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Mechanical properties and microstructure of mullite modified zirconia ceramic for dental applications

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Objectives: The aim of this study tried to find an appropriate addition of mullite to modify zirconia in order to improve the shortcomings of zirconia for clinical applications.

Methods: 10%, 20%, 30%, 40%, 50% (on weight basis) mullite modified zirconia (MDZ) were fabricated.The hardness, fracture toughness and elastic modulus were tested on specimens prepared through respective methods.

Results: The flexural strength, hardness and elastic modulus of these five groups decreased with an increase in the percentage of mullite, which may be ascribed to the increasing presence of a glassy phase. The fracture toughness of the 30% mullite content showed a similar result with the 10% group.

Conclusions: In general, an increase in the content of mullite is accompanied with a decrease of the strength and fracture toughness. The MDZ with a 10% content of mullite presents better mechanical properties and a better comprehensive clinical performance may be expected from.

Key words: Mullite, 3Y-TZP, Fracture toughness, Flexural strength, Elastic Modulus, Crystalline phase.

Introduction

Mullite ($3Al_2O_3$-$2SiO_2$) has a high fracture strength at high temperature, excellent resistance to heat, corrosion and oxidation as well as a low Young's modulus. Thus, mullite is becoming an important advanced ceramic material and has received signicant attention during the past decades as a potential structural material for high temperature applications [1]. Due to the fact that a zirconia dispersion in a mullite matrix improves the toughness by transformation and microcrack toughening, zirconia is extensively used to modify mullite for engineering applications [2, 3, 4]. However, in the present study, mullite was used to modify zirconia for dental applications based on the following demands in the dental clinical community.

Zirconia-based ceramics as restorative dental materials have generated considerable interest in the dental community. A phase transformation endows it with both high mechanical properties and alters the phase integrity of the material and increases the susceptibility to aging [5]. The low temperature degradation (LTD) of zirconia is a well-documented phenomenon, exacerbated notably by the presence of water [6, 7, 8]. High density crystalline phase with a low Si content leads to a modest combination with veneer [9] and modest cementation performance [10-17]. Furthermore, the elastic modulus of Y-TZP mismatching [18] with natural dentin [19] leads to a stress concentration on all ceramic crown margins and further to denture failure. Accordingly, corresponding researches found that the hydration resistance of zirconia is improved by the incorporation of mullite [20, 21]. It is found that the element Si is promising for the future denture cementation property [22] and the combination of a veneer porcelain [23, 24].

Based on the appealing particularity of mullite and imperative advancement of zirconia, the purpose of the present investigation is to introduce the elastic gradients of mullite to modify zirconia. Various mullite modified zirconia composites containing up to 50 wt.% of mullite were made using uniaxial pressing in order to evaluate their microstructural and mechanical features for future applications as dental restorative materials.

Experiment Procedure

Sol-gel derived, fine-grained mullite powder and zirconia powder partially stabilized by yttria were used as starting materials (supplied by Sansai Company, Jiangsu province, PRC.). The mean particle size of the powder was 400 nm and the specic surface area was 3.575 m^2g^{-1} (measured by an X-ray centrifugal sedimentation method, BI-XDC, Brookhaven Instrument Corporation, USA). The particle diameters of the powders are shown in Fig. 1. Appropriate amounts of mullite and zirconia were mixed by conventional ball milling using zirconia balls in ethanol for 6 h.

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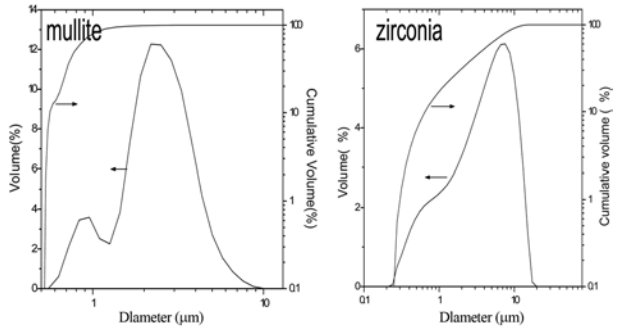

Fig. 1. Particle diameters of mullite and zirconia powder.

The resulting paste obtained after milling was dried in an oven, then, grounded and sieved to produce agglomerate-free powders. Next, the powder mixtures were pressed uniaxially at 20 MPa and isostatically at 200 MPa prior to a subsequent sintering at 1500 ºC for 2 h in air.

