THE EFFECT OF SINTERING PROCESS ON ZIRCONIA'S OPTICAL AND PHYSICAL PROPERTIES

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ABSTRACT

Lida Swann: The effect of sintering process on zirconia's optical and physical properties
(Under the direction of Lyndon F. Cooper)

Zirconia restorations present an alternative dental restorative option with an average flexural strength of 1000 MPA. One of the challenges of this material is the decreased translucency when compared with less strong ceramic materials like feldespatic porcelain or lithium disilicate. A potential solution to this challenge is to the increase of sintering temperature and or increase holding times.

The present study evaluated the effect of different sintering temperatures and holding times on contrast ratio as a measure of translucency, and evaluated if any temperatures or holding times could have a negative effect on materials strength.
We also looked at the effect of cyclic loading vs conventional load to failure testing.

One hundred and twenty (120) milled zirconia disks with .2mm thickness and 14mm diameter were sintered. Temperatures vary in 50-degree increments from 1450 to1600 F. Each of those temperatures was held for different times including 1h, 2h, 3h. The zirconia disks used were pure white Zenostar, 10 disks were obtained to test each variable.

Contrast ration was measured on a spectophotometer for all specimens. 60 specimens (5 per group) were subjected to mechanical cyclic loading under water at a load of 100N for 100,000 cycles at a frequency of 1.5Hz.
After fatigue loading samples and control group were tested on an Instron machine until catastrophic failure occurred.

Under the conditions measured, increasing temperature and / or holding time did not alter translucency or significantly affected physical properties.

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Introduction

Biomaterials in dentistry must address several requirements that include biocompatibility, strength related to intended purpose and esthetics. The history of dental prostheses reflects a progression from function to esthetics with gold restorations being largely replaced by porcelain fused to metal restorations during a period from the 1970's to 1990's. The introduction of various all-ceramic restorations beginning in the 1980's initiated a continuous transition from metal-based ceramics to different multilayered and monolithic all ceramic restorations.

The central issue for all ceramic restorations has been the balancing of esthetics (color and translucency) with strength or function. Different materials have been utilized (Table 1) and their esthetic value traditionally has been inversely related to strength. The basis for this clinical paradox is the use of glass phase ceramics to impart translucency to dental ceramics and the use of relatively opaque crystalline ceramics to achieve strength. Today, lithium disilicate restorations (e.g., IPS e-max Ivoclar Vivadent (175 Pineview Drive, Amherst, NY 14228 USA) exemplifies a glass phase ceramic with remarkable translucency and color adaptability that achieves only 50 % strength represented by traditional porcelain fused to metal restorations. In contrast, contemporary zirconia-based ceramics can achieve nearly 80- 90% strength of traditional porcelain fused to metal restorations, but in its strongest monolithic form offers little translucency.

Table 1- Ceramic restorations in dentistry

CERAMIC RESTORATIONS IN DENTISTRY						
MATERIAL	STRENGHT	TRANSLUCENCY	LAYERED	MONOLITHIC	SINGLE UNITS	MULTI UNITS
FELDESPATHIC Vita Mark	-	+++	yes	Yes	yes	no
LEUCITE REINFORCED IPS Empress	+ / -	+++	yes	Yes	yes	no
LITHIUM DISILICATE IPS e-max	+	++	yes	Yes	yes	+ / -
ALUMINA In-ceram Rondo	+ / -	+ / -	yes	No	yes	+
ZIRCONIA Lava Everest In Ceram Cercon	++	+ / -	yes	Yes	yes	+++

Despite the esthetic limitations of zirconia-based restorations, the dental profession has seen remarkable penetration into clinical practice. A recent survey of dental laboratory owners indicates that all ceramic restorations are largely replacing porcelain fused to metal. The reasons for this replacement of metal and metal ceramic restorations is attributable to several factors including the relative cost of gold alloys, the integration of Zirconia materials into the CAD CAM workflow, and the esthetic value of ‘white’ dental materials. Suggested by this migration of clinical preferences from metal ceramics to all ceramic materials is the satisfactory performance of the all-ceramic material.

The past decade of clinical research has provided some insight regarding the performance of zirconia prostheses. A systematic review by Raigrodski looked at the survival and complications of zirconia FDP. He reported survival rates that ranged from 73.9% to 100% within 12 studies. Five studies reported 100% survival rates during the observations period. One study reported 73.9% survival of frameworks and the rest (6 studies) had survival rates ranging between 88.2% and 96.6%. The common complication reported was chipping and it was suggested that with the development of new layering porcelains better clinical properties would be expected. [2]

In a second report, a 2010 systematic review on the performance of zirconia based fixed dental prosthesis evaluated not only the survival but also the complication rates for this type of prosthesis up to 5 years. Three hundred and ten prosthesis were included. The 5-year survival rate for all FDP was 94.29% and 76.41% were considered free of complications with chipping being the most reported complication [3]. Very rarely, do we seem to see fractures within the zirconia framework itself. For example, the systematic review by Sailer [4], indicated that compared to chipping rates of 13.6%, framework fractures occurred only 6.5 %. Observed fractures were reported most commonly in connectors of multiunit posterior restorations, and, or second molar abutments. Larsson's systematic review in 2014 [5], suggested that the success rate of tooth-supported and implant-supported zirconia-based crowns is adequate, similar, and comparable to that of conventional porcelain-fused-to-metal crowns. A recent laboratory study utilized indentation to induce chipping of monolithic zirconia and lithium disilicate materials. The results confirm that ceramic veneered-zirconia displayed high chipping and monolithic lithium disilicate resisted this chipping, monolithic zirconia was most resistant to this induced chipping behavior [6].

When considering the outcome of zirconia single unit full coverage restorations, less information is available. The earliest clinical efforts of zirconia-based restorations involved the creation of a milled zirconia coping supporting a compatible ceramic veneer. Most recently, a 5 – year cohort study revealed that less than 60% of the crowns demonstrated success at 5 years and 11 of 47 crowns at 5 years required replacement due to chipping. This 2014 paper advised that new materials should be more carefully evaluated before introduction to clinical use. [7]

Previous outcomes for zirconia restorations including crowns have been considered in several systematic reviews. A 5-year retrospective study of survival of zirconia single crowns fitted in a private clinical setting by Anders showed promising results for zirconia single crowns. Most crowns (78%) were placed on premolars and molars. Among the 143 crowns that were followed for 5 years, 88% did not have any complications. The reported complications were: extraction of abutment tooth (7; 3%), loss of retention (15; 7%), need of endodontic treatment (9; 4%) and porcelain veneer fracture (6; 3%). No zirconia cores fractured [8].

Jung's systematic review focused on single crowns. The five to ten year results showed high survival rates for tooth and implant supported single crowns, but technical, biological and aesthetic complications were common. It is possible to suggest that many of the complications were mostly related to restoring implants compared to tooth supported restorations [9].

As revealed in the aforementioned reviews concerning zirconia restoration performance, one of the early and prominent observations made regarding the clinical performance of zirconia-based all ceramic restorations was chipping of the veneering porcelain from the zirconia frameworks. While many different investigators have suggested fundamental reasons for this phenomenon (reviewed below), the clinical response to chipping is a concern for layered zirconia restorations.

When used as a framework, zirconia has an inherent basic esthetic value, due to the fact that it is white and can be alternatively colored to mimic surrounding dentin. Further it can be provided with high opacity to cover discolored teeth and implant components [10]. This can be advantageous to the technician who is trying to conceal a dark underlying tooth structure, a metal post, or the remainder of amalgam restorations left after initial preparation.

Zirconia framework based- restorations, when veneered with an appropriate ceramic layering system designed for zirconia, may result in exceptional aesthetics and can achieve an imperceptible match to the surrounding dentition. The talented technician may develop appropriate color and optical properties of the restoration within the veneering ceramics. However, the past decade of investigation has revealed that chipping within the veneering ceramic or at the framework/veneer interface frustrates higher clinical success and survival of these restorations. Veneer chipping, not framework fracture, appears to be the weak link in zirconia-based restorations.

