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Chemical durability and microhardness of dental ceramics immersed in acidic agents

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Abstract

Objective. To evaluate the microhardness and surface elemental compositions of ceramics immersed in acidic agents. ***Material and methods.*** Thirty-five ceramic disc specimens were made from each of four types of ceramic (VMK 95, Vitadur Alpha, Empress Esthetic and IPS e.max Ceram). Before immersion, baseline data of Vicker's microhardness and elemental composition were recorded. Four groups of discs (seven per group) were then immersed in acidic agents (citrate buffer solution, pineapple juice and green mango juice) and deionized water (as a control) for 168 h at 37°C. One group was immersed in 4% acetic acid at 80°C for 168 h. After immersion, specimens were evaluated and data were analyzed using two-way ANOVA with repeated measurements and a paired *t*-test at a significance level of 0.05. ***Results.*** The microhardness values of four types of ceramic significantly decreased after being immersed in acidic agents ($p < 0.05$). The elemental compositions of ceramics mainly comprise silicon, aluminium and potassium. These compositions also decreased after immersion ($p < 0.05$). ***Conclusions.*** The acidic agents used in this study affected the microhardness and elemental dissolution of ceramics. The main elemental compositions of ceramics (silicon, aluminium and potassium) decreased after being immersed in acidic agents.

Key Words: *Alumina, energy-dispersive X-ray, fluorapatite, leucite, microhardness*

Introduction

Dental ceramics are widely used for both anterior and posterior restorations such as inlays, onlays, veneers, metal–ceramic and all-ceramic restorations [1]. Their uses mainly reflect their excellent aesthetic properties, biocompatibility and resistance to wear. In addition, dental ceramics are considered to be chemically inert restorative materials. However, there are large differences in the chemical compositions and microstructures of ceramics. Different kinds of ceramics possess different chemical properties. Because of this, the inertness of a specific dental ceramic cannot be generalized.

Basically, the chemical durability of dental ceramics is good, but it may be influenced by many factors, such as the composition and microstructure of the ceramic materials, the chemical character of the ceramic materials, the chemical character of the erosive or acidic agents, the exposure time and the temperature [2]. Degradation of dental ceramics occurs when ceramics are exposed to aqueous solutions or erosive agents [3]. This phenomenon takes place as a result of selective leaching of alkaline ions. Environmental conditions may also impair resistance to surface and bulk degradation. Variations in ceramic and processing techniques may result in materials with reduced hydrolytic stability. Alkaline metal ions are far less stable in the glass phase than in the crystalline phase [3]. Some alkaline ions are leached after exposure to acidic solutions [4–6]. Variations in pH, solution chemistry, wear and mechanical load make the oral cavity a complex environment [3]. Crack propagation in ceramics is increased when ceramics are exposed to the aqueous environment [3]. Consequences of ceramic degradation include coarseness of the exposed surface [6,7], which promotes plaque accumulation [3–8], promotion of wear to the antagonist teeth or restorative materials and change to the colour of dental ceramics, thereby

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compromising the aesthetic appearance of ceramic restorations [3,6].

There are several different types of ceramic used in dentistry. Feldspathic ceramics, i.e. Vita VMK 95 (Vita Zahnfabrik, Bad Zackingen, Germany), are formed from a mixture of potassium feldspar and glass, forming 19 weight percent (wt%) of leucite crystals ($K_2O\ Al_2O_3\ 4SiO_2$) after incongruent melting [9]. Feldspathic ceramics are used as the veneering material in metal–ceramic restorations. Aluminous ceramics, i.e. Vitadur Alpha (Vita Zahnfabrik), are composed of mixtures similar to the feldspathic ceramics, but with increased amounts of 40–50 wt% aluminium oxide crystals [10]. Aluminous ceramics may be used as laminate veneers, inlays, onlays and as a covering material for all-ceramic restorations. Feldspathic and aluminous ceramics generally provide excellent aesthetics and compressive strength. The mean flexural strengths for feldspathic and aluminous ceramic are 67 and 91 MPa, respectively [11].

The injection-moulded or pressable ceramics are supplied as ceramic ingots. They are melted at high temperatures and pressed into a mould, using the lost-wax technique. IPS Empress Esthetic (Ivoclar Vivadent AG, Schaan, Liechtenstein) is an example of this ceramic, which originates from IPS Empress Original. These ceramics contain 40–50 wt% leucite crystals [12]. Recently, the new all-ceramic systems, IPS e.max (Ivoclar Vivadent AG), have been introduced to the market. IPS e.max Ceram is a veneering ceramic of this system, which belongs to the feldspathic-based ceramics group. This glass–ceramic consists of dispersed fluorapatite crystals [$Ca_{10}(PO_4)_6F_2$] in a feldspathic glassy matrix and has a microstructure unlike that of any other commercially available dental ceramic-s [13]. Fluorapatite crystals, 2–5 μm in length and 300 nm in diameter with a needle-like morphology, are known to be contained in natural bone and teeth. The very small crystals in dental microstructures result in very special optical properties, such as translucence and opalescence, which are also seen in dental restorations [12].

