EFFECTS OF SINTERING HOLDING TIME ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TRANSLUCENT ZIRCONIA

by

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DEDICATION

All challenging work requires self-effort as well as support, especially from people who are very close to our hearts.

With humble effort, I gratefully dedicate this thesis to my beloved parents, for their guiding support, which inspired me with motivation, and for their devotion to me throughout my life.

I would also like to dedicate this thesis to my lovely wife, for her love, patience, and encouragement during my study.

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INTRODUCTION

Zirconia is known as a polymorphic material that demonstrates three crystalline forms: monoclinic, tetragonal, and cubic. The monoclinic phase is stable from room temperature to 1170°C, while the tetragonal phase is stable at temperatures above 1170°C up to 2370°C. The cubic becomes dominant over 2370°C. [1-3] The cubic form at higher temperatures does not have technical significance and is not routinely studied.

In the early 20th century, Passerini [4] and Ruff et al. [5, 6] discovered that zirconia retained tetragonal metastability at room temperature by adding metal oxide, which “alloyed” the zirconia. Zirconia oxide could prevent catastrophic fracture better than pure zirconia. Although zirconia was introduced in orthopedics for hip head replacement in 1969, [7] zirconia was not used in dental treatment until the 1990s. [8] Metal oxide can be added into zirconia as a stabilizer, including CaO, MgO, Y_2O_3, CeO_2, Er_2O_3, Eu_2O_3, Gd_2O_3, Sc_2O_3, La_2O_3 and Yb_2O. [9-11] Among all the metal oxides, CaO, MgO, Y_2O_3 are major chemical compounds that have been utilized in dental zirconia. Meanwhile, Y_2O_3 is considered as one chemical compound that reaches the ISO standard[12] of surgical application.[11] Several *in-vitro* studies also support that zirconia provides reliable long-term longevity in clinical application.[13, 14]

During the sintering procedure, the monoclinic-tetragonal phase transformation takes place. In order to retain metastable tetragonal phase at room temperature, several metal oxides can be added to prevent catastrophic failure of pure zirconia. By alloying zirconia, it can be retained in the tetragonal phase at room temperature.[15]

With the recent development of advanced dental ceramics combined with computerized-aided design and computerized-aided manufacturing (CAD/CAM) technologies, zirconia-based CAD/CAM ceramic is now widely used in dentistry. The advantages of zirconia-based ceramic over conventional metal-ceramic in fixed dental prostheses (FDP) include its biocompatibility, durability, and esthetic quality.

The introduced CAD/CAM technology using zirconia ceramic requires an enlarged dimension (approximately 25 percent) to compensate for the shrinkage occurring in the sintering.[16] Meanwhile, depending on the manufacturer's recommendation, the green stage of zirconia usually requires an extended period of time in a conventional oven at a temperature usually between 1350°C to 1550°C to reach the final dimension and metastability of the tetragonal phase.

Compared with conventional feldspathic porcelain crowns (PJCs),[17, 18] zirconia-based ceramics demonstrate better mechanical performance, superior strength, and higher fracture resistance.[19, 20] Due to their high opacity and whitish optical appearance, zirconia-based ceramics are traditionally used as core materials that require a veneer layer for clinically-acceptable aesthetics.[21] However, ceramic veneer possesses some disadvantages like low tensile strength and fracture toughness. The inherent imperfections in the crystal structure and the existence of voids make porcelain prone to cracking when subjected to stress. Therefore, chipping in the veneer has been identified as a main reason for failure[22, 23] and also as the most common complication in all-ceramic crowns.[24] Recently, a new generation of zirconia, commonly referred to as "full-contour zirconia," has been introduced. Manufacturers claim that full-contour zirconia restorations have higher translucency than traditional zirconia and therefore do not require a veneer layer for posterior restorations.[22, 23] There are several potential clinical benefits with full-contour zirconia restorations. Without the need for a veneer, the amount of tooth reduction and possibility of chipping are less. Furthermore, heat treatment for the veneer, which has been shown to decrease the flexural strength and the microhardness of the zirconia, is unnecessary. [25]

Another review of the recent literature [21] shows that the processing conditions for ceramic materials, including heating rate, sintering temperature and duration, source of stabilizing oxides, and heating source, can have a strong impact on the final mechanical and optical properties of zirconia restorations. However, detailed studies on the effects of the processing variables on the mechanical and optical properties of these full-contour zirconia materials are still lacking.

Potentially, the shorter sintering schedule will lead to finer microstructures and higher mechanical properties of the final CAD/CAM zirconia prosthesis. Also, due to higher strength of full-contour zirconia, it is proposed that less tooth structure reduction is required in tooth preparation compared with conventional full-ceramic restorations. However, the mechanical properties of these novel full-contour zirconias still remain unclear. Further scientific investigations regarding these novel materials are required. This research therefore investigated the effects of different heating programs on the microstructure and mechanical properties of three of four full-zirconia materials (BruxZir, KDZ Bruxer, CAP FZ). [26]

The objective of this study was to investigate the effects of holding time during sintering on the flexural strength, microhardness, grain dimension/shape, and translucency of three different full-contour zirconia materials.

Null Hypothesis

The null hypothesis was that sintering zirconia specimens with a longer holding time would not influence 1) flexural strength, 2) microhardness, 3) grain dimension/size under SEM, and 4) translucency compared with specimens sintered with the recommended heating schedule.

REVIEW OF LITERATURE

CONVENTIONAL ZIRCONIA

Compared with other dental ceramic materials, yttria-stabilized tetragonal zirconia (Y-TZP) is characterized by high flexural strength, high fracture toughness, high compressive strength, and low modulus of elasticity.[3] The particle size of the zirconia is usually between 0.1 µm to 0.5 µm.[27]

With the improvement of technology, the as-received CAD/CAM zirconia blocks are made highly porous to allow milling by the CAD/CAM machines. A sintering process is therefore needed after milling to fabricate high-density restorations. In zirconia, the sintering procedure not only increases the density of the block accompanied by an increase in mechanical properties, but also transforms the monoclinic phase to the tetragonal phase. [28] Factors associated with transformation metastability include size and shape of zirconia nano-particles, composition of zirconia, type and amount of stabilizing oxides, and interaction of zirconia with other phases. Therefore, variables of processing can have significant effects on final microstructural development and should be studied carefully.

FULL-CONTOUR ZIRCONIA

Yttria-stabilized zirconia has been recognized as a strong and tough dental material among many available dental ceramics. However, the innate opacity has limited its application to cores or frameworks of dental restorations. [22] In order to achieve a favorable esthetic outcome, veneering porcelains are used to imitate natural tooth shade. However, chipping of the veneering porcelains has been identified as the main mechanism for its failure.[22, 23, 29-34] The introduced full-contour zirconia eliminates the porcelain veneer layer and therefore less tooth reduction is required during tooth preparation than conventional porcelain fused to metal (PFM) and conventional all-ceramic restorations.

An *in-vitro* study by Jung[35] tested the wear ability by comparing full-contour zirconia and feldspathic porcelain against human enamel with a chewing simulator for 240,000 cycles. The author concluded that the degree of wear on the antagonistic teeth was less with polished full-contour zirconia than with feldspathic porcelain. The author also speculated that a polished full-contour zirconia crown without glazing is more effective than a polished full-contour zirconia crown with glazing in reducing antagonistic teeth wear. Another systemic review[36] concluded that polished zirconia surfaces showed favorable wear behavior when opposed to natural enamel. However, the author also agreed that long-term investigation for stability and abrasiveness of polished zirconia is needed.

Considering failure mode and fracture resistance of full-contour zirconia, an experiment produced by Preis in 2012[23] tested failure and fracture resistance of full-contour zirconia *in vitro*. Full-contour zirconia samples underwent four different surface treatments: veneering, glazing, polishing, and grinding. The article concluded that full-contour zirconia demonstrated superior resistance to failures and fracture over the general chewing forces. Meanwhile, full-contour zirconia-based fixed partial dentures had a high tolerance for fracture when polishing was performed after surface treatments and adjustments.

The multiple superior properties of zirconia compound versus those of conventional dental ceramics or traditional veneered zirconia may extend the clinical application of full-contour zirconia. However, detailed properties of these full-contour zirconias still require further investigation and experiment.

TRANSFORMATION TOUGHENING OF ZIRCONIA

Pure zirconia has three allotropes (monoclinic, tetragonal, and cubic phases) that maintain stability in different temperature ranges. With appropriate stabilizers added, the high temperature tetragonal phase can be stabilized to appear at room temperature. As the crack initiates, the crack tip propagates through the tetragonal phase, and a tetragonal-monoclinic transformation takes place.[1] This transformation is accompanied by a 3-percent to 4-percent volumetric expansion, exerting compressive stress on the crack tip and hindering further crack propagation. This phenomenon contributes to higher toughness and mechanical strength.[37] This is known as the transformation toughening of zirconia.[2, 38]

LOW-TEMPERATURE DEGRADATION (LTD) OR AGING OF ZIRCONIA

The tetragonal phase of zirconia undergoes transformation to the monoclinic phase most rapidly at temperature 200°C to 300°C.[39] However, tetragonal-to-monoclinic phase transformation can also happen at room temperature when tetragonal phase zirconia is in contact with water, which is called low-temperature degradation (LTD) or aging.[40-42] According to Lughi, factors related to aging included the type and content of metal oxide; the residual stress, and the grain size.[11] Aging is a long-term and continuous processing of tetragonal-to-monoclinic phase transformation in the presence of water or body fluid. Denry et al. [43] reported that some forms of zirconia are susceptible to aging and therefore the sintering process could play a critical role in the aging of zirconia. The excessive progression of LTD caused unfavorable phase transformation, and a loss of strength and surface degradation that further resulted in surface roughness.[36]

In Lughi's review article, an assumption had been made that accelerated LTD may lead to unacceptable outcomes in full-contour zirconia restoration surfaces.[11] Therefore, long-term wear behavior of full-contour zirconia should be evaluated and considered for the polishing and abrasiveness over time.[36]

THE EFFECT OF SINTERING ON ZIRCONIA

In ceramic engineering, it is known that the processing conditions for ceramic materials, including heating rate, sintering temperature, sintering duration, and cooling rate, can have a strong impact on the final mechanical and optical properties of the ceramics.[21] The same principle applies to dental ceramic restorations as well.[1]

Considering the factor of sintering duration, Hjerppe et al. investigated the mechanical properties of yttrium-stabilized zirconia by using different sintering times. The conclusion was that thermocycling treatment might induce a higher amount of monoclinic phase even though thermocycling had no statistically significant influence on mechanical properties of zirconia.[2] However, more monoclinic phase was found in thermocycled samples compared with the group without thermocycling. Meanwhile, samples stored in distilled water also showed a higher proportion of monoclinic phase in longer sintering times than in shorter periods of time.

