Microstructural changes and fracture resistance of nano-crystalline monolithic zirconia restorations upon aging

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Abstract. To assess the effect of nano-modification of two CAD/CAM monolithic Zirconia systems (wet and dry-milled) on microstructural changes and fracture resistance upon aging. Twenty monolithic Zirconia discs (10mm x 1.5mm) were divided into 2 groups (n=10) according to fabrication system; wet-milled (Incoris TZI) and dry-milled (CeramillZolid). Each group was subdivided into two subgroups (n=5), whether subjected to aging or not. Aging procedures included accelerated hydrothermal aging and cyclic loading. Microstructural changes were assessed quantitatively and qualitatively using x-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. Discs were subject to fracture resistance test using universal testing machine. Mean and standard deviations were recorded for phase transformation (t-m) of Zirconia and repeated ANOVA was used to correlate phase transformation with fracture resistance results (p≤0.05). For aged subgroups, XRD analysis revealed significantly higher phase transformation of wet-milled than dry-milled (p≤0.05) and SEM analysis revealed wide zone phase transformation for wet-milled zirconia and minimal zone for dry-milled. For both systems, no significant difference between the mean flexural strength values of non-aged and aged zirconia (p≤0.05). Nanocrystalline microstructure of monolithic zirconia improved its resistance to aging. The fracture resistance of the two systems was not affected by aging.
1. Introduction

Esthetics is becoming a major demand in modern dentistry. The advances in recent dental ceramics are concerned with providing materials with high esthetic parameters, together with function to provide long term success for the restorations [1]. Zirconia is one of the materials has the potential to substitute the metal-ceramic fixed dental prosthesis (FDP) due to their high biocompatibility [2] and similar mechanical properties [3][4] with those of metal-ceramic restorations. The superior mechanical properties are due to the finer grain size and the tetragonal-monoclinic transformation toughening mechanism (t→m) of yttria-stabilized Zirconia (3Y-TZP) which leads to compressive stresses in the material and results in reduced crack propagation [5].

On the other hand, Zirconia shows inferior optical properties than those of natural tooth structure due to its inherent opacity [6]. This opacity required veneering of zirconia with more translucent ceramic to simulate the natural esthetic appearance of the tooth structure. The veneering process had a negative impact on the strength and longevity of the zirconia-based restorations, [7], [8][9]. The oral cavity is an inhospitable environment due to the presence of moisture, temperature and PH fluctuations and biting forces that induce zirconia degradation, hence a→m phase transformation [10][11]. This phenomenon is known as low temperature degradation (LTD) [12]. One of the hypotheses currently most favored is that the filling of oxygen vacancies by “water derived species” (hydroxyl, oxygen, or hydrogen ions) probably leads to accumulation of internal tensile stresses in the grains in contact with water. (t→m) transformation is accompanied by surface uplift of grains and large stresses that can provoke the creation of cracks along the grain boundaries [13][14]. Previous studies [15][16], [17] discussed the relation between (t→m) transformation of zirconia and the reduction of its mechanical properties. Long term exposure to hydrothermal aging, has produced significant reduction in its mechanical parameters, including flexural strength and Young’s modulus of elasticity. CAD/CAM machined Zirconia showed initial high resistance to hydrothermal aging but deteriorated at a faster rate upon prolonged exposure to oral conditions [18][19].

Many studies [20][21][22], [23] clarified the role of nano technology in improving the properties of zirconia, regarding to the optical properties and resistance to aging. Reducing the grain size to nano scale (70 – 82 nm) together with high density and eliminating the internal porosity had been proposed as a solution for enhancement of aging resistance [24][25]. These nanomodifications of Zirconia had led to introduction of monolithic translucent zirconia which in turn overcomes the drawbacks of Zirconia-based systems. By reviewing the literature, the impact of the nanocrystalline microstructure on the fracture and aging resistance of 3Y-TZP requires further investigations. So, the aim of the present study was to assess the effect of nano-modification of two CAD/CAM monolithic Zirconia systems (wet and dry) on microstructural changes and fracture resistance upon aging. The null hypothesis of this study was that nano-modification of two CAD/CAM monolithic Zirconia systems (wet and dry) had no effect on the microstructural changes and the fracture resistance upon aging.

