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# A comparative study on biaxial flexural strength and Vicker`s microhardness of different zirconia materials: Effect of glazing and thermal cycling

Estudo comparativo da resistência à flexão biaxial e microdureza Vicker`s em diferentes materiais à base de zircônia: Efeito do glazeamento e da ciclagem térmica

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## ABSTRACT

**Objective:** This study evaluated the effect of glazing and thermal cycling on biaxial flexural strength and Vickers hardness of different zirconia framework materials. **Material and Methods:** Disc shaped zirconia specimens (15 mm x 1.15 mm) were fabricated using three systems (ZirkonZahn, Cercon, Ceramill) according to each manufacturer`s instructions. The specimens of each system were randomly divided into 2 groups. While half of the specimens were glazed, the other half was left unglazed. Each group was further divided into 4 subgroups to be subjected to thermal cycling (0-control, 1000, 3000, 5000 cycles, 5-55 ºC). Biaxial flexural strength was tested in a universal testing machine (1 mm/min). Unglazed zirconia specimens were subjected to Vickers microhardness with and without thermal cycling (0-control, 1000, 3000, 5000 cycles, 5-55 ºC). Data were statistically analyzed using one-way ANOVA, two-way ANOVA and Tukey's test ($p < 0.05$). **Results:** In non-aged conditions (1104-1388 MPa), glazing significantly decreased the biaxial flexural strength of all zirconia ceramics (845.65-897.35 MPa) ($p = 0.000$). While in the non-glazed groups, all thermal cycling regimens significantly decreased the biaxial flexural strength (864 -1156 MPa) ($p = 0.000$), in glazed groups thermal cycling did not affect the results (829.4-854.9 MPa) ($p = 0.405$). Compared to the non-aged group (1414.1 VHN), thermal cycling decreased the Vickers hardness significantly only for Cercon (1365.9 VHN) ($p = 0.005$). **Conclusion:** Glazing decreased the biaxial flexural strength of the zirconia ceramics tested. Unglazed

## RESUMO

**Objetivo:** Este estudo avaliou o efeito do glazeamento e da ciclagem térmica na resistência à flexão biaxial e na dureza Vicker's de diferentes materiais à base de zircônia. **Material e Métodos:** Espécimes de disco (15 mm x 1,15 mm) de zircônia foram confeccionados usando 3 sistemas (ZirkonZahn, Cercon, Ceramill) de acordo com a recomendação de cada fabricante. Os espécimes de cada sistema cerâmico foram randomicamente divididos em 2 grupos. Enquanto metade dos espécimes foram glazeados, a outra metade permaneceu não glazeado. Adicionalmente, cada grupo foi divido em 4 subgrupos submetidos a diferentes ciclagens térmicas (0-control, 1000, 3000, 5000 ciclos, 5-55 ºC). A resistência à flexão biaxial foi realizada em uma máquina de teste universal (1 mm/min). As amostras não glazeadas foram submetidas a microdureza Vicker's antes e após a ciclagem térmica (0-control, 1000, 3000, 5000 cycles, 5-55 ºC). Os dados foram estatisticamente analisados usando ANOVA 1-fator, ANOVA 2-fatores e teste de Tukey's ($p < 0,05$). **Resultados:** Nas amostras não cicladas (1104-1388 MPa), o glazeamento reduziu significativamente a resistência à flexão biaxial de todos os sistemas cerâmicos (845.65-897.35 MPa) ($p = 0,000$). Enquanto nos grupos não glazeados todas as modalidades de ciclagem térmica reduziram significantemente a resistência à flexão biaxial (864-1156 MPa) ($p = 0,000$), nos grupos glazeados a ciclagem térmica não afetou os resultados (829.4-854.9 MPa) ($p = 0,405$). Comparados aos grupos não envelhecidos (1414.1 VHN), a ciclagem térmica reduziu significantemente a dureza Vickers apenas para o Cercon (1365.9 VHN) ($p = 0,005$). **Conclusão:** O glazeamento reduz a resistência à flexão biaxial

zirconia ceramics were weaker against thermal cycling compared to glazed ones. For the long-term durability of monolithic zirconia reconstructions, this information may have clinical significance.

## KEYWORDS

Biaxial flexural strength; Glazing; Thermal cycling; Vickers microhardness; Zirconia.

dos sistemas à base de zircônia testados. As amostras não glazeadas foram mais afetadas pela ciclagem que as amostras glazeadas. Estas informações podem ter relevância clínica na durabilidade de reconstruções em zircônia monolítica.

## PALAVRAS-CHAVE

Resistência à flexão biaxial; Vitrificação; Ciclagem térmica; Microdureza Vickers; Zirconia.

## INTRODUCTION

With the increasing aesthetic demands of the patients, all-ceramic materials are increasingly used in dentistry for fixed dental prosthesis (FDP). Among different options, zirconia presents the best mechanical properties compared to other oxide ceramics. Zirconia is a polymorphic material with 3 allotropes. Pure zirconia is monoclinic at room temperature and this phase is stable up to 1170 ºC. Above this temperature, it transforms into the tetragonal phase which is stable up to 2370 ºC. The cubic phase on the other hand is stable up to 2680 ºC. Due to 'transformation toughening' property that increases the resistance to crack growth, zirconia has a high initial strength and fracture toughness.[1,2] As a result of transformation, the metastable tetragonal particles transform into monoclinic ones, their volume increases and consequently, compressive stresses develop on the zirconia surface.[2] Because of this metastability, zirconia is subjected to aging in the presence of water.[3,4] This phenomenon, the so called low temperature degradation (LTD), was first described by Kobayashi and Masaki.[3,4] LTD of zirconia causes micro and macro cracks within the material that yields to the degradation and eventually decreases in the mechanical properties.[4-6] LTD occurs as a function of time and more rapidly at temperatures between 65 ºC and 500 ºC with a peak rate at approximately 250 ºC.[3,5] LTD in the presence of water is explained in two ways: Firstly, as a result of the reaction with water ($H_2O$) and Zr-O-Zr bonds on the surface, Zr-OH bond is formed. This causes strain energy to accumulate, yielding to t→m phase transformation. Secondly, as a result of the reaction between $H_2O$ and yttria ($Y_2O_3$), $Y(OH)_3$ forms. Eventually, stabilizing oxides decrease and t→m phase transformation occurs.[3,7]