As regards the sintering temperature, in Jiang's experiment in 2011, nano-particles of 40-nm zirconia powder reached 99 percent of the theoretical density value at 1400°C to 1500°C and 90-nm zirconia powder at 1500°C. As for the transmittances, 40-

nm particle powders gained the highest transmittance at temperatures above 1400°C while the critical temperature for 90 nm was 1450°C.[44] Conclusively, sintering temperature between 1450°C to 1500°C would gain nearly full density (>99%) and 17-percent to 18-percent transmittance for the nano-particle zirconia. Meanwhile, when nano-particle size decreased, the density and transmittance became higher compared with that of the higher nano-particle sintering result.[44]

Another article about the sintering temperature effect was written by Stawarczyk in 2012.[45] Instead of utilizing two different nano-particle zirconia powders like Jiang's study, only one zirconia was introduced in this study. All samples were divided into nine groups and sintered with different final sintering temperatures from 1300°C to 1700°C. This experiment found the highest flexural strength at final sintering temperatures between 1400°C and 1500°C. Meanwhile, grain size enlarged with the increase of sintering temperature and crystal structure became hollow and collapsed when the temperature rose over 1600°C.

Besides using a conventional oven to sinter zirconia, a novel sintering method using a microwave has been advocated recently. Microwave sintering has several favorable features compared with conventional oven sintering like rapid volumetric heating, lower cost, higher production rate, and lower energy requirement.[3] Almazdi conducted a study comparing the surface quality, mechanical and physical properties, and dimensional stability by sintering yttria-stabilized zirconia (Y-TZP) in a conventional oven versus a microwave furnace. The result of this study revealed that a microwave sintering method could satisfy general clinical requirements for dental use. No significant difference was observed regarding the mechanical properties. However, the author stated that microwave energy provides a greater uniformity of heating and is more efficient in productivity and saving energy.

An experiment conducted by Oilo et al. [21] investigated whether firing cycles affect the mechanical properties of zirconia ceramics. During the experiment, zirconia samples were divided into three groups: the first group consisted of non-heat-treated samples; the second group underwent a one-time firing cycle to correspond to the first step of veneering procedure; and the third group was heat-treated five times to mimic all veneering processes. The conclusion provided was that zirconia core material had a statistically significant reduction in flexural strength and microhardness after the first firing cycle. However, no detrimental effect was observed for the subsequent firing cycles.

Even the cooling procedure may have an effect on the strength of zirconia. According to Avramov,[46] viscous flow of glasses over or around Tg has influence on structural relaxation, which related to shear viscosity ŋ of the glass-forming melt. Renan Belli et al.[47] introduced two different porcelains: VM9 (VITA Zahnfabrik) and Lava Ceram (3M ESPE) to investigate their properties after different cooling procedures.[47] They found Lava Ceram contained more amorphous and smaller crystals than VM9, which may be a result of a less temperature-sensitive nature of Lava Ceram to cooling stresses arising from fast cooling.

Another variation may cause mechanical property change is thermocycling treatment. When zirconia ceramics are sintered at higher temperature, depending on the sintering temperature and duration, cubic grains may exhibit 6- to 7-mol % yttria, which coexists with the tetragonal phase retaining less than 2-mol % yttria.[48] Therefore, theoretically, thermal treatment at high temperature is correlated to a greater capability for transformation toughening and for gaining a tougher and stronger zirconia compound.[25, 49] Nevertheless, a higher proportion of monoclinic grains in proportion may induce a higher rate-of-aging effect by a nucleation and growth mechanism.[50] The theory of equilibration between the tetragonal and cubic phases at hydrothermal stability is questionable.

An *in-vitro* study evaluated the shear bond strength between three different dual-cure resin cements and silica coated zirconia with and without thermocycling treatment.[51] All resin cements showed lower shear bond strength with thermocycling treated zirconia crowns. The same result was also provided by Söderholm[52] and Isidor.[53]

MECHANICAL PROPERTIES

Flexural Strength

As mentioned earlier, in Oilo's article,[21] zirconia after sintering possesses the highest flexural strength and micro-hardness. After heat treatment, the zirconia core material shows reduced flexural strength after the first firing and with no statistically significant difference for the subsequent firings. This research provides the possibility of property degradation during the veneering process of zirconia-based core restorations.[1]

Sundh et al. utilized yttria-stabilized zirconia (Y-TZP) (Vita YZ) and magnesia partially stabilized zirconia (Mg-PSZ) (Denzir-M) to investigate fracture strength before/after veneering or heat treatment materials. Their research shows that veneered Vita YZ has the highest fracture strength, which may be due to the infiltration of the veneering porcelain into defects and/or increased compressive stress on the surface of the frameworks from the veneering porcelain. As for Denzir-M, the fracture resistance is significantly decreased after heat-treatment and veneering. This might be because of the phase transformation induced by heat, which also influences its mechanical properties.

Johansson et al.[54] studied and evaluated the fracture strength of monolithic translucent zirconia. An experiment was performed between two different monolithic translucent zirconia with and without a veneer, one heat-pressed monolithic lithium disilicate, and one veneered Y-TZP crown core. All samples were thermocycled for 5000 cycles, and cemented onto dies with resin cement. Samples were cyclically pre-loaded at a 100° angle for 10,000 cycles before being loaded to fracture. The experiment demonstrated that two brands of monolithic translucent zirconia represented a statistically significant higher fracture strength (2,795-3,038 N) compared with the other groups (1480 N to 2229 N).

Hardness

Hardness is a mechanical property, which is related to surface microstructure. The demonstration of monoclinic phase in transformation toughening majorly represents on the surface of the zirconia[15, 48] before the tetragonal to monoclinic transformation starts inside the zirconia.[55] In Oilo's article,[21] a correlation between the decrease of hardness and multiple heat firing procedures was demonstrated.

However, in Hjerppe's article,[2] the author utilized a different sintering program to test zirconia Vickers hardness. No difference was found in different sintering program groups. The null hypothesis was not rejected because the author concluded that the microhardness change did not depend on tetragonal to monoclinic phase change on the surface of the specimens during this experiment.

Grain Size/ Dimension of Zirconia

Hjerppe et al. concluded that zirconia sintered with a shorter sintering time has slightly smaller grain size compared with longer sintered zirconia, but the difference was not statistically significant.[2] The smaller grain size of zirconia from shorter sintering time seemed to generate less monoclinic phase than a longer sintering time.

However, a significant grain size change was noticed in Inokoshi's study. An experiment tested the effect of different sintering conditions on zirconia and demonstrated an average grain size that was 0.26 μm at 1450°C versus an average grain size of 0.69 μm at 1650°C. This study also concluded that sintering temperatures between 1450°C to 1550°C did not result in enlarged microstructure. But elongated dwell times at 1650°C clearly enlarged the grain size.[56]

In Chevalier's experiment,[48] yttria-stabilized zirconia became bimodal when the sintering temperature reached 1550°C within a five-hour sintering program. The occurrence of grain sizes larger than 2 μm could be observed. According to Rühle et al., these larger grains were cubic form in nature.[57] Ruiz and Readey [25] also proved the appearance of cubic form when the sintering temperature was above 1500°C. Cubic grains demonstrated higher yttria content than tetragonal grains at grain boundaries and caused a change of mechanical properties.

OPTICAL PROPERTY OF ZIRCONIA

Due to the innate opacity of conventional zirconia, few processing techniques have endeavored to improve translucency in processed zirconia. One technique investigated by Radford and Bratton added titanium oxide to yttrium-stabilized zirconia and it was reported to be effective in densifying yttria-stabilized zirconia. Tsukuma [58] studied the effect of TiO_2 on the transparency of zirconia, instead of translucency. He added 10 mol % TiO_2 to 8 mol % yttria-zirconia powder and sintered it to 1430°C for 12 hours and 1630°C for 7 hours[59]. X-ray diffraction indicated that TiO_2 stimulates grain growth during sintering. The grains size in TiO_2 doped zirconia were larger than in TiO_2 undoped. The author found that the added TiO_2 provides a fairly high transmittance to the zirconia. Moreover, the pressure associated with the TiO_2-adding technique led to pore migration, which is thought to be the factor of increasing transparency and strength.

Another processing technique is Hot Isostatic Pressing (HIP) used to increase the translucency.[59, 60] In this technique, the zirconia powder is heated by a heating coil and pressed at the same time. The introduced pressure eliminates pores in the sintered material, but also results in increased grain size,[59] which in turn deteriorates the mechanical and optical properties due to a reduction in grain boundaries.[61]

Spark Plasma Sintering (SPS) is an alternative method used to counterbalance the overgrown grain size associated with the HIP technique. In SPS, a high density current flux runs through the sample and the die to provide the required heat while pressure is applied. This technique allows low temperature sintering (about 1200 ^{o}C) and reduced heating and cooling time. Grain growth was minimized while nanostructure was maintained with this technique.[62] The addition of high pressure endowed this technique to produce dense materials of less than 20-nm grain size. [63] This results in an elimination or decrease of pores in the material while creating more grain boundaries. In other words, a tougher material could be obtained, at least theoretically.