In several countries, such as Australia, the Philippines and Thailand, people frequently consume acidic food, sour fruits and drinks resulting in a high incidence of dental erosion [14,15]. The potential erosive effect of these acidic foodstuffs on enamel occurs primarily by dissolution of apatite crystals [15,16]. In an oral environment, both surface degradation and erosion of ceramic restoration may occur. Therefore, the purpose of this in vitro study was to evaluate changes in the surface microhardness and chemical durability of four types of dental ceramic (feldspathic, aluminous, high-leucite and fluorapatite ceramics) after immersion in acidic agents (pineapple juice, green mango juice, citrate buffer solution and 4% acetic acid).

Material and methods

Specimen preparation

Four dental ceramics were chosen for the test as representatives of the various ceramic types available, including feldspathic ceramic (Vita VMK 95), aluminous ceramic (Vitadur Alpha), high-leucite ceramic (IPS Empress Esthetic) and fluorapatite ceramic (IPS e.max Ceram) (Table I). Thirty-five disc specimens (12.0-mm diameter; 2.0-mm thick) were produced from each ceramic. For groups of sintered ceramics, ceramic powder was mixed with deionized water using a plastic spatula on a glass slab at the recommended powder/liquid ratio according to the manufacturer's instruction. The creamy mixed ceramic was then condensed into the silicone mould (Provil; Haraeus Kulzer, Wehrheim, Germany). Platinum foil and a glass slide were then placed over the filled mould. Excess liquid on the surface of the specimen was blot-dried with a piece of absorbent paper. After condensation, specimens were removed from their moulds and then non-sintered test specimens were left on the platinum foil prior to the sintering process. The test specimens were cured in a chamber furnace according to the manufacturer's instructions (Table II). Subsequently, the specimens were polished (model Phoenix 4000; Buehler GmbH, Düsseldorf, Germany) under running water on a rotating disc at 150 rev/min using 600- and 1200-grit silicon carbide paper (3M ESPE, St. Paul, MN). Then, the specimens were ultrasonically cleaned in distilled water for 10 min. Finally, the specimens were submitted to self-glazing according to the manufacturer's instructions (Table II).

For the high-leucite ceramic, the specimens were fabricated according to the instructions for use issued by Ivoclar. Briefly, 35 wax patterns (dental wax sheets; Mizzy Inc., Cherry Hill, NJ; 12-mm diameter, 2.0-mm thick) were prepared, sprued and cast in a phosphate-bonded investment (Ivoclar Vivadent AG) using a lost-wax casting technique. A E TC 2 ingot (Ivoclar Vivadent AG), investment and plunger were heated in a burn-out furnace (KDF model H7; Denken, Tokyo, Japan) starting at 23°C and increased to 250°C, which was maintained for 30 min. The temperature was then increased in 5°C-increments until 850°C was reached and this temperature maintained for 90 min. Subsequently, the ingot was placed into a mould followed by compression in a press furnace (EP 600 Press Furnace; Ivoclar Vivadent AG). The compression process was performed at a pressure of 0.5 MPa and a starting temperature of 700°C and increased to 1075°C. After the specimen had cooled down to room temperature (23°C) (≈60 min), the casting was disassembled and the specimen was cleaned by blasting with glass beads (particle size 90 μm) at 0.4 and 0.2 MPa with a distance of 10 mm between the specimen and the blasting tip.

Table I. Elemental compositions (wt%) of the four dental ceramics used according to information received from the manufacturers.

	Type of ceramic			
	Feldspathic ceramic (VMK 95)	Aluminous ceramic (Vitadur Alpha)	High-leucite ceramic (IPS Empress Esthetic)	Fluorapatite ceramic (IPS e.max Ceram)
SiO_2	52.0–68.0	62.0–65.0	59.0–63.0	60.0–72.0
Al_2O_3	14.0–19.0	14.0–15.0	19.0–23.0	2.0–8.0
K_2O	10.0–13.0	7.0–8.0	10.0–14.0	10.0–23.0
Na_2O	6.0–7.0	4.0–5.0	3.5–6.5	†
CaO	†	1.0–2.0	0.5–3.0	1.0–10.5
B_2O_3	3.0–4.0	6.0–7.0	0.0–1.0	†
ZrO_2	5.0–6.0	0.2–0.8	†	†
P_2O_5	†	†	†	0.5–6.0
Li_2O	†	†	†	1.0–5.0
ZnO	†	†	†	8.5–20.0
BaO	†	†	0.0–1.5	†
CeO_2	†	†	0.0–1.0	†
TiO_2	2.0–3.0	†	0.0–0.5	†
SnO_2	4.0–5.0	†	†	†
Rb_2O	0.0–1.0	†	†	†
Fe_2O_3	†	†	†	†
MgO	†	†	†	†
F^-	†	†	†	0.1–1.0

†Data unavailable.

