

Evaluation of hardness and fracture toughness, coupled with microstructural analysis, of zirconia ceramics stored in environments with different pH values

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The aim of this study was to evaluate the effects of pH changes in the oral cavity on the mechanical properties of zirconia and feldspathic ceramics. Bilayered zirconia-feldspathic samples were prepared from three different commercial brands of Y-TZP blocks: Zirkon Zahn, Cercon, and Everest. Samples were stored in artificial saliva with different pH values (3.5, 7.0, and 10.0) for 10 days at 37°C. Flexural strength, Vickers hardness, and fracture toughness were calculated after samples were subjected to biaxial flexure test. Microstructural analysis of the materials was also performed.

Data were analyzed by one-way analysis of variance (ANOVA), and multiple comparisons were performed using Tukey's test ($\alpha=0.05$). Acidic and alkaline environments adversely affected the mechanical properties of zirconia, resulting in material degradation, loss of stabilizer content, and increase in tetragonal-monoclinic phase transformation. Commercial dental zirconia blocks have varied mechanical properties, but they are generally susceptible to degradation when exposed to corrosive environments.

Keywords: Y-TZP, Low-temperature degradation, XRD, Corrosion

INTRODUCTION

In prosthetic dentistry, strength and esthetics are of paramount importance^{1,2}. Recently, the introduction of zirconia-based ceramics as restorative dental materials has generated considerable interest in the dental community. Zirconia offers the best mechanical properties unparalleled by any other dental ceramic, bringing to realization reliable and non-metal posterior fixed partial dentures with a substantial reduction in core thickness. It also offers superior esthetics which enables the fabrication of esthetic all-ceramic restorations in all areas of the mouth. By embodying both strength and esthetics, zirconia-based ceramics have been used for the fabrication of dental implants and implant abutments *via* hard machining, and for the fabrication of posterior crowns and fixed partial prostheses *via* soft machining and sintering.

At ambient pressure, unalloyed zirconia can assume three crystallographic forms depending on the temperature. Pure zirconia has a monoclinic structure at room temperature, which is stable up to 1,170°C. It has a tetragonal structure between 1,170 and 2,370°C, and a cubic structure above 2,370°C which remains stable up to the melting point. On cooling from high temperature, a reversible transformation from the tetragonal (t) phase to the monoclinic (m) phase begins at about 950°C. This phase transformation is accompanied by a substantial increase in volume (~4.5%), which can cause catastrophic failure. Alloying pure zirconia with stabilizing oxides such as CaO, MgO, Y₂O₃, or CeO₂ allows the retention of the tetragonal structure at room

temperature. Elimination of the stress-induced t→m transformation efficiently prevents crack propagation and enhances fracture toughness^{1,3-7}.

Partially stabilized zirconia (PSZ) has been extensively studied for decades and is now widely used in numerous industrial and biomedical applications. PSZ owes its high strength and toughness to its metastability: it is toughened as it undergoes stress-induced tetragonal to monoclinic (t-m) martensitic transformation at room temperature. However, it was first reported by Kobayashi *et al.* in 1981 that PSZ is also susceptible to low-temperature degradation (LTD) owing to deterioration in mechanical properties⁸⁻¹⁰.

LTD of zirconia is a well-documented phenomenon, exacerbated notably by the presence of water. The consequences of this aging process are multiple, including surface degradation with grain pullout, microcracking, and strength degradation. The main factors that affect this low-temperature aging phenomenon include grain size, shape, and distribution, stabilizer type and content, and the presence of residual stresses in the ceramics^{1,6,7,10-13}.

The oral cavity is a dynamic environment where changes constantly occur. It is also a warm and moist environment which presents many occasions and factors that would adversely affect the mechanical properties of ceramic restorations: (a) water from saliva; (b) water from luting cements and dentinal tubules; (c) masticatory stresses; (d) stresses due to differences in the coefficients of thermal expansion of restorative materials; (e) temperature variations; and (f) pH variations^{14,15}. The normal pH of saliva is 6.8–7.2, but it can be easily lowered or raised by the consumption of food and drink. For example, each time a carbohydrate-

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rich food is ingested, organic acids are produced by dental plaque, lowering the pH of the oral cavity to an acidic pH of about 4.5¹⁶. In response, increased salivary flow, and hence an increase in bicarbonate flux, would raise oral pH to normal levels again. However, acidic products such as lemonade and soft drinks lower oral pH and create an acidic environment in the mouth without bacterial involvement¹⁴.

Partially stabilized yttria tetragonal zirconia polycrystalline (Y-TZP) ceramics are a relatively new class of dental ceramics introduced to the market. Scientific data on the behavior of Y-TZP-based materials, especially in response to pH changes in the oral cavity, are scarce. The aim of this study was to evaluate the effects of pH changes in the oral cavity on the mechanical properties of zirconia and feldspathic ceramics. The null hypothesis of this study was that an acidic environment would adversely affect the mechanical properties and microstructural characteristics of bilayered zirconia-feldspathic structures.

MATERIALS AND METHODS

Preparation of bilayered zirconia-feldspathic samples

To simulate the clinical application of zirconia, bilayered samples were fabricated from three different commercial brands of non-HIP zirconia blanks: Zirkonzahn (Steger, Ahrntal, Italy), Cercon (DeguDent, Hanau, Germany), and Everest (KaVo, Biberach, Germany). For each zirconia group, 100 disk-shaped samples of 15.0 mm diameter and 1.3 mm thickness were prepared according to ISO 6872 guidelines. A total of 300 disk-shaped zirconia samples were mirror-polished to a final thickness of 1.00 (± 0.13) mm using a polishing machine (LaboPol-5, Struers, Denmark).

For 90 samples from each zirconia group, a 1.0-mm-thick feldspathic layer was applied on the surface of each sample using a stainless steel mold. According to manufacturer's recommendations, Cerabien ZR (Noritake Dental Supply, Aichi, Japan) feldspathic ceramic was layered on Zirkonzahn group, Vita VM9 (Vita Zahnfabrik, Germany) on Cercon group, and IPS e.max Ceram (Ivoclar Vivadent, Schaan, Liechtenstein) on Everest group. The remaining 10 samples of each zirconia group without feldspathic layering, to be used as control, were stored in ambient air.