The temperature change in the oral cavity is expected to range between 4.5 ºC [8] and 50-55 ºC.[9] Thus, thermal cycling process is typically used to expose the materials to hydrothermal aging that is considered as the worse case scenario. The abrupt change in temperature when specimens are submerged into the water baths creates stresses in the specimens.[10] The number of chewing cycles intraorally is not well known but it is predicted to be 20-50 cycles per day, corresponding to approximately 10000 cycles per year.[11]

When dental restorations are cemented and subjected to the oral cavity, several factors may cause physicochemical changes in dental materials. Repeated chewing forces results in stress concentration, and thermal variations and saliva induce fatigue in the materials that may eventually shorten their clinical longevity.[12] In fact, veneering ceramics and luting cements protect the direct exposure of zirconia framework to the oral environment. Yet, it has been postulated that commonly used luting cements absorb water via dental tubules or from the oral environment in the marginal areas,

exposing the zirconia framework to moisture that may lead to aging over a shorter period of time than anticipated.[13] There are several other scenarios where exposure of zirconia in the oral environment could be expected such as the common clinical problem, chipping of the veneering ceramic from zirconia framework that may also expose zirconia to the oral environment. Occasionally, during occlusal adjustments, zirconia may likewise be exposed to the oral cavity. Recently, in order to eliminate the chipping phenomenon in bilayered zirconia FDPs and also reduce the technician costs, monolithic zirconia materials have been introduced to the dental market. Although optical features are not favourable, they can be used as such where zirconia is completely exposed to the oral cavity. Alternatively, glazing or using ceramic tints could improve optical properties of zirconia. However, the effect of heat treatment on zirconia in the course of veneering and glazing procedures was reported to decrease the fracture resistance of the bilayered complex.[14] To date the effect of glazing without veneering ceramic on the mechanical properties of monolithic zirconia is not studied.

The objectives of this study therefore were to verify the effect of glazing and thermal cycling on biaxial flexural strength and Vicker's hardness of different zirconia framework materials. The null hypothesis tested was that both glazing and thermal cycling would decrease the mechanical properties of zirconia framework materials.

## MATERIAL AND METHODS

The brands, chemical compositions and manufacturers of the materials used in this study are listed in Table 1. Three different zirconia systems indicated for the fabrication of FDPs, namely ZirkonZahn system (Steger, Ahrntal, Italy), Cercon system (DeguDent GmbH, Hanau, Germany) and Ceramill system (Amann Girrbach GmbH, Koblach, Austria) were used for the experiments.

Disc shaped metallic rings (inner diameter: 15 mm; thickness: 2 mm) were used for the fabrication of composite discs. The composite discs were then ground to a thickness of 1.4 mm.

### *Specimen preparation*

Specimens of ZirkonZahn group were produced by means of a copy-milling system using presintered zirconia blanks. Composite models were fixed to the holding plate of the scanning unit. Scanning was performed with the stylus and enlarged by a lever arm system based on the pantographic principle. Presintered zirconia blank was fixed to the holding plate of the milling unit. After obtaining the zirconia specimens, they were sintered at 1500 ºC (Zirkonofen, ZirkonZahn, Steger) according to

**Table 1 -** The brands, chemical composition and manufacturers of the ceramic materials used in this study

| Brand | Chemical Composition | Manufacturer |
|---|---|---|
| ZirkonZahn | $ZrO_2$ (+$HfO_2$) w% main component, $Y_2O_3$ 4.95~5.26 w%, $Al_2O_3$ 0.15~0.35 w%, $SiO_2$ 0.02 w%, $Fe_2O_3$ 0.01 w%, $Na_2O$ 0.04 w% | Steger, Ahrntal, Italy |
| Cercon | $ZrO_2$ (+$HfO_2$) w% main component, $Y_2O_3$ 5 w%, $Al_2O_3$ + $SiO_2$ 1 w%, $HfO_2$ 2 w% | DeguDent GmbH, Hanau, Germany |
| Ceramill | $ZrO_2$ w% main component, $Y_2O_3$ 4-6 w%, $Al_2O_3$ 0-1 w%, $HfO_2$ 1-5 w% | Amann Girrbach GmbH, Koblach, Austria |
| ZirkonZahn Glaze, ZirkonZahn ICE Stain Liquid | 60-70 w% ceramic powder and pigments 30-40 w% Glycol | Steger, Ahrntal, Italy |
| Ceramco PFZ Overglaze, Ceramco PFZ Stain & Glaze Liquid | 60-70 w% ceramic powder and pigments 99 w% Propylene glycol | Dentsply, York, PA, USA |

the manufacturer`s recommendations. Then, the zirconia specimens were initially wet ground with 60 grit silicone carbide papers to a thickness of 1.15 (± 0.02) mm and wet polished with 600, 800, 1200 grit silicone carbide papers in sequence each for 15 s at 300 rpm using a polishing machine (Phoenix Beta Grinder/ Polisher, Buehler, Lake Bluff, IL, USA).