Table II. Firing schedules for the dental ceramics used.

Ceramic	Type of firing	Starting temperature (°C)	Heating rate (°C/min)	Firing temperature (°C)	Holding time (min)
Vita VMK 95	Dentine	600	55	930	1
	Glaze	600	83	930	1
Vitadur Alpha	Dentine	600	60	960	1
	Glaze	600	85	940	1
IPS e.max Ceram	Dentine	403	50	850	0
	Glaze	403	50	800	0

A sprue was cut with a thin diamond disk. The specimens were polished and cleaned as described above. Subsequently, the specimens were glazed (IPS Empress Universal Glaze; Ivoclar Vivadent AG) according to the manufacturer's instructions. All of the specimens were ultrasonically cleaned in distilled water for 10 min and dried in a stream of oil-free compressed air and kept at room temperature before testing.

Immersion in acidic agents and microhardness measurement

Twenty-five ceramic discs were randomly divided into five groups (five discs per group). Before immersion, all groups were subjected to microhardness measurements for baseline data and they were also tested after immersion in acidic agents. For the microhardness measurement, disc specimens were measured with a microhardness tester (Buehler Micromet II; Buehler Ltd, Lake Bluff, IL) using a Vickers diamond tip under a 200-g indentation load for 15 s [17]. Five indentations per specimen were performed on the top surface and the mean value of each specimen was calculated. Subsequently, four groups of discs were immersed manually in 25 ml of three acidic agents (citrate buffer solution, pineapple juice and green mango juice; see Table III) and deionized water (which served as a control) for 168 h at 37°C. One group of discs was immersed in 4% acetic acid at 80°C for 168 h (a modified method of

Table III. Acidic agents used and pH.

Acidic agent	pH; mean (SD)	Form	Lot number	Manufacturer
Citrate buffer solution	4.99 (0.01)	Instant	OC553005	BDH Laboratory Supplies, Poole, UK
100% pineapple juice	3.64 (0.01)	Instant	140807	Tipco Foods Co. Ltd., Bangkok, Thailand
Green mango juice	2.39 (0.01)	Prepared from fresh green mango	N/A	N/A
4% acetic acid	2.47 (0.01)	Diluted from 100% acetic acid	K32712763 347	Merck KGaA, Darmstadt, Germany

ISO 6872 [18]). After the immersion sequence was completed, the specimens were rinsed with deionized water, blotted dry and subjected to microhardness testing at intervals of 24, 96 and 168 h. The specimens were rotated through the microhardness tester clockwise at random angles.

Energy dispersive X-ray analysis

Ten disc specimens were randomly divided into five groups of two. Specimens were dried at room temperature for 24 h before surface elemental analysis, which was performed on the same test specimens before and after in vitro immersion. Specimens were subjected to a standard cleaning procedure prior to analysis. The variation of the elemental compositions at the specimen surfaces before and after acidic immersion (at 24, 96 and 168 h) was evaluated using an energy-dispersive X-ray (EDX) spectrometer (Link ISIS 300; Oxford Instruments, Oxfordshire, UK) attached to a scanning electron microscope (JSM-5800LV Scanning Microscope; JEOL, Tokyo, Japan) under vacuum on uncoated specimens fixed on stubs. Ten areas per specimen were selected and tested on a scanning electron microscope (20 kVp, 20 mm distance, 5 nm spot size). Each of the surface elemental compositions was calculated in terms of a mean weight percentage and standard deviation (SD). Hydrocarbon contamination, which consistently showed as a carbon peak in all groups, was disregarded [19].

Statistical methods

A two-way analysis of variance (ANOVA) with repeated measurements was performed to assess the influence of different acidic agents and ceramics on the microhardness values and elemental compositions before and after exposition to acidic agents. Statistical differences in the ceramics and acidic agents were further analyzed with one-way ANOVA and a Tukey HSD post-hoc test ($\alpha = 0.05$). Within-groups analysis was performed on microhardness and elemental compositions between baseline and each time point.