Storage in solutions of different pH values

Three solutions with pH values of 3.5, 7.0, and 10.0 were prepared as described by Pinto *et al.*¹⁴. For the neutral solution of pH 7.0, artificial saliva of the following composition was thus prepared: 100 mL of KH_2PO_4 (2.5 mM), 100 mL of Na_2HPO_4 (2.4 mM), 100 mL of KHCO_3 (1.50 mM), 100 mL of NaCl (1.0 mM), 100 mL of MgCl_2 (0.15 mM), 100 mL of CaCl_2 (1.5 mM), and 6 mL of citric acid (0.002 mM). The pH of neutral artificial saliva solution was lowered to 3.5 by adding HCl, and raised to 10.0 by adding NaOH.

Ninety bilayered samples of the three zirconia groups were equally divided for storage among the three

solutions. A total of nine test groups were thus formed. All samples were stored at 37°C for 10 days.

Biaxial flexure test

After 10-day storage, biaxial flexure test was carried out according to ISO 6872 standard, using a piston-on-three-ball technique in a universal testing machine (Autograph AG-IS, Shimadzu, Kyoto, Japan). Three hardened steel balls, 3.2 mm diameter each, were evenly spaced around a support circle of 6 mm radius. Each bilayered sample was placed in the test apparatus with the feldspathic veneer layer at the top and the zirconia layer supported on the three steel balls. Flexural loading was applied using a steel cylinder of 1.4 mm diameter at a crosshead speed of 1 mm/min until fracture.

The thickness and fabrication method of bilayered samples used in this study were different from ISO 6872 specifications. Therefore, flexural strengths had to be calculated using a different method in this study. Calculations were made according to the formulae proposed by Thompson, where bilayered samples were “transformed” into a single material¹⁷.

Vickers microhardness and fracture toughness tests

Hardness and fracture toughness were determined for 10 polished control disks stored in ambient air from each zirconia group, as well as 10 fragments of fractured samples (recovered from biaxial flexure test) from each of the nine test groups. Microhardness and fracture toughness tests were performed on a LEICA VMHT machine (Leica, Germany) using a 4.9 N load with a dwell time of 20 s.

To measure fracture strength, a stress rate of 1 MPa/s was used. To measure Vickers hardness, an indentation was made on the zirconia surface of each sample at room conditions (22°C and 60% relative humidity). Crack length was digitally obtained using an optical microscope within 30 s after indentation. Fracture toughness (K_{Ic}) was calculated using the equation below:

$$K_{Ic} = 0.203(c/a)^{-3/2}Ha^{1/2}$$

where c is the half-diagonal of the indentation, a is the average median/radial crack length, and H is Vickers hardness number (VHN).

Microstructural analysis

Microstructural characterization was conducted using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) analysis. In addition to samples randomly selected from each of the nine test groups, one as-sintered zirconia disk from each of the three zirconia groups (Zs, Cs, Es) were also analyzed.

Cross-sections of the samples were evaluated using SEM (JSM-7000F, Jeol, Tokyo, Japan) at $\times 100$, $\times 1,000$, and $\times 10,000$ magnifications to observe their crack pattern, grain size and shape, and porosity. Y_2O_3 stabilizer contents of the different zirconia surfaces were analyzed by EDS. XRD patterns were collected

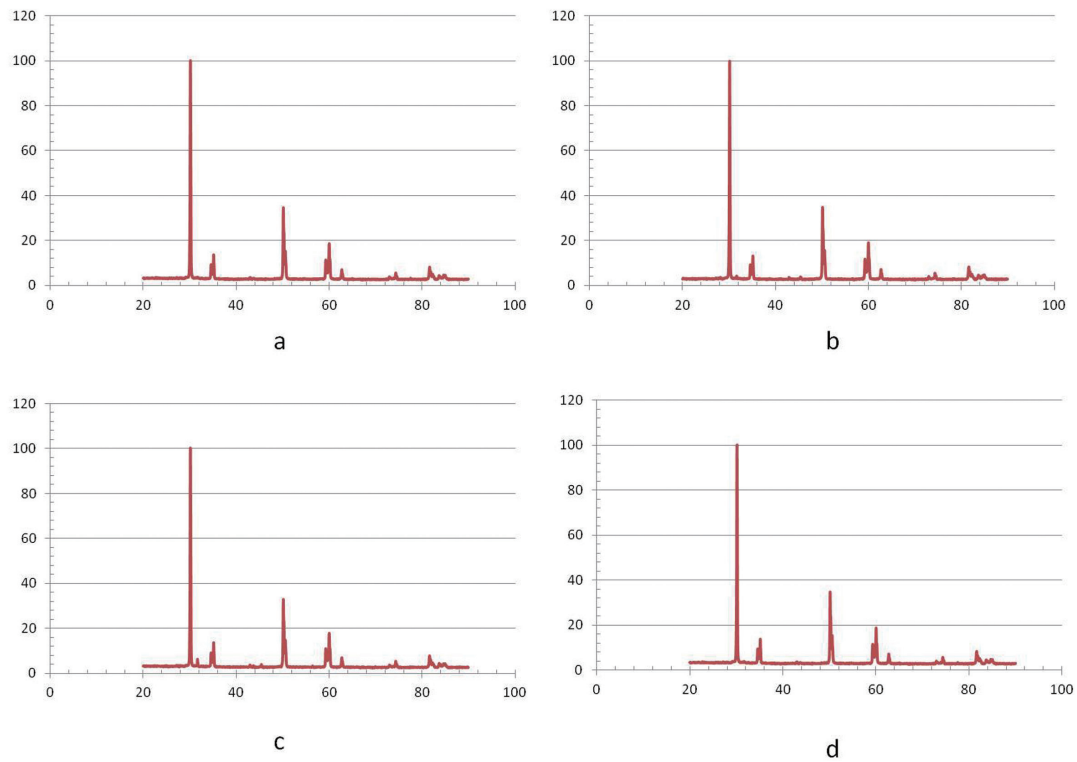


Fig. 1 XRD patterns of Zirkonzahn samples: (a) as-sintered; (b) stored in neutral solution; (c) stored in acidic solution; (d) stored in alkaline solution (relative intensity vs. 2θ angle).