Cassock et al. and Anselmi-Tumburini et al. used an electric current sintering technique to test transparence with cubic (8 mol % yttria) and tetragonal (3 mol % yttria) nanostructured powders. Both studies had an average grain size between 50 nm to 55 nm and transparence for the fully stabilized (8 mol % yttria) zirconia was higher than partially stabilized (8 mol % yttria) zirconia (60 % versus 50 %).[64, 65] In these two studies, the shade change of the zirconia had been achieved. Alaniz[62] found that transmission, reflectance, and absorption coefficients are reported for various wavelengths, and absorption coefficient were highly dependent on processing time. An annealing test determined that oxygen vacancies are the primary absorption centers in the visible wavelength. These vacancies absorb the light and result in coloration. An annealing in oxidizing atmospheres diffuses back oxygen and reduces those color centers. Meanwhile, holding temperature at 1200 ˚C during sintering is also a determination for the level of coloration.

In summary, though zirconia has been shown to be stronger than conventional glass-ceramics, the final mechanical properties of zirconia depend on many processing variables, including the type of stabilizing oxides, sintering methods, sintering time, sintering sequences, heating rate, cooling rate, surface sand blasting, or even the veneering procedures. The impact of processing techniques on the mechanical properties of full contour zirconia is not well investigated and there are few studies that tested this type of material.

In one previous study, Janabi had investigated the mechanical properties of four groups of translucent zirconia (BruxZir, KDZ Bruxer, CAP FZ, Suntech zirconia), one group of traditional zirconia (CAP QZ) and IPS e.maxCAD) by using crown shape and bar shape specimens sintered under manufacturer-recommended heating schedules. Since CAD/CAM zirconia material has nano-size particles and porosity, the surface area is comparatively higher than micron-size particles and results in a higher driving force for sintering. Therefore, the higher surface area offers the more opportunity to utilize a shorter sintering schedule to achieve the desirable sintering density. Meanwhile, a longer holding time during sintering seems to lead to larger microstructures and changes mechanical properties of the final CAD/CAM zirconia prosthesis. This research therefore investigated the effects of sintering holding time on the microstructure and mechanical properties of three zirconia materials (BruxZir, KDZ Bruxer, CAP FZ).[26]

MATERIALS AND METHODS

Three full-contour zirconia brands were selected to be compared in this study (Table 1). They are BruxZir (Shaded blank 100 (A1, B1, C1), Glidewell Dental labs, Newport Beach, CA, USA), KDZ Bruxer (Shade: A2, Keating Dental Arts, Irvine, CA, USA), and CAP FZ (Shade: A1, Custom Automated Prosthetics, Stoneham, MA, USA).

BAR SAMPLE PREPARATION

Bar samples of each material were cut from the CAD/CAM material blocks by using a cutting machine (Isomet 1000, Buehler, IL, USA.) (Figure 1). Sample size was thirty for each material (n = 30 and total N = 90) with final dimensions of 20 (±0.3) mm x 1.8 (±0.1) mm x 5 (±0.1) mm were made. Due to the shrinkage associated with sintering zirconia, the zirconia samples were cut oversized by a percentage specified by the manufacturers (ranging from 24.5-25 %) (Table II, Figure 2). All samples were polished in the sequence of 240-, 320-, 400-, 600-, to 1200-grit (EXAKT Technologies, Oklahoma City, OK, USA) with diamond discs before sintering. All samples were then diamond paste-polished in the sequence of 10 μm, 6 μm, 1 μm, to 1/10 μm after sintering. Each material was divided randomly into three groups (n = 10 for each group) and sintered separately by three different heating programs: 1) The manufacturer-recommended heating schedule (control group, n = 10) (Table III); 2) The first experimental group, sintered to 1000°C at a rate of 10°C/minute, then increased to a target temperature of 1600°C at a rate of 2°C/minute and held three hours before furnace cooling (n = 10) (Table IV), and 3) The second experimental group sintered with the same rate as first experiment group, but with a holding time of 6 hours before furnace cooling (n = 10)

(Table V). All groups were tested for flexural strength, microhardness, and grain size under SEM.

SQUARE SAMPLE PREPARATION

Square samples of each material were also prepared with the same methods as the bar samples (Figure 1). The sample number was nine for each material ($n = 9$ and total $N = 27$) with final dimensions of 8 (±0.3) mm x 8 (±0.3) mm x 1.5 (±0.1) mm. The shrinkage factor was considered and oversized samples were prepared to compensate, according to the specific percentage identified by each manufacturer (ranging from 24.5-25 %) (Table II, Figure 2). All samples were polished in the sequence of 240-, 320-, 400-, 600-, to 1200-grit (EXAKT Technologies, Oklahoma City, OK, USA) with diamond discs before sintering. After sintering, all samples were polished with diamond paste in the sequence of 10 μm, 6 μm, 1 μm, to 1/10 μm. Each material was divided randomly into three groups ($n = 3$ for each group) and sintered following the same procedure as described for the bar sample preparation. Square samples were used to test translucency.

FLEXURAL STRENGTH

The three-point bending test (Figure 3) was used to measure the uniaxial flexural strength (F) of bar samples on a universal testing machine (MTS Sintech ReNew 1123, MTS Systems Corporation, St. Paul, MN) (Figure 4). The following formula was used:

$$F = \frac{3P_f L}{2BH^2}$$

Where P_f is the measured load at the fracture, L is the length, B is the width, and H is the height of the specimen. The loading rate of the cross head was 1 mm/minute at room temperature (25±1°C).

MICROHARDNESS

Three broken specimens from each flexural strength test group were randomly chosen for the microhardness test. This prevented the introducing indentations in the samples that could influence the flexural strength results. The Knoop microhardness testing machine (M-400 Hardness Tester, Computing Printer ACP-94, LECO®, Knoop Diamond Indenter 860-538) (Figure 5) was used to test samples. Five indentations were made on each sample.

The load of the microhardness test was set at 300g, and an indentation dwell time of 15 seconds dwell time was used. The Knoop hardness number (KHN) is the ratio of the load applied to the area of the indentation. The calculation of KHN used the following equation:

$$\mathrm{KHN} = \frac{\mathrm{L}}{\ell^2 \mathrm{Cp}}$$

Where L is the load applied (kgf), ℓ is the measured length of the long diagonal of the indentation (mm), and Cp is the constant ($7.028 * 10^{-2}$) which is the relationship of the projected area of the indentation to the square of the long diagonal. The unit for KHN is kg/mm^2. Higher values represent harder materials.

THERMAL ETCHING AND CHORD LENGTH MEASUREMENT

According to “Ceramography: Preparation and Analysis of Ceramic Microstructures," etching is a method to enhance microstructure by selective corrosion.[66] Etching enables easier observation of grain boundaries and other microstructural features that are not apparent on a polished surface. Meanwhile, etching the microstructure should not be executed before a mechanical property test or a microindentation hardness test.

Methods of etching include thermal, chemical, electrolytic, ion, molten salt, and so on. Among all the available etching methods, thermal etching is usually considered as the simplest, cleanest, and most effective method of delineating grain boundaries in ceramic microstructures. For ceramic thermal etching, a temperature that is approximately 100 k to 200 k lower than the sintering temperature is usually utilized with a holding time of 5 minutes to 30 minutes.[66]

Therefore, a 1500-˚C thermal etching temperature with a 20-minute holding time was introduced in this experiment. One sample of each group that was not used in the microhardness test was randomly chosen (n = 9). All selected samples were put in the furnace followed the pre-set setting thermal etching program.

After thermal etching, all nine samples were ultrasonically cleaned in distilled water and isopropanol. Samples were then gold plated and imaged under a scanning electron microscope (SEM) (JEOL 6390 LV, Jeol USA, Peabody, MA) operating at 10 kV with a working distance of 11.2 mm to 11.3 mm and magnification of X25000.

Grain size analysis was performed with chord length measurement technique.[67] The advantages of chord length distribution technique include ease of use, little maintenance or calibration equipment required, the freedom of electronic or *in-situ* analysis.[68] Meanwhile, chord length measurement had been considered as a reliable method for the grain size distribution analysis.[69]

TRANSLUCENCY

Sintered square samples were used for the translucency test. The translucency parameter (TP) used in this study was developed by Johnson et al. (1995).[70] This parameter uses visible light that ranges between 380 nm to 780 nm and calculates the difference between the color reflectance data of white and black. The equation used for TP is as follows:

$$\mathrm{TP} = \sqrt{[(L*B \;\; - L*W)^2 + (a*\ B - a*W)^2 + (b*B - b*\ W)^2]}$$

Where, L* refers to the brightness, a* represents redness to greenness, and b* is yellowness to blueness. B refers to the color coordinates on the black background, and W refers to the coordinates on the white background.

The translucency parameter (TP) of all samples was measured with a spectrophotometer (CM-2600D, Konica Minolta Sensing Americas, Inc., Ramsey, NJ) (Figure 6). The device settings were controlled at 10-percent observer angle, UV 100 percent and standard illuminant D65 as the standard wavelength between 300 nm to 780 nm. The light reflected through target samples that were 1.5-mm thick. The SCI numbers were measured with zirconia samples inserted underneath a spectrophotometer device and on a white (Figure 7) and black background (Figure 8).

STATISTICAL METHODS

Two-way ANOVA followed by Tukey's pairwise multiple comparisons were used to determine the significance of different material groups (BruxZir, KDZ Bruxer, and CAP FZ) on flexural strength, microhardness, and translucency. All tests were performed at a significance level of 5 percent.

RESULTS

FLEXURAL STRENGTH

Mean flexural strength, standard deviation, the highest value, and the lowest value are listed in Table VI and Figure 9. For the flexural strength, CAP FZ with holding time 3 hours showed the highest mean value (1586 MPa) whereas the BruxZir manufacturing group represented the lowest mean value (823 MPa). The differences in flexural strength between different materials were significant ($p < 0.05$). Considering the difference between two different holding time programs and the manufacturer's program for each material, BruxZir (1204 MPa) and KDZ Bruxer (996 MPa) had a higher average value in the 6-hour holding time group than the manufacturer's programs (BruxZir: 823 MPa; KDZ Bruxer: 896 MPa). CAP FZ had a higher average value in the 3-hour holding time group (1586 MPa) than the manufacturer's program (1258 MPa). The statistical analysis (Table VII (a), (b), and (c)) indicated that the value of both 3-hour (1188 MPa) and 6-hour (1246 MPa) holding time groups were significantly ($p < 0.05$) higher than the manufacturer's recommended sintering program (992 MPa). Meanwhile, the interaction between these two variables was also significant ($p < 0.05$). However, even though the 6-hour holding time had higher flexural strength than the 3-hour holding time program, there is no statistical significance ($p > 0.05$).

