Original Article

pISSN, eISSN 0125-5614
M Dent J 2019; 39 (2) : 99-105

The effect of accelerated aging on phase transformation and flexural strength of conventional and translucent zirconia-based dental ceramics

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Low temperature degradation (LTD) occurs by tetragonal-to-monoclinic phase transformation of yttria-stabilized tetragonal zirconia polycrystal dental ceramics (Y-TZP). In this study, the influence of the hydrothermal aging on phase transformation and flexural strength of Y-TZP ceramics was investigated. Bar-shaped specimens (22.0mmx1.5mmx4.0 mm) of two Y-TZP (Ceramill ZI and Ceramill zolid FX) were subjected to hydrothermal aging at 134°C under 0.2 MPa for 0, 1 and 2 hours (n=6). The phase transformation (tetragonal-to-monoclinic) was evaluated by x-ray diffraction (XRD). The flexural strength was determined using four-point bending test. The amount of monoclinic phase conversion and flexural strength data were statistically analyzed by two-way ANOVA at α=.05. The results from the XRD analysis showed that the monoclinic phase increased from 0.1 to 4.8 % for Ceramill ZI with an increase in the autoclaving time from 0 to 2 hours. For Ceramill Zolid FX, an increase in monoclinic phase fraction was minor, ranging between 0.8 (control) to 1.7 % after autoclaving for 1-2 hours. The flexural strengths of these materials were not significant different after aging for 2 hours. In conclusion, the hydrothermal aging induced monoclinic-phase transformation in Y-TZP ceramics. However, an increase in monoclinic phase caused from hydrothermal aging in this study did not significantly affect the flexural strength of Ceramill ZI and Ceramill zolid FX.

Key words: accelerated aging, flexural strength, low temperature degradation, phase transformation, Y-TZP, zirconia

How to cite: Limsamai N, Pongpruaksa P, Supttamongkol K. The effect of accelerated aging on phase transformation and flexural strength of conventional and translucent zirconia-based dental ceramics. M Dent J 2019; 39: 99-105.

Introduction

The major drawback of Y-TZP zirconia ceramics is their sensitivity to low temperature degradation which has been reported by some studies [1, 2]. This mechanism is the stress-induced phase transformation of the metastable tetragonal grains to the monoclinic structure around the crack tip especially in the presence of the water [3, 4]. The low-temperature degradation processes are boosted by water at temperature of 200-300 degree Celsius. With the presence of water, phase transformation proceeds rapidly and transformation occurs from the surface to the bulk of zirconia materials. The grain size, stress, and stabilizing content affect the phase transformation process [5].

Zirconia ceramic had been used in orthopedics since 1990s especially for manufacturing hip-prostheses [6]. Unfortunately, failure due to fracture occurred repeatedly and low-temperature aging was reported to be the cause of failure. In 2001, the FDA and the Australian Therapeutic Goods Administration (TGA) announced

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Received : 19 April 2019 Accepted : 18 June 2019

for recalling all series of Y-TZP hip prostheses. In dental fields, zirconia commonly contains 3 mol % of yttria (3Y-TZP) to achieve chemical and dimensional stability, high mechanical strength, and fracture-toughness [7-9]. Zirconia ceramics are usually used as framework of 3- and 4-unit partial fixed prostheses and then veneered with dental veneering materials [10]. Recently, some translucent zirconia has been developed to gain the esthetic improvement with lower mechanical properties. Dental prosthesis is regularly exposed to moisture with alternating pH and temperature. Chevalier reported that the result from aging of zirconia in autoclave in 1 hour at 134ºC under 2 bar pressure was in resemblances of phase transformations equivalent to those occurred in oral cavity within the period of three to four years [11]. Clinical studies concerning the longevity of zirconia restoration rarely reported fracture of zirconia framework of posterior fixed partial denture for at least 5 years [12, 13].

