirconia at higher temperatures, or increasing the Y₂O₃ content and introducing more cubic phase zirconia [50].

Our results showed that prolonged hydrothermal aging could indeed decrease the translucency of aging-sensitive zirconia, as it was observed that 60 h of hydrothermal aging significantly decreased translucency of 3Y-TZP zirconia ceramics but did not influence the translucency of aging-resistant 5Y-PSZ ceramics, regardless of the employed sintering technique. Due to aging or mechanical stress, the crystal structure of Y-TZP zirconia can change from tetragonal to monoclinic phase, which is known to reduce the translucency of Y-TZP [54]. Even though both monoclinic and tetragonal crystals are

anisotropic and birefringent, they have different optical properties. Besides the difference in the grain boundary orientation between monoclinic and tetragonal phases (crystals), monoclinic crystals are known to scatter more light [55]. Moreover, the surface phase transformation during aging results in surface alterations such as porosity, micro-cracking, higher roughness and reflection, which can all influence light transmission in zirconia ceramics [56,57].

Even though there were statistical differences in hardness between speed-sintered and conventionally sintered 3Y-TZP zirconia ceramics, all values fell in the typical range of fully dense zirconia ceramics (1240 - 1376 kg/mm²) [37,58]. On the other hand, the fracture toughness of zirconia ceramics is highly dependent on the transformation toughening, phenomenon which is closely related to the grain size and tetragonal phase composition [59]. Therefore, it was not a surprise that the tested 3Y-TZP zirconia ceramics resulted in higher toughness values than the 5Y-PSZ ceramics. Although a statistical difference was observed between the 3Y-TZP zirconia ceramics, the fracture toughness values for both 3Y-TZP and 5Y-PSZ zirconia grades are also in accordance with previously published studies [10,33].

Regarding the biaxial flexural strength, a piston-on-3-balls (P3B) test was performed. Although this set-up has already been used for some time, multiple studies have tried to validate and adjust the P3B test with respect to specimen size and geometry [30,60–62]. Minimizing the applicable specimen size is considered to be crucial as most of the ceramic CAD/CAM materials are supplied in the form of small CAD/CAM blocks or disks intended for fabrication of small dental restorations, such as inlays, onlays or single crowns. Compared to the set-up described in ISO standard 6872, the set-up applied in this work was adjusted for testing square disk samples (length of 12-16 mm), without losing the accuracy of the tests [63]. Importantly, finite element analysis showed the same stress distribution when testing disk- and round-shaped samples using the applied test set-up, thus rendering comparable biaxial strength values by substituting the radius value of the disk-shaped specimen by half the length of the square-plate specimen [30]. As most commercial dental ceramic materials are supplied in the form of blocks, one of the main advantages of this set-up is that it allows the fabrication of samples for biaxial flexural strength testing without reshaping the sample. Another advantage of the present set-up is related to the testing of the recently introduced multilayered CAD/CAM zirconia ceramics blocks or disks. It is known that the addition of different types of pigments or coloring agents can significantly influence its microstructure, optical and mechanical properties [64]. Coloring of multilayered zirconia is usually done by pressing various layers consisting of ZrO₂ powder doped with different amount of metal oxides. Since the ceramic block is gradually colored through its thickness, including all the layers in the analysis is of high importance.

Additionally, the flexural strength of both speed-sintered and conventionally sintered zirconia ceramic was evaluated using Weibull distribution analysis, which allows to predict material failure at