MICROHARDNESS

The mean Knoop microhardness number (KHN) and standard deviation of each group are presented in Table VIII and Figure 10. CAP FZ represented the highest mean KHN (1370 kg/mm^2) with the manufacturer's recommendation sintering program whereas the lowest mean KHN happened on BruxZir with the manufacturer's recommendation sintering program (906 kg/mm^2). For BruxZir and KDZ Bruxer, both the 3-hour (BruxZir: 973 kg/mm^2; KDZ Bruxer: 1222 kg/mm^2) and 6-hour (BruxZir: 965 kg/mm^2; KDZ Bruxer: 1234 kg/mm^2) holding-time groups had a higher average KHN than the manufacturer's program groups (BruxZir: 906 kg/mm^2; KDZ Bruxer: 1124 kg/mm^2). CAP FZ had higher mean KHN in the manufacturer's recommendation sintering program group (1370 kg/mm^2) than in the 3-hour (1255 kg/mm^2) and 6-hour (1261 kg/mm^2) holding-time groups. The statistical analysis (Table IX (a), (b), and (c)) indicated that the KHN was statistically significant among the different materials ($p < 0.05$). The interaction between these two variables was also significant ($p < 0.05$). However, there was no statistical significance with different sintering programs within the same material ($p > 0.05$).

SCANNING ELECTRON MICROSCOPE (SEM)

The SEM images from Figure 11 to Figure 19 represent the three different sintering programs (manufacturer's recommendation, 3-hour, and 6-hour holding-time sintering programs) for the three materials (BruxZir, KDZ Bruxer, and CAP FZ). The chord length measurement showed that the grain size was homogeneous for samples sintered following the manufacturer's recommendation programs. An average grain size of 0.38 µm was obtained for the three materials following the manufacturer's recommended programs. The cumulative mean, standard deviation for grain size (µm) of the three materials and three different sintering programs are listed in Table X and Figure 20.

Compared with manufacturers' recommendation groups, the 3-hour holding-time sintering program exhibited more irregular grain arrangement in all three materials. Partial grains also represented an enlarged size. For BruxZir, the 3-hour holding-time sintering program showed noticeable partial grain size enlargement and irregular arrangement. Figure 21 (a), (b), and (c) represents BruxZir grain size proportion change by percentage for different sintering programs. For KDZ Bruxer, partially enlarged grains could be seen in both experimental holding time groups compared with the manufacturer's sintering program. The grain size proportion change by percentage for different sintering programs is presented in Figure 22 (a), (b), and (c). CAP FZ had partially enlarged grains in the 3-hour holding-time sintering program compared with the manufacturer's recommended sintering program. Moreover, in the CAP FZ 6-hour holding-time group, an even enlargement of grains was discovered compared with the manufacturer's recommended sintering program. The CAP FZ grain size proportion change by percentage for different sintering programs is presented in Figure 23 (a), (b), and (c). In conclusion, all three materials had a tendency to generate increased grain size when holding time was prolonged.

The statistical analysis (Table XI (a), (b), and (c)) indicated no statistical difference among the three materials in grain size in the manufacturers' recommended sintering programs ($p > 0.05$). However, both longer holding time groups had statistically significant differences compared with the manufacturer's program ($p < 0.05$). Meanwhile, when comparing the two longer holding-time sintering programs, although the 6-hour holding-time sintering group had higher mean value than the 3-hour's, no statistical significance was found between them.

Grain size greater than 2 μm was not discovered in any SEM image. This finding was in contrast to Chevalier's article.[48] However, mechanical property changes were still observed in other mechanical properties tests.

TRANSLUCENCY

For BruxZir, the mean translucency parameter (TP) was higher in the manufacturer's recommendation group (0.472) than in the 3-hour (0.109) and 6-hour (0.100) holding-time sintering programs. KDZ Bruxer represented similar TP mean values (3.476 ~ 3.576) in three different groups. As for CAP FZ, the highest TP mean value (3.634) fell in the 6-hour holding-time sintering program and both experimental sintering programs demonstrated greater TP mean values than the manufacturer's recommendation group (2.793). However, the statistical analysis (Table XII (a), (b), and (c)) indicated there was no significance among the manufacturer's recommendation sintering program and different holding-time sintering programs. Moreover, BruxZir represented a significantly lower TP value than KDZ Bruxer and CAP FZ, and no statistical difference was found between KDZ Bruxer and CAP FZ. The interaction between these two variables was also insignificant ($p > 0.05$). The mean translucency parameter (TP) and standard deviation of each group are presented in Table XIII and Figure 24.

TABLES AND FIGURES

TABLE I

The materials used in this study

Brands	Manufacturers	Materials	Shade
BruxZir	Glidewell Dental labs, Newport Beach, CA, USA	Translucent Zirconia	100 (A1, B1, C1)
KDZ Bruxer	Keating Dental Arts, Irvine, CA, USA	Translucent Zirconia	A2
CAP FZ	Custom Automated Prosthetics, Stoneham, MA, USA	Translucent Zirconia	A1

TABLE II

Shrinkage factor and oversize cutting percentage
(to compensate for the shrinkage after sintering)

Brands	Shrinkage factor	Oversize cutting percentage
BruxZir	1.2291	23 %
KDZ Bruxer	1.243	24.3 %
CAP FZ	1.2546	25 %

TABLE III

The manufacturer recommended sintering program

	BruxZir	KDZ Bruxer	CAP FZ
Temp 1	25°C	25°C	25°C
Rate	15°C/minute (1 hour 18 minutes)	8°C/minute (≃2 hours 2 minutes)	6°C/minute (≃2 hours 40 minutes)
Temp 2	1200°C	1000°C	980°C
Hold	1 hour	(No Holding)	1 minute
Rate	2°C/minute (50 minutes)	2°C/minute (≃4 hours 55 minutes)	4°C/minute (≃2 hours 25 minutes)
Temp 3	1300°C	1590°C	1560°C
Hold		3 hours	2 hours
Temp 4	1580°C	1590°C	1560°C
Rate	10°C/minute (28 minutes)		
Hold	2 hours 30 minutes		
Temp 5	155°C		
Cool rate	15°C/minute		
Cooling time	1 hour 30 minutes		10°C/minute (2 hours)
Temp 6			400°C
Free cooling	To 25°C	To 25°C	To 25°C

TABLE IV

The three-hour holding-time sintering program

	BruxZir	KDZ Bruxer	CAP FZ
Temp 1	25°C		
Rate	10°C/minute (1 hour 38 minutes)		
Temp 2	1000°C		
Rate	2°C/minute (5 hours)		
Temp 3	1600°C		
Hold	3 hours		
Free cooling	25°C		

TABLE V

The six-hour holding-time sintering program

	BruxZir	KDZ Bruxer	CAP FZ
Temp 1	25°C		
Rate	10°C/minute (1 hour 38 minutes)		
Temp 2	1000°C		
Rate	2°C/minute (5 hours)		
Temp 3	1600°C		
Hold	6 hours		
Free cooling	25°C		

TABLE VI

The mean, standard deviation, minimum and maximum for flexural strength (MPa) of three materials and three different sintering programs

		Mean	SD	Min	Max
BruxZir	Manufacturer	823	121.4	610	957
	3-hour	1112	146.3	875	1360
	6-hour	1204	109.5	1000	1419
KDZ Bruxer	Manufacturer	896	85.3	765	993
	3-hour	865	70.0	758	959
	6-hour	996	87.2	822	1119
CAP FZ	Manufacturer	1258	299.5	774	1690
	3-hour	1586	262.7	1101	1866
	6-hour	1538	158.0	1280	1782

TABLE VII (a)

The two-way ANOVA statistical analysis of flexural strength

	DF	**ANOVA SS**	**Mean Square**	**F Value**	**Pr > F**
Manufacturer variables	2	4807978.703	2403989.352	80.95	<.0001
Sintering variables	2	1058182.459	529091.229	17.82	<.0001
Interaction	4	453925.007	113481.252	3.82	0.0068

TABLE VII (b)

The Tukey’s comparisons of different materials

<table>
<tr><th colspan="4">Means with the same letter are not significantly different.</th></tr>
<tr><th>Tukey Grouping</th><th>Mean</th><th>N</th><th>Manufacturer variables</th></tr>
<tr><td>A</td><td>1046</td><td>30</td><td>BruxZir</td></tr>
<tr><td>B</td><td>919</td><td>30</td><td>KDZ Bruxer</td></tr>
<tr><td>C</td><td>1460</td><td>30</td><td>CAPFZ</td></tr>
</table>

TABLE VII (c)

The Tukey's comparisons of different sintering programs

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Sintering variables
A	992	30	Manufacturer
B	1188	30	3-hour holding time
B	1246	30	6-hour holding time

TABLE VIII

The mean, standard deviation for Knoop microhardness number (kg/mm^2) of three materials and three different sintering programs

	Manufacturer		3-hour		6-hour	
	Mean	SD	Mean	SD	Mean	SD
BruxZir	906	62.4	973	58.3	965	70.2
KDZ Bruxer	1124	71.2	1222	61.1	1234	73.7
CAP FZ	1370	226.9	1255	109.8	1261	78.6

TABLE IX (a)

The two-way ANOVA statistical analysis of Knoop microhardness number

	DF	ANOVA SS	Mean Square	F Value	Pr > F
Manufacturer variables	2	2868124.844	1434062.422	125.14	<.0001
Sintering variables	2	10578.311	5289.156	0.46	0.6314
Interaction	4	264186.044	66046.511	5.76	0.0003

TABLE IX (b)

The Tukey’s comparisons of different materials.