2. Materials and Methods

2.1. Sample grouping

Twenty monolithic Zirconia discs (10 mm diameter x 1.5 mm thickness) were divided into 2 groups (n=10 each) according to the system used for fabrication. Group I, fabricated from wet-milled monolithic nanocrystalline Zirconia system (incoris TZI, Dentsply Sirona, Germany), Group II; fabricated from dry-milled monolithic nanocrystalline Zirconia (CeramillZolid, Ammangirbach, Austria). Each group was further subdivided into 2 subgroups (n=5) a: not subjected to aging and b: subjected to aging.

2.2. Discs Fabrication

For the purpose of standardization of monolithic Zirconia discs, a copper mould was designed with diameter of 10 mm and thickness of 1.5 mm. For the wet-milled monolithic zirconia discs; the mould was scanned by an Intraoral scanner (Omnican, Dentsply Sirona, Germany) and discs were designed using Inlab 3D software (V4.2) (Dentsply Sirona, Germany). Zirconia discs were milled using InLab MCX5 machine (Dentsply Sirona, Benseheim, Germany). Sintering process was carried out for all...
the discs inFire HTC speed(Dentsply Sirona, Germany) following the manufacturer’s recommendations. While for Dry-milled monolithic Zirconia discs, scanning of the mould was carried out with digital optical scanner (Ceramillmap 400, Ammannigirbach, Austria), designing of the disc with CAD software (Ceramillmind, Ammannigirbach, Austria), milling using Ceramill motion (Ammangirbach, Austria) and finally sintering process was carried out in furnace (Ceramiltherm, Ammannigirbach, Austria) following the manufacturer’s recommendations.

2.3. Aging Procedures
Zirconia discs of group Ib and IIb were subjected to 2 types of aging to simulate the conditions existing in the oral cavity (hydrothermal aging and cyclic loading). For hydrothermal aging, discs were placed in a steam autoclave (Hydra, Carlo Di Georgi, Italy) at temperature 121°C and 1 bar pressure for 5 hours to simulate hydrothermal aging for 5 years inside the oral cavity. To simulate cyclic loading, a custom-made machine loading device was designed (figure 1). The machine delivers 1,250,000 cycles at right angle to the discs at frequency of 300 cycle/min using load of 50 N forces[26].

2.4. X-ray diffraction analysis (XRD)
XRD analysis was used to detect the crystalline phases inside the monolithic Zirconia samples. XRD analysis were performed with a powder diffractometer (Xpert pro, PANalytical B.V, Netherlands), using Cr Ka radiation (40 mA, 40 kV), a scan range of 0°–90(2θ), a step size of 0.02 and a scan time per step of 4 s. Zirconia fractions were determined with software support. The percentage of Zirconia transformation (t-m) was calculated using Gravie-Nicholson equation [27].

\[ X_m = \frac{I_m(-1,1,1) + I_m(1,1,1)}{I_m(-1,1,1) + I_m(1,1,1) + I_t(1,0,1)} \]  
where \( X_m \) is the amount of transformed monoclinic phase, \( I_m(-1,1,1) \) is the peak recorded at 2θ angle 28.40°, \( I_m(1,1,1) \) is the peak recorded at 2θ 31.41° and \( I_t(1,0,1) \) is the tetragonal peak recorded at 2θ 30.34°.

2.5. Fracture testing
Discs sample strength was determined using biaxial flexural test in a universal mechanical testing machine (Instron, University Ave, Norwood, USA) at a cross-head speed of 1 mm/min. Custom made sample holder was designed for flexural strength testing (figure 2). Samples were successively placed on the testing platform on the universal testing machine to remain stable during load application and the maximum breaking loads were recorded in Newton (N).

**Figure 1.** Diagram showing custom made cyclic loading machine.: (a) digital panel to control the number of load cycles and load intensity, (b) attachment for cyclic load application, (c) acrylic base to hold the disc, (d) monolithic Zirconia disc and (e) machine platform to hold acrylic base – zirconia disc assembly.

**Figure 2.** Custom made holder for zirconia discs: (a) top view with 3 equidistant stainless-steel balls (b) Zirconia disc (c) Stainless steel balls projecting from the base (d) Stainless steel base of (12 mm in diameter).
2.6. Scanning Electron Microscope Analysis (SEM)

The microstructure of fractured disc fragments (aged and non-aged groups) was assessed using Scanning electron microscope (FEI company, Netherlands) model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V and magnification of 10000x.