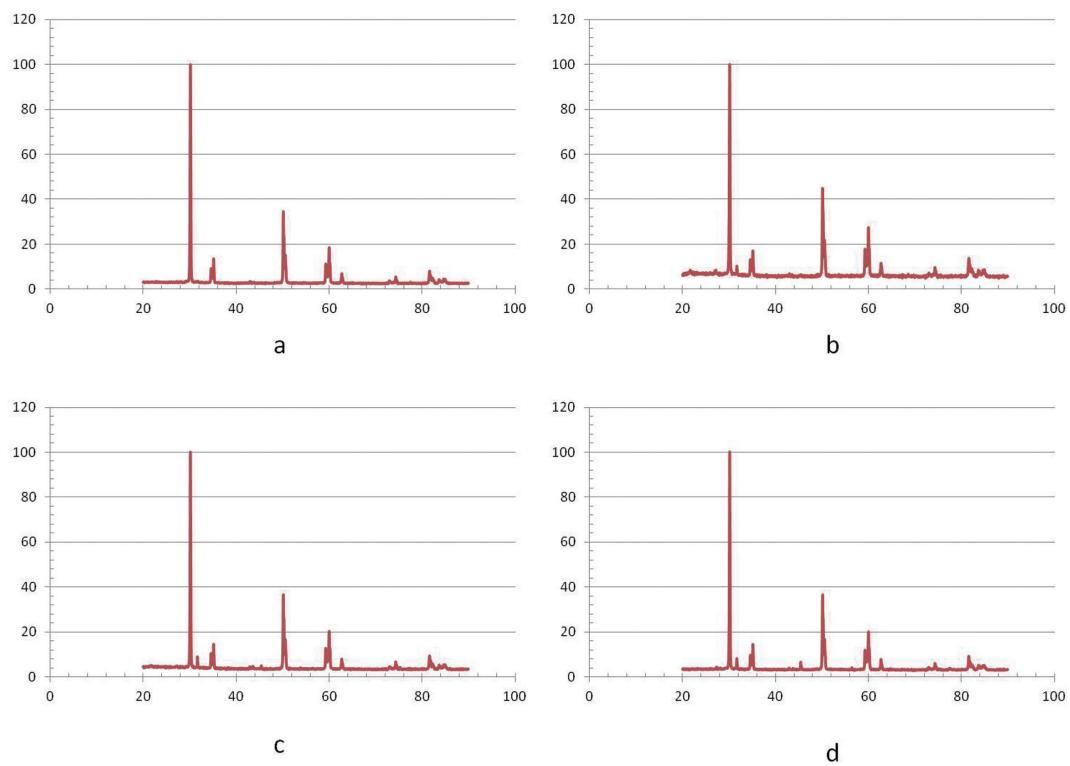


Fig. 2 XRD patterns of Cercon samples: (a) as-sintered; (b) stored in neutral solution; (c) stored in acidic solution; (d) stored in alkaline solution (relative intensity vs. 2θ angle).

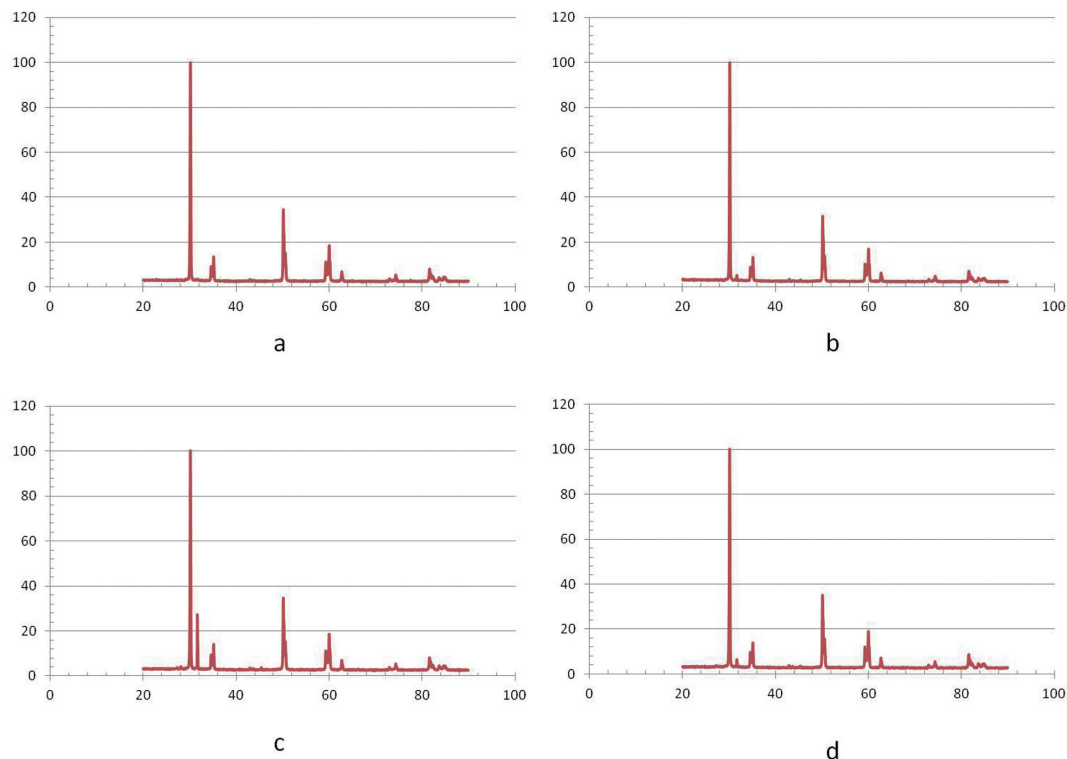


Fig. 3 XRD patterns of Everest samples: (a) as-sintered; (b) stored in neutral solution; (c) stored in acidic solution; (d) stored in alkaline solution (relative intensity *vs.* 2θ angle).

using a diffractometer (X'Pert Pro, PANalytical, The Netherlands) within the 2θ range of 25–65, covering the positions of the highest peaks of tetragonal and monoclinic phases of ZrO_2 . $\text{CuK}\alpha$ radiation was generated at 40 kV and 45 mA (Figs. 1–3).

Mass fraction of monoclinic phase (X_m) was calculated using Garvie and Nicholson's formula¹⁸⁾:

$$X_m = [I_m(-111) + I_m(111)] / [I_m(-111) + I_m(111) + I_t(101)]$$

where X_m is the mass fraction of monoclinic phase, $I_m(-111)$ is the intensity of monoclinic peak at 28.2° , $I_m(111)$ is the intensity of monoclinic peak at 31.5° , and $I_t(101)$ is the intensity of tetragonal peak at 30.2° .

Volume fraction (V_m) of monoclinic phase was calculated using the following formula proposed by Toraya *et al.*¹⁹⁾:

$$V_m = 1.311X_m / (1 + 0.311X_m)$$

where V_m is the volume fraction of monoclinic phase and X_m is the mass fraction of monoclinic phase.

Statistical analysis

Flexural strength, fracture toughness, and Vickers hardness data were analyzed by one-way analysis of variance (ANOVA) and multiple comparisons were performed using Tukey's test at a pre-set significance

level of 5%. All analyses were performed using a statistical software package (SPSS 17.0, SPSS Inc., Chicago, IL, USA).