Results

The microhardness values of the four types of ceramic before and after immersion are reported in Table IV. The results of the two-way ANOVA found statistically significant differences among the different types of ceramics ($p = 0.001$), the different acidic agents ($p = 0.001$) and the interaction between the two ($p = 0.001$). Before immersion, all groups of each ceramic showed no statistically significant difference in microhardness values ($p > 0.05$). Overall, the IPS Empress Esthetic groups yielded the highest microhardness values and were significantly different compared to the VMK 95, Vitadur Alpha and IPS e.max Ceram groups ($p = 0.001$). After immersion, from the post-hoc test results, the mean microhardness for the control group (deionized water) of all types of ceramic showed no significant differences at subsequent time periods ($p > 0.05$). For the acetic acid and citrate buffer solution groups of all types of ceramic, the microhardness values significantly decreased during the first 24 and 96 h, respectively ($p < 0.05$), while the microhardness values in the green mango juice or pineapple juice groups decreased with time for all types of ceramic. The green mango juice groups of VMK 95, IPS Empress Esthetic and IPS e.max Ceram showed a significant decrease in microhardness values during the first 96 h ($p < 0.05$), as opposed to a significant decrease during the first 24 h for the Vitadur Alpha ($p = 0.001$). Similarly to the pineapple juice groups, the microhardness values for VMK 95, IPS Empress Esthetic and IPS e.max Ceram decreased significantly during 168 h ($p < 0.05$), and Vitadur Alpha similarly decreased significantly during 24 h ($p = 0.001$).

The background values of the elemental compositions of different dental ceramics before immersion are presented in Tables V–VIII. Overall, silicon was found at the highest weight percentage, followed by oxygen. Phosphorus [1.7 (0.2) wt%] was only found in IPS e.max Ceram, the fluorapatite ceramic. After immersion, the EDX results for all groups of dental ceramics are reported in Tables V–VIII. The results of the two-way ANOVA found statistical differences among the different types of ceramics ($p = 0.001$), the different acidic agents ($p = 0.001$) and the

Table IV. Mean microhardnesses of dental ceramics immersed in acidic agents at different times.

Type of ceramic	Acidic agent	Microhardness (GPa); mean (SD) at different times (h) 0	24	96	168
VMK 95	Control	5.75 (0.37)	5.76 (0.33)	5.77 (0.36)	5.76 (0.42)
	Citrate buffer solution	5.75 (0.40)	5.61 (0.15)	5.44 (0.29)*	5.27 (0.12)*
	Mango juice	5.75 (0.30)	5.57 (0.31)	5.16 (0.29)*	5.09 (0.22)*
	Pineapple juice	5.76 (0.29)	5.67 (0.53)	5.59 (0.24)	5.31 (0.34)*
	4% acetic acid	5.74 (0.21)	5.21 (0.40)*	4.51 (0.23)*	4.49 (0.19)*
Vitadur Alpha	Control	5.66 (0.15)	5.64 (0.21)	5.63 (0.21)	5.67 (0.17)
	Citrate buffer solution	5.73 (0.18)	5.49 (0.39)	5.08 (0.57)*	5.06 (0.56)*
	Mango juice	5.81 (0.23)	5.45 (0.23)*	4.87 (0.39)*	4.66 (0.78)*
	Pineapple juice	5.71 (0.11)	5.48 (0.31)*	5.33 (0.38)*	5.25 (0.20)*
	4% acetic acid	5.86 (0.21)	5.23 (0.16)*	4.59 (0.47)*	4.55 (0.54)*
IPS Empress Esthetic	Control	6.64 (0.57)	6.64 (0.46)	6.66 (0.48)	6.66 (0.51)
	Citrate buffer solution	6.61 (0.21)	6.38 (0.35)	6.03 (0.49)*	5.95 (0.16)*
	Mango juice	6.64 (0.19)	6.49 (0.42)	5.89 (0.31)*	5.87 (0.26)*
	Pineapple juice	6.58 (0.92)	6.44 (0.23)	6.14 (0.25)	6.03 (0.72)*
	4% acetic acid	6.64 (0.34)	6.25 (0.31)*	5.82 (0.35)*	5.51 (0.27)*
IPS e.max Ceram	Control	5.60 (0.27)	5.60 (0.25)	5.59 (0.31)	5.59 (0.18)
	Citrate buffer solution	5.57 (0.12)	5.31 (0.27)	4.64 (0.42)*	4.63 (0.40)*
	Mango juice	5.63 (0.26)	5.43 (0.34)	4.71 (0.42)*	4.68 (0.37)*
	Pineapple juice	5.58 (0.17)	5.51 (0.31)	5.29 (0.28)	5.07 (0.51)*
	4% acetic acid	5.63 (0.32)	5.21 (0.17)*	4.32 (0.29)*	4.31 (0.26)*

*Significant difference from baseline value ($p < 0.05$).

Table V. Mean elemental compositions of VMK 95 immersed in acidic agents at different times.