X-ray diffraction (XRD) is a nondestructive, quantitative assessment of the transformation kinetics of zirconia. XRD analysis is conventionally used to examine the surface phase transformation by measuring the phase fraction evolution by diffraction of the x-ray beam [14]. The XRD measurements characterize the whole sample behavior. In the event of using XRD with fixed incidence angle to assess the information, the volume of zirconia polycrystalline is influenced by the incidence angles of x-ray beam which small incidence angles give information at the near-surface, whereas high angles can investigate more in-depth information. This technique can be used as the first step to investigate the aging sensitivity of zirconia [8]. The monoclinic-to-tetragonal (m/t) peak intensity ratio was used to calculate the monoclinic phase fraction using the well-known Garvie and Nicholson method [15] and Toraya equation [16]. The Rietveld refinement technique described by Hugo Rietveld is also used to analyze the phase identifications (crystalline and amorphous), crystal structure determination, crystal structure refinements, quantitative phase analysis, microstructural analyses, texture analysis, residual stress analysis and thin films [17].

Several studies have used x-ray diffraction techniques for quantitative analysis of monoclinic phase as the predictor to the presence of aging [7, 11, 15, 18-22]. The effect of phase transformation on the mechanical property of zirconia ceramics was also investigated. Flinn et al stated that the autoclaving for 200 h at 134ºC under 2 bar could decrease the flexural strength [19]. Kim proposed that the flexural strength began to decrease when monoclinic phase fraction was about 12-75% [23]. Conversely, De Zouza et al reported that the flexural strength test was not sensitive enough to detect the change in mechanical properties of initial aged Y-TZP [24]. Borchers et al indicated no significant influence of any aging treatment on biaxial flexural strength of 3Y-TZP ceramics, although significant amounts of monoclinic phase were presented [25]. Eleni and co-worker described that a slight increase in monoclinic phase fraction after aging for 5 h would increase the flexural strength slightly and decrease after aging for 10 h [20]. However, some studies concluded that flexural strength of Y-TZP depended on brand, aging protocol and different composition such as yttria content [26, 27]. The aims of this study were to evaluate the effect of autoclaving times on the phase transformation and flexural strength of conventional and translucent yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) ceramics.

Materials and Methods

I. Specimen preparation

Two commercially available yttria-stabilized tetragonal zirconia (Y-TZP) materials were selected in this study. Their compositions and manufacturers are presented in Table 1. Bar-shaped specimens of each material were prepared according to the recommendations by the manufacturers and the guidelines described in ISO 6872: 2015-Dentistry-ceramic materials.

Six bar-shape specimens of each group (2 mm x 5 mm x 27 mm) were cut from a zirconia disc using a low-speed cutting machine and diamond-coated disk (Isomet®, BUEHLER®, Illinois, USA) under water lubrication. They were wet-polished with 600,800, 1000, 1500 and 2000 grit silicon carbide (SiC) abrasive papers subsequence. The four sharp edges of these specimens were removed at 45° angle to the length with a 600-grit SiC paper. After polishing, these bars were sintered to their final density according to the manufacturers' instruction. The final dimensions of all ceramic specimens were 1.5 mm x 4 mm x 22 mm.

II. Aging procedure

The zirconia specimens were artificially aged using an autoclave machine at 134°C and 2 bar pressure (n=6) for 0, 1, and 2 hours. After autoclaving, the tetragonal-to-monoclinic phase transformation was determined by an x-ray diffractometer (Bruker D8 advance, city, Germany). The data were collected in the 2θrange of 20 to 80 degrees, step size 0.01 degree/step, at 40 mA, and 40 kV. Three specimens from each group were used for an x-ray diffraction analysis (XRD). The monoclinic phase fraction was determined from XRD data using the Match phase identification software version 3.3 (Crystal Impact, Bonn, Germany) and Rietveld refinement method.

III.Flexural strength test

The flexural strength of all specimens was measured using a 4-point bending flexure set up with a universal testing machine (Instron 8872, Instron, MA, USA). The specimen was placed centrally on the bearers (10 mm inner span, 20 mm outer span)) of the test fixture. The load was applied on the specimen at the cross speed of 0.5 mm/min. The loads required to break the test specimens were recorded. flexural strength was calculated according to the following equation;

$$\sigma = 3PL/4wt^2$$

when σ = maximum flexural strength (MPa), P = maximum fracture load exerted on a specimen, L = distance between two support (mm), t = thickness or height of the specimen (mm), w = width of specimen (mm)

The statistical analysis of the strength data was performed using two-way ANOVA at a significance level of .05.