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Manufacturer variables
A	948	45	BruxZir
B	1193	45	KDZ Bruxer
C	1295	45	CAPFZ

TABLE IX (c)

The Tukey’s comparisons of different sintering programs

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Sintering variables
A	1133	45	Manufacturer
A	1150	45	3-hour holding time
A	1153	45	6-hour holding time

TABLE X

The mean and standard deviation for grain size (µm)
for three materials and three different sintering programs

	Manufacturer		3-hour		6-hour	
	Mean	SD	Mean	SD	Mean	SD
BruxZir	0.33	0.120	0.48	0.178	0.53	0.178
KDZ Bruxer	0.44	0.131	0.49	0.136	0.48	0.212
CAP FZ	0.36	0.107	0.46	0.151	0.54	0.159

TABLE XI (a)

The two-way ANOVA statistical analysis of the chord length measurement

	DF	ANOVA SS	Mean Square	F Value	Pr > F
Manufacturer variables	2	0.08205129	0.04102565	1.73	0.1783
Sintering variables	2	1.50201172	0.75100586	31.71	<.0001
Interaction	4	0.28289575	0.07072394	2.99	0.0190

TABLE XI (b)

The Tukey’s comparisons of different materials

<table>
<tr><th colspan="4">Means with the same letter are not significantly different.</th></tr>
<tr><th>Tukey Grouping</th><th>Mean</th><th>N</th><th>Manufacturer variables</th></tr>
<tr><td>A</td><td>0.44</td><td>120</td><td>BruxZir</td></tr>
<tr><td>A</td><td>0.47</td><td>133</td><td>KDZ Bruxer</td></tr>
<tr><td>A</td><td>0.44</td><td>132</td><td>CAPFZ</td></tr>
</table>

TABLE XI (c)

The Tukey's comparisons of different sintering programs

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Sintering variables
A	0.37	143	Manufacturer
B	0.48	122	3-hour holding time
B	0.52	120	6-hour holding time

TABLE XII (a)

The two-way ANOVA statistical analysis of translucency parameter (TP)

	DF	ANOVA SS	Mean Square	F Value	Pr > F
Manufacturer variables	2	61.14251467	30.57125733	150.87	<.0001
Sintering variables	2	0.07413356	0.03706678	0.18	0.8344
Interaction	4	1.35856978	0.33964244	1.68	0.1992

TABLE XII (b)

The Tukey's comparisons of different materials.

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Manufacturer variables
A	0.2268	9	BruxZir
B	3.5408	9	KDZ Bruxer
B	3.2814	9	CAPFZ

TABLE XII (c)

The Tukey's comparisons of different sintering programs

Means with the same letter are not significantly different.			
Tukey Grouping	Mean	N	Sintering variables
A	2.2784	9	Manufacturer
A	2.3676	9	3-hour holding time
A	2.4030	9	6-hour holding time

TABLE XIII

The mean, standard deviation for translucency parameter
(TP) of three materials and three different sintering programs

	Manufacturer		3-hour		6-hour	
	Mean	SD	Mean	SD	Mean	SD
Brux Zir	0.472	0.056	0.109	0.010	0.100	0.070
KDZ Bruxer	3.571	0.551	3.576	0.271	3.476	0.208
CAP FZ	2.793	0.288	3.417	0.587	3.634	0.228

FIGURE 1. Isomet 1000, a cutting machine.

FIGURE 2. Zirconia bar samples, left: pre-sintered, and right: sintered.

[redacted]

FIGURE 3. Three point bending test.

FIGURE 4. MTS Sintech 123, a loading machine.

FIGURE 5. M-400 Hardness Teste, Knoop Diamond Indenter 860-538.

FIGURE 6. CM-2600D, Konica Minolta Sensing Americas, Inc., Ramsey, NJ.

FIGURE 7. White background for translucency parameter testing.

FIGURE 8. Black background for translucency parameter testing.

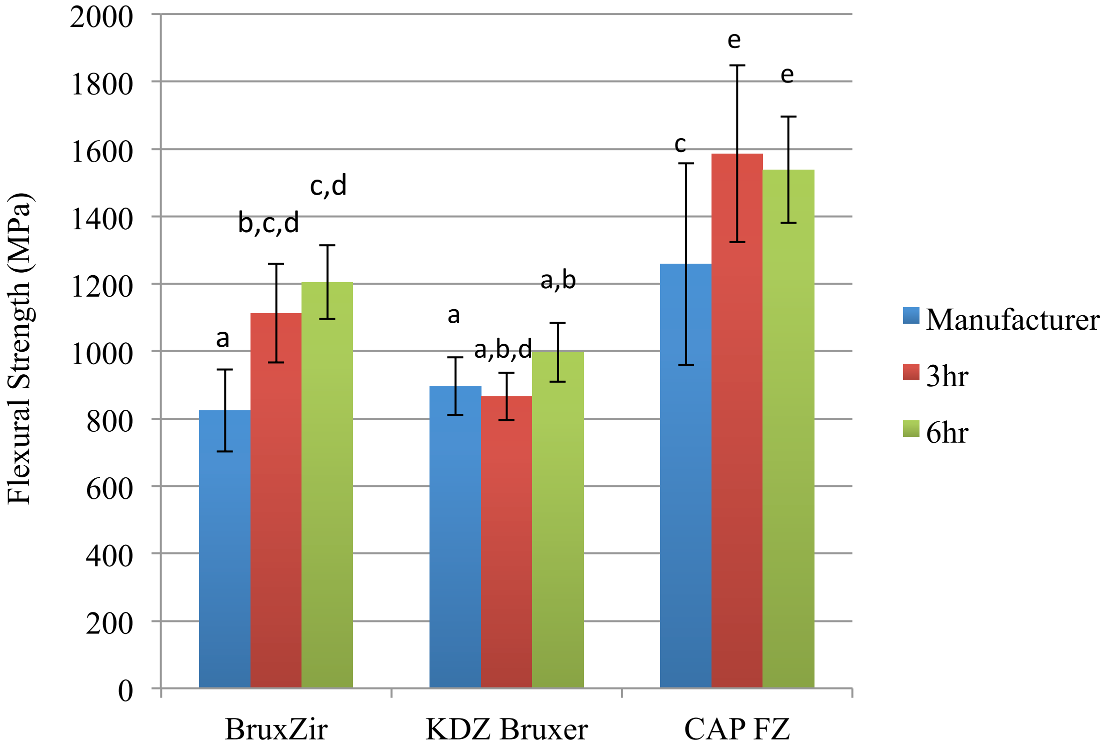

FIGURE 9. Mean flexural strength with standard deviation.

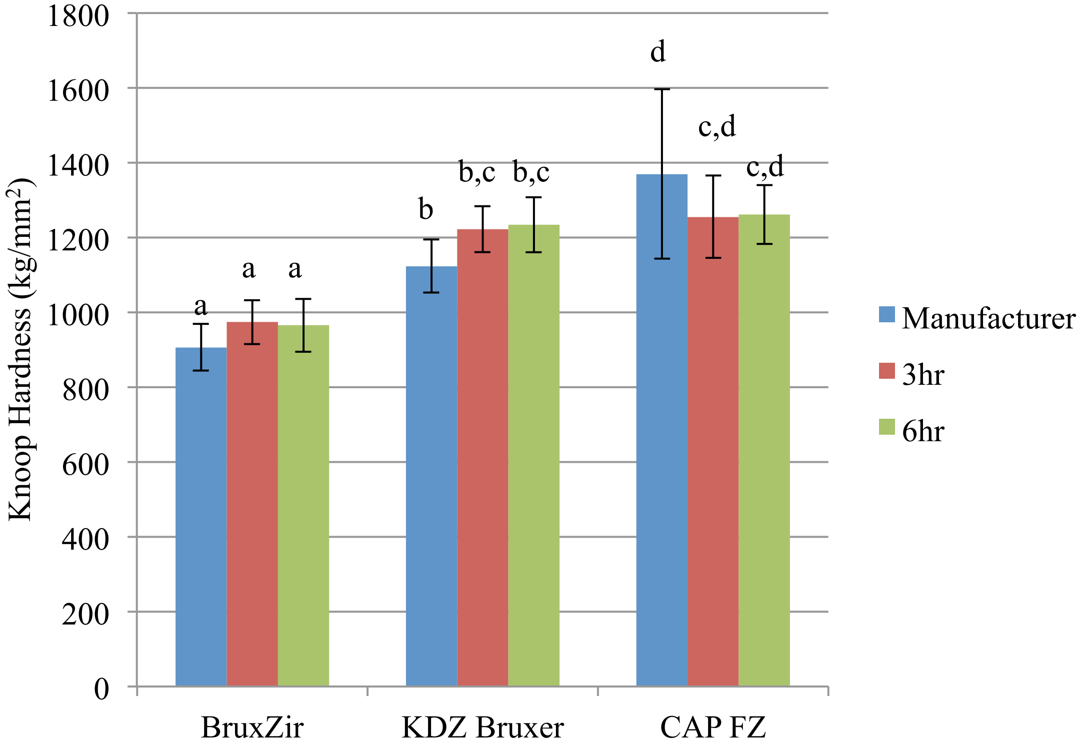

FIGURE 10. Mean Knoop microhardness with standard deviation.

FIGURE 11. SEM image: BruxZir with the manufacturer’s recommendation sintering program.

FIGURE 12. SEM image: BruxZir with the 3-hour holding-time sintering program.

FIGURE 13. SEM image: BruxZir with the 6-hour holding-time sintering program.

FIGURE 14. SEM image: KDZ Bruxer with the manufacturer’s recommendation sintering program.

FIGURE 15. SEM image: KDZ Bruxer with the3-hour holding-time sintering program.

FIGURE 16. SEM image: KDZ Bruxer with the 6-hour holding-time sintering program.

FIGURE 17. SEM image: CAP FZ with the manufacturer’s recommendation sintering program.