2.6. Statistical Analysis

Quantitative data were presented as mean and standard deviation (SD). Data were explored for normality by checking the data distribution, calculating the mean and median values and using Kolmogorov-Smirnov and Shapiro-Wilk tests. Flexural strength data showed parametric distribution. For parametric data; repeated measures Analysis of Variance (ANOVA) was used in testing the effect of milling system, aging and their interactions on mean flexural strength. Turkey’s post-hoc test was used for pair-wise comparison between the groups when ANOVA test is significant. Whereas for the values of XRD measurements, mean and standard deviation (SD). The amount of (t-m) transformation were recorded for aged and non-aged groups. The significance level was set at P ≤ 0.05.

3. Results

3.1. XRD Results
XRD pattern for wet-milled and dry-milled monolithic nanocrystalline Zirconia systems were recorded for non-aged samples (figure 3a and b). Peak for tetragonal Zirconia was recorded at 2Θ angle of 30.3. No peaks for monoclinic Zirconia were recorded at 2Θ angle of 28. The amount of each phase was measured by counts for each phase or element.

In samples subjected to aging, peak for monoclinic Zirconia was recorded at an angle of 28 for both systems (figure 4). The monoclinic peak in case of dry-milled Zirconia was smaller than that of wet-milled Zirconia.

The mean and the standard deviations of the amount of phase transformation (t-m) calculated by Gravie- Nicholson equation shown that wet-milled system showed a statistically significantly higher mean amount of transformation of (t-m) (0.101±0.006) than dry-milled system (0.027±0.005) (figure 5).
Figure 5. Bar chart representing mean values for comparison between amounts of transformation of (t-m) in the aged two milling techniques.

3.2. Fracture Resistance results
Regardless of aging; wet-milled system showed statistically significantly lower mean flexural strength value (1326.4 ± 171.0) than dry-milled system (1949.8 ± 76.4) (figure 6).

Figure 6. Bar chart representing mean values for comparison between wet-milled and dry-milled Zirconia systems

Flexural strength results have shown that, either with wet or dry milling systems, there was no statistically significant difference between the mean flexural strength values of non-aged (wet-milled 1382.1 ± 209.6 N, dry-milled 1946.2 ± 98.9 N) and aged samples (wet-milled 1270.7 ± 118.9 N, dry-milled 1953.4 ± 57.6 N) (figure 7).
3.3. Scanning Electron Microscope (SEM) Analysis
For non-aged samples, the SEM photomicrograph of wet-milled disc (Incoris TZI) showed areas of subsurface porosities, no surface cracks and very narrow zone of transformation below the surface (figure 8a). While, the SEM photomicrograph of dry-milled disc (CeramilZoild) showed homogeneous microstructure, no zone of transformation and/or subsurface porosities (figure 8c). Aged, the SEM photomicrograph of wet-milled disc (Incoris TZI) showed an area of transformation below the surface, subsurface porosities and/or grain pull-out at the surface (figure 8b). While, the SEM photomicrograph of dry-milled disc (CeramilZoild) showed minimal zone of subsurface transformation, no subsurface porosities and/or grain pull-out from the surface (figure 8d).

Figure 7. Bar chart representing mean values for comparison between flexural strength of milling systems for non-aged and aged samples.