	Mean elemental composition[†]; wt% (SD)							
	IA		IIA		IVB	IIIA	IVA	VIA
Acidic agent and time (h)	Na	K	Mg	Ca	Ti	Al	Si	O
Before								
	3.6 (0.2)	12.9 (2.5)	0.3 (0.1)	2.6 (0.7)	1.5 (0.6)	8.7 (0.2)	34.8 (2.1)	22.4 (2.5)
Control								
24	3.6 (0.1)	10.4 (1.3)*	0.2 (0.1)	2.6 (0.4)	1.5 (0.4)	7.6 (0.4)*	30.1 (1.6)*	22.5 (0.9)
168	3.7 (0.1)	8.6 (0.9)*	0.2 (0.1)	2.6 (0.4)	1.5 (0.3)	7.5 (0.3)*	27.9 (1.6)*	24.3 (1.3)
Citrate buffer solution								
24	3.6 (0.1)	4.4 (0.3)*	0.2 (0.1)	0.7 (0.1)*	1.5 (0.3)	7.9 (0.2)*	28.2 (0.8)*	23.4 (0.8)
168	3.6 (0.1)	4.1 (0.6)*	0.2 (0.1)	0.6 (0.2)*	1.5 (0.3)	7.7 (0.4)*	28.1 (1.5)*	23.7 (0.5)
Green mango juice								
24	3.1 (0.8)	6.5 (1.9)*	0.2 (0.1)	1.1 (0.6)*	1.5 (0.3)	6.4 (1.4)*	25.9 (3.1)*	23.5 (1.3)
168	2.7 (0.2)*	2.8 (1.2)*	0.2 (0.1)	0.6 (0.2)*	1.5 (0.3)	4.7 (0.6)*	15.4 (2.4)*	25.9 (2.3)
Pineapple juice								
24	3.1 (0.5)	9.7 (1.5)*	0.2 (0.1)	1.8 (0.3)*	1.5 (0.3)	7.8 (0.3)*	29.8 (1.8)*	21.9 (1.7)
168	2.7 (0.1)*	6.7 (1.2)*	0.2 (0.1)	1.3 (0.3)*	1.5 (0.2)	7.1 (0.5)*	25.9 (1.9)*	24.1 (1.3)
4% acetic acid								
24	3.1 (0.1)*	3.5 (0.2)*	0.2 (0.1)	0.8 (0.1)*	1.5 (0.3)	6.4 (0.2)*	29.7 (0.9)*	23.8 (1.3)
168	2.6 (0.2)*	1.1 (0.2)*	0.2 (0.1)	0.8 (0.1)*	0.6 (0.2)*	4.4 (0.3)*	21.9 (1.6)*	30.5 (1.2)

[†] The elements are ordered according to the division of the periodic table (IA, IIA, etc.).

*Significant difference from baseline value ($p < 0.05$).

Table VI. Mean elemental compositions of Vitadur Alpha immersed in acidic agents at different times.

	Mean elemental composition†; wt% (SD)							
	IA		IIA		IVB	IIIA	IVA	VIA
Acidic agent and time (h)	Na	K	Mg	Ca	Ti	Al	Si	O
Before								
	2.4 (0.1)	10.2 (1.3)	0.4 (0.1)	1.3 (0.2)	0.6 (0.1)	7.4 (0.2)	38.8 (1.8)	21.9 (0.5)
Control								
24	2.4 (0.2)	8.5 (0.1)*	0.2 (0.1)*	1.1 (0.1)*	0.6 (0.1)	6.8 (0.4)*	31.8 (1.7)*	24.4 (0.9)
168	2.4 (0.1)	8.4 (0.5)*	0.2 (0.1)*	0.9 (0.1)*	0.6 (0.1)	6.2 (0.4)*	29.4 (1.6)*	25.0 (1.2)
Citrate buffer solution								
24	2.4 (0.1)	3.7 (0.2)*	0.2 (0.1)*	0.4 (0.1)*	0.6 (0.1)	6.6 (0.3)*	30.6 (1.8)*	24.7 (0.6)
168	2.5 (0.1)	3.1 (0.5)*	0.2 (0.1)*	0.3 (0.1)*	0.6 (0.1)	6.3 (0.3)*	33.7 (0.7)*	24.4 (0.7)
Green mango juice								
24	2.2 (0.2)	7.7 (1.7)*	0.2 (0.1)*	0.8 (0.3)*	0.6 (0.1)	6.5 (0.3)*	34.7 (0.6)*	24.4 (2.7)
168	2.1 (0.1)*	7.3 (0.8)*	0.2 (0.1)*	0.7 (0.1)*	0.6 (0.1)	6.3 (0.3)*	30.7 (1.7)*	26.8 (2.7)
Pineapple juice								
24	2.2 (0.4)	8.4 (1.1)*	0.2 (0.1)*	0.8 (0.1)*	0.6 (0.1)	6.5 (0.3)*	30.1 (0.9)*	24.5 (1.1)
168	2.1 (0.2)*	6.8 (1.1)*	0.2 (0.1)*	0.8 (0.1)*	0.6 (0.1)	6.2 (0.8)*	27.2 (1.2)*	26.8 (1.6)
4% acetic acid								
24	1.9 (0.2)*	2.4 (0.3)*	0.2 (0.1)*	0.9 (0.1)*	0.4 (0.1)	5.9 (0.6)*	30.5 (1.2)*	27.4 (1.5)
168	1.9 (0.1)*	1.3 (0.6)*	0.2 (0.1)*	0.8 (0.1)*	0.4 (0.1)	5.1 (0.6)*	24.9 (3.9)*	31.7 (2.9)

†The elements are ordered according to the division of the periodic table (IA, IIA, etc.).
*Significant difference from baseline value ($p < 0.05$).