The fractured specimens obtaining from the 4-point bending test were used for a scanning electron microscope observation. The representative specimens from each group were cleaned in ultrasonic cleanser with absolute ethanol for 10 min, air-blow dried and coated with gold in a sputter coater (PolaronSC7620, Quorum Technologies Ltd, East Sussex, UK). These specimens were examined using a scanning electron microscope (JSM-6610LV, JEOL USA Co. Ltd, Massachusetts, USA).

Table 1 Zirconia-based ceramics used in this study

Manufacturer	Product	Composition	
Amann Girrach®	Ceramill ZI (Conventional)	ZrO_2+HfO_2+Y_2O_3	≥ 99.0%
		Y_2O_3	4.5-5.6%*
		Al_2O_3	≤ 0.5%
		Other oxides (except Er_2O_3)	≤ 0.5%
	Ceramill zolid FX ML (Translucent)	ZrO_2+HfO_2+Y_2O_3	≥ 99.0%
		Y_2O_3	8.5-9.5%*
		Al_2O_3	≤ 0.5%
		Other oxides (except Er_2O_3)	≤ 0.1%

Results

The results from XRD observed on Ceramill ZI group showed that the monoclinic phase increased from 0.1 to 4.5 and 4.8 % with an increase in the autoclaving time from 0 to 1 and 2 h, respectively. For Ceramill zolid FX, an increase in monoclinic phase fraction was minor, ranging between 0.8 (control) to 1.7 % after autoclaving for 1 and 2 h. Before autoclaving, all Y-TZP zirconia materials had very small amount of monoclinic phase. The autoclaving appeared to have very little effect on the T-M transformation of Ceramill zolid FX.

The mean flexural strengths with standard deviations of two dental ceramics are shown in the Table 2. The results from the Shapiro-Wilk test showed that the flexural strength values of Ceramill ZI and Ceramill zolid FX were normally distributed ($p>0.05$). The homogeneity of variances was tested using Levene's test. The results from two-way ANOVA showed that only the type of material had an effect on the flexural strength of zirconia-based materials used in this study. The flexural strengths of each material were not significantly different at all autoclaving times. However, the flexural strength of Ceramill zolid FX was significantly lower than that of the Ceramill ZI at all autoclaving times.

The representative SEM images of zirconia-based materials used in this study are shown in Fig.1. For non-autoclaving groups, the grain size of all zirconia-based materials ranged within submicron scales with some in a micron level. Ceramill ZI seemed to have smaller grain sizes when compared with Ceramill zolid FX. For non-autoclaving groups, the zirconia grains were clearly observed. After autoclaving for 2 hours, there were some deposits as a result of autoclaving procedure observed on the surface of all specimens. There was no significant change in the microstructure of these zirconia materials.

Table 2 The flexural strength of zirconia material at 1 and 2 hours of autoclaving

Materials	Strength (MPa)		
	Control	1 hr	2 hrs
Ceramill ZI	1107.0±57.0 ^{A}	1035.7±164.2 ^{A}	987.5±206.2 ^{A}
Ceramill zolid FX	686.1±67.1 ^{B}	638.0±36.1 ^{B}	573.1±35.6 ^{B}

*Mean pairs with different superscripts represent statistically different.

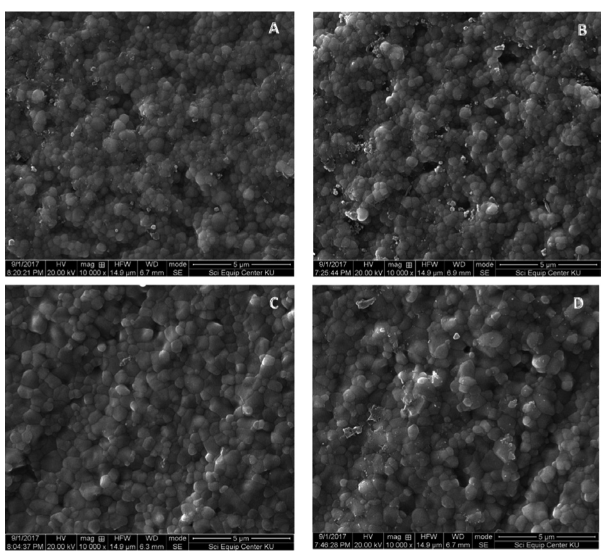

Figure 1 The SEM images of zirconia-based materials used in this study: A) Ceramill ZI control, B) Ceramill ZI after autoclaving for 2 h, C) Ceramill zolid FX control, and D) Ceramill zolid FX after autoclaving for 2 h

Discussion

Low temperature degradation (LTD) of Y-TZP zirconia caused from tetragonal-to-monoclinic phase transformation which acted by nucleated-and-growth process starting from the surface into the bulk material [11]. It has been suggested that hydrothermal and mechanical exposure could induce unexpected phase transformation [18]. Y-TZP materials that experienced the LTD exhibited inferior mechanical properties and alternation of microstructure [23, 28, 29].