For specimens of Cercon system, composite discs were fixed to the holding plate of the scanning unit (Cercon Brain Unit, DeguDent GmbH, Hanau, Germany) and were scanned by a non-contact laser scanner. The conversion of the data for milling process was achieved using the corresponding software. The milling process started automatically when the presintered Cercon blank was fixed to the holding plate of the milling unit. The zirconia specimens were then sintered at 1350 ºC (Cercon furnace, Degudent GmbH) according to the manufacturer`s recommendations. Then the specimens were wet ground with 60 grit silicone carbide papers to a thickness of 1.15 (± 0.02) mm and wet polished with 600, 800, 1200 grit silicone carbide papers in sequence each for 15 s at 300 rpm using a polishing machine (Phoenix Beta Grinder/ Polisher, Buehler).

The specimens of Ceramill system (AmannGirrbach GmbH) were produced similar to ZirkonZahn by a copy-milling system using presintered zirconia blanks. Composite models were duplicated by Ceramill Gel model acrylic (Amann Girrbach GmbH) that were then fixed in the holding plate of the scanning unit and presintered zirconia blank was fixed in the holding frame of the milling unit. The zirconia specimens were sintered at 1450 ºC (Ceramill Therm, AmannGirrbach AG, Koblach, Austria) according to the manufacturer`s recommendations. The specimens were wet ground with 60 grit silicone carbide papers to a thickness of 1.15 (± 0.02) mm and wet polished with 600, 800, 1200 grit silicone carbide papers in sequence each for 15 s at 300 rpm using a polishing machine (Phoenix Beta Grinder/ Polisher, Buehler).

For biaxial flexural strength test from 3 zirconia systems 120 specimens were made (n = 40 per material). Half of them were glazed (n = 60, n = 20 per material) and the other half left unglazed (n = 60, n = 20 per material).

To study the effect of thermal cycling on the biaxial flexural strength, from 3 zirconia systems 120 specimens were made and each group was further divided into 4 subgroups to be subjected to thermal cycling (0-control, 1000, 3000, 5000 cycles at 5-55 ºC) (n = 10 per group).

To study the effect of thermal cycling on the Vickers hardness of unglazed zirconia, from 3 zirconia systems 60 specimens were made and each group was further divided into 4 subgroups to be subjected to thermal cycling (0-control, 1000, 3000, 5000 cycles at 5-55 ºC) (n = 5 per group).

***Glazing***

The glaze ceramics recommended by each manufacturer was used to glaze the zirconia specimens. For ZirkonZahn and Ceramill zirconia, ZirkonZahn Glaze and ZirkonZahn ICE Stain Liquid (ZirkonZahn, Steger, Ahrntal, Italy), and for Cercon zirconia Ceramco PFZ Overglaze, Ceramco PFZ Stain&Glaze Liquid (Dentsply, York, PA, USA) was used as glaze ceramics. The glaze powder was mixed with their corresponding glaze liquids strictly obeying the mixing procedures and applied to the surfaces of the zirconia specimens to create a glaze layer of approximately 0.1 mm thick by one experienced dental technician. All glazed specimens were sintered at the stated firing temperatures according to the manufacturer's instructions (Table 2).

**Table 2 -** Firing procedures of the glaze ceramics

| Brand | Idle (°C) | Dry (s) | Highest Temperature (°C) | Holding time | Heat Rate (°C/min) | Vacuum |
|---|---|---|---|---|---|---|
| ZirkonZahn Ceramill | 350 | 5 | 820 | 2 min | 55 | + |
| Cercon | 450 | 5 | 850 | 30 s | 60 | - |

***Thermal cycling***

While one group of all systems were considered as control groups and not aged, the other groups were subjected to thermal cycling. Thermal cycling was performed for 1000, 3000 and 5000 cycles between 5 and 55 ºC in distilled water (Salubristechnica, Salubris A.S., Istanbul, Turkey). The dwelling time at each bath was 30 s and the transfer time from one bath to the other was 2 s. After thermal cycling, the specimens were subjected to biaxial flexural strength test.

***Biaxial flexural test***

The biaxial flexural tests were performed in a universal testing machine (Instron, 3345, Instron Corp., Norwood, MA, USA) (1 mm/min) according to ISO 6872 [15] using Equations 1, 2 and 3:

$$S=-0.2387P(X-Y)/d^2 \quad \text{(Eq. 1)}$$

where 'S' was the maximum tensile stress (MPa), 'P' the total load causing fracture (N);

$$X=(1+\nu)In(r2/r3)2+[(1-\nu)/2](r2/r3)2 \quad \text{(Eq. 2)}$$

$$Y=(1+\nu)[1+In(r1/r3)2]+(1-\nu)(r1/r3)2 \quad \text{(Eq. 3)}$$

($\nu$): Poisson ratio was considerd as 0.25 [15];

r1: radius of support circle (mm);

r2: radius of loaded area (mm);

r3: radius of the specimen (mm);

d: specimen thickness at fracture origin (mm).

***Vickers microhardness test***

Unglazed zirconia specimens were made and tested for Vickers microhardness (VHN) measurements with and without thermal cycling (0-control, 1000, 3000, 5000 cycles, 5-55 ºC).

The hardness measurements were carried out employing Vickers hardness test (Indentamet™1100, Buehler) according to ASTM standards.[16]

Vickers hardness (HV) values were calculated using Equation 4 where "P" was the applied load (N) and "d" was the mean of the diagonal length (m) and α the angle between the opposite faces of the indenter:

$$H_V = \frac{a \cdot P}{d^2} \quad \text{(Eq. 4)}$$

Each specimen was subjected to 3 indentations that were performed under a load of 1 kg (9.8 N) at a velocity of 0.015-0.070 mm/s, and the loading time was 15 s.