Flexural strengths were tested in three-point bending tests on 3 × 4 × 36 mm^3 sized samples, using a 30 mm span and a crosshead speed of 0.5 mm $minute^{-1}$ on a universal testing machine (EASYTEST, LLOYD Inc., England). The reported values are the average data obtained from ten tests of samples with the same raw powder composition and heat treatment procedure. The fracture toughness, K_{IC} ($MPa^{1/2}$), was determined on polished surfaces using a Vickers indentation method (Wilson-Wolpert Tukon-2100B) in accordance with Marshall and Evan's method [25]. Each sample was measured under a load of 10 kgf for 30 s.

Young's modulus was determined with the help of a nanoindentor (FISCHERSCOPE H100, Germany) the load force was 200 mN, the loading and holding time was 20 s and 5 s respectively.

Microstructures were characterized by a JSM-6700F field emission scanning electron microscope. Qualitative and quantitative analysis of micro areas of the materials were established by an electron microprobe analysis instrument (EPMA-8705QH2, Japan). IPP image pro-plus was assumed to measure the volume fraction of each crystal phase.

Each test item datum was analyzed using one-way ANOVA followed by Student-Newman-Keuls pairwise tests (a = 0.05).

Result and Discussion

The mechanical properties measurement data are listed in Table 1 and curved in Fig. 2. Chemical components and spectra from the electron microprobe analysis are

Table 1. Mechanical properties of each group

Group	Ingredients (Based on weight)		Elastic Modulus (GPa)	Hardness HV(GPa)	Toughness, KIC ($MNm^{-1.5}$)	Strength, σ_f (MPa)
	Zirconia	Mullite				
1	90%	10%	214.2	13.59	5.129322	737.8
2	80%	20%	206.4	12.30	4.545152	354.83
3	70%	30%	202.4	12.33	5.394458	264
4	60%	40%	185.9	11.26	4.179853	255.589
5	50%	50%	177.35	7.03	3.976161	213.68

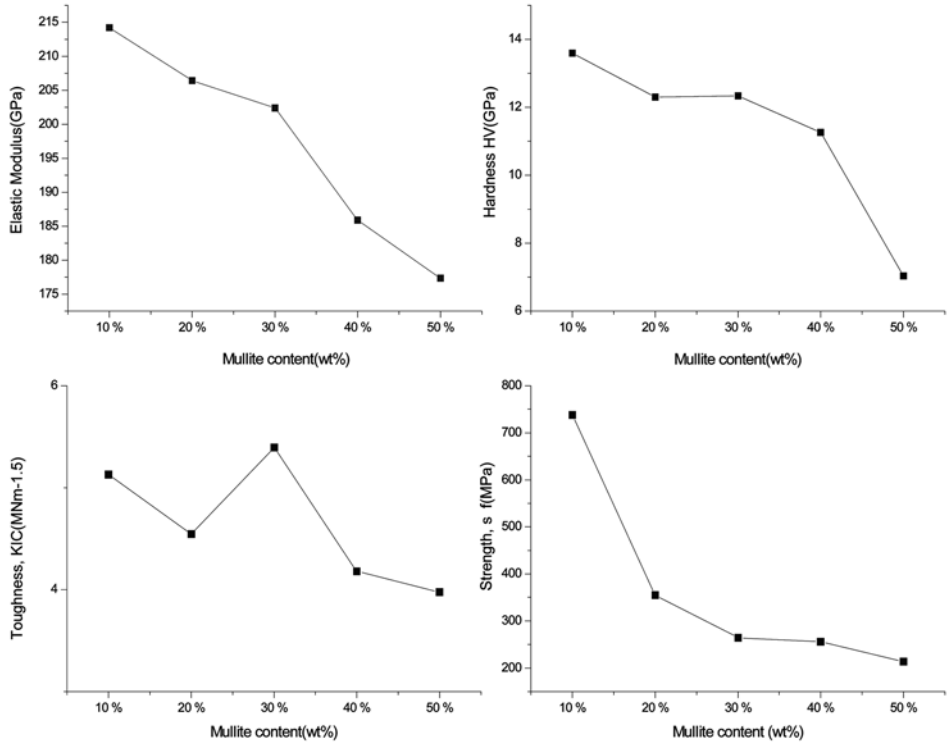

Fig. 2. Curves of mechanical properties as a function of mullite content.

listed in Table 2 and Fig. 3. Scanning electron micrographs and images treated by IPP image pro-plus are shown in Fig. 4, the phase volume computation results are shown in Table 3.