For traditional porcelain fused to metal restorations, layering porcelains possess a lower coefficient of thermal expansion (CTE) than the metallic substrate. In this manner the veneering porcelain gains strength by compressive loading. Unfortunately, the simple mis-matching of CTEs doesn't work effectively for zirconia-layered restorations. This results in the creation of stress fields throughout the restoration leading to cracking and delamination during the cooling phase of the veneering process. [11]. Fortunately, specific ceramic veneering materials have been developed for application to Zirconia frameworks. Given that veneering materials and framework zirconia CTEs are today well matched, it is unlikely that CTE represents the root cause of veneered zirconia framework chipping.

Laboratory processes can inevitably have an effect on final physical properties of a restoration. Zirconia does possess important physical properties that influence its behavior with respect to veneering with ceramics. For example, it has a relatively high modulus of elasticity that encourages its use in larger prostheses with longer spans. It displays high toughness. Most veneering porcelains have a low fracture toughness Z (K) values (0.7-0.9MPa. m ½) that is about 1/8 of the values for zirconia core ceramics. Zirconia as a crystalline material is a relatively poor conductor of heat and this is in striking contrast to metals traditionally used in dental prostheses and this affects the processing of zirconia based prostheses. Thus the rate of change in temperature may, in addition to differences in CTE, influence the strength of the veneer / framework bond. For example, Belli et al (2013) demonstrated by chewing simulation and compressive loading that attempts to minimize the thermal residual stresses within the veneer (closer CTEs) and application of slow-cooling cycles (< 30oC/minute) delayed the experimental failure of zirconia-veneer crowns. This was more important where larger differences in CTE were displayed. In an interesting and related paper Belli, the fractographic analysis of zirconia –veneered crowns demonstrated failures occurred solely within the veneering porcelains [12]. Others have also reported that a longer the cooling rate after firing will affect negatively bond strength of ceramic veneered restorations [13,14]. The number of firing cycles has also been considered to affect the bond strength, and it has been reported that between 3 and 5 firing cycles would be recommended to obtain a better bonding [15,16]. On the other hand one report argues than more than six firings will reduce bond strength [17].

Additionally, the influence of veneer thickness on residual stresses is another variable that may influence chipping of zirconia-veneer crowns. Mainjot et al (2012) compared 1mm - 3 mm veneers modeled on zirconia disks versus metal disks. They observed that stresses in the surface of metal samples were not influenced by veneer thickness. Zirconia samples exhibited a stress depth profile of larger magnitude and the role of crystalline transformation may contribute to this elevated stress profile. [18].

The surface finish of a zirconia framework could also affect the core- veneer bond strength. Roughening of zirconia by the means of air abrasion could potentially improve bond strength but in the same time it could also make the core more susceptible to fractures. 50 um alumina oxide particles create less severe damage than when 120 particles are used [19].

Finally, the application of wet thick layers of porcelain onto a dried zirconia facilitates the t-m conversion and can create residual stress [20]. This too may result from water-mediated crystalline transformation of the zirconia framework. Contemporary workflow for veneered zirconia restorations include very long drying periods to assure firing occurs in the absence of water. It may be concluded that the process of veneering application has an important role in is the bond between the zirconia surface and the veneering porcelain.

In three different reports, using different systems (lava, DC-Zircon) , zirconia frameworks that were veneered with layering porcelain all developed cracking or crazing over two years of observation, ranging from 80% to 50% loss of material [21,22,23]. These studies may indicate that the observed porcelain fractures were material-system specific. It also indicates that factors such as type of zirconia framework thickness, and framework design, may very well be a cause for ceramic fracture.

1.1 Biocompatibility

Research regarding zirconia as biomaterial was started in the late 60s. Helmer and Driscoll [24], published the first paper 1969. Christel, in 1988, offered the use of zirconia, as an alternative to other materials used at time, to manufacture the ball heads for total hip replacements [25]. Zirconia is still used in this application and other medical prosthetics to this day. Implied was acceptable biocompatibility. Clark showed that zirconia was found to be better than other ceramic biomaterials in use circa 1990, because it possessed higher strength and hardness [4].

Direct assessment of biocompatibility of zirconia has been achieved. In vivo testing in rats (Christel, 1989) showed satisfactory results on the biological reactions of zirconia into muscle and bone. [27] [28]. Earliest studies by Hayashi et al demonstrated biocompatibility of end osseous Zr. In vitro studies of Zr powders also suggested safety using human osteoblast cell culture [29]. This underscores the interest in Zr as a material for dental implants [30]. Other recent studies using gingival epithelial cells reiterate this observation of biocompatibility [31]. The interaction of zirconia with oral soft tissues may be central to the performance of tooth and implant supported restorations [32]. The formation of biofilm on dental prostheses, either natural tooth - or implant – supported is material-related. A recent investigation [33] measured the colonization of dental implant abutments. DNA checkerboard analysis revealed that, compared to Zirconia abutment materials, higher total bacterial counts were greater on cast or machined titanium disks after 24 hours. This confirms the work of Bremer et al who showed that biofilm was lowest and thinnest on zirconia compared to lithium disilicate restorations [34]. The clinical impression that low biofilm formation and limited inflammation at zirconia restorations is supported by such in vitro and in vivo studies. Bacterial adhesion has proven to be slightly better that titanium. Scarano reported a degree of coverage by bacteria of 12.1% for zirconia as compared to 19.3% on titanium [35]. Rimindini confirmed these results with an in vivo study where y-TZP accumulated fewer bacteria than Ti in terms of total numbers of bacteria and presence of potential pathogens such as rods [36]. It may be concluded that zirconia materials offer advantages of biocompatibility for use as endosseous biomaterials and oral biomaterials due, both to its remarkable strength and durability as well as the surface properties of the material.

1.2 Strength

Introduction of zirconia-based ceramics as a restorative dental material has generated much interest in the dental profession. The mechanical properties of zirconia are the highest ever reported for any ceramic used prosthetic dentistry. The strength of zirconia has allowed the incorporation of high-strength all ceramics, into its use for posterior FDP [37]. High-strength, coupled with the possible high aesthetics that zirconia offers, allows the material to become a highly valuable option in our prosthetic armamentarium.

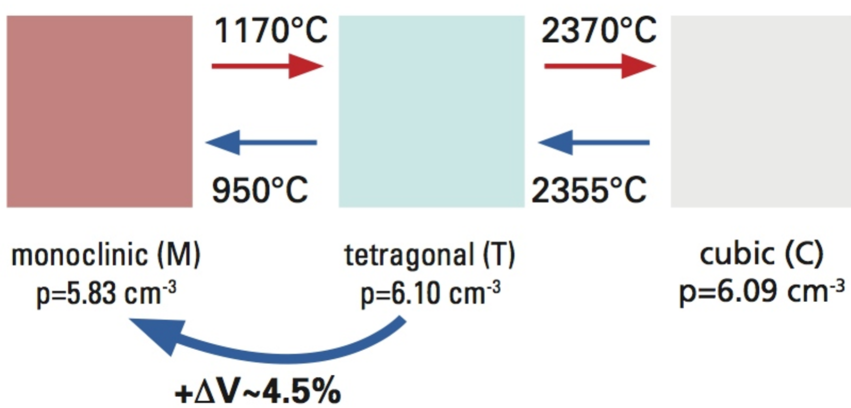
The basis for the valued strength displayed by Zirconia is its unique crystalline structure and its behavior under loads. Zirconium dioxide (ZrO2), also known as zirconia, is a white crystalline oxide of the metal element zirconium. Its most naturally occurring form is the rare mineral baddeleyite though zirconium metal used for dentistry is obtained from the zirconium- containing mineral ore called zircon. After being processed and purified these powders can be further processed to produce somewhat porous bodies that can be CAD/CAM milled with great precision. Once densely sintered, a polycrystalline ceramic material is produced which, unlike most other dental ceramics, contains no glass phase.