***Statistical analysis***

Statistical analysis was performed using SPSS Version 15 for Windows (SPSS INC, Chicago, IL, USA). The means of each group were analyzed by two-way analysis of variance (ANOVA), where biaxial flexural strength was the dependent variable and the zirconia systems and glazing as the independent factors. The effect of repeated thermal cycling on the unglazed and glazed specimens was analyzed by two-way analysis of variance (ANOVA) with biaxial flexural strength test as the dependent variable and the zirconia systems, glazing and thermal cycling (experimental conditions) as the independent factors. Multiple comparisons were made using Tukey's adjustment test. The effect of repeated thermal cycling on the Vickers hardness was analyzed by one-way analysis of variance (ANOVA). P values less than 0.05 were considered to be statistically significant in all tests.

## DISCUSSION

While glazing significantly affected the biaxial flexural strength results (p = 0.000), zirconia type did not significantly affect the results (p = 0.088). Interaction terms were significant (p = 0.009) (Table 3a). In non-aged conditions (1104-1388 MPa), glazing significantly decreased the biaxial flexural strength of all zirconia ceramics (846-897 MPa) namely, for ZirkonZahn 39%, Cercon 18.84%, Ceramill 23.46%, respectively compared to non-glazed ones (p = 0.000) (Figure 1).

In the non-glazed groups, all thermal cycling regimens (1000, 3000, 5000 cycles) significantly decreased the biaxial flexural strength (864-1156 MPa) (ZirkonZahn 16.71%, Cercon 21.7%, Ceramill 25.7%) (p = 0.000), in glazed groups thermal cycling did not significantly affect the results (829-855 MPa) (p = 0.405) (Table 3b, Figure 2). In the non-glazed groups, increased number of cycles decreased the results significantly (p=0.000) whereas in the glazed groups, no significant effect was observed between any of the thermal cycle regimen (p = 0.802) (Table 3c, Figure 3). The nature of the failures were brittle.

Compared to the non-aged group (1414 VHN), thermal cycling decreased the Vickers hardness significantly only for Cercon (1366 VHN) (3%) (p = 0.005) (Table 4, Figure 4).

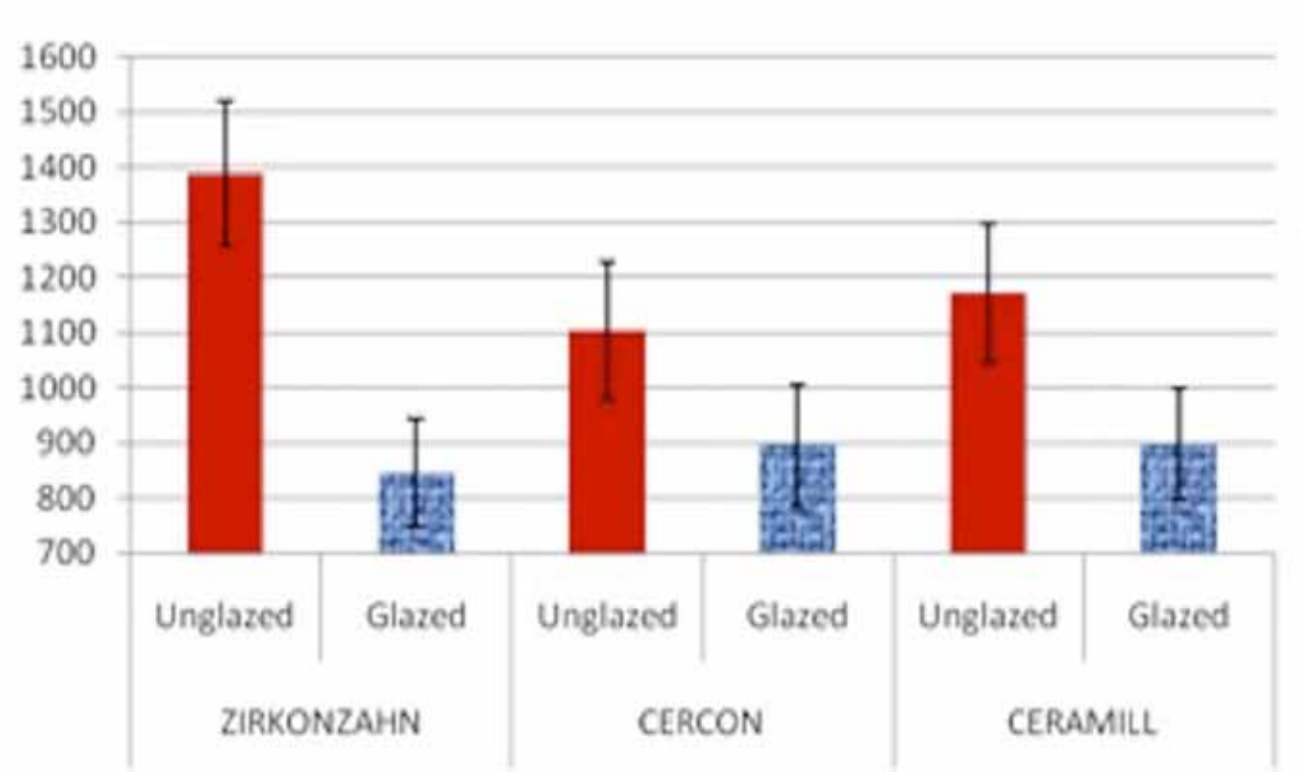


**Figure 1 -** The mean biaxial flexural strength values (MPa) for zirconia systems with and without glazing.

**Table 3a -** Results of two-way analysis of variance (ANOVA) for the effect of glazing of zirconia on the biaxial flexural strength (*p < 0.05)

| Source of variation | Sum of squares | Degree of freedom | Mean ratio square | Probability | |
|---|---|---|---|---|---|
| | | | | F | p |
| Glazing | 875060 | 1 | 875060 | 65.06 | 0.000* |
| Zirconia type | 72422 | 2 | 36211 | 2.69 | 0.088 |
| Zirconia x Glazing | 156847 | 2 | 78424 | 5.83 | 0.009* |
| Error | 322809 | 24 | 13450 | | |
| Total | 1427139 | 29 | | | |