Microstructure

Scanning electron micrographs of the five groups are shown in Fig. 4. All the samples had a dense microstructure with a low residual porosity. There is no preferential direction or orientation of the mullite grains in the microstructure of these materials.

Processed under the same conditions, composite material with a 10% mullite content shows a higher sintering grade with a lower porosity. Different aluminosilicate composites were observed and characterized by electron microprobe analysis: white color grains (spectrum 1 in Fig. 3) are $23.35ZrO_2 \cdot 8.58SiO_2 \cdot 0.84Al_2O_3$ which can be observed in all cases, gray tint grains (spectrum 2 in Fig. 3) of $4Al_2O_3 \cdot 3SiO_2 \cdot ZrO_2$, dark gray grains (spectrum 3 in Fig. 3) of $13.45Al_2O_3 \cdot 20.74SiO_2$. All these three composites can be observed as products of zirconia and mullite under a high temperature sintering reaction. The small black areas are the gas pores.

IPP image analysis showed the zirconia phase volume fraction to be 73.65, 65.26, 51.78, 35.71, 21.13 percent as shown in Table 3. As the main phase givings crack resistance, the TZP volume fraction might be the best interpretation of the fracture toughness and flexural strength differences among the specimens. The amorphous matrix contributed to the low elastic modulus, fracture toughness, as well as flexural strength of the higher mullite content group of the MDZ.

Considering the volume fraction of the three principal phases, it is clear that microstructure changes in the groups with 40% and 50% mullite content appear. In these materials mullite is the continuous phase and acts as a matrix for the glass and zirconia grains. From the microstructure of group with 30% in Fig. 4, the mullite content appears all as intermediate between the other two configurations showing the difficulty of determining which component acts as the matrix.

Fracture toughness

Fracture toughness is an important material parameter which characterizes the resistance of a material against a propagating crack. The higher the fracture toughness the better is the mechanical behavior of a dental composite ceramic.

Theoretically speaking, fracture toughness of these groups should differ considerably, i.e. the 10% percent group must have a higher fracture toughness than the other

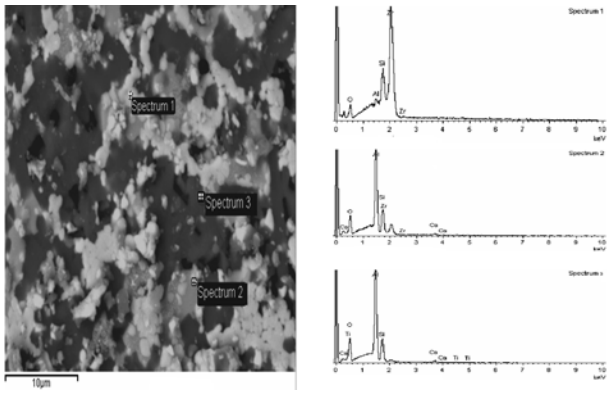

Fig. 3. Scanning electron microscope imags and electron microprobe analysis of the three phases.