Table VII. Mean elemental compositions of IPS Empress Esthetic immersed in acidic agents at different times.

	Mean elemental composition†; wt% (SD)							
	IA		IIA		IVB	III	IV	VI
Acidic agent and time (h)	Na	K	Mg	Ca	Ti	Al	Si	O
Before								
	2.8 (0.1)	18.5 (0.9)	0.3 (0.1)	2.8 (0.2)	0.7 (0.2)	9.9 (0.2)	37.9 (0.8)	15.8 (0.7)
Control								
24	2.8 (0.1)	17.8 (0.7)	0.2 (0.1)	2.8 (0.1)	0.7 (0.1)	9.1 (0.5)*	35.8 (0.5)	17.5 (1.3)
168	2.8 (0.1)	14.8 (1.4)*	0.2 (0.1)	2.8 (0.1)	0.7 (0.1)	8.3 (0.7)*	34.9 (1.5)*	18.8 (1.5)
Citrate buffer solution								
24	2.8 (0.1)	8.7 (0.5)*	0.2 (0.1)	1.3 (0.1)*	0.6 (0.1)	9.2 (0.4)*	34.7 (0.6)	19.1 (0.5)
168	2.8 (0.1)	8.1 (0.5)*	0.2 (0.1)	1.2 (0.1)*	0.6 (0.1)	8.4 (0.5)*	34.4 (0.9)*	21.3 (1.9)
Green mango juice								
24	2.5 (0.1)*	17.1 (1.1)*	0.2 (0.1)	2.5 (0.5)*	0.7 (0.1)	9.2 (0.5)*	36.8 (1.1)	16.4 (0.8)
168	2.2 (0.3)*	12.1 (1.6)*	0.2 (0.1)	1.8 (0.2)*	0.7 (0.1)	7.9 (0.4)*	30.8 (2.7)*	17.6 (1.4)
Pineapple juice								
24	2.6 (0.2)*	16.1 (1.3)*	0.2 (0.1)	2.3 (0.5)*	0.7 (0.1)	8.8 (0.6)*	35.3 (1.4)*	17.7 (0.9)
168	2.1 (0.4)*	10.5 (2.8)*	0.2 (0.1)	1.3 (0.4)*	0.7 (0.1)	6.6 (1.5)*	24.3 (2.5)*	28.9 (5.3)
4% acetic acid								
24	2.5 (0.2)*	5.1 (0.4)*	0.2 (0.1)	0.8 (0.1)*	0.5 (0.1)*	7.7 (0.1)*	30.4 (1.2)*	24.3 (0.7)
168	1.6 (0.1)*	3.1 (0.7)*	0.2 (0.1)	0.3 (0.2)*	0.4 (0.1)*	5.7 (0.5)*	29.4 (1.3)*	26.9 (0.8)

†The elements are ordered according to the division of the periodic table (IA, IIA, etc.).
*Significant difference from baseline value ($p < 0.05$).

Table VIII. Mean elemental compositions of IPS e.max Ceram immersed in acidic agents at different times.