**Table 3b -** Results of two-way analysis of variance (ANOVA) for the effect of thermal cycling of the unglazed zirconia on the biaxial flexural strength (*p < 0.05)

| Source of variation | Sum of squares | Degree of freedom | Mean ratio square | Probability | |
|---|---|---|---|---|---|
| | | | | F | p |
| Zirconia (Unglazed) | 896589 | 2 | 448295 | 31.17 | 0.000* |
| Thermal cycling | 531313 | 3 | 177104 | 12.31 | 0.000* |
| Zirconia x Thermal cycling | 26432 | 6 | 4405 | 0.31 | 0.931 |
| Error | 690401 | 48 | 14383 | | |
| Total | 2144736 | 59 | | | |

**Table 3c -** Results of two-way analysis of variance (ANOVA) for the effect of thermal cycling of the glazed zirconia on the biaxial flexural strength (*p < 0.05)

| Source of variation | Sum of squares | Degree of freedom | Mean ratio square | Probability | |
|---|---|---|---|---|---|
| | | | | F | p |
| Zirconia (Glazed) | 18742 | 2 | 9371.0 | 0.92 | 0.405 |
| Thermal cycling | 10150 | 3 | 3383.4 | 0.33 | 0.802 |
| Zirconia x Thermal cycling | 2045 | 6 | 340.9 | 0.03 | 1.000 |
| Error | 487975 | 48 | 10166.1 | | |
| Total | 518912 | 59 | | | |

**Table 4 -** Mean Vickers hardness (VHN) of unglazed zirconia ceramics after thermal cycling regimens and significant differences between groups (*p < 0.05)

| Experimental condition | ZIRKONZAHN (VHN) | CERCON (VHN) | CERAMILL (VHN) | F | p |
|---|---|---|---|---|---|
| Control | 1378±51 | 1414±27 | 1357±24 | 3.2 | 0.07 |
| 1000 cycles | 1376±50 | 1413±20 | 1358±27 | 3.12 | 0.08 |
| 3000 cycles | 1373±19 | 1388±18 | 1353±26 | 3.48 | 0.06 |
| 5000 cycles | 1368±36 | 1366±14 | 1351±7 | 0.89 | 0.43 |
| F | 0.05 | 6.37 | 0.11 | | |
| p | 0.98 | 0.005 | 0.94 | | |

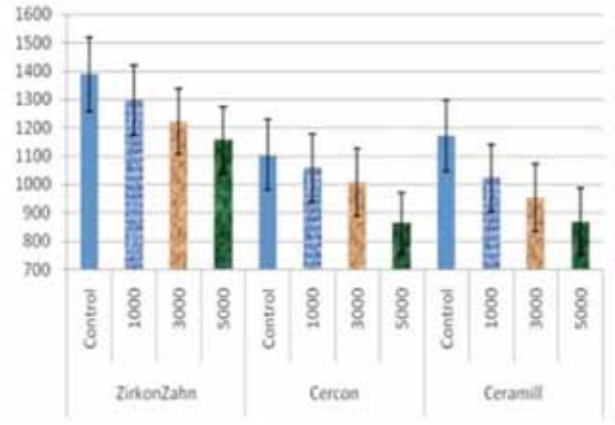


**Figure 2 -** The mean biaxial flexural strength values (MPa) for unglazed zirconia systems without and with thermal cycling.

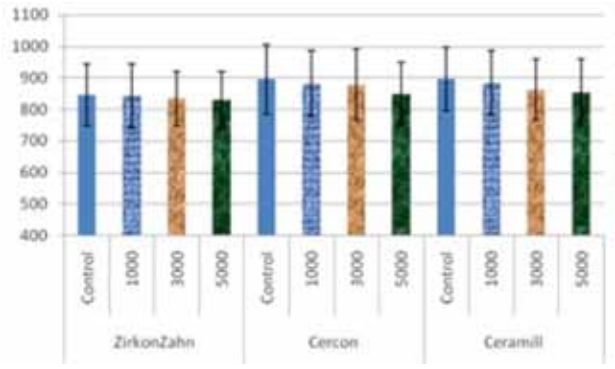


**Figure 3 -** The mean biaxial flexural strength values (MPa) for glazed zirconia systems without and with thermal cycling.

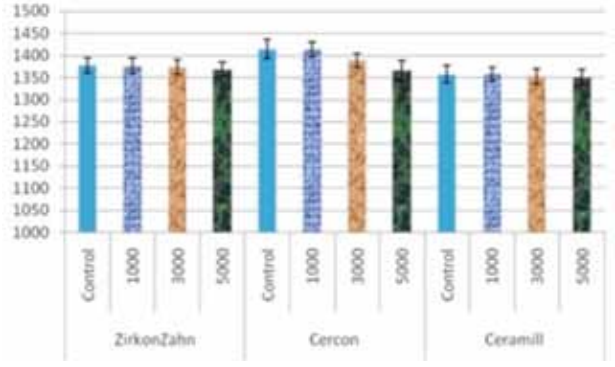


**Figure 4 -** The mean Vickers hardness values (VHN) for unglazed glazed zirconia systems without and with thermal cycling.