Zirconium dioxide (ZrO_2, zirconia) has a unique crystallographic property that greatly improves its strength and toughness. Zirconia crystals can have a monoclinic (M), tetragonal (T) or cubic structure depending on temperature. Figure 1

A crystal structure is the spacing of the atoms of zirconium and oxygen and produces a resulting volume. At high temperatures, zirconia has a cubic structure. As the temperature is lowered, the atoms rearrange themselves and the structure becomes tetragonal. Further cooling results in additional rearrangement into a monoclinic structure. The transformation from tetragonal to monoclinic is accompanied by a volume change. The volume change accompanying the tetragonal to monoclinic transformation is what makes zirconia stronger and tougher than aluminum oxide and therefore, unique as a dental structural material for multiple unit posterior bridges.

Certain oxides, such as magnesium oxide (MgO), yttrium oxide, (Y_2O_3), calcium oxide (CaO), cerium(III) oxide (Ce_2O_3), and others are added to zirconia to stabilize the tetragonal crystal structure at room temperature. The conversion from the tetragonal phase to the monoclinic then occurs when the material is stressed and a crack starts to propagate. However, because of the volume increase accompanying the T to M transformation, the crack is closed until a much higher stress is applied. [62]. When considering yttria – doped zirconia (Y-TZP) ceramics, the flexural resistance has been measured to be from 700 MPa to 1200 MPa. These values exceed typical masticatory loads during chewing. The fracture resistance has been measured to be greater than 2,000N, a value that is two to three times greater than alumina or lithium disilicate materials used in dentistry [38].

Over the last several years, many high strength ceramics have been developed for the construction of metal free restorations [39]. Several studies have evaluated different all ceramic systems, and offered conclusions on where these ceramic systems may be used in the oral environment with success. Luthy, measured average load bearing capacities for several ceramic systems, and found 518 N, for alumina-based restorations, 282 N, for lithium disilicate based restorations, and 755 N, for zirconium restorations [40]. Raigrodski, also analyzed several different all ceramic systems, and concluded that the all ceramic systems he studied, were only to be used in the anterior, for single crown restorations, and possibly three unit FPDs. He also concluded that because of the higher strength of zirconia, this material offers a wider area of restorative options in the oral cavity, including posterior single units, and multiunit FDPs [39].



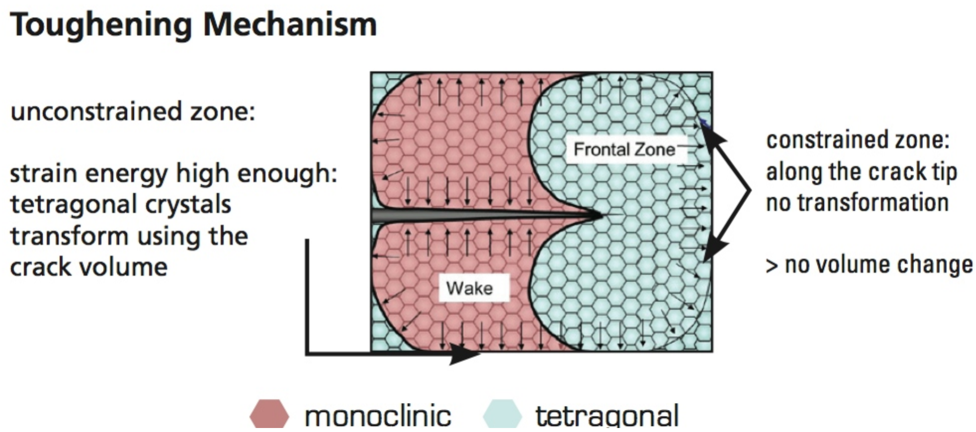


Figure 1- Transformation toughening of zirconia

Biomedical grade zirconia usually contains 3 to 5 mol% yttria ($Y2\ O3$) as a stabilizer (3Y-TZP). The mechanical properties of 3Y-TZP strongly depend on its grain size. Above a critical grain size, 3Y-TZP is less stable and more susceptible to spontaneous t → m transformation whereas smaller grain sizes (<1 um) are associated with a lower transformation rate [41]. Moreover, below a certain grain size (~0.2 um), the transformation is not possible, leading to reduced fracture toughness [42]. Consequently, the sintering conditions have a strong impact on both stability and mechanical properties of the final product as they dictate the grain size Higher sintering temperatures and longer sintering times lead to larger grain sizes [43,44]

Along with learning of the positive attributes possessed by zirconia, there is also a growing realization of process and fabrication challenges when using zirconia to fabricate dental prostheses. Grinding and sandblasting can trigger the (t-m) transformation, possibly leading to the increase of the formation of surface compressive strength stresses, but at the same time, can also alter the phase integrity of the material and increase the susceptibility of aging [45]. When considering bulk zirconia as required for an anatomical, monolithic prosthesis, laboratory manipulation and clinical alterations required following sintering may influence the strength of the material. For example, air abrasion is utilized as a cleaning step during veneering and cementation procedures. Air abrasion was shown to increase the flexural strength of zirconia by T-M phase transformation that places the surface ceramic in compression. Machining with fine diamond instruments (<40 um) provided a similar effect on the compression surface zone, where as large grit instruments (> 125 um) created flaws beyond the depth of the surface zone, thereby weakening the structure [46]. It should be acknowledged that beyond the physical damage, heat induced by grinding might be of the magnitude to induce low temperature degradation of the material that leads to weakness.

Other factor to consider for the long-term success of zirconia-based restorations in multiunit FPD's is the size of the interproximal connectors. The minimal interproximal connector surface should be at least 6.25mm. Also, the height of the terminal abutments, is fundamental to achieving proper interproximal connectors, and should be evaluated with utmost care [37].

Reich looked at the influence of different finish lines and its influence on fracture resistance and found that chamfer finish lines had a higher fracture resistance in comparison to featheredge margins while Clausen found no differences at all. [47,48].

To circumvent the need for veneering altogether, another option is to develop fracture resistant, partially translucent monolithic ceramics. Monolithic all ceramic restorations are becoming more accepted due to higher strength, by avoiding weak veneer-core interfaces. All ceramic restorations, such as, IPS e-max (lithium disilicate), Wieland (zirconia), 3M lava Plus (zirconia), offer several all ceramic monolithic, restorative options, that have acceptable aesthetics, and eliminate the need for veneering ceramics altogether. [41]

1.3 Wear

During the early 2000's zirconia was perceived as a material that would cause high wear to the opposing dentition. Today this perception is being challenged [49] and multiple studies have shown how zirconia can be a material gentle to opposing dentition, in comparison to glass ceramics that are layered on PFM restorations. This low wear property can be attributed to zirconia's microstructure, and it's small grain size, that allows for a mirror polished surface to be created, that is kind to opposing enamel surfaces. [50-51]

An *in vitro* study by Yu-Seok evaluated the wear of enamel opposing zirconia surface. They found that zirconia surfaces appear to be less abrasive to enamel than feldespathic porcelains. They also found that polished zirconia without glazing is less abrasive than Zirconia glazed surfaces. [52]. A second study by Burgess also evaluated the wear of enamel by full contour zirconia polished and glazed. A wear simulator and producing a 4mm slide at 20 N rate was applied and samples evaluated using a non-contact 3D profilometer. Although the wear of glazed zirconia was more than polished zirconia, it was still less than commonly used porcelains for PFM restorations [53]. See figure 2