Variability of flexural strength data was analyzed using a two-parameter Weibull cumulative distribution function. The equation for Weibull cumulative distribution function is as follows:

$$P(\sigma) = 1 - \exp[-(\sigma/\sigma_0)^m]$$

where P is the probability of failure, σ_0 is the characteristic parameter corresponding to the fracture probability of 63.2%, and m is the Weibull modulus (Figs. 4–6). The Weibull moduli of the nine test groups are given in Table 1.

RESULTS

Flexural strength

Table 2 shows the mean flexural strengths of the nine test groups of this study. In the acidic environment, there were no statistically significant differences in flexural strength between Za and Ea groups, which were significantly higher than that of Ca group. In the neutral environment, the flexural strength of En was significantly lower than Zn and Cn. In the alkaline environment, there were no statistically significant differences among Zb, Cb, and Eb groups.

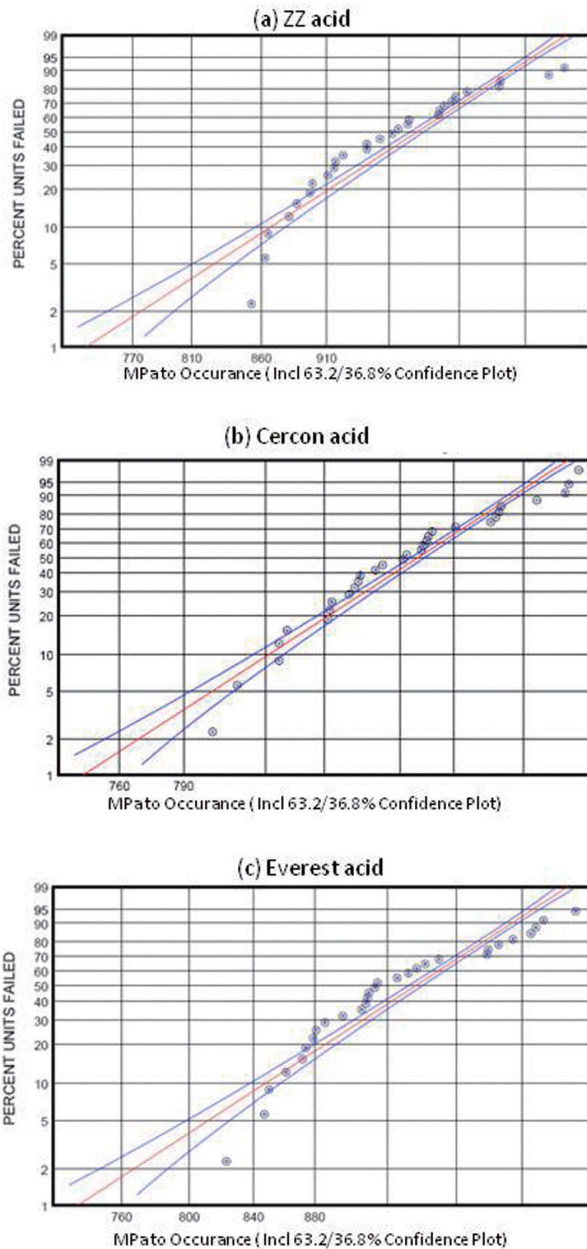


Fig. 4 Weibull distribution of samples stored in acidic pH solution.

For each zirconia group, the sample stored in acidic environment yielded the lowest flexural strength whereas that stored in the neutral environment yielded the highest. Moreover, in each zirconia group, flexural strength significantly decreased from the neutral to the alkaline environment, and from the alkaline to the acidic environment.

Vickers microhardness

Table 3 shows the mean Vickers microhardness values of the nine test groups of this study. In the acidic environment, there were no statistically significant

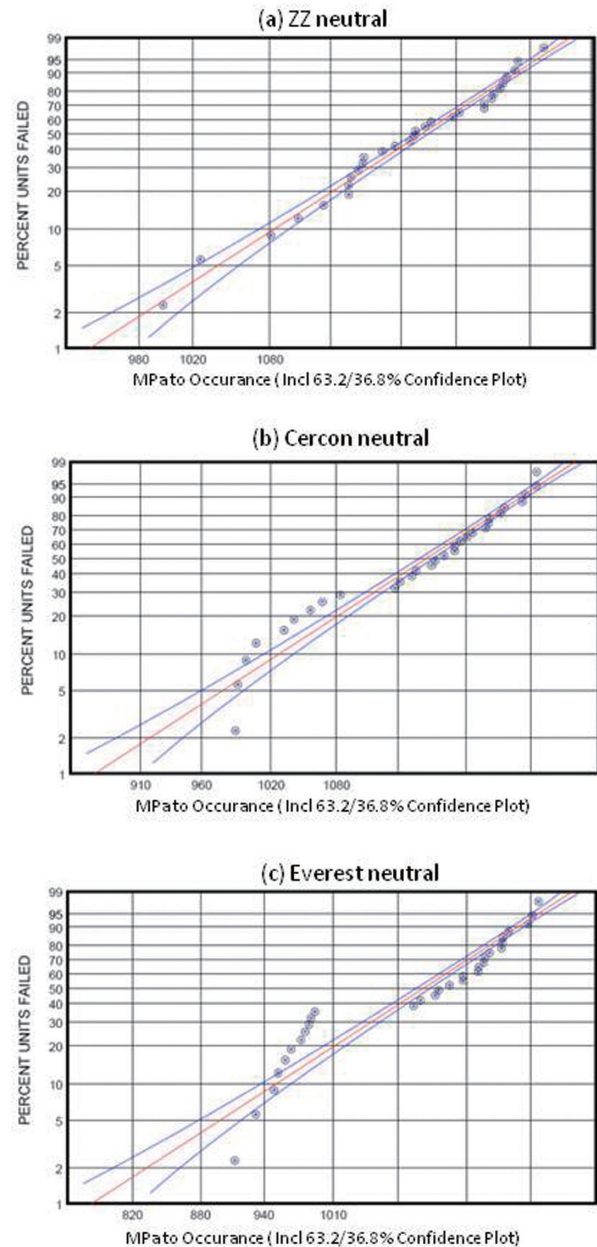


Fig. 5 Weibull distribution of samples stored in neutral pH solution.

differences in Vickers microhardness among Za, Ca, and Ea groups. Similarly in the neutral environment, there were no statistically significant differences in hardness among Zn, Cn, and En groups.

Within Z group, Vickers microhardness was significantly different between Za and Zn. Within E group, the microhardness value of En was significantly higher than those of Ea and Eb.