## DISCUSSION

The present study was undertaken in order to evaluate the effect of glazing and thermal cycling on the biaxial flexural strength and Vickers hardness of different zirconia ceramics. Based on the results of this study, both glazing and thermal cycling decreased the biaxial flexural strength of zirconia specimens. Thermal cycling caused a significant decrease in the Vickers hardness of Cercon group only. Therefore, the hypothesis was partially accepted.

Due to its low contrast ratio, zirconia frameworks are veneered with veneering ceramic in order to achieve more natural looking FDPs. [17,18] The rough surfaces of zirconia during milling is also smoothed by glazing with which also optimum biocompatibility is obtained. [12,19] In the course of veneering and glazing, the material is subjected to firing. In this study, no veneering ceramic was used and glazing was performed directly on the zirconia framework material. This situation in fact represents the clinical application of monolithic zirconia FDPs.

Previous studies demonstrated decrease in the strength of zirconia after heat treatments. [6,14,20] Some researchers reported that keeping zirconia at 900 ºC for 1 hour or at 900-1000 ºC for 1 min caused reverse transformation (also referred as m→t transformation).[14,20] This phenomenon occurs with the reduction of the compressive stresses on the zirconia surface and the consequent decrease in strength. Hence, the veneer firing induces reverse transformation.[3,20] In other studies, it has been shown that both m and t phases exists before sintering zirconia specimens at 1500 ºC, whereas only t phase was seen after sintering. [3,21] Manufacturing processes may develop compressive stresses on the zirconia surface that may in turn be relieved by heat treatment and veneering. The other possible explanation could be that the change in the particle size during heat treatment or veneering may cause this phenomena.[14] Similarly, in this study, heat treatment during glazing caused significant decrease in the biaxial flexural strength of all zirconia systems (ZirkonZahn, Cercon and Ceramill). The decrease in strength may be due to t→m phase transformation of zirconia when subjected to thermal stresses.

When presintered zirconia is used for dental restorations, it is subjected to final sintering at a temperature of 1350-1550 ºC according to the manufacturers' instructions. As sintering temperature and time increase, the particle size increases.[22] The mechanical properties of zirconia depends on the particle size. There is a critical size, above which the stability of zirconia decreases and becomes more sensitive to t→m transformation. In the presence of smaller particles (<1 $\mu$m), transformation ratio decreases. Moreover, under a specific particle size (~0.2 $\mu$m), transformation is impossible and that reduces the fracture toughness. Finally, because sintering conditions affect the particle size, it affects the stability and the mechanical properties of the final product. Chevalier et al.[22] sintered pure zirconia specimens at 1450 ºC for 2 and 5 h, and at 1550 ºC for 2 and 5 h. They found out that the particle size was very small and homogenous in the specimens sintered at 1450 ºC for 2 h. The particle sizes were larger but homogenous in the specimens sintered at 1450 ºC for 5 h and at 1550 ºC for 2 h where a few big particles (~1 $\mu$m) were observed. In the specimens sintered at 1550 ºC for 5 h, with the 2 $\mu$m particles, the structure was heterogeneous. Ruiz and Readey showed the presence of cubic phase above 1500 ºC.[23] These particles contain more yttria than tetragonal particles [24]. It is reported that while cubic particles include more yttria, the tetragonal particles around them include less yttria where cubic particles pull yttria from the tetragonal particles. Principally, zirconia sintering should be carried out at a temperature low enough to prevent the dual cubic-tetragonal phase formation and high enough to achieve a full density material. This means that a narrow temperature range between 1400-1450 ºC should be chosen. [22] In this study, the highest decrease in the biaxial flexural strength after glazing was in the ZirkonZahn group. A possible explanation could be that the ZirkonZahn specimens were sintered at 1500 ºC whereas the Cercon and the Ceramill specimens were sintered at 1350 ºC and 1450 ºC, respectively.

The tetragonal particles transform into monoclinic ones under external stresses such as grinding and air-borne particle abrasion. Kosmač et al. [25] reported that grinding reduces the monoclinic content of zirconia. The microcracks formed after grinding and milling processes can progress into the material because of the change in the borders of the particles and in the particle size during heating. Heat treatment can alter the shapes of the porosities and facilitate the crack propagation. It is suggested that the transformation capacity that prevents crack formation can be reduced by heat treatment. [6] Grinding with coarse grit abrasives causes a significant decrease in the biaxial flexural strength of zirconia.[26-28] Moreover, many studies have shown that heat treatment after grinding reduced the flexural strength of zirconia.[26,29,30] It is emphasized that heat treatment caused reverse transformation and reduced the m content.[13,30]

The glaze layer of 0.05 mm thickness was reported to be sufficient to prolong its integrity. [31] Therefore, 0.05 mm thickness of glaze was applied to the surface of zirconia specimens. Since glaze layer is applied free hand, the thickness may vary in real-life situations that may consequently change the results. This aspect needs further investigations.