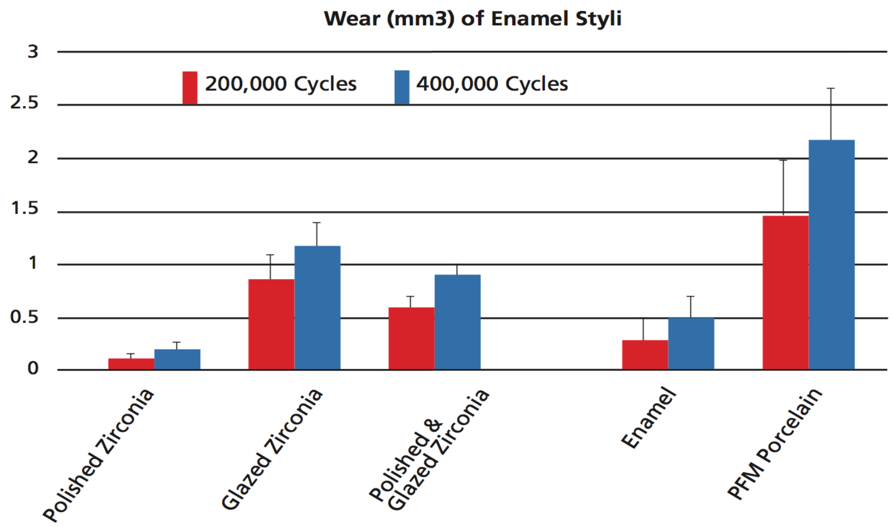


Figure 2- Wear of zirconia vs enamel

These results were further investigated in a six-month clinical study that evaluated the wear on opposing dentition for monolithic full contour zirconia prostheses. 20 monolithic crowns were placed in patients and mean vertical loss for specimens, antagonists and contralateral was recorded. Both mean and maximum enamel wear were significantly different between the antagonists of the zirconia crowns and the contralateral antagonists. Under clinical conditions, monolithic zirconia crowns seem to be associated with more wear of opposed enamel than are natural teeth, but the amount of wear is comparable if not less than other ceramic systems. [54]

1.4 Accuracy

Zirconia is currently utilized in construction of dental prostheses by CAD-CAM milling of partially sintered materials. These materials shrink in dimension with sintering. When utilized as a framework with veneered ceramic, further distortion may occur. However, when compared to the internal fit and marginal adaptation of metal ceramic crowns, there was no difference in the fit of the different restorations. However, prior to veneering, metal copings displayed better internal fit [55]. When extended to larger restorations, the ceramic veneering of CAD/CAM frameworks did lead to distortion as measured by higher strain development using strain gauges. Non-veneered anatomic zirconia restorations showed little distortion and significantly less strain upon measurement [56].

There are many dental CAD_CAM systems offered on the market today, for commercial laboratories. The majority of these Systems, can mill partially sintered zirconia, into a full contour, anatomical tooth shape. Denry and Kelly [37] reported that the milling of partially sintered zirconia offers a final surface virtually free of the monoclinic phase. Even with these observations, damage to the surface of zirconia can be created during the milling process. Several commercially available zirconia's, were evaluated after milling, and specimens showed flakes, debris, and a smear layer, and also observed were micro cracking that penetrated 4-6um into the surface. While the evaluation of post-sintered zirconia following its milling in the pre-sintered state reveals that micro-cracking is evident, it is not clear to what extent this influences the zirconia's physical properties. Several investigations suggest that the use larger grit burs or abrasives can negatively influence the resulting prosthesis. It is not clear what the influence of other milling parameters (rate, speed, tool path) will impose on the ultimate integrity of the surface layer [57].

With regards to marginal integrity several studies have been done and showed that with the aid of new milling systems and in some instances digital impression systems. Seelbach looked at the marginal adaptation of alumina and zirconia restorations various CAD CAM Systems including Lava COS, CEREC and iTero, conventional impressions were used as well. The overall marginal fit for the groups was 44+/- 26. He reported that within the limitations of his in-vitro study the marginal adaptation of this all-ceramic crowns is acceptable and comparable to the ones made with conventional methods. [58]

A systematic review described the marginal discrepancies for zirconia FDP. The occurrences of marginal gaps for six studies were reported as follows. Marginal integrity was clinically unacceptable for 16.7% [59], marginal integrity was considered a success [60], marginal discrepancies were detected in 11.5 %[61], visible evidence of ditching along the margins 5-26% [62], marginal gaps were evident in 58.7 [63] , and visible evidence and or catch of the explorer was present in one case [2].

Similar results were observed by Martinez-Rus. The measurement of marginal discrepancy of four different milled zirconia copings was shown to result in mean marginal openings of 8.7 – 29.9 um, demonstrating that all offered accuracy within the range of clinical acceptability 120 um [64]. Larger, more complex frameworks also demonstrate relatively good marginal adaptation. The marginal gaps reported for milled zirconia framework 3 unit FDPs was less than 90 um in all cases [65]. A report of the marginal fit of a 14 - unit zirconia FDP framework produced using Zeno CAD CAM on master dies was reported. The mean marginal gaps were again small (25 +/-29 um), but larger than that measured for single unit crowns placed on the retainers. The quality of fit was location dependent, suggesting that large frameworks are subject to complex changes. It should be further noted that these frameworks were not veneered [66].

1.5 Esthetics

The difficulty in reproducibly achieving good esthetics with PFM restorations and the desire for metal free solutions has led to the increased use of zirconia. The unique optical properties of zirconia require new and different understanding of how the materials are managed [67].

Translucency and color are important and often inseparable variables for dental restorations. Translucency may be an innate optical property of the zirconia material related to its crystalline structure. Colorants may be infused within the partially sintered zirconia and incorporated during sintering. Hjerppe examined the influence of shading on zirconia disks [68]. Differences in biaxial strength were measured among the samples (885 MPa – 1007MPa) compared to the control group (1132 MPa).

Traditionally, all ceramics could be classified into 2 groups: highly translucent and those with a high strength opaque core that will require the application of an esthetic layering ceramic. Among translucent porcelains we have feldespathic porcelains like Empress and Vita glass ceramics. Feldespathic dental porcelain and its additives manipulate light in a favorable manner. Scattering occurs at the boundaries between the various phases and is influenced by the crystals' particle size, shape, volume concentrations, and relative refractive indices. Physical properties for these types of materials are optimized by the use of bonding techniques, but still it is recommended the use of these of materials to be limited to the esthetic zone.

Examples of the high strength cores are alumina, and zirconia. Opaque ceramic cores allow the clinician to be able to hide dark underlying tooth structures or the color of a metal implant abutment. The optical properties of core materials play an important role in matching ceramic restorations to the appearance of natural teeth. Kelly indicated that core translucency was one of the primary factors in achieving esthetics and affected the shade of the restoration greatly [69]. Spink in 2009 measured the level of translucency for several all-ceramic materials. (Table 1) In addition to the data that shows the different contrast ratios, she also reported that the increase of thickness of the specimen would decrease the percentage of light transmission [70]. The issue of translucency of high strength ceramics becomes more important today, as efforts focus on the elimination of the issues with layering porcelain on full contour milled zirconia restorations that are being fabricated. The translucency of zirconia may be controlled by several properties including grain size, distribution of grains, processing methods and additives [71].

0.5 mm										
Tukey HSD										
0.5 mm	N	Subset for alpha = 0.05								
		1	2	3	4	5	6	7	8	9
Empress Esthetic LT (HC)	3	.695733								
Empress CAD HT (LC)	3		.719767							
Empress CAD LT (HC)	3			.746133						
Empress Esthetic LT (LC)	3			.759400	.759400					
Empress CAD LT (LC)	3				.773833					
Vita In-Ceram Spinell (HC)	3					.824267				
Vita In-Ceram Spinell (LC)	3					.831867				
Vita Y-Z zirconia (LC)	3						.884500			
Vita Y-Z zirconia (HC)	3						.890500			
Lava zirconia (LC)	3						.897600			
Vita Alumina (HC)	3							.913833		
Vita Alumina (LC)	3							.915767	.915767	
Vita In-Ceram Alumina (HC)	3							.925833	.925833	
Lava zirconia (HC)	3							.926300	.926300	
Vita In-Ceram Alumina (LC)	3								.929200	
Vita In-Ceram Zirconia (LC)	3									1.001 000
Sig.		1.000	1.000	.135	.072	.871	.146	.199	.124	1.000
Means for groups in homogeneous subsets are displayed.										

Table 2- Translucency- contrast ratio of dental ceramics

Regarding the present knowledge pertaining to zirconia – based dental prostheses, the following conclusions are suggested:

1) Milled zirconia restorations fabricated by pre-sintering CAD CAM display acceptable fit. Greater accuracy is displayed for smaller prostheses.

2) Layered zirconia restorations display chipping of the veneer ceramic material, but framework fracture is rare.
3) Anatomic, monolithic zirconia restorations may offer promises of improved physical strength and absence of chipping, but the translucency of the bulk zirconia may challenge esthetics.