FIGURE 18. SEM image: CAP FZ with the 3-hour holding-time sintering program.

FIGURE 19. SEM image: CAP FZ with the 6-hour holding-time sintering program.

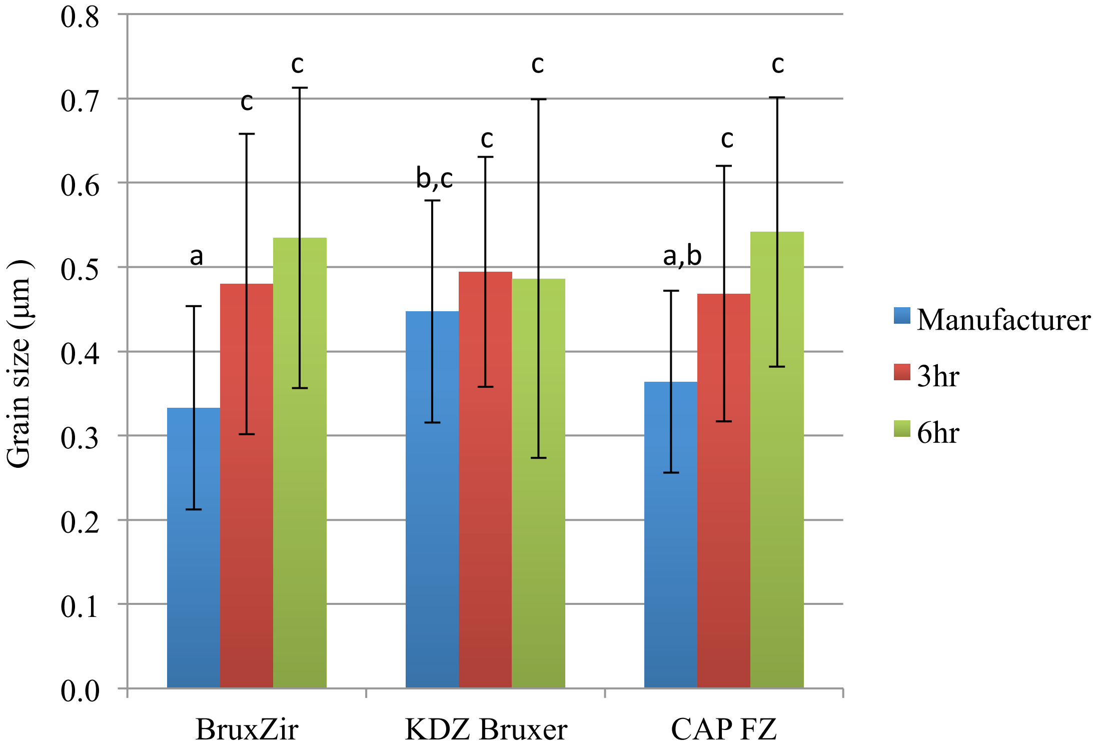

FIGURE 20. Mean grain size value with standard deviation.

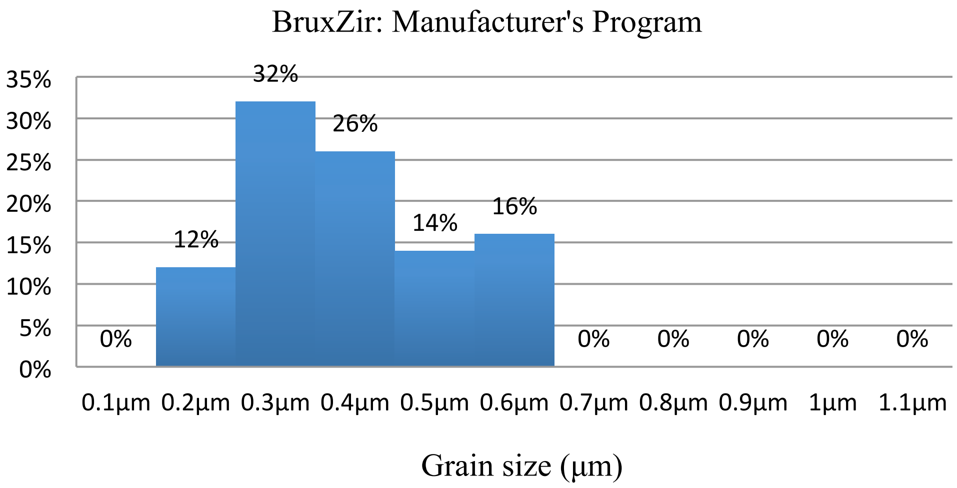

FIGURE 21 (a). BruxZir grain size distribution change by percentage.

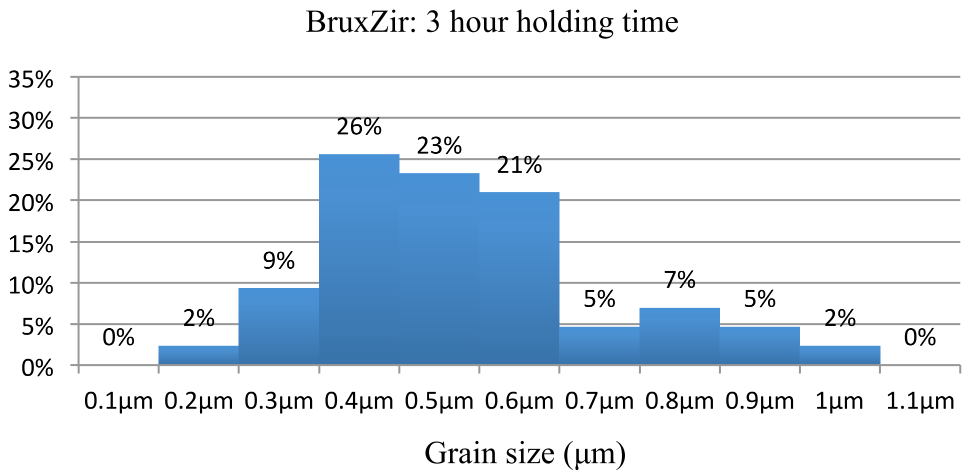

FIGURE 21 (b). BruxZir grain size distribution change by percentage.

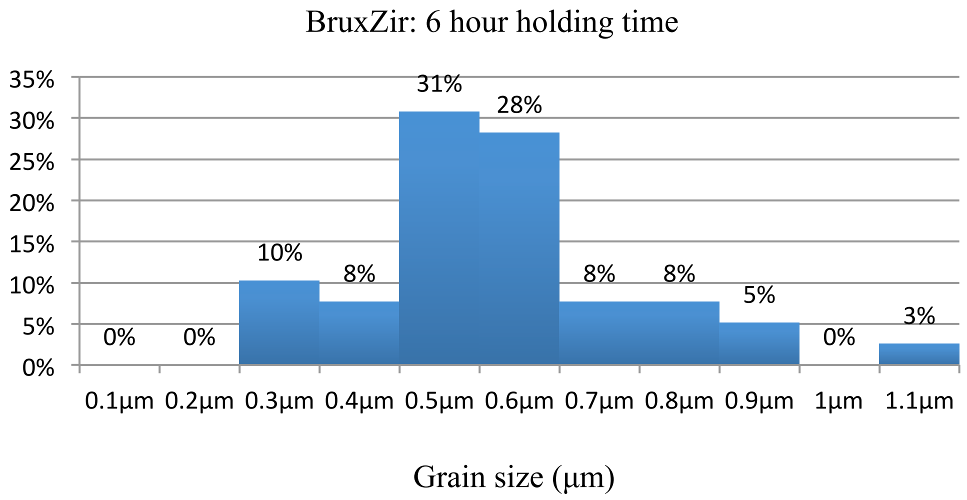

FIGURE 21 (c). BruxZir grain size distribution change by percentage.

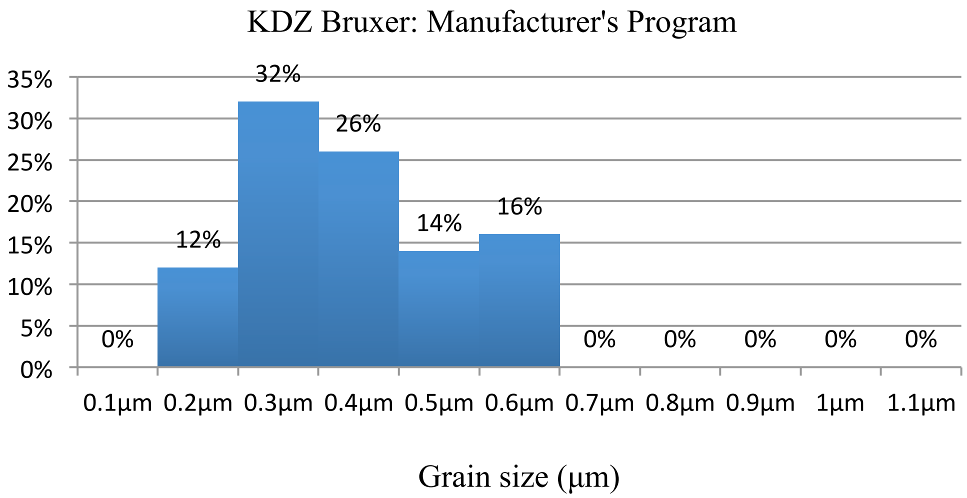

FIGURE 22 (a). KDZ Bruxer grain size distribution change by percentage.