Fracture toughness

Table 4 shows the mean fracture toughness values of the nine test groups of this study. Fracture toughness results

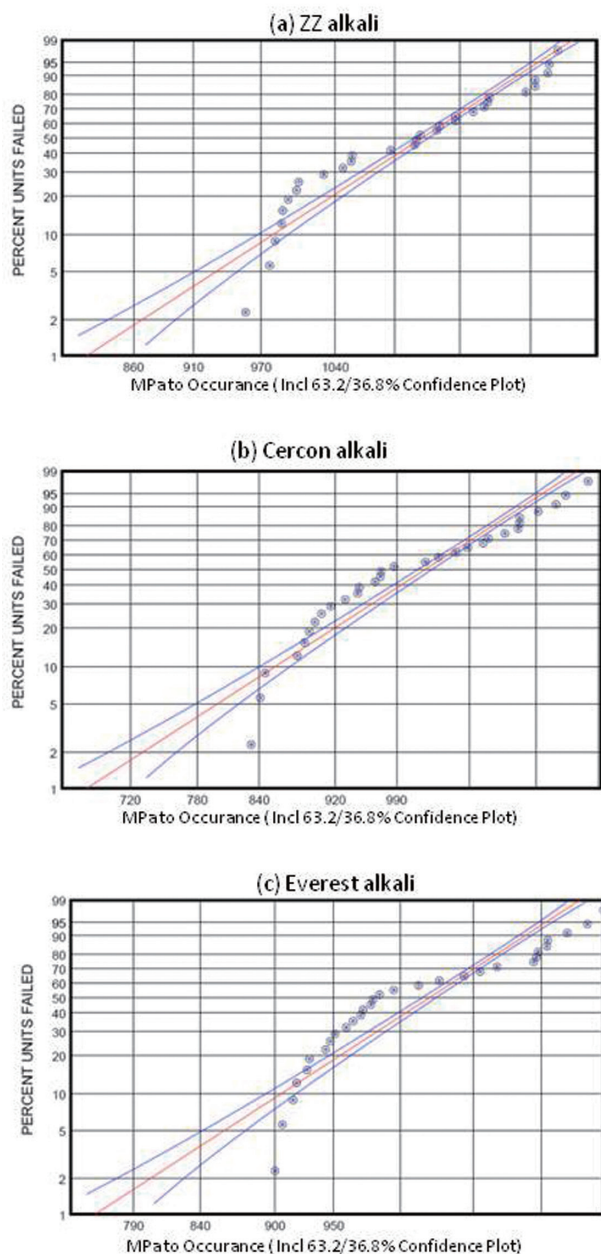


Fig. 6 Weibull distribution of samples stored in alkaline pH solution.

were similar to Vickers microhardness test results. In the acidic environment, there were no statistically significant differences in fracture toughness among Za, Ca, and Ea groups. In neutral pH environment, there were also no significant differences among Zn, Cn, and En. In the alkaline environment, differences among Zb, Cb, and Eb were also not significant.

Microstructural analysis

Table 5 displays the XRD volume fraction (V_m) results of the monoclinic phase. In every zirconia group, the as-sintered sample had the lowest V_m value but that stored

Table 1 Weibull moduli of the nine test groups of this study

Test group	Weibull modulus (m)
Zirkonzahn Acidic (Za)	14.3
Zirkonzahn Neutral (Zn)	17.1
Zirkonzahn Alkaline (Zb)	13.3
Cercon Acidic (Ca)	20.0
Cercon Neutral (Cn)	14.6
Cercon Alkaline (Cb)	10.4
Everest Acidic (Ea)	16.2
Everest Neutral (En)	12.1
Everest Alkaline (Eb)	13.4

in the acidic environment had the highest value. For all the three zirconia groups, samples stored in the alkaline environment had close but higher V_m values than those stored in the neutral solution.

EDS results for Y_2O_3 stabilizer content (weight%) are also displayed in Table 5. In every zirconia group, the as-sintered sample had the highest Y_2O_3 content followed by that stored in the neutral solution. Lowest Y_2O_3 content was observed in samples stored in the acidic solution.

SEM photographs revealed that among the three different brands of zirconia products, they had similar microstructural appearances as a function of the storage environment. For neutral pH-stored samples, round particles of different radii were observed and porosity was absent (Figs. 7–9). For acidic pH-stored samples, there was a pronounced change in microstructural appearance: grains became rough and sharp, and porosity was observed (Figs. 10–12). Alkaline pH-stored samples had similar characteristics as the neutral pH-stored ones, where round particles of varied sizes were observed and there was miniscule porosity between the grains (Figs. 13–15).

DISCUSSION

Effects on pH changes on zirconia

The importance of prosthodontic restorations imitating the appearance of missing natural teeth fuels the impetus for manufacturers to develop new restorative materials that promise higher biocompatibility with excellent functional and esthetic outcomes. Zirconia frameworks are reportedly highly biocompatible, durable, and more esthetically pleasing than metal frameworks by virtue of their translucency and all-white color^{20–23}. However, the long-term effects of a dynamic oral environment on zirconia await thorough investigation^{1,24}.

Various studies have shown that ceramic restorations were affected by periodic pH changes during their

Table 2 Mean flexural strengths of nine test groups expressed in MPa (\pm SD)

	Zirkonzahn	Cercon	Everest
Acidic	975.57 \pm 86.23 ^{A,a}	873.67 \pm 163.14 ^{A,b}	942.47 \pm 73.34 ^{A,a}
Neutral	1,198.53 \pm 81.84 ^{B,a}	1,158.00 \pm 95.68 ^{B,a}	1,098.53 \pm 111.30 ^{B,b}
Alkaline	1,118.30 \pm 90.88 ^{C,a}	1,013.90 \pm 122.3 ^{C,a}	1,028.53 \pm 99.83 ^{C,a}

Means with different capital letter superscripts in the same column and with different small letter superscripts in the same row were statistically different at $p < 0.05$.

Table 3 Mean Vickers microhardness values expressed in VHN (\pm SD)

	Zirkonzahn	Cercon	Everest
Acidic	1,346 \pm 29 ^{A,a}	1,347 \pm 29 ^{A,a}	1,347 \pm 33 ^{A,a}
Neutral	1,368 \pm 28 ^{B,a}	1,362 \pm 39 ^{A,a}	1,368 \pm 40 ^{B,a}
Alkaline	1,356 \pm 33 ^{A,B,a}	1,348 \pm 27 ^{A,a}	1,350 \pm 30 ^{A,a}

Means with different capital letter superscripts in the same column and with different small letter superscripts in the same row were statistically different at $p < 0.05$.