LTD causes t→m phase transformation and volume expansion referred as transformation toughening. The volume expansion caused by transformation toughening, which is initiated by a crack, seals the crack. However, LTD is not desired overall because if transformation occurs in great amounts, the ceramic is degraded and the strength decreases.[32] Since transformation can be induced at body temperature in the presence of water and pressure, phase transformation may occur clinically.[33] The US Food and Drug Administration (FDA) has informed the critical effect of the steam sterilization procedure at 134 ºC (2 bar pressure) on zirconia implants. [34] As a result, this procedure is restricted for zirconia. Earlier studies investigated the effect of low temperature aging (autoclave at 120 ºC

for 15 days, autoclave at 120 ºC for 14 days) on the flexural strength of zirconia and found that the monoclinic content increased dramatically whereas the flexural strength decreased.[3,35] In the present study, thermal cycling caused a statistically significant decrease in the biaxial flexural strength of unglazed ZirkonZahn, Cercon and Ceramill specimens. It could be anticipated that the monoclinic content could have increased after thermal cycling and this may have led to decrease in flexural strength.

Addison et al. reported that thermal cycling reduced the flexural strength of glazed porcelain specimens.[36] In this study, thermal cycling did not create any significant difference in the biaxial flexural strength of the glazed groups. The difference in the results of the studies may be due to the different glazing techniques. In this study, overglazing technique was used. It is shown that the flexural strength of overglazed specimens was higher than the autoglazed ones.[37] This may show that overglazing is more resistant than autoglazing.

In this study, all unglazed zirconia ceramics showed similar Vickers hardness and thermal cycling decreased the hardness values of only Cercon significantly. Controversial reports are present on the microhardness of zirconia in the literature. The difference between reports may be due to the variation in the magnitude of applied loads.[6,28,38,39] As the applied load gradually increases, microhardness decreases.[40] Hjerppe et al. investigated the Vickers hardness of ZirkonZahn specimens after 20000 thermal cycling and reported that thermal cycling did not reduce the microhardness of zirconia specimens.[41] Similarly, Roy et al., reported that there was no decrease in the microhardness of explanted zirconia hip joints after 6 years.[42] In another study, aging zirconia specimens at 134 ºC for 49 h caused an increase in m content and surface roughness and caused a decrease in the Vickers hardness.[7] Curtis et al. observed no significant change in Vickers hardness of Lava specimens after aging in water at 37 °C for 24 h.[28] The microhardness of thermal cycled zirconia specimens is expected to decrease due to microcracks developed by phase transformation and LTD.[43,44] In this study, the decrease in the microhardness of Cercon specimens after 5000 thermal cycling may be due to phase transformation and low temperature degradation.

Microcracks that occur during grinding and polishing and manufacturing processes may lead to internal stresses at a depth of 20 $\mu$m.[45] The grinding and polishing procedures applied could also in part have affected the flexural strength. Also, during glazing, the specimens are subjected to moisture, which might have affected the flexural strength.[14] The reduction in the mechanical properties after glazing and thermal cycling may be due to moisture, aging conditions and a combination of manufacturing, grinding, polishing and heat treatment processes. The testing of the discs by biaxial flexure does not represent a clinically relevant condition since the discs are not supported by simulated dentin or support material. Further investigations should consider these aspects. Clinical relevancy of the glaze firing and 55 ºC of aging in thermal cycling may be of significance in the future for monolithic zirconia systems that require no veneering ceramic.

## CONCLUSIONS

From this study, the following could be concluded:

1. Glazing decreased the biaxial flexural strength of all zirconia materials tested.

2. Thermal cycling decreased the biaxial flexural strength of all unglazed zirconia ceramics but did not decrease the strength in the glazed groups.

3. Unglazed ZirkonZahn presented significantly higher biaxial flexural strength than those of unglazed Cercon and unglazed Ceramill with or without thermal cycling.

4. All unglazed zirconia ceramics showed similar Vickers hardness values with and without thermal cycling, except for Cercon zirconia where thermal cycling significantly decreased the hardness.