Monolithic zirconia restorations were recently introduced to address the strength and chipping complications reported. The concept of avoiding veneering porcelains is directed at elimination of chipping. However, elimination of the veneering porcelains may reduce the technician and clinician ability to impart natural appearances attributable to translucency. It is the aim of this project to examine the relationship of translucency and strength of zirconia as a function of sintering conditions.

2.The Effect of Sintering Process on Zirconia's Optical and Physical Properties.

Introduction

One of the emerging challenges inherent to the adoption of new CAD-CAM procedures for fabricating dental prosthesis is identifying the physical limitations presented. Anusavice (2012) described many of the limitations in dental materials testing in prediction of clinical outcomes [72]. For the emergent use of Zirconia restorations that are presently supported by work-flow (digital), cost (versus gold) and esthetics (all-ceramic) issues, a complex set of concerns must be addressed. For example, if the strength of zirconia is sufficient for fabrication of single as well as multiunit restorations, can it be utilized in a highly esthetic manner? Although Zirconia is white, it is relatively opaque. Clinical strategies to utilize this promising dental material in an effective, efficient and esthetic manner require careful assessment.

Zirconia is strong and tough. Its strength is based on its crystalline structure. In its tetragonal form, stresses lead to local transformation to monoclinic form that resists or stops crack propagation [73]. This can be measured in bulk and observed by fractography. Zirconia is white. This appeals to dentists and patients alike.

However, teeth are subtly colored and not white. Using bulk zirconia to develop prosthesis that functions and resists imposed loads over time requires its clinical alteration. Presently, two different approaches have emerged. A third approach, milling zirconia from the sintered state has been largely discounted in recent years.

One approach to utilizing zirconia for reproducibly esthetic and lasting restorations is by CAD CAM generation of a framework that is veneered with a compatible veneering ceramic. The other approach involves the generation of a fully anatomical prosthesis or 'monolithic' zirconia prosthesis that is devoid of veneering ceramic. Modification of the zirconia's white color occurs by infusion of colorants prior to sintering.

Ceramic veneered zirconia prostheses require the careful design and manufacture of a framework that is produced by CAD CAM procedures from bulk zirconia. Recent reports suggest that proper contour and design of the framework be employed to assure ceramic veneer integrity [74]. Other studies confirm that milled zirconia frameworks fit with acceptable fidelity [75]. Beautiful ceramics can be applied to these frameworks and remarkable prostheses can be made. However, when considering the growing data set regarding the clinical outcomes for this approach to using zirconia for clinical dentistry, chipping of the framework (often an irreversible complication) occurs with relatively high frequency [76]

The use of anatomical or 'monolithic' zirconia prosthesis to provide lasting and esthetic restorations offers other clinical challenges [77]. Generally these prostheses are complex in architecture, especially when made for screw retained implant prostheses. The complex milling procedures requires confidence in design. Thus, a resin prototype prosthesis is a necessary intermediary step [78]. Further, the monolithic nature of the prosthesis also refers to the white color. The coloring of a monolithic prosthesis is a complex procedure requiring the use of multiple colors and a precise drying and sintering procedure. When completed, a monolithic zirconia prosthesis lacks a ceramic veneer that is susceptible to chipping. However, compared to veneered prostheses, relative opacity may be noted [79].

Monolithic zirconia restorations were recently introduced to address the strength and chipping complications reported. The concept of avoiding veneering porcelains is directed at elimination of chipping. However, elimination of the veneering porcelains may reduce the technician and clinician ability to impart natural appearances attributable to translucency. **It is the aim of this project to examine the relationship of translucency and strength of zirconia as a function of sintering conditions**.

2.1 Materials and Methods

One hundred and twenty (120) zirconia disks were created using Materialize software and milled using Wieland's Zenotec Mini, Wieland Dental + Technik GmbH & Co. KG Lindenstraße 2 Germany - 75175 Pforzheim. The zirconia blanks used were Zenostar Zr Translucent, Shade Pure 98x18mm, Ivoclar Vivadent, Inc. 175 Pineview Drive Amherst, NY. File design was created to meet the following post sintering dimensions: 1.2 mm thickness by 14mm diameter. Figures 3 and 4.

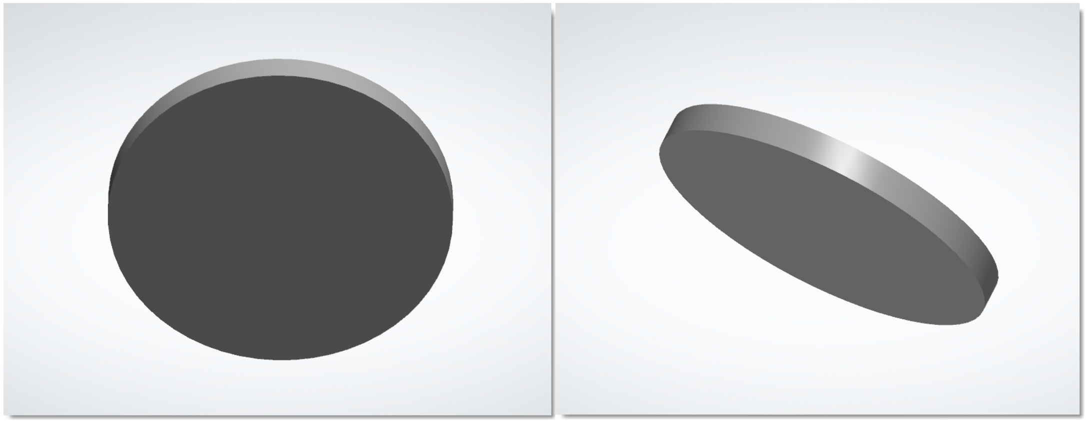


Figure 3- Disks design file

Figure 4- Milled zirconia disk

All di5sks were subsequently subjected to a processing and polishing protocol (Figure 5)

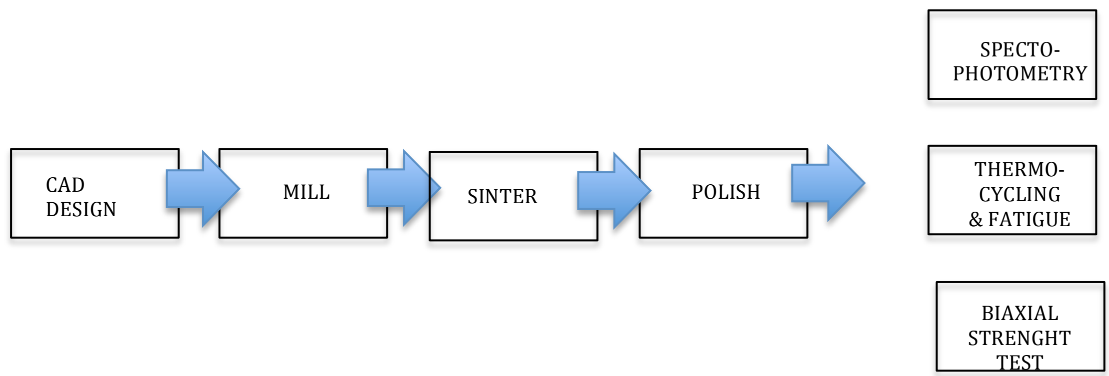


Figure 5- Diagram of research sequence

All disks were sintered in a four stage protocol using Origin® DuoTron™ Pro Furnace , B&D Dental Technologies 2371 S. Presidents Dr., Ste. E ,West Valley City, UT, and were sintered according to manufacturer's recommendations in regards to Stages 1,2 and 4 (Closing, heat ramp and Cooling). Stage 3 (holding temperature) was the variable considered in this study as the holding temperature and times were modified to explore what combination would give the best outcome as far as optical and physical properties.

Disks were divided into 12 groups and each groups was assigned a holding (sintering) temperature and holding time according to table 1.

Table 3- Sintering temperatures

Max temperature / Holding time	1450	1500	1550	1600
1H	10	10	10	10
2H	10	10	10	10
3H	10	10	10	10

All disks were surfaced after sintering using table top polisher Ecomet 3 (Buehler 41 Waukegan Road Lake Bluff, Illinois), using water at 100 RPM. Buelher Carbimet disks were used first grit 320/P400 followed by 600/P1200. Each of the 12 groups was later subdivided into 2 subgroups representing fatigued and non-fatigued (control) samples (n=5).