Table 4 Mean fracture toughness values expressed in MPa \cdot m^{1/2} (\pm SD)

	Zirkonzahn	Cercon	Everest
Acidic	6.9 \pm 0.5 ^{A,a}	7.0 \pm 0.6 ^{A,a}	6.9 \pm 0.3 ^{A,a}
Neutral	7.3 \pm 0.3 ^{B,a}	7.3 \pm 0.3 ^{A,a}	7.4 \pm 0.2 ^{B,a}
Alkaline	7.1 \pm 0.4 ^{A,B,a}	7.1 \pm 0.3 ^{A,a}	7.0 \pm 0.5 ^{A,a}

Means with different capital letter superscripts in the same column and with different small letter superscripts in the same row were statistically different at $p < 0.05$.

Table 5 Microstructural analysis results

Test group	Monoclinic phase (Volume%)	Y ₂ O ₃ (Weight%)
Za	12.6	1.70
Zn	9.9	2.25
Zb	10.7	1.36
Zs	9.4	2.97
Ca	18.3	1.41
Cn	11.2	2.21
Cb	13.2	1.43
Cs	10.1	2.61
Ea	14.6	1.35
En	11.2	2.33
Eb	11.9	1.63
Es	8.6	2.53

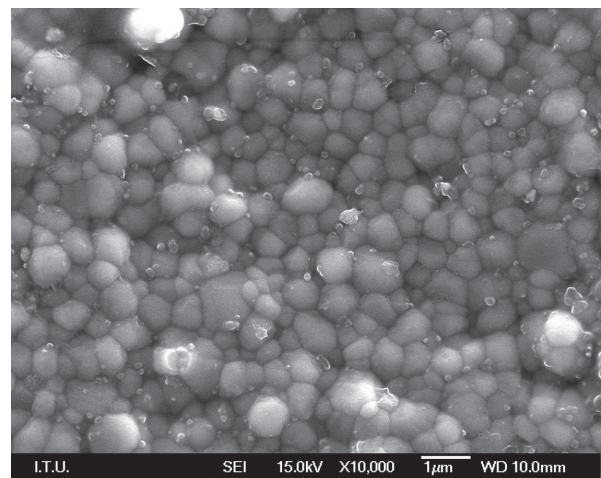


Fig. 7 Surface of a bilayered Zirkonzahn sample stored in neutral pH solution ($\times 10,000$).

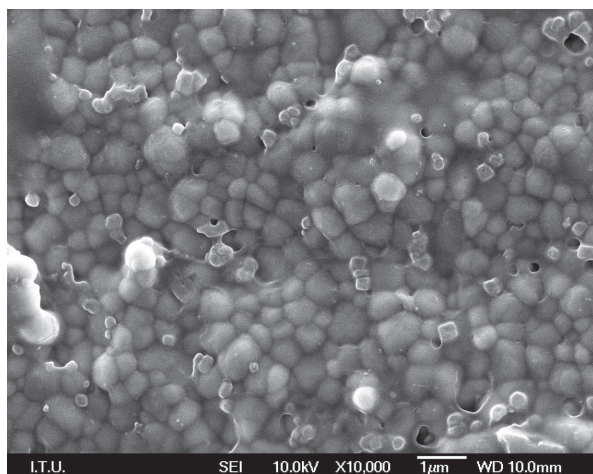


Fig. 8 Surface of a bilayered Cercon sample stored in neutral pH solution ($\times 10,000$).

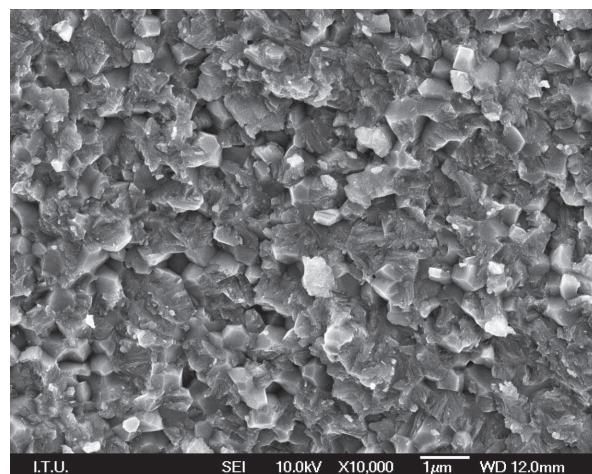


Fig. 11 Surface of a bilayered Cercon sample stored in acidic pH solution ($\times 10,000$).

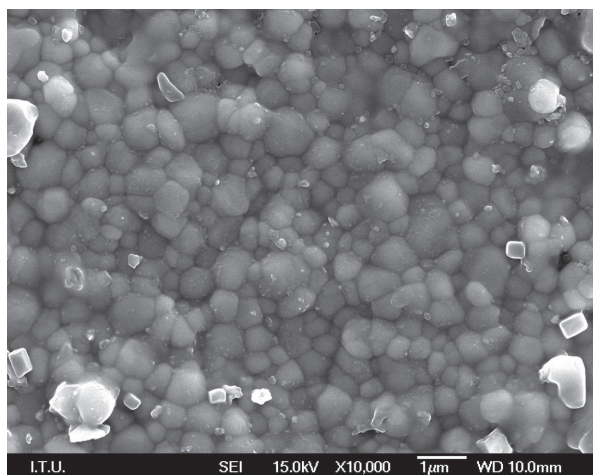


Fig. 9 Surface of a bilayered Everest sample stored in neutral pH solution ($\times 10,000$).

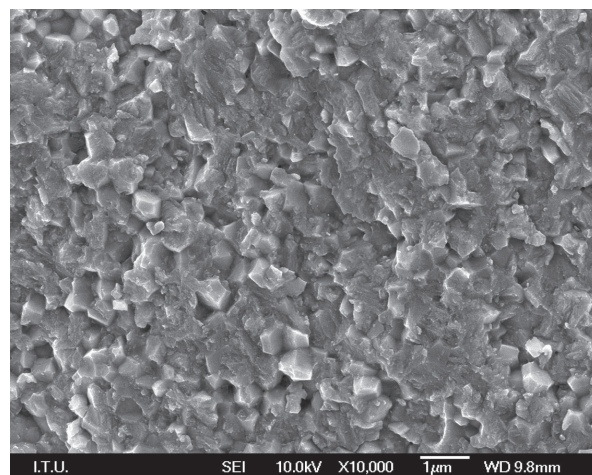


Fig. 12 Surface of a bilayered Everest sample stored in acidic pH solution ($\times 10,000$).