any stress level by assessing the mechanical reliability of the material [65]. Speed sintering of both 3Y-TZP and 5Y-PSZ zirconia grades showed no differences in mean biaxial flexural strength as their conventionally sintered references. These values are also comparable with the flexural strength reported in other studies [66]. It is noteworthy that there might be a difference between the surface treatment of the samples used in this study (mirror polishing) and the ones that are usually applied in dental clinics. Even though polishing of zirconia restorations using various zirconia polishing kits is highly recommended to reduce opposing tooth wear, it is quite difficult to achieve the same level of smoothness as compared with mirror polishing performed in the laboratory. Previously, it has been widely reported that different clinical surface treatments of Y-TZP zirconia ceramics, such as machining, grinding and sandblasting, could cause phase transformation and consequently introduce compressive stress and micro-cracked layers in the zirconia (sub)surface [68]. Depending on the balance between compressive stress and the depth of surface flaws, the surface treatment can result in a decrease or increase of flexural strength and mechanical reliability of zirconia ceramics [69,70]. In particular, processes, such as sandblasting, are able to transform the zirconia surface; however, the length of generated micro-cracks will not largely exceed the thickness of the transformed compressive surface layer. On the other hand, high stresses developed during rough grinding can form severe cracks, which can propagate through the stress compressive layer and behave as major flaws and stress concentrators, thus significantly diminishing mean flexural strength and reliability of the material [71,72]. Since the focus of this work was on the effect of sintering, mirror polishing allows standardization of the test by dismissing all additional factors (such as deep scratches or defects) that could vastly influence the mechanical reliability and failure predictability of zirconia ceramics. Furthermore, *in-vitro* studies represent a low-cost effective tool, which is relatively easy to perform, control and interpret, and they also allow evaluation of the effect of isolated factors and prediction of material behavior [73]. The Weibull distribution analysis, however, revealed lower shape values (m values) for the speed-sintered zirconia ceramics, which implies a reduced mechanical reliability. Since the strength of brittle materials, in general, is determined by the size of the major flaw in the specimen [73], the reduction in mechanical reliability might be attributed to the high heating or cooling rates imposed during speed sintering. It has already been described that a thermal shock provoked by extremely rapid cooling can generate high tensile stress at the surface and compressive stress inside the ceramic material [74]. When the tensile surface stress exceeds the strength of the material, it cause the formation of surface micro-cracks and subsequent material failure. On the other hand, the crack propagation could also be stopped by the compressive stress in the bulk before the failure, which would consequently result in low mechanical reliability of material. For this reason, more studies are necessary in order to optimize the speed-sintering protocol of Y-TZP zirconia ceramics.

5. CONCLUSION

For the 5Y-PSZ and 3Y-TZP zirconia ceramics investigated (Katana STML_{SS} and CEREC Zr_{SS}), speed sintering revealed a similar density, microstructure, hardness, fracture toughness and average biaxial flexural strength, and hydrothermal aging resistance as compared to the conventionally sintered references. Irrespective of the sintering method applied, 5Y-PSZ Katana STML_{SS/CS} had a lower fracture toughness and flexural strength than the 3Y-TZP CEREC Zr_{SS} and inCoris TZI_{CS} ceramics. However, speed sintering of 3Y-TZP CEREC Zr_{SS} caused a decrease in translucency, while the optical properties of 5Y-PSZ were not affected by the sintering method. Moreover, speed sintering lowered the mechanical reliability of both the 3Y-TZP and 5Y-PSZ zirconia ceramics. Future research is needed to optimize the sintering programs in order to improve the optical properties and the mechanical reliability of speed-sintered zirconia ceramics.

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TABLES

Table 1. Density of sintered zirconia ceramics

	Density (g/cm ³)	
	Mean	SD
Katana STML _{CS}	6.03	0.01
Katana STML _{SS}	6.03	0.01
CEREC Zr _{SS}	6.06	0.02
inCoris TZI _{CS}	6.09	0.02

Table 2. The elemental composition of the commercial ceramics, as obtained by XRF

Composition (wt%)	Katana STML _{CS}	Katana STML _{SS}	CEREC Zr _{SS}	inCoris TZI _{CS}
ZrO ₂	89.6	89.7	93.1	92.4
Y ₂ O ₃	8.9	9.04	4.89	5.5
HfO ₂	1.12	1.15	1.12	1.44
MgO	0.15	/	/	/
Er ₂ O ₃	/	/	0.4	0.29
Fe ₂ O ₃	/	/	0.1	/

Table 3. Phase composition and lattice parameters, as obtained by Rietveld analysis