Table 4- Test fatigued group

Total specimens 60

Max temperature / Holding time	1450	1500	1550	1600
1H	5	5	5	5
2H	5	5	5	5
3H	5	5	5	5

Table 5- Control group

Total specimens 60

Max temperature / Holding time	1450	1500	1550	1600
1H	5	5	5	5
2H	5	5	5	5
3H	5	5	5	5

Using a calibrated spectrophotometer (UltraScan VISDelta TRAC with EasyMatch QC, Calibration date 11-6-13, Hunter Associates Laboratory Inc. Reston VA samples were evaluated for contrast ratio(CR) as a measure of translucency. Contrast Ratio is the ratio between the reflectance of a specimen over a black background to that over a white background of a known reflectance [80, 81]. The CR values are calculated according to the equation CR = Yb/Yw, in which Yb represents the spectral reflectance of light of the specimen over a black background and Yw over a white background. The CR value of a totally transparent material is 0, while the value of a totally opaque material is 1.

Specimens were later fatigued and thermo cycled using SD Mechatronik chewing simulator CS-4 (*SD MECHATRONIK GMBH Miesbacher Straße 34 D-83620 Feldkirchen-Westerham GERMANY*). Samples where mounted in a customized supporting device using Bosworth acrylic. Combined thermal cycling

(TC: 6000 58/558; 2 min each cycle) and mechanical loading (100 N; 1.6 Hz 100.000 cycles) was performed with parameters based on previous reports.

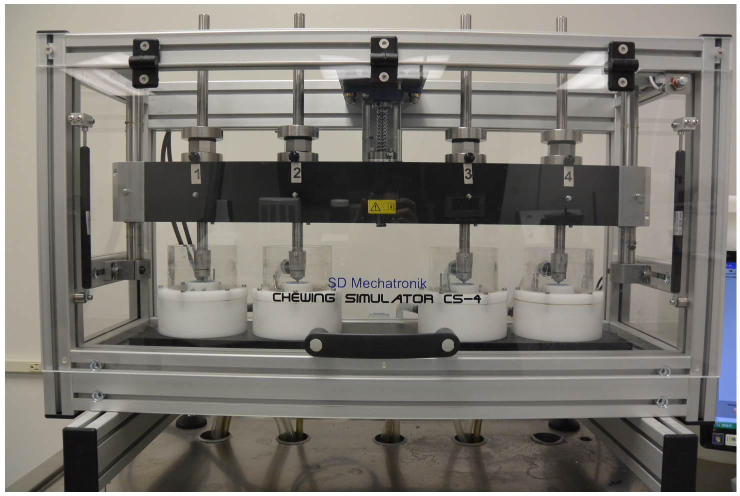


Figure 6- SD Mechatronik chewing simulator CS-4

Specimens in group A (fatigued) and group B (control), were measured for strength with a biaxial strength test (piston on 3 balls) as described in the ISO standard 6872 for dental ceramics [82]. Each disk was measured with digital caliper and values were taken into account up to 2 decimal points. Average disk thickness of 1.20 was observed for the specimens.

Figure 7- Samples measurement

Tension-compression test machine Instron 33R4204 ,Instron Worldwide Headquarters 825 University Ave. Norwood, MA. with a crosshead speed of 0.15 mm/min was used (Calibration day 04/10/13). To support the specimen 3 steel balls with a diameter of (3mm) were positioned in a support circle with (16mm) diameter The disk - shaped specimens were positioned concentrically on these supports and load was applied centrally with a stainless steel stylus 1.4 mm in diameter at the tip. The load at the point of fracture was recorded and biaxial strength for each specimen recorded and the mean and standard deviations were calculated. Figure 8

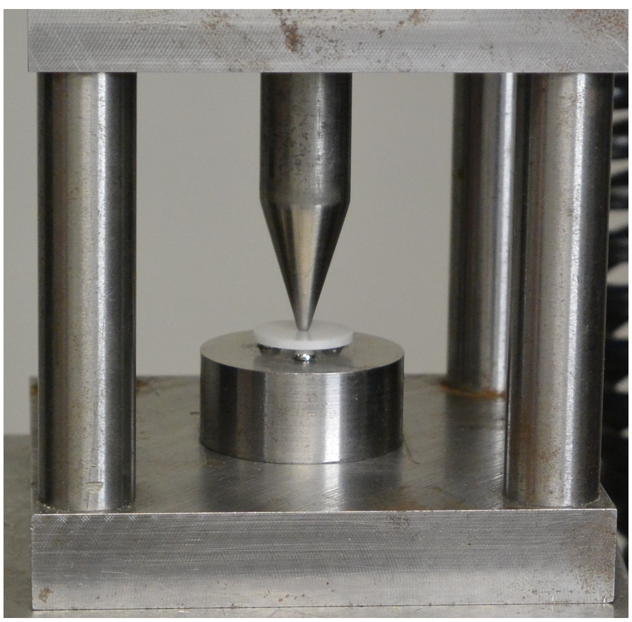


Figure 8 - Instron 33R4204

2.2 Statistics

The outcomes of the study were strength and translucency, measured as a contrast ratio. The explanatory variables of interest were group, temperature and holding time for strength and temperature and holding time for translucency. The statistical method used separately for each outcome was a factorial ANOVA with main effects only, no interactions were included because of small sample size. Level of significance was set at 0.05. Pairwise contrasts using least mean squares were performed when a main effect was statistically significant.

2.3 Results

2.3.1 Model for Strength

The results obtained from biaxial loading of samples revealed only modest differences among samples created using all conditions. Generally, a trend for greater strength with higher temperatures and longer holding times was observed (Table 4 and 5). More specific observations are revealed by the statistical evaluations.

The model can be summarized in the following formula,

$$\text{Strength} = \text{group} + \text{temperature} + \text{holdtime}$$

The Type 3 results for this model are,

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Group	1	0.0424	0.0424	0.00	0.9988
Temp	3	143180.9626	47726.9875	2.68	0.0506
Holdtime	2	112575.1159	56287.5580	3.16	0.0464

The average strength was not statistically different among the groups (P=0.99). Holding time was statistically significant (P=.046) after adjusting for temperature and group. The pairwise comparisons indicate that the average material strength with 1 hour holding time is statistically significantly different (smaller) than that with 2 hour holding time (P=0.016). But the comparisons between 1 hr and 3 hrs and between 2 hrs and 3 hrs were not statistically significant (P =0.078 and P=0.515 respectively). In addition, temperature approached statistical significance (p = 0.0506). The pairwise comparisons show that the average material strength obtained using the 1550-degree temperature was statistically significantly different (smaller) than that with 1600 degree temperature (p=0.0072). But the differences between other pairs (i.e. 1450 vs 1500, 1450 vs 1550, 1450 vs 1600, 1500 vs 1550 and 1500 vs 1600) are not statistically different.