	Mean elemental composition†; wt% (SD)								
	IA		IIA		IVB	IIIA	IVA	VA	VIA
Acidic agent and time (h)	Na	K	Mg	Ca	Ti	Al	Si	P	O
Before									
	5.2 (0.3)	11.3 (2.8)	0.5 (0.1)	1.8 (0.5)	1.3 (0.4)	2.1 (0.2)	30.1 (2.9)	1.7 (0.2)	22.9 (2.3)
Control									
24	5.2 (0.5)	11.3 (0.8)	0.5 (0.1)	1.6 (0.2)	1.3 (0.4)	2.1 (0.3)	29.9 (1.8)	1.3 (0.1)*	23.9 (1.1)
168	5.2 (0.3)	9.4 (0.7)*	0.5 (0.1)	1.4 (0.2)*	1.3 (0.3)	1.8 (0.1)*	26.3 (0.9)*	0.9 (0.1)*	24.1 (1.6)
Citrate buffer solution									
24	5.2 (0.2)	5.5 (1.1)*	0.5 (0.1)	0.6 (0.2)*	1.2 (0.3)	2.1 (0.1)	29.6 (1.9)	0.8 (0.1)*	23.5 (0.7)
168	5.3 (0.2)	3.4 (1.5)*	0.4 (0.1)	0.4 (0.2)*	1.2 (0.1)	1.7 (0.2)*	27.4 (1.8)*	0.8 (0.1)*	24.5 (1.3)
Green mango juice									
24	4.3 (0.1)*	10.9 (0.4)	0.5 (0.1)	1.6 (0.2)	1.3 (0.3)	2.1 (0.1)	29.6 (0.9)	1.1 (0.1)*	23.6 (1.5)
168	3.6 (0.2)*	8.1 (1.3)*	0.4 (0.1)	1.2 (0.2)*	1.3 (0.4)	1.6 (0.1)*	25.6 (1.9)*	0.9 (0.2)*	23.4 (1.1)
Pineapple juice									
24	4.6 (0.4)*	9.6 (0.3)*	0.5 (0.1)	1.6 (0.4)	1.3 (0.3)	2.1 (0.1)	29.2 (0.6)	1.1 (0.1)*	23.8 (1.3)
168	3.2 (0.4)*	5.4 (0.7)*	0.4 (0.1)	1.1 (0.3)*	1.3 (0.3)	1.5 (0.3)*	25.7 (2.5)*	0.9 (0.2)*	24.1 (1.2)
4% acetic acid									
24	4.2 (0.2)*	2.2 (0.6)*	0.5 (0.1)	0.6 (0.2)*	1.1 (0.1)*	1.4 (0.1)*	29.7 (0.8)	1.2 (0.1)*	28.6 (0.9)
168	3.3 (0.2)*	0.9 (0.2)*	0.4 (0.1)	0.4 (0.1)*	0.9 (0.1)*	1.3 (0.6)*	25.9 (1.3)*	0.9 (0.1)*	31.5 (1.5)

†The elements are ordered according to the division of the periodic table (IA, IIA, etc.).
*Significant difference from baseline value ($p < 0.05$).

interaction between the two ($p = 0.001$). All the immersed ceramics displayed evidence of surface elemental changes on the exposed surfaces, but to varying degrees at subsequent times as compared to baseline values. All groups of acidic agents, including the control groups of four dental ceramics, showed decreases in the elemental percentages, mainly in potassium, aluminium and silicon ($p < 0.05$), while oxygen remained unchanged, or even increased. For Vitadur Alpha, magnesium significantly decreased in all groups ($p < 0.05$). For all types of ceramic, calcium decreased significantly in the citrate buffer solution, green mango juice, pineapple juice and acetic acid groups and only decreased in the control group of Vitadur Alpha ($p < 0.05$). Sodium significantly decreased in the green mango juice, pineapple juice and 4% acetic acid groups ($p < 0.05$), while titanium decreased in the 4% acetic acid group ($p < 0.05$). For the IPS e.max Ceram, there was a statistically significant decrease in phosphorus after 168 h of immersion in all acidic agents, including the control group ($p < 0.05$).

Discussion

Basically, dental ceramics have been considered to be the most chemically inert restorative materials. However, the results of this study have clearly demonstrated that, after 168 h of immersion in acidic agents, all ceramics examined had surface changes in microhardness and elemental compositions. Possible explanations for these changes could be the effects of pH, environmental conditions and microstructural differences of different types of ceramic in determining microhardness values and elemental dissolution.

The green mango juice was the most acidic agent (pH 2.39) used in this study, followed by acetic acid (pH 2.47), pineapple juice (pH 3.64) and citrate buffer solution (pH 4.99), which corresponded to the significant decrease in microhardness values before and after acidic immersion. The pH of the agents resulted from the composition of each solution. The acidic agents used in this study, including pineapple and green mango juices, are considered to be favourite sour fruits in many countries, such as Australia, the Philippines and Thailand. They consist of citric acid and other organic acids [14–16]. These acids may affect the elemental dissolution of ceramics due to their chelating effect. Acetic acid has been used as the acid for chemical stability testing according to ISO standard 6872 [18]. Although acetic acid has been found to be a weak organic acid, it was still fairly corrosive to ceramics due to its chelating effect. According to ISO 6872 [18], the chemical stability of the ceramics was tested at a high temperature, 80°C, which in this study showed changes in microhardness and elemental dissolution more than other acidic agents. These results clearly demonstrate the effect of environmental conditions such as high temperature on ceramic degradation. However, the degradation of dental ceramics does not depend on just the temperature and pH of acidic agents. The important point concerns the value of the iso-electric point (IEP) [19]. This IEP value depends on the composition of the ceramics. Different dental ceramics behave differently in the various acidic solutions. The dental ceramics used in this study have a variety of compositions according to Table I; therefore, they may vary in IEP value. The ceramic with the highest IEP value had the lowest corrosion resistance. All of these reasons may explain the degradation of the ceramics.