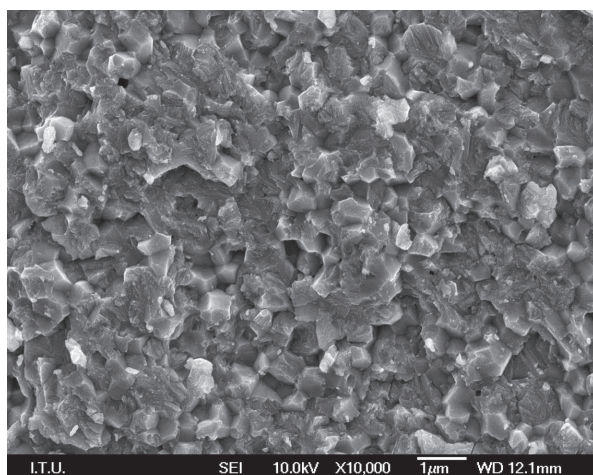


Fig. 10 Surface of a bilayered Zirkozahn sample stored in acidic pH solution ($\times 10,000$).

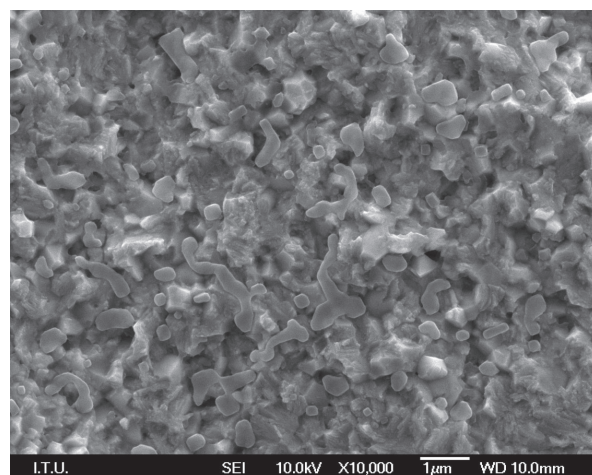


Fig. 13 Surface of a bilayered Zirkozahn sample stored in alkaline pH solution ($\times 10,000$).

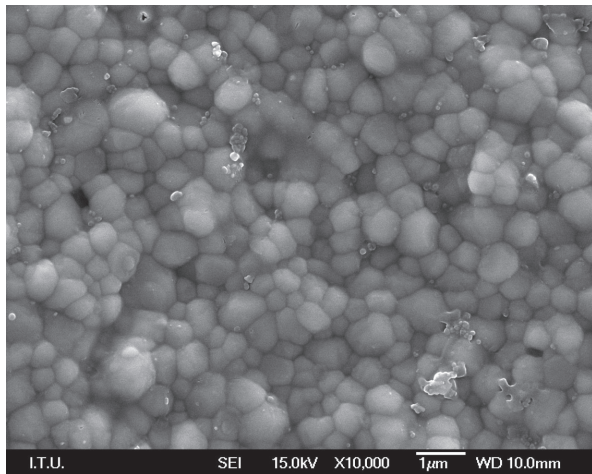


Fig. 14 Surface of a bilayered Cercon sample stored in alkaline pH solution ($\times 10,000$).

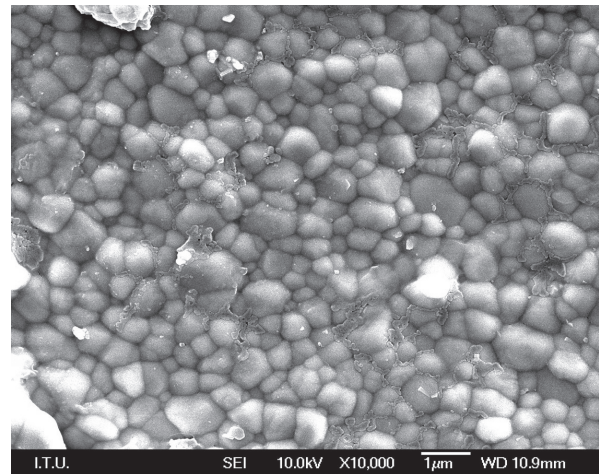


Fig. 15 Surface of a bilayered Everest sample stored in alkaline pH solution ($\times 10,000$).

service time in the oral cavity. The normal pH value of saliva is 6.8–7.2. However, several mechanisms cause pH changes in the mouth. Consumption of carbohydrate-rich food, leading to production of organic acids by microorganisms, may lower the pH value to as low as 4.5^{16,25–27}. Acidic beverages such as lemonade and orange juice may lower the pH to a lower value. The pH of the oral cavity is returned to neutral by the buffering effect of bicarbonate ions in increased saliva flow^{14,15}. In this study, bilayered zirconia-feldspathic samples were stored in artificial saliva solutions of pH 3.5 and pH 10.0 to evaluate the effects of long-term exposure to acidic and alkali environments on the mechanical properties and microstructural characteristics of zirconia.

Clinically, zirconia ceramics are veneered with feldspathic ceramics with lower mechanical properties to achieve better esthetic results. This means that zirconia is usually not in direct contact with oral fluids. However, some clinical occasions cause zirconia to become exposed: cracking or chipping of veneer ceramic, overdentures with zirconia abutments, or telescopic fixed partial dentures with zirconia copings^{28–30}. Besides, microleakage due to the dissolution of conventional cements or exposure of crown margins due to periodontal problems may cause the zirconia substructure to come into contact with oral fluids³¹.

Effects of pH changes on flexural strength

Results of biaxial flexure tests showed that the mechanical properties of zirconia were adversely affected by pH changes in the environment. Samples stored in the acidic and alkaline environments exhibited lower flexural strengths than those stored in the neutral solution. For all the three zirconia groups, samples stored in the acidic solution yielded the lowest flexural strength.

Studart *et al.*¹⁵ reported that in all-ceramic restorations, cracks developed in the veneer surface as

the mechanical properties deteriorated, propagating toward the veneer-framework interface by slow crack growth mechanism. This may cause restorations with weaker frameworks, such as lithium disilicate, to fail clinically. For zirconia frameworks, crack propagation is stopped at the interface with transformation toughening mechanism. In short term, this is a merit which increases the durability of the restoration; in the long term, oral fluids may reach zirconia through cracks on the veneer.

In this study, SEM analysis revealed that the zirconia layer was able to stop cracks propagating from the feldspathic veneer surface. Based on this observation, it could be said that cracks developed in and propagated from the uppermost layer were stopped at the veneer-framework interface by the transformation toughening mechanism of zirconia. The catastrophic failure of each sample, therefore, was a result of flexural stress in the lower zirconia layer of the bilayered sample. According to the results of similar studies involving bilayered samples, the bottom layer determined the overall mechanical strength of the sample^{32,33}.