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## REFERENCES

1. Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. Biomaterials. 1999;20(1):1-25.
2. Garvie RC, Hannink HR, Pascoe RT. Ceramic Steel? Nature. 258,703-704;1975. doi:10.1038/258703a0 .
3. Ban S. Reliability and properties of core materials for all-ceramic dental restorations. Jpn Dent Sci Rev. 2008;44(1):3-21.
4. Lawson S. Environmental degradation of zirconia ceramics. J Eur Ceram Soc. 1995;15(6):485-502.
5. Haraguchi K, Sugano N, Nishii T, Miki H, Oka K, Yoshikawa H. Phase transformation of a zirconia ceramic head after total hip arthroplasty. J Bone Joint Surg Br. 2001;83(7):996-1000.
6. Oilo M, Gjerdet NR, Tvinnereim HM. The firing procedure influences properties of a zirconia core ceramic. Dent Mater. 2008;24(4):471-5.
7. Roy ME, Whiteside LA, Katerberg BJ, Steiger JA, Nayfeh T. Not all zirconia femoral heads degrade in vivo. Clin Orthop Relat Res. 2007;465:220-6.
8. Palmer DS, Barco MT, Billy EJ. Temperature extremes produced orally by hot and cold liquids. J Prosthet Dent. 1992;67(3):325-7.
9. Plant CG, Jones DW, Darvell BW. The heat evolved and temperatures attained during setting of restorative materials. Br Dent J. 1974;137(6):233-8.
10. Vult von Steyern P, Ebbesson S, Holmgren J, Haag P, Nilner K. Fracture strength of two oxide ceramic crown systems after cyclic pre-loading and thermocycling. J Oral Rehabil. 2006;33(9):682-9.
11. Gale MS, Darvell BW. Thermal cycling procedures for laboratory testing of dental restorations. J Dent. 1999;27(2):89-99.
12. Oyafuso DK, Özcan M, Bottino MA, Itinoche MK. Influence of thermal and mechanical cycling on the flexural strength of ceramics with titanium or gold alloy frameworks. Dent Mater. 2008;24(3):351-6.
13. Kosmač T, Oblak Č, Marion L. The effects of dental grinding and sandblasting on ageing and fatigue behavior of dental zirconia (Y-TZP) ceramics. J Eur Ceram Soc. 2008;28(5):1085-90.
14. Sundh A, Molin M, Sjogren G. Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing. Dent Mater. 2005;21(5):476-82.
15. International Organization For Standardization, ISO 6872. Geneva: ISO, 1998.
16. American Society for Testing and Materials. C1327-03: Standard test method for Vickers Indentation Hardness of Advanced Ceramics. West Conshohocken, PA: ASTM International, 2003.
17. Sundh A, Sjogren G. A comparison of fracture strength of yttrium-oxide- partially-stabilized zirconia ceramic crowns with varying core thickness, shapes and veneer ceramics. J Oral Rehabil. 2004;31(7):682-8.
18. White SN, Miklus VG, McLaren EA, Lang LA, Caputo AA. Flexural strength of a layered zirconia and porcelain dental all-ceramic system. J Prosthet Dent. 2005;94(2):125-31.
19. Raimondo RL Jr, Richardson JT, Wiedner B. Polished versus autoglazed dental porcelain. J Prosthet Dent. 1990;64(5):553-7.
20. Denry I, Kelly JR. State of the art of zirconia for dental applications. Dent Mater. 2008;24(3):299-307.
21. Tsalouchou E, Cattell MJ, Knowles JC, Pittayachawan P, McDonald A. Fatigue and fracture properties of yttria partially stabilized zirconia crown systems. Dent Mater. 2008;24(3):308-18.
22. Chevalier J, Deville S, Munch E, Jullian R, Lair F. Critical effect of cubic phase on aging in 3mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis. Biomaterials. 2004;25(24):5539-45.
23. Ruiz L, Readey M. Effect of heat treatment on grain size, phase assemblage, and mechanical properties of 3 mol % Y-TZP. J Am Ceram Soc. 1996;79(9):2331-40.
24. Scott H. Phase relationships in the zirconia-yttria system. J Mater Sci. 1975;10(9):1527-35.
25. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. Dent Mater. 1999;15(6):426-33.
26. Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. Strength and reliability of surface treated Y-TZP dental ceramics. J Biomed Mater Res. 2000;53(4):304-13.
27. Xu HKK, Jahanmir S, Ives LK. . Effect of grinding on strength of tetragonal zirconia and zirconia-toughened alumina. Machining Science and Technology. 1997;1(1):49-66.
28. Curtis AR, Wright AJ, Fleming GJ. The influence of surface modification techniques on the performance of a Y-TZP dental ceramic. J Dent. 2006;34(3):195-206.
29. Ho CJ, Liu HC, Tuan WH. Effect of abrasive grinding on the strength of Y-TZP. J Eur Ceram Soc. 2009;29(12):2665-9.
30. Guazzato M, Quach L, Albakry M, Swain MV. Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic. J Dent. 2005;33(1):9-18.
31. Anusavice K. Dental Ceramics In: KJ A (editor). Phillips' Science of Dental Materials. 11th ed. St. Louis: Saunders; 2003. p. 665-719.
32. Swab J. Low temperature degradation of Y-TZP materials. J Mater Sci. 1991;26(24):6706-14.
33. Kim Y. Comparison of polyethylene wear associated with cobalt-chromium and zirconia heads after total hip replacement. J Bone Joint Surg 2005;87(8):1769-76.
34. Drug AUSFa. Steam Sterilization, IL: FDA, 2003 [cited November 1, 2003]].
35. Ban S NM, Suehiro Y, Nakanishi H. Mechanical properties of zirconia/ alumina nano-composite after soaking in various water based conditions. Key Eng Mater. 2006;309-11:1219-22.

36. Addison O, Fleming GJ, Marquis PM. The effect of thermocycling on the strength of porcelain laminate veneer (PLV) materials. Dent Mater. 2003;19(4):291-7.

37. Brackett SE, Leary JM, Turner KA, Jordan RD. An evaluation of porcelain strength and the effect of surface treatment. J Prosthet Dent. 1989;61(4):446-51.

38. Pittayachawan P, McDonald A, Petrie A, Knowles JC. The biaxial flexural strength and fatigue property of Lava Y-TZP dental ceramic. Dent Mater. 2007;23(8):1018-29.

39. Kanno T, Milleding P, Wennerberg A. Topography, microhardness, and precision of fit on ready-made zirconia abutment before/after sintering process. Clin Implant Dent Relat Res. 2007;9(3):156-65.

40. Quinn G. Hardness testing of ceramics. Adv Mater Proces. 1998;154(2):23-7.

41. Hjerppe J, Vallittu PK, Froberg K, Lassila LV. Effect of sintering time on biaxial strength of zirconium dioxide. Dent Mater. 2009;25(2):166-71.

42. Roy ME, Whiteside LA, Katerberg BJ, Steiger JA. Phase transformation, roughness, and microhardness of artificially aged yttria- and magnesia-stabilized zirconia femoral heads. J Biomed Mater Res A. 2007;83(4):1096-102.

43. Chevalier J, Cales B, Drouin JM. . Low temperature aging of Y-TZP ceramics. J Am Ceram Soc. 1999;82(8):2150-4.

44. Chevalier J. What future for zirconia as a biomaterial? Biomaterials. 2006;27(4):535-43.

45. Shimizu K, Oka M, Kumar P, Kotoura Y, Yamamuro T, Makinouchi K, et al. Time-dependent changes in the mechanical properties of zirconia ceramic. J Biomed Mater Res. 1993;27(6):729-34.

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