Table 6- Results for holding time

holdtime	strength LSMEAN
1 hour	999.30664
2 hours	1072.35000
3 hours	1052.85000

Least Squares Means for Effect holdtime t for H0: LSMean(i)=LSMean(j) / Pr > |t| Dependent Variable: strength			
i/j	**1 hour**	**2 hours**	**3 hours**
1 hour		-2.4298	-1.78113
		0.0167	0.0776
2 hours	2.429804		0.652963
	0.0167		0.5151
3 hours	1.781132	-0.65296	
	0.0776	0.5151	

Table 7- Results for temperature

temp	strength LSMEAN
1450 deg	1031.70000
1500 deg	1034.23333
1550 deg	1002.44218
1600 deg	1097.63333

i/j	1450 deg	1500 deg	1550 deg	1600 deg
1450 deg		-0.07346	0.84104	-1.91201
		0.9416	0.4021	0.0584
1500 deg	0.073464		0.913863	-1.83854
	0.9416		0.3628	0.0686
1550 deg	-0.84104	-0.91386		-2.73635
	0.4021	0.3628		0.0072
1600 deg	1.912008	1.838544	2.736349	
	0.0584	0.0686	0.0072	

The following graphics summarizes the above results:

Figure 9- Biaxial strength test for control group

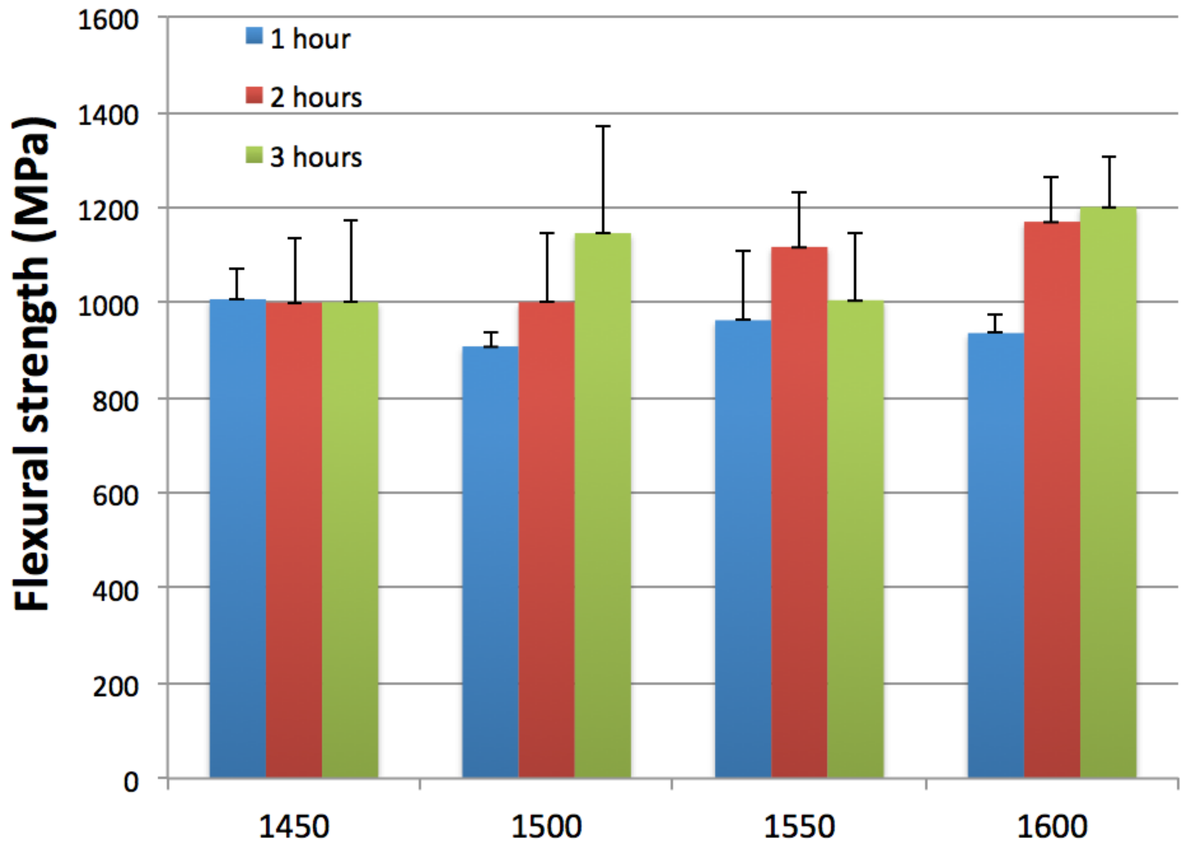
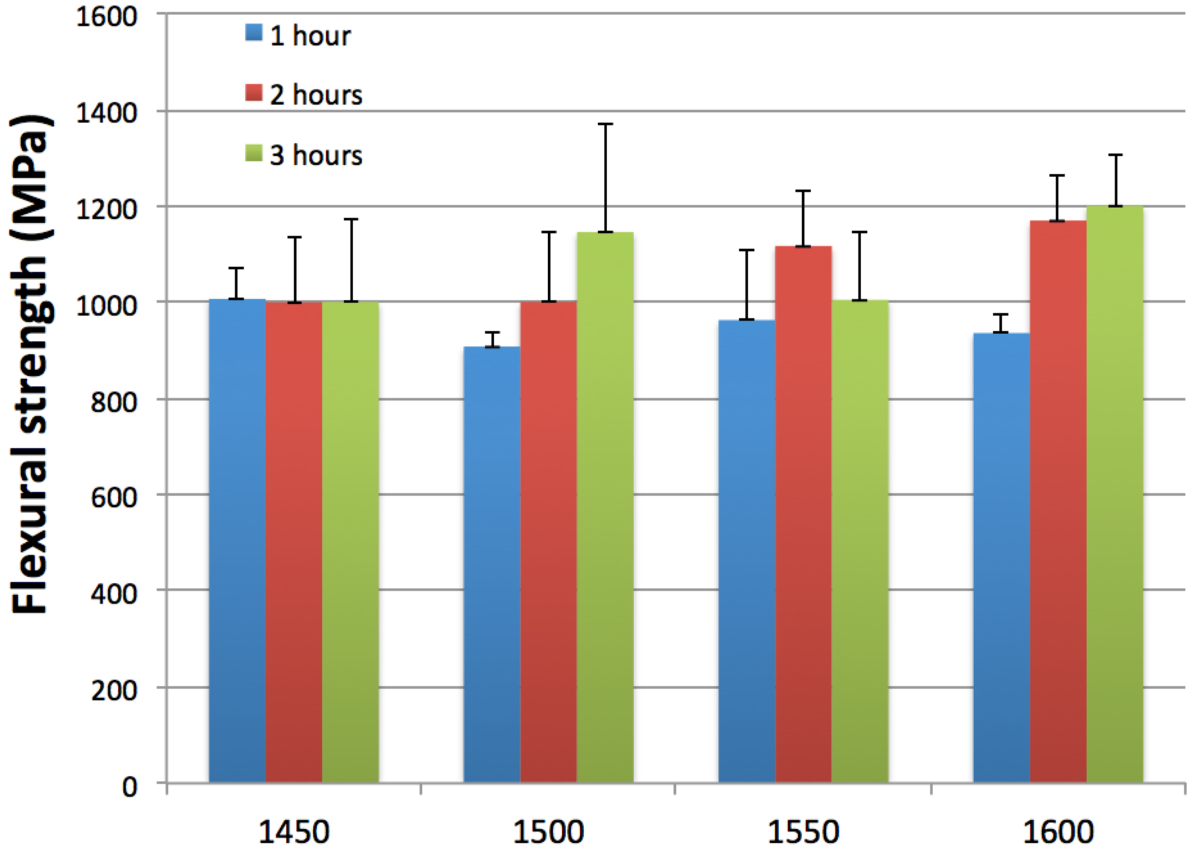


Figure 10- Biaxial strength test for fatigued group



2.3.2 Model for Translucency

The results obtained from spectrophotometric of samples revealed minor changes in the translucency of the samples created using all conditions. Generally, a trend for higher translucency with higher temperatures and longer holding times was observed (Table 3). More specific observations are revealed by the statistical evaluations.

The model can be summarized in the following formula,

$$translucency = temperature + holdtime$$

The Type 3 results for this model are,

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp	3	0.00156971	0.00052324	7.02	0.0005
Holdtime	2	0.00004025	0.00002012	0.27	0.7644

Average translucency was not statistically significantly different among the 3 holding times (P=0.76) but was statistically significantly different for the 4 temperatures after adjusting for holding time. The average contrast ratio (i.e. translucency) between 1450 and 1550 degrees , 1450 degree and 1600 degrees, and 1500 and 1600 degrees are significantly different. The average contrast ratios between the other pairs of temperatures (1450 vs 1500; 1500 vs 1550; and 1550 vs 1600) are not statistically significantly different.