Effects of pH changes on hardness

Different Vickers microhardness behaviors were displayed by the three zirconia brands. In Zirkonzahn group, samples stored in the acidic solution had a significantly lower hardness value than in the neutral solution. Cercon samples had the lowest VHN values among the three zirconia groups in all pH environments, but pH of the storage solution did not seem to significantly affect their microhardness behavior. In Everest group, VHN values yielded in the acidic and alkaline solutions were significantly lower than in the neutral solution.

Several studies have reported that low temperature degradation (LTD) and excessive t-m phase transformation decreased zirconia microhardness^{9,34,35}. In this study, VHN of all the three zirconia groups decreased because of LTD and adverse effect of increased

t-m transformation.

Effects of pH changes on fracture toughness

Fracture toughness of all the three zirconia groups was also adversely affected by pH changes of the storage environment. Samples stored in the neutral solution had significantly higher fracture toughness than those stored in acidic and alkali solutions.

Effects of pH changes on microstructural characteristics

Biaxial flexure test results have clearly shown that pH changes of the storage environment adversely affected the mechanical properties of zirconia. Apart from LTD which takes place in a humid environment, mechanical evaluation results of this study should be explained by another mechanism since storage temperature and humidity were constant in this study.

EDS revealed that samples stored in the acidic environment had a lower amount of Y_2O_3 compared to other environments. Decrease in stabilizer content positively correlated with decrease in mechanical properties. Zn, which demonstrated the highest flexural strength, also had the highest stabilizer content. Ea, which demonstrated the lowest flexural strength, had the lowest amount of Y_2O_3 . In all the three zirconia groups, as-sintered samples had the highest Y_2O_3 content; even samples stored in the neutral solution had a decrease in stabilizer content. Several studies have reported that increase in Y_2O_3 content decreased t-m transformation which occurs with aging of the material^{36–38}. It was also reported that as the stabilizer content in the material decreased, Y-TZP became more susceptible to degradation even in environments less humid and less corrosive than normal³⁹.

XRD analysis revealed that samples stored in the neutral solution had a higher monoclinic volume fraction than the as-sintered samples. Increase in monoclinic volume became even more pronounced in acidic and alkaline solutions, with the highest monoclinic volume yielded in the acidic solution in all the three zirconia groups. Among the nine test groups, Ca exhibited the highest monoclinic volume. Conversely, Zn—which had the highest flexural strength—exhibited the lowest monoclinic volume. Therefore, an increase in monoclinic volume was accompanied with a decrease in mechanical properties. Environmental effects weakened the surfaces of zirconia materials mechanically by t-m transformation and corrosion.

Correlation between mechanical properties and microstructural characteristics of zirconia

A positive correlation was observed between the results of mechanical and microstructural evaluations. In all the three zirconia groups, samples stored in the acidic environment showed the lowest flexural strength. They also had the lowest stabilizer content and the highest monoclinic volume fraction. Similar correlations were observed for samples stored in the alkaline and neutral environments. SEM analysis further revealed the presence of porosity and loss of grains from the surface.

Therefore, a low-pH environment induced a loss of yttria from the zirconia surface and weakened the structure by t-m transformation, resulting in deterioration of flexural strength.

Fang *et al.* reported similar results when Y-TZP samples were exposed to a corrosive environment for 115 h⁴⁰. As duration in the corrosive solution increased, so did the monoclinic phase on the surfaces of the samples. They concluded that t-m phase transformation increased the incidence of cracks and pores on the surfaces of the samples, resulting in decreased mechanical properties.

Novak and Kalin compared the wear behaviors of zirconia and alumina in pH range of 4.0–13.0⁴¹. The wear of zirconia was 100 times greater than that of alumina at higher pH values, and the vast difference was attributed to LTD of zirconia. SEM observation also revealed wear debris formation at low pH created by dissolution and precipitation, which in turn were assisted by chemical processes.

Similar results were reported by Ardlin for Y-TZP samples stored in 4% acetic acid at 80°C for 168 h⁹. SEM observation revealed irregularities and porosity on the surfaces of the samples. There was also an increase in monoclinic phase: from 2% in the control group not affected by low-temperature aging up to 25% in the corroded test group. Correspondingly, flexural strength decreased with increase in the monoclinic phase.

Structural reliability of zirconia ceramics

The Weibull modulus (m) describes the flaw size distribution or data scatter of a given volume of ceramic under a uniform stress. It is a factor used in analytical design approaches to brittle materials such as ceramics. In the present study, the Weibull moduli of all the three zirconia materials tested were within the typical range for ceramic materials⁴². However, differences in Weibull modulus were observed between samples stored in different environments. For Zirkonzahn groups, Zn in the neutral solution had the highest Weibull modulus. Interestingly, for Cercon and Everest groups, Ca and Ea in the acidic solution had higher m values. This difference in distribution might be due to differences in the compositions of the materials. Differences in Weibull modulus corresponded to differences in flexural strength and fracture toughness of the zirconia groups (Tables 2 and 4). These results agreed with those reported by Bona *et al.*⁴³, in that the structural reliability of veneered core ceramic in veneer-core bilayered systems is controlled primarily by that of the core ceramic.

CONCLUSIONS

Acidic and alkaline environments caused and exacerbated the corrosion of three commercial brands of zirconia materials used in this study. Therefore, the hypothesis of this study was accepted since increase in corrosion led to loss of yttria stabilizer, increase in surface irregularities, and increase in t-m transformation, culminating in significantly reduced mechanical properties. The clinical significance is that since the mechanical properties of

zirconia substructures may degrade pronouncedly in humid and/or corrosive (acidic or alkaline) conditions, zirconia substructures should be completely veneered with feldspathic ceramic to increase their durability in the oral cavity.

In general, decrease in the fracture toughness of zirconia is caused by low-temperature degradation and corrosion, which occur simultaneously as a result of pH changes. On the other hand, dental zirconia blocks from different manufacturers—which possess varying mechanical properties—are affected in different degrees by the corrosive environments. Differences in mechanical properties among the different brands of zirconia stem from differences in material purity and homogeneity at the production stage, amount and distribution of stabilizer, grain size, and production method.

Considering the availability of many zirconia brands in the market, further studies with a larger number of different commercial brands would provide more useful insight into the corrosive behavior of zirconia and the long-term clinical acceptance of zirconia frameworks.

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