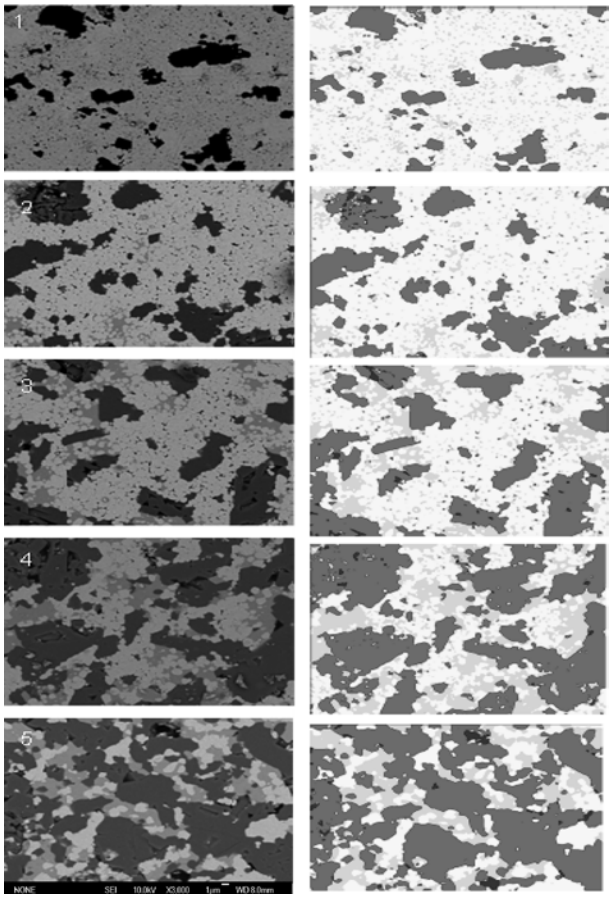

Fig. 4. Scanning electron micrographs of each group and corresponding images treated by IPP image pro-plus.

Table 2. Electron microprobe analysis of three-phase atom components

Atomic(%) Elements	Al	Zr	Si	O	Ca	Ti	Molecular Formula
Spectrum1	1.68	23.35	8.58	66.39	/	/	$23.35ZrO_2 \cdot 8.58SiO_2 \cdot 0.84Al_2O_3$
Spectrum2	24.18	3.25	9.62	62.48	0.47	/	$4Al_2O_3 \cdot 3SiO_2 \cdot ZrO_2$
Spectrum3	26.90	/	10.37	62.03	0.47	0.24	$13.45Al_2O_3 \cdot 20.74SiO_2$

Table 3. Respective phase volume fraction of each group computed by image pro-plus

Volume Fraction (%)	Spectrum 1	Spectrum 2	Spectrum 3	pore	Total
Group 1	73.65	11.51	14.84	0	100%
Group 2	65.26	10.16	24.04	0.54	100%
Group 3	51.78	18.35	29.15	0.72	100%
Group 4	35.71	16.86	47.10	0.32	100%
Group 5	21.13	23.49	54.18	1.2	100%

groups, it was found to be very close with the 30% percent group. No statistically significant difference between these two groups was detected. This anomaly may be explained on the basis of their phase component, content (shown in Tables 2 and 3) and the base values of fracture toughness of each phase.

Compared with the 10 $MNm^{-3/2}$ of the present commercial Y-TZP, the fracture toughness of MDZs were far lower [26]. While compared to 2 $MNm^{-3/2}$ of mullite [27], the MDZ has a fracture toughness value above 3.3 $MNm^{-3/2}$. It was contributed by the glassy amorphous matrix formation by the introduction of mullite. Similar results were found in a dental ceramic with a glassy matrix, which exhibits low values (1.25-4.4 $MPam^{1/2}$) of fracture toughness by consisting of polycrystalline particles [28-32].

Different mechanisms are involved in the toughening: a stress-induced transformation, microcracking, crack bowing and crack deflection. In all cases, the operative toughening mechanism depends on such variables as matrix stiffness, zirconia particle size, chemical composition, temperature and strength [33-37].

It may be inferred that the main mechanism is based on the tetragonal-monoclinic ZrO_2-phase transformation, which occurs during the crack growth and generates a bulk-expansion between 3 vol.% and 6 vol.%, and microcrack formation around m-ZrO_2 (microcrack toughening) during crack propagation. This is in coincidence with the researches concerning zirconia-toughened mullite [38-41].

Flexural strength

Flexural strength tests are considered to be sensitive to surface imperfections such as voids, cracks, and related flaws which can influence the strength of brittle materials. High flexural strength values reflect a limited tendency to crazing and a high resistance to surface defects and erosion. Flexural and tensile strengths are therefore considered the most important mechanical properties of core materials used as all-ceramic dental restorations, and efforts in developments of these materials should be directed towards improving these physical properties.

The values of flexural strength of the composites were well supported by the concentration of mullite and zirconia phases. It may be inferred therefore, that the tetragonal zirconia phase was responsible for the attainment of high mechanical strength. The phase volume fraction results showed consistency with this point.

The flexural strength of the composites was dependent on the phase composition in the range of study. Compared to other dental ceramics [42, 43], the flexural strength of group 1 is higher, and group 2 is comparatively lower. For groups 3 and 4, these flexural strengths are slightly lower than those given in the literature for pure mullite (254 MPa) [44]. The difference may be explained by the residual porosity, the presence of a non-crystalline phase, and the processing conditions used.