			Katana STML _{CS}	Katana STML _{SS}	CEREC Zr _{SS}	inCoris TZI _{CS}
XRD	Tetragonal	fraction (%)	47 ± 2	47 ± 4	92 ± 0.5	80 ± 1
		<i>c</i> (Å)	5.1689 ± 0.0007	5.1650 ± 0.0000	5.1733 ± 0.0003	5.1768 ± 0.0004
		<i>a</i> (Å)	3.6146 ± 0.0002	3.6144 ± 0.0003	3.6080 ± 0.0002	3.6055 ± 0.0002
		<i>c/a</i> √2	1.0112 ± 0.0002	1.0104 ± 0.0001	1.0139 ± 0.0001	1.053 ± 0
		Y ₂ O ₃ (mol%)	4.2 ± 0.1	4.5 ± 0.02	3.2 ± 0.04	2.7 ± 0.01
	Cubic	fraction (%)	53 ± 2	53 ± 4	8 ± 0.5	20 ± 1
		<i>c</i> (Å)	5.1354 ± 0.0001	5.1354 ± 0.0003	5.1429 ± 0.0014	5.1369 ± 0.0005

Table 4. Mean biaxial flexural strength, Weibull modulus and characteristic strength of the tested zirconia ceramics

	Descriptive analysis (MPa)	Weibull modulus	
	Mean $\pm$ SD	m	σ_0
Katana STML _{CS}	702 $\pm$ 127 ^a	6.3	754
Katana STML _{SS}	619 $\pm$ 13 ^a	5.4	672
CEREC Zr _{SS}	918 $\pm$ 135 ^b	6.8	977
inCoris TZI _{CS}	823 $\pm$ 99 ^b	9.7	865

FIGURES:

Figure 1.

Figure 2.

Katana STML_{cs}	Katana STML_{ss}	CEREC Zr_{ss}	inCoris TZI_{cs}
Heating rate (°C/min)	10 °C/min (1550 °C)	350 °C/min (1300 °C) 150 °C/min (1500 °C) 10 °C/min (1560 °C)	330 °C/min (1050 °C) 150 °C/min (1580 °C)	25 °C/min (800 °C) 15 °C/min (1510 °C)
Sintering	1550 °C for 120 min	1560 °C for 16 min	1580 °C for 3 min	1510 °C for 120 min
Cooling rate (°C/min)	10 °C/min (200 °C)	170 °C/min (1200 °C) 480 °C/min (37 °C)	175 °C/min (1200 °C) 400 °C/min (37 °C)	30 °C/min (200 °C)

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

(a)

(b)

Figure 8.

FIGURE CAPTIONS:

Fig. 1: Flow chart of the experimental study set-up

Fig. 2: Speed sintering (SS) and conventional sintering (CS) protocol as a function of temperature and time.

Fig. 3: (a) XRD patterns of the zirconia ceramics. The characteristic peaks of cubic and tetragonal zirconia are indexed in the patterns of speed-sintered and conventionally sintered zirconia ceramics. (b) Expanded view of the 29-30, 33-37 and 70-78 2θ range.

Fig. 4: SEM micrograph of speed-sintered (Katana STMLSS and CEREC ZrSS) and conventionally sintered (Katana STMLCS and inCoris TZICS) ceramics. Katana STMLSS and Katana STMLCS had the largest average grain size of 0.96 μm and 0.36 μm , respectively. CEREC ZrSS and inCoris TZICS have a similar average grain size of 0.29 μm and 0.31 μm , respectively. The particle size distribution histogram of Katana STMLSS showed wide distribution tendency of a bimodal grain-size distribution, while unimodal grain-size distribution was observed in Katana STMLCS, CEREC ZrSS and inCoris TZICS.

Fig. 5: Monoclinic ZrO_2 phase content in function of hydrothermal aging time at 134 °C up to 60 h.

Fig. 6: Translucency of speed-sintered and conventionally sintered materials before and after hydrothermal aging up to 60 h. Letter annotation and asterisk represent the significant difference between the tested materials and between non-aged and aged samples at the significance level $p < 0.05$, respectively.

Fig. 7: Vickers hardness and fracture toughness of speed-sintered and conventionally sintered zirconia ceramics.

Fig. 8: Biaxial flexural strength of speed-sintered and conventionally sintered zirconia ceramics. Weibull plot with 95% confidence bands. The horizontal dotted line represents the Weibull characteristic strength (failure probability of 63.2%).