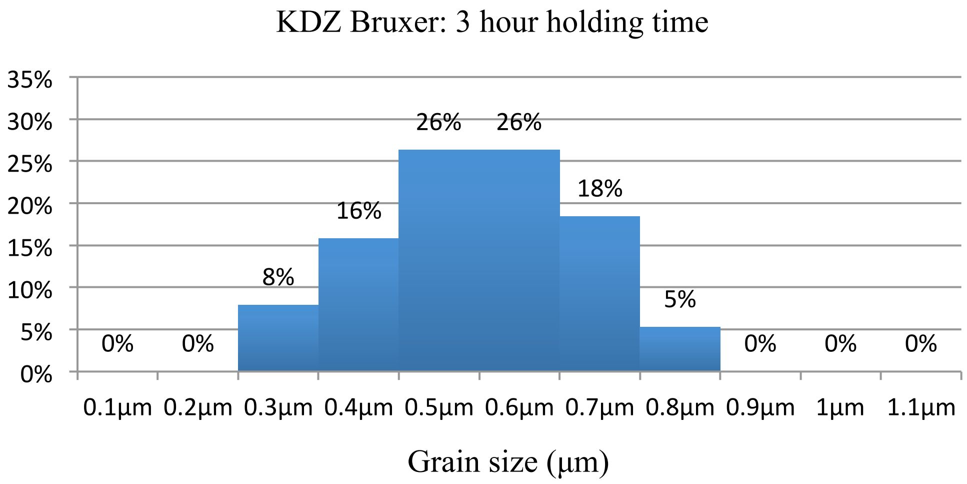

FIGURE 22 (b). KDZ Bruxer grain size distribution change by percentage.

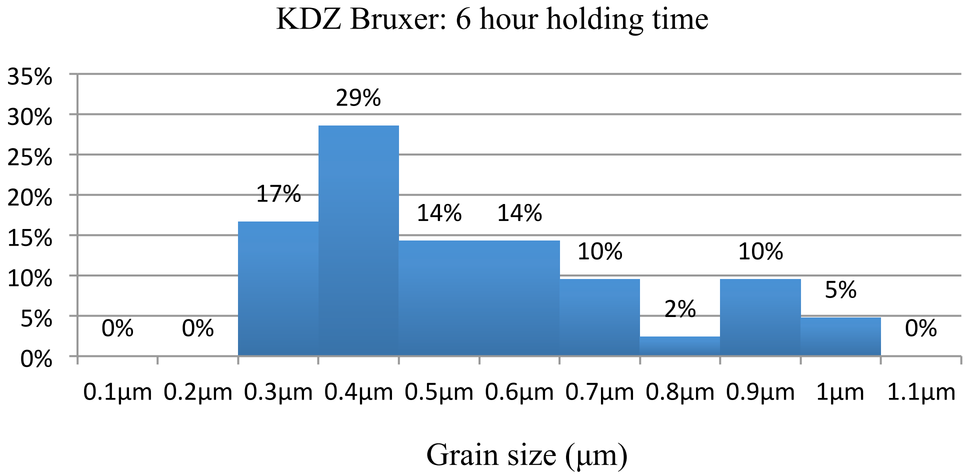

FIGURE 22 (c). KDZ Bruxer grain size distribution change by percentage.

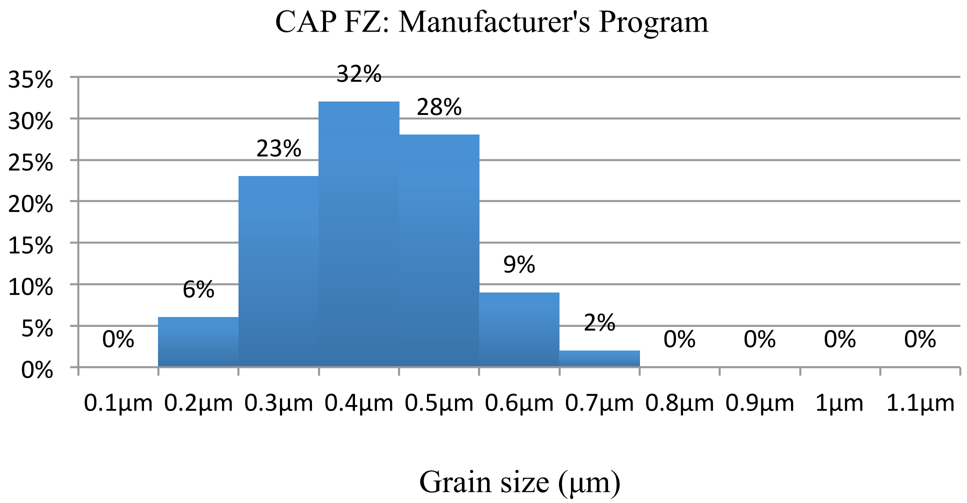

FIGURE 23 (a). CAP FZ grain size distribution change by percentage.

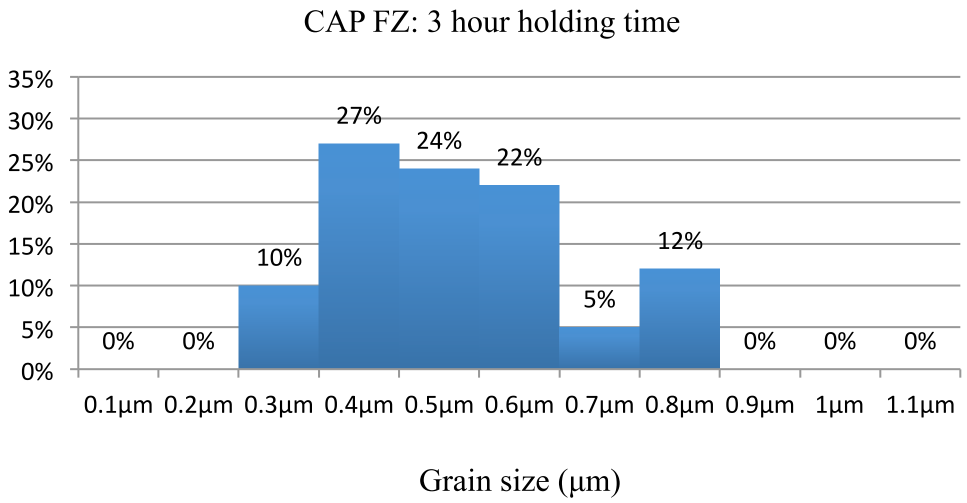

FIGURE 23 (b). CAP FZ grain size distribution change by percentage.

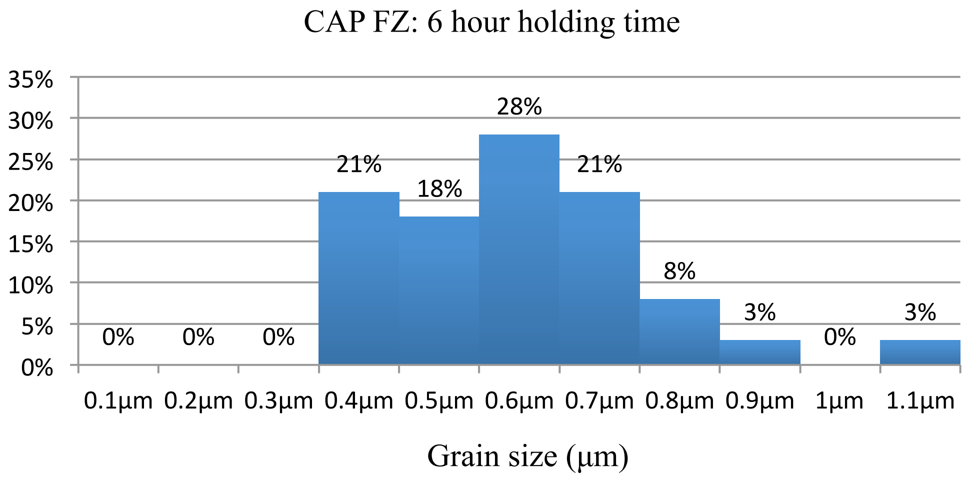

FIGURE 23 (c). CAP FZ grain size distribution change by percentage.

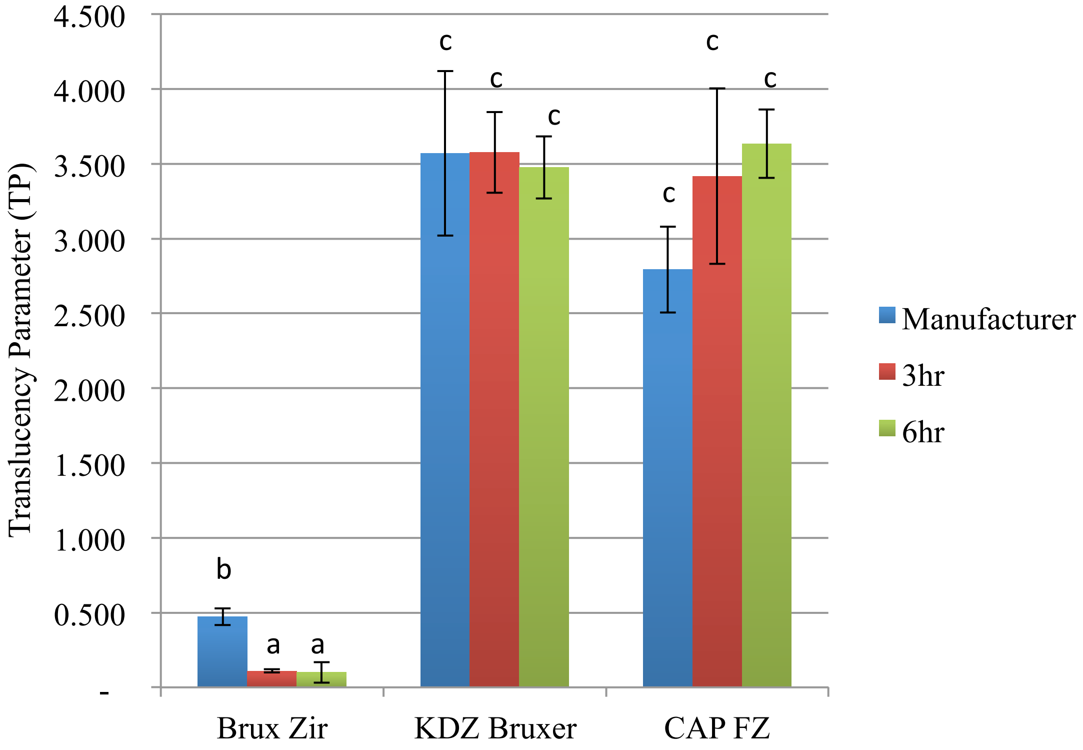

FIGURE 24. Mean translucency parameter (TP) with standard deviation.