A previous study reported that an occurrence of LTD was time–dependent phenomenon [11]. The higher duration of aging time, the higher tetragonal-to monoclinic phase transformation rate [23]. Chevalier proposed that autoclaving for 1 hour at 134°C under 2 bar pressure of zirconia was equivalent to an exposure in oral cavity within the period of three to four years [11]. Accordingly, the standard ISO 13356;2015 defines 5 hours in an autoclave at 134°C at 0.2 MPa is similar to 5 - 20 years of exposure at body temperature [30].

From the results of this study, phase transformation and flexural strength were influenced by hydrothermal aging. The monoclinic phase increased from 0.1% to 4.8 % for Ceramill ZI after aging for 2 h. For Ceramill zolid FX, the autoclaving for 2 h appeared to have insignificant phase transformation effect. According to a previous study, three main factors that influenced LTD included type and amount of stabilizing agents, residual stress in material structure, and grain size [29]. Ceramill ZI showed gradually occurrence of monoclinic conversion. The average grain size of Ceramill ZI was small (0.4 μm). According to Lu and his co-worker, increasing grain size, tetragonal to monoclinic phase transformation would increase [31].

For Ceramill zolid FX, however, the grain size was not the reason for lower monoclinic phase fraction [19]. One possible reason in this case could be the variation in yttria stabilizer content. According to the manufacturers' instructions, Ceramill zolid FX had 8.5-9.5 % of Y_2O_3 which was higher than Ceramill ZI. It was reported that the yttria content higher than 8% displayed as a stabilizer for the cubic phase, which was a more translucent phase than tetragonal [6]. Interestingly, the cubic phase would not undergo the martensitic phase transformation. Hence, the monoclinic phase of Ceramill zolid FX barely increased under aging condition [32].

Besides the crystal microstructure, the alteration in macro-mechanical property was also evaluated. There were few studies reported the effect of LTD-induced phase conversion on the flexural strength [19, 23]. In this work, the flexural strengths of all 3Y-TZP materials without aging were similar to that claimed by the manufacturer. Nevertheless, no significant reduction in the flexural strength of the materials was reported after aging. This evidence was inconsistent to some previous reports. In those studies, long period (50 to 200 hours) of hydrothermal aging was made [28]. With those extreme aging condition, significant deterioration of the flexural strength could be expected.

In this study, short or initial period of aging condition was performed. Thus, the flexural strength might not be decreased within this time frame. Recently, there have been some reports about the effect of short aging period on the flexural strength of 3Y-TZP materials [20]. This study did not show a decrease in the flexural strength. Additionally, the flexural strength of the materials slightly increased during this initial period. This could be explained by the local compressive model during initial aging state. With minimal phase transformation, the alteration in microstructure would be limited superficially. The volumetric expansion can cause compressive stress that resist the crack or flaw initiation [20].

This proposed mechanism also supported the evidence that Ceramill system did not show an increase in the flexural strength under aging condition due to less monoclinic conversion.

In this study, the T-M transformation caused from a hydrothermal process was conducted to examine the transformation behavior of conventional and translucent zirconia-based dental ceramics. An increase in monoclinic fraction was observed after 1-2 hours for a conventional Ceramill ZI with no significant change in its flexural strength. The translucent Ceramill zolid FX appeared to be more resistant to phase transformation than a conventional Ceramill ZI ceramic.

Conclusions

The amount of tetragonal to monoclinic phase transformation and flexural strength of zirconia-based dental ceramics used in this study were influenced by the hydrothermal aging with varied effect.

Ceramill zolid FX translucent zirconia material exhibited lower amount of t-m phase transformation and lower *fl*exural strength values than Ceramill ZI dental ceramics.

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