Figure 8. SEM photomicrographs of monolithic zirconia systems: a; non-aged wet-milled disc (Incoris TZI). b; aged wet-milled disc (Incoris TZI). c; non-aged dry-milled disc (CeramilZoild). d; aged dry-milled disc (CeramilZoild). P, represents subsurface porosity. T, represents transformation zone (magnification 10000x).
4. Discussion
The nano technological evolution stood behind the development of a new class of nano ceramic materials that has been remarkably and intensively used in dentistry [28,29]. Previous studies [30,31] summarized the benefits connected to the use of nanostructured ceramics with reduced grain size that leads to an improvement of the strength; since finer grain size (≤200nm or ≤0.4 µm) [31,32] leads to stronger materials, while other study Hallman et al. [33] has shown critical grain size of ≤0.36 µm to resist LTD. So, the aim of the present study was to assess the impact of the nano microstructure of two monolithic Zirconia systems (wet and dry-milled) on its aging resistance, (t-m) transformation and finally its flexural strength. The null hypothesis of the study was partially accepted, as the wet milling system induced significant (t-m) phase transformation, yet this transformation of nano crystalline Zirconia was below the level of inducing reduction of flexural strength.
In the present study, accelerated hydrothermal aging was selected and simulated extraorally by subjecting samples to steam autoclaving for 5 hours, as 1 hour of steam autoclaving at 1210C at 1 bar pressure simulates one year of hydrothermal aging in the oral cavity. Cyclic loading mechanical stress in the oral cavity was simulated by custom made machine delivering 1250,000 cycles at frequency of 300 cycle/ min using load of 50 N force. This load was found to simulate 5 years inside the oral cavity [26].
XRD has been chosen as method for the assessment of microstructural changes. XRD has the advantage of revealing the phase’s count of the same element or crystalline structure inside the material based on its volumetric change [34][35]. The same condition which occurs within the structure of Zirconia due to phase transformation of tetragonal to monoclinic phase accompanied by volumetric change of crystal sizes.
In the present study, XRD analysis for non-aged samples of both tested systems didn’t show any peaks of monoclinic phase indicating (t-m) transformation (figure 3 a &b) which appeared as homogeneous microstructure, no zone of transformation and /or subsurface porosities in the SEM photomicrograph of dry milling system CeramillZolid (figure7 c) and very narrow zone of transformation below the surface in the SEM photomicrograph of wet-milled system Incoris TZI (figure 7a). WhileXRD analysis of aged samples showed the appearance of monoclinic peaks in both wet and dry-milled system which appeared as an area of transformation below the surface, subsurface porosities and/or grain pull-out at the surface in the SEM photomicrograph of wet milling system (Incoris TZI) (figure 6 b). While, the SEM photomicrograph of dry milling system (CeramillZolid) showed minimal zone of subsurface transformation, no subsurface porosities and/or grain pull-out from the surface (figure 6d). The results may be attributed to LTD under the effect of moisture of aging procedure. These results were in accordance with many studies [10], [11].They studied the impact of oral conditions on aging resistance of Zirconia. They claimed that phase transformation and appearance of monoclinic phase occurred under the effect of moisture and cyclic loading.
Further description for the role of water in the process of Zirconia degradation has been described in Lange’s thermodynamic model [39]. Where the chemical free energy associated with the transformed particles provoked the creation of cracks along the grain boundaries [13]].
In the present study, the amount of phase transformation of aged two monolithic Zirconia systems (Incoris TZI (0.101±0.006) & CeramillZolid (0.027±0.005)) were less than those of other studies[35-37].They found increased in the amount of phase transformation of monolithic nano-crystalline ultra-transparent Zirconia following aging process. This contrast in the results may be attributed to the difference in the microstructure modification. The presence of cubic phase of ultra-transparent Zirconia was responsible for reduction of its strength and overall aging resistance compared to the tetragonal nano-crystalline tetragonal translucent Zirconia tested in the present study.
The impact of microstructural changes (phase transformation) on the function was assessed by measuring the flexural strength of monolithic Zirconia. Yet non-aged dry-milled system showed significantly higher strength values (1946.2±98.9N) than that of wet-milled system (1382.1±209.6 N).This can be attributed to the effect of water during the milling process as previously discussed.
Aging process didn’t significantly affect the flexural strength of both monolithic Zirconia systems (wet milling 1270.7±118.9N, dry milling 153.4±57.6N). These results may be attributed to the beneficial effect of nano modification of the grain size [31-33], as both Zirconia systems (wet and
dry-milled) have grain size less than 400nm [32,33]. The results of the present study were consistent with those of Zhang et al [40]. They claimed that densification of microstructure enhanced the aging resistance of monolithic Zirconia, as it minimized the effect of moisture on acceleration the aging process overtime. Also, Kim et al. [41] clarified that the flexural strength started to decrease significantly after monoclinic phase reached 12 to 54 %. This explanation was behind the non-significant effect of aging and phase transformation on the flexural strength of both monolithic Zirconia systems.

Limitations of this study were the inability to simulate all the aging conditions in the oral cavity. So, further future studies are required to study the effect of different aging conditions within the oral cavity on the performance of monolithic Zirconia for longer periods of time.

5. Conclusions
Within the limitations of this study, the following can be concluded: 1) Nanocrystalline microstructure of monolithic Zirconia positively improved its resistance to aging. 2) Dry-milled monolithic Zirconia system is more resistant to microstructural changes than wet-milled Zirconia. 3) Microstructural changes of both systems did not negatively affect the fracture resistance.

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