DISCUSSION

Full-contour zirconias have recently caught many dentists' attention due to claims of higher translucency than traditional zirconia and no need for a veneer layer in dental restorations.[23] These potential superiorities support full-contour zirconias' application in clinical practice. Numerous articles have shown the effects of sintering conditions on properties of these materials.[2, 3, 21, 25, 44, 45, 47, 61, 71-74] However, due to the variables in full-contour zirconia materials and different sintering conditions, no consensus has been reached. Meanwhile, limited articles were found investigating the effect of different holding times in the sintering programs on full-contour zirconias. The purpose of this study was to investigate the effects on mechanical properties by using different holding time in the sintering programs.

For the flexural strength test, the statistical analysis showed an increase in load at fracture in sintering programs with longer holding time compared with the manufacturers' recommendation sintering programs. A longer holding time contributed to a greater grain sizes just as an increase in sintering temperature contribute to greater grain sizes. With the prolonged sintering time, grains are sintered together and defects or pores on grain boundaries are reduced or covered by solid-state diffusion.[44] This might be a reason for longer holding-time groups achieving higher flexural strength than manufacturers' recommendation sintering programs.

Another reason for the increased flexural strength is the tetragonal to monoclinic transformation toughening factor. Lazar[37] concluded that the presence of coarser grains in the microstructure of yttria-stabilized zirconia ceramics is an indicator of monoclinic form existence. The tetragonal to monoclinic transformation of the zirconia in the superficial layer contributed to the increment of surface compressive stresses and balancing tensile stresses in bulk.[75] The transformed zirconia is mainly in the outer layer, while zirconia in the central layer retained the tetragonal form. This induces outer layer compressive stresses that also cover potential advancing cracks and therefore result in an increase in strength of zirconias.[11, 76] These conclusions are consistent with the finding in this experiment. Therefore, the null hypothesis that sintering zirconia specimens with a longer holding time would not have an influence on flexural strength compared with specimens sintered with the manufacturers' recommended heating schedule was rejected.

For the microhardness test, theoretically, the existence of monoclinic phase transformation on the surface would result in an increase of surface microhardness. However, in the present study, no statistical significance was found with different sintering programs. This result corresponded to Hjerppe's study.[2] In Hjerppe's article, the microhardness test was performed on zirconia samples with different holding times (3 hours and 1 hour 40 minutes respectively). The author found no significant difference in the microhardness test. Meanwhile, Cottom et al. also reported that the hardness of zirconia ceramics was unrelated to grain size.[77] In the present study, nevertheless, even though there was no statistical significance between different sintering programs, an incremental KHN mean value from manufacturers' recommendation sintering programs to the 3-hour and 6-hour holding-time sintering programs was found (Table IX (c)). It is speculated that the microhardness change from the surface microstructure with longer holding time was not as significant as sintering at a higher temperature. Further studies into the microhardness change in different sintering conditions will be needed. Due to the absence of significance in statistics, the null hypothesis that sintering zirconia specimens with a longer holding time would not have an influence on microhardness compared with specimens sintered with the manufacturers' recommended heating schedule could not be rejected.

The property of translucency depends on chemical components, volume of crystals, size of particles, and sintered densities. These factors influence the amount of light that is absorbed, reflected, or transmitted.[44] Smaller crystals have higher transmittance with less refraction and less absorption when light passes through directly. However, due to the increased particle number per unit volume, scattering of light increases the opacity. On the contrary, greater particle materials have reduced numbers of crystals per unit volume that cause less scattering and also decreased opacity.[78] In the present study, with the prolonged holding time, the mean TP value increased, even though it was not statistically significant (Table XII (c)). In CAP FZ, there is an increase in TP value that is consistent with other articles, even though it is not statistically significant. Meanwhile, in BruxZir, there is a noticeable decrease in TP value for both longer holding-time sintering programs. It is speculated that the decrease of translucency was attributed to the increased scattering from irregular grain arrangement and inhomogeneity after the sintering (Figure 12 and Figure 13). Therefore, the null hypothesis that sintering zirconia specimens with a longer holding time would not have an influence on translucency compared with specimens sintered with the manufacturers' recommended heating schedule was partially rejected.

Based on articles, the higher the sintering temperature, the greater the grain size. Several experiments had provided the same conclusion regarding this theory. The greater grain size may potentially increase full-contour zirconias' strength,[15, 45] but full-contour zirconias may also be subject to a higher isk of low-temperature degradation (LTD).[15] Meanwhile, low-temperature degradation (LTD) is considered a possible cause of catastrophic fracture.[11, 14, 15, 39, 48, 50, 51, 55, 73, 79, 80]

For the yttria-stabilized zirconias sintered at a higher temperature, the migration of yttrium toward the grain boundaries was found.[81] The uneven distribution of the yttria-stabilizing ions caused the lower average yttria content in the remaining tetragonal phase to be more vulnerable to LTD.[43, 73] A greater number of monoclinic phase particles on the outer layer of the zirconia might encounter microcracking and lead to a faster aging process.[15] The gained flexural strength from surface compressive stresses due to the transformation toughening might therefore be lost, and the zirconias become more susceptible to acidic and aqueous environments.[80] In order to keep the stability of zirconias, they should be fabricated and sintered without inducing phase transformation. It is hence understandable that manufacturers suggest sintering programs that are at lower sintering temperatures or use faster sintering programs. The zirconias may be weaker in strength but more stable in crystal phases.

In conclusion, longer holding time at high temperature may be utilized to increase full-contour zirconias' strength by promoting transformation toughening. However, the effect of LTD in zirconia with longer holding-time sintering programs is unclear. Meanwhile, the present study had limitations in simulating oral environment changes. The applied loading was static instead of cyclic fatigue force. For future studies, investigation of different sintering programs' effects on full-contour zirconias – LTD effects, hardness changes, optic properties, phase compositions by X-ray diffraction, and oral environment simulations – are indicated.

SUMMARY AND CONCLUSION

The mechanical properties of full-contour zirconias greatly depend on the grain size. Enlarged grain size potentially increases flexural strength that is statistically significant.

1. Greater grains could be achieved, similar to raising the sintering temperature, by increasing holding time. The longer the holding time, the more chance to acquire greater grains.
2. No obvious relationship between prolonged holding times and the change of microhardness was found statistically. No consensus was reached regarding the change in microhardness in different sintering conditions.
3. BruxZir had a significant decrease in translucency after longer holding time, while CAP FZ had a significant increase in translucency with the 6-hour holding time group. Overall, a tendency of increasing translucency with increasing holding time was found. However, there is no statistical relationship between these two variables.

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ABSTRACT

EFFECTS OF SINTERING HOLDING TIME ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TRANSLUCENT ZIRCONIA

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Background: With the great improvements in CAD/CAM technology, zirconia-based CAD/CAM ceramic is now widely used in dentistry. The CAD/CAM zirconia block offers the more efficient way to fabricate dental prostheses. However, the effects of sintering conditions and concomitant microstructure of zirconia-based materials (ZrO_2) remain unclear. This study investigated the effects of varying the holding times on microstructure and mechanical properties of three different translucent zirconia materials.

The objective of this study was to investigate the effects of holding time during sintering on the flexural strength, microhardness, grain dimension/shape, and translucency of three full-contour zirconia materials.

The alternative hypothesis was that zirconia specimens sintered with a longer holding time would have influences on 1) flexural strength; 2) microhardness; 3) grain dimension/size under SEM; and 4) translucency compared with specimens sintered with

the recommended heating schedule.

Materials and Methods: The experiment used three different translucent zirconias: BruxZir, KDZ Bruxer, and CAP FZ, (n = 30 for each material). Each material was exposed to three heating programs: 1) The manufacturer's recommended heating schedule (control group, n = 10); 2) The first experimental group sintered to 1000°C at a rate of 10°C/minute, then increased to a target temperature of 1600°C at a rate of 2°C/minute and held three hours before furnace cooling (experiment group, n = 10), and 3) The second experimental group sintered with the same rate as the first experimental group, but with a holding time of 6 hours before furnace cooling (experiment group, n=10). All samples were polished in the sequence of 240-, 320-, 400-, 600-, to 1200-grit (EXAKT Technologies, Oklahoma City, OK, USA) with a diamond disc before sintering. Then, all samples were polished in the sequence of 10 μm, 6 μm, 1 μm, to 1/10 μm with diamond paste after sintering. Three groups were tested for flexural strength, microhardness, grain size under SEM, and translucency.

Statistical methods: Two-way ANOVA was used to test the properties of different material groups. Tukey's pairwise multiple comparisons were used to compare the different sintering programs in this experiment.

Results: (1) Flexural Strength: Flexural strength between different materials were significant ($p < 0.05$). The interaction between these two variables was also significant ($p < 0.05$). However, there is no statistical significance ($p > 0.05$) between two longer holding-time sintering programs. (2) Microhardness: It was statistically significant among different materials ($p < 0.05$). The interaction between these two variables was also significant ($p < 0.05$). However, there was no statistical significance with different

sintering programs within the same material ($p > 0.05$). (3) SEM: An average grain size of 0.38 μm was obtained for samples processed according to the manufacturer's recommendation programs. No statistical difference among the three materials in the manufacturers' recommended sintering programs ($p > 0.05$). However, both longer holding time groups had statistically significant differences compared with the manufacturer's program ($p < 0.05$). (4) Translucency: No significance among the manufacturer's recommendation sintering program and different holding-time sintering programs. BruxZir represented a significantly lower TP value than KDZ Bruxer and CAP FZ, and no statistical difference was found between KDZ Bruxer and CAP FZ.

Conclusion: The mechanical properties of full-contour zirconias greatly depend on the grain size. Enlarged grain size may potentially increase flexural strength, but full-contour zirconias may also be subject to a higher risk of low-temperature degradation (LTD). No obvious relationship between prolonged holding times and the change of microhardness was found statistically. A tendency of increasing translucency with increasing holding time was found.

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