Another factor that may influence the mechanical properties of dental porcelains is the main mean crystal size. It has been determined that the retention of the tetragonal phase is critically governed by the grain size [45]. That is elevation of the grain size is predicted to decrease the critical stress that induces the tetragonal-monoclinic transformation. SEM showed that the particle diameter of group 1 was around 500 nm, group 2 was 600 nm-1000 nm, and groups 3, 4 and 5 were all above 1000 nm. Another factor affecting the flexural strength might be the initial particle adoption initiative powder size adopted, as shown in Fig. 1, the zirconia powder size was 300 nm-400 nm, while the mullite powder diameter was 600 nm. Based on that the smaller size of the powder, the bigger is the specific surface area and the driving energy, a small particle size administers to the process of sintering [46, 47]. For the submicrometer-sized zirconia and micro-sized mullite, their sintering affected their mechanical properties in further.

Besides this, some other factors such as porosity, the shape and orientation are important in determining the mechanical properties.

Elastic modulus

Elastic modulus describes the relative stiffness of the material within the elastic range. Natural tooth hard tissues have a range of intrinsic stiffness or modulus values and the addition of restorative materials of different modulus can affect the overall stiffness of the restored tooth and the interfacial stresses that are generated. The clinical outcome will be related to the mismatching of moduli values, and if the modulus mismatch is too great, an interfacial stress may result from either a thermal, or mechanical effect in the material [48].

Therefore, restoration materials should have similar elastic modulus of dentin to withstand the forces of mastication. Consequently, the determination of elastic modulus is valuable in the evaluation of restorative materials.

Recently, nanoindentation tests have been used to measure the hardness and the elastic modulus of small filler particles in resin composites and other dental restoratives [49]. Nanoindentation is able to test mechanical properties with a resolution of better than 1 μm and does not require visual resolution of the indentation. Taking into account the microstructural features of a composite ceramic, the nanoindentation technique offers a means by which the intrinsic mechanical properties of the individual microstructural components of a ceramic may be

measured in a manner which avoids the influences of the inherent defects and heterogeneities in the microstructure and also allows the mechanical properties to be measured in several different directions at the microstructural level.

In order to testify the validation of the nanoindention method, the modulus of pure 3Y-TZP was tested and gave 217 GPa, which was slightly higher than previously reported values of 200-210GP, the elastic modulus of Procera, Cercon, Lava Zirconia Y-TZP [26]. The discrepancy among values may be due to differences in test methods, as the previously reported values were measured using tensile tests and three-point bending tests. The elastic modulus results of MDZ were considered to be acceptable since for a similar result from 3Y-TZP was obtained with the reported values.

The values obtained are slightly lower than that of pure mullite ceramics (204GPa) [50]. Residual porosity of the composites was probably the main cause of the low measured modulus in comparison with the two single component materials.

In the present study, the elastic modulus of groups 40% and 50% were found to be lower than that for the other three groups, and statistical analysis revealed prominent difference, and that there was no statistical difference between groups 4 and 5. The amorphous matrix contributed to the low modulus of elasticity of the higher mullite content groups of MDZ.

Generally speaking, the present study offers one method to modify 3Y-TZP. By the addition of mullite, the glassy matrix formation decreased the hardness and elastic modulus of 3Y-TZP, approached the tooth hard tissues levels more than before, avoided stress concentration susceptibility. In addition, the element Si in the glassy matrix may potentially contribute to the better combination with a veneer porcelain and a better cementation effect with adhesives which will be validated in a follow study.

Notwithstanding the above, detailed group division should be continued between 10% and 20%, because the proportion among this range might compromise the best mechanical properties, furthermore, finer powder and a different sintering schedule might make for ideal properties. These systems continue to be evaluated in clinical studies for their predictability and long-term success.

Conclusions

Generally, the present study has shown that an increase in the content of mullite is accompanied with a decrease of the strength and fracture toughness. The MDZ with 10 wt.% mullite content presented better mechanical properties and a better comprehensive clinical performance may be expected from it. Based on the microstructural features of the MDZ, it was possible to determine that the main toughening mechanism of MDZ is a phase transformation and microcrack toughening. Furthermore experiments should be executed to realize a lower elastic modulus matching with tooth hard tissues. Additional studies are necessary to fully understand the role of mullite on MDZ cementation with an adhesive, a combination with a veneer porcelain and water aging status.

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