Table 8- Translucency results for temperature

temp	trans LSMEAN
1450 deg	0.79922784
1500 deg	0.79648005
1550 deg	0.79137061
1600 deg	0.78583723

Least Squares Means for Effect temp
t for H0: LSMean(i)=LSMean(j) / Pr > |t|
Dependent Variable: trans

i/j	1450 deg	1500 deg	1550 deg	1600 deg
1450 deg		0.871674	2.492523	4.247859
		0.3872	0.0158	<.0001
1500 deg	-0.87167		1.620849	3.376185
	0.3872		0.1109	0.0014
1550 deg	-2.49252	-1.62085		1.755336
	0.0158	0.1109		0.0849
1600 deg	-4.24786	-3.37619	-1.75534	
	<.0001	0.0014	0.0849	

2.4 Discussion

In this investigation, the influence of firing time and temperature on zirconia's physical properties of strength and translucency were examined. Using disks and a biaxial model of strength testing, the current results confirm the relatively high strength of zirconia that approximates 1,000 MPa. This is a central advantage of zirconia among other dental ceramics available today. For example the reported strength of other materials are: Lithium disilicate 400 MPa, Leucite reinforced ceramics (Empress) 140 MPa.

The samples made in this investigation were disks of 14 mm diameter. This was mandated by our need to adapt samples to the UltraScan VIS spectrophotometer (Hunter Associates Laboratory Inc. Reston VA). Because of this, strength was measured using a biaxial strength test. In the biaxial flexural test a disk shaped specimen is supported below by 3 ball bearings distributed o a circular pattern. The load is applied from above by use of a piston concentric with the support ball bearings.

The 3 - point flexural strength test that has been commonly used to test dental ceramics presents a problem since it can be sensitive to flaws along the specimen edges [82]. Biaxial flexure described in ISO 6872 is a reliable method of choice, since the effect of possible flaws in the edges is eliminated by applying the load in the central area [82]. Several studies have used biaxial flexural strength as a method to predict performance of all-ceramic materials [83-85]. For example, Pittayachawan in 2007 tested the biaxial strength of lava and reported Biaxial flexural strength around 1100 MPa. [86]

This study employed a thermocycling regimen in the evaluation of fatigue. This may be of particular relevance to zirconia testing. Low-temperature degradation (LTD) has been associated with several 3Y-TZP-based biomaterials, but it is difficult to simulate in the laboratory. Thermocycling has been described as an effective way to simulate the oral environment and evaluate the effect of (LDT). Currently, Y_2O_3 (yttria) or CeO_2 (ceria) are being incorporated to zirconia. These stabilizers improve the retention of the tetragonal structure at room temperature. Perdigao in 2012 evaluated the effect of thermocycling in zirconia with yttria and Ceria as stabilizers and reported lower monoclinic fraction in the group that contained Ceria as stabilizer. The group that contained yttria reflected greater susceptibility to LTD.

A spectrophotometric method was used to measure translucency. They are useful in measuring the amount of light reflected from a sample and the amount of light adsorbed from the sample to calculate translucency. There exist other methods of measuring translucency that include spectroradiometry. These instruments measure different parameters of irradiance and radiance. When Lim et al compared the measures of translucency using both spectroradiometry and spectrophotometry; values were higher for the spectroradiometry measures. The measures were highly correlated. A previous study measured translucency of various ceramics and the CR results were between 0.82 and 0.89 for zirconia samples such as Vita Y Z zirconia and Lava, and for more translucent materials such as Empress values range from 0.69 to 0.77. [70].

An important phenomenon that affects measurement of translucency is 'edge-loss'. This refers to the scattering of incident light to the edges of a translucent material without being adsorbed and thus, not being detected by the spectrophotometer. Edge-loss is influenced by the physical characteristics of the spectrophotometer, the properties of the material, the thickness of the translucent layer and the reflectance of the backing layer. In this study, the various parameters affecting edge loss were well controlled using a single investigation, a single sample thickness and consistent measurement. However, the properties of the material were hypothesized to vary with holding temperature and time. One other variable that could have influenced the measured values is the surface topography. These samples were polished using 300 and 600 grit abrasives after sintering. The imposed or resultant roughness may have induced or permitted scatter of incident light and an induced edge-effect. While this may be important, it should be noted that all samples were polished equally resulting in similar surface roughness (polish) among all groups. Further studies may be performed with an immersed sample or highly polished sample to reduce the influence of scatter and edge-effect. The opportunity to use glazed samples was avoided in response to the report of Heffernan (2002) that revealed modestly higher translucency for glazed materials. In this regard, the clinical use of polished zirconia may be preferred due to favored wear versus natural teeth or prostheses. [87,88]

A clinically relevant zirconia substrate dimension was studied. Its use in anatomic monolithic prostheses often requires 16 – 20 mm^2 connector dimensions minimally. Implant supported prostheses with anterior tooth display will have incisor thicknesses approaching or exceeding anatomic limits. Here, samples were 1.2 mm thick. Among the many variables affecting translucency, thickness reduces translucency of dental porcelains [87-88].

Sintering temperatures are one variable that influences the strength of zirconia. Previous investigations demonstrated zirconia demonstrated highest strengths with sintering temperatures of 1400 C and 1550 C. Sintering temperatures of 1650 C and above lead to changes in the microstructure that decreased the materials strength. One of the limitations described in this study was the fact that they only used one type of zirconia and those results might not be applicable for all brands. [70].

The laboratory or clinical manipulation of zirconia for dental prostheses must follow careful guidelines. Here, significantly lower strength was noted for zirconia sintered at the relatively low temperature of 1450 degrees C. A trend for higher strength was seen when high temperatures >1550 or long holding times > 2 hours were used. It may be suggested that clinical manipulations of zirconia be conducted in calibrated ovens. Further, under no circumstances should firing be conducted using reduced holding times.

The hypothesis that elevated sintering temperatures will increase the translucency of the resulting zirconia was not supported by the spectrophotometric analyses. Globally, translucency values of 0.78 to 0.82 were observed. These values reflect previous measures of zirconia and confirm that zirconia is less translucent than lithium disilicate materials with translucency values measured to be approximately 0.7 [71]. We speculate that further polishing, glazing or wet measurement of these samples would reduce the reflectance component of the measurement and improve translucency. Whether or not highly polished or glazed materials that are represented clinically are more or less translucent than the samples measure here cannot be determined. However, the issue of reflectance would affect all samples similarly and mask translucency with equal magnitude. Although there is a trend toward greater translucency with higher sintering temperatures and times, it is unclear how this may translate into the clinical environment.

One limitation of this study may reflect the choice to polish and not glaze these samples [87] evaluated translucency for several ceramics and performed several measurements before and after the glazing process. Significant differences (CR) were found and between glazed and non-glazed specimens. The glass disc Vitadur Alpha, IPS Empress, In-Ceram Spinell, and Procera glazed specimens were significantly more translucent than their corresponding non-glazed specimens, respectively. No significant difference was found in the opacity of glazed and non-glazed specimens of IPS Empress 2, In-Ceram Alumina, In- Ceram Zirconia, and metal-ceramic. Glazing cycles decreased the opacity for all veneered materials, except for In-Ceram Zirconia and metal-ceramic specimens. We could possibly suggest that the effect of glazing for translucency measures is material dependent.

Clinical performance of contemporary all ceramics systems depend on a variety of factors that finally would determine how a material would perform in the oral environment. Prior to clinical manipulation evaluation of material properties in vitro might help to predict its clinical performance. The opportunity to compare the measured translucency with previous reports is limited. Existing studies have used very different samples of different thickness and made of different zirconia substrates. This work, however, demonstrates the modest sensitivity of zirconia translucency to holding temperatures and times.

One potential clinical implication that may be suggested from this investigation is that while 'fine-tuning' of the firing cycle can provide minor enhancement of zirconia translucency without deleterious effects on strength, other approaches to creating highly translucent restorations using monolithic zirconia are needed.

2.5 Conclusions

Within the limitations of these experiments, the follow observations were made:

1) Increasing temperature from 1450 – 1600^{o}C led to minor increase in biaxial flexural strength that were not significantly different

2) Increasing the holding times from 1 to 2 to 3 hours at temperatures ranging from1450 – 1600°C led to increased flexural strength when holding times exceed 1 hour.

3) Under the conditions measured, increasing temperature and / or holding time did not alter translucency. Further investigations may be required to fully explore the influence of firing technique on translucency.

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