Overall, before immersion the IPS Empress Esthetic had the highest microhardness values, while VMK 95, Vitadur Alpha and IPS e.max Ceram were comparable. A possible explanation for this result could be the microstructural differences of these ceramics [12]. The IPS Empress Esthetic consisted of high-leucite-reinforced crystals from the K_2O Al_2O_3 SiO_2 system. The leucite crystals (40–50 wt%) were distributed more evenly and an increased density appeared to result in improved material properties as well as heightened aesthetics. The VMK 95, a feldspathic ceramic, also consisted of leucite crystals, but had a lower proportion of them (19 wt%) [9]. The IPS e.max Ceram consisted of dispersed fluorapatite crystals in a feldspathic glassy matrix [13], while Vitadur Alpha had 50 wt% alumina crystals [11]. The high leucite content of IPS Empress Esthetic could be the key factor in this issue. In essence, the large thermal contraction mismatch between leucite ($22–25 \times 10^{-6}/^\circ C$) and the glassy matrix ($8 \times 10^{-6}/^\circ C$) associated with a phase transformation of leucite from cubic to tetragonal appeared to lead to the development of tangential compressive stresses in the glass around the leucite crystal upon cooling [20,21]. Such residual stresses may counteract the crack driving force and act as crack deflectors, resulting in strength and hardness increases [22,23] of the IPS Empress Esthetic, a high-leucite ceramic.

After immersion, when considering the effect of acidic agents on microhardness values, the results demonstrated that all types of ceramics examined, except Vitadur Alpha, gave similar results. The microhardness values changed during the first 96 and 168 h after being immersed in mango and pineapple juices, respectively. In contrast, microhardness values changed after 24 h for Vitadur Alpha. This result seemed to show that the alumina crystals in Vitadur Alpha had the lowest durability compared to the leucite crystals in IPS Empress Esthetic and VMK 95 and the fluorapatite crystals in IPS e.max Ceram. However, further study is required to confirm this result.

In this study, the method used for the analysis of the elemental composition was the EDX technique. This equipment was attached to a scanning electron microscope to provide information on the elemental composition beneath the surface. Ideally, electronic spectroscopy for chemical analysis (ESCA) equipment will give information from the most superficial layer of the material, whereas other analysis techniques also add some information from subsurface regions. From the results of elemental analysis by EDX, the background value played a decisive role in the accuracy and precision of the analytical results. The background values and SDs were generally small, indicating well-controlled analytical procedures. In this study, as expected, the surface composition of all types of ceramics was dominated by silicon, oxygen, aluminium, sodium and potassium elements. These elements constitute leucite and alumina crystals. In addition, phosphorus, an element that constitutes fluorapatite crystals, was only found in IPS e.max Ceram. Compared with information available from the manufacturers (Table I), the surface elemental compositions determined by EDX were largely found to be comparable and differed only in some details. Not all of the elements declared in the list of contents from the manufacturers were detected in the EDX results. Fluoride (which is found in fluorapatite), barium or boron, which are declared in the manufacturer's information, were not found in the EDX results of this study. This may be interpreted as an effect of the specimen production procedure, during which concentration on the surface layers or an evaporation of certain elements from the surface layers may have taken place. Another explanation could be reaction of the surface with small amounts of water at the elevated temperature used during firing. A few elements were not detected in the EDX analysis, either due to interference with peaks of other elements or perhaps simply be due to the fact that the specific element was not available at the surface [19]. To take account of this fact, a number of measurements were carried out at different locations on the specimen in this study.

After the immersion of all groups of ceramic in acidic agents, as seen from the EDX analysis, decreases in aluminium, sodium and potassium elements of all types of ceramics can be observed, which is consistent with previous studies [2,19]. Surprisingly, silicon decreased, which was not the same as the previous studies [2,19]. However, a possible reason might be the immersion time used here. The total exposure time used in the present study was 168 h. The time period of the experiment was longer than that in previous studies [2,19]. Acid may wash out some elements, resulting in alterations to the surface layer of ceramic. The present study demonstrated that none of the examined ceramics were found to be chemically inert. Even in a neutral aqueous environment, i.e. the control group, a very low level of degradation was observed. It can be assumed that similar degradation processes will also occur for many dental ceramics because their microstructure is dominated by a glassy matrix [2]. It is generally believed that two dominant mechanisms are responsible for the aqueous corrosion of sodium–silicate glasses, such as dental ceramics [3]. Even though the dental ceramics were not simple sodium–silicate glasses, the materials dominated by the glassy matrix and the reactions of the primary glass network former, silica, largely controlled the degradation process, firstly, by the selective leaching of alkali ions and secondly, by dissolution of the glass network (Si–O–Si). These mechanisms were controlled by the diffusion of hydrogen ions or hydronium ions (H_3O^+) from an aqueous solution into the glass and loss of alkali ions from the glass surface to maintain electrical neutrality. In general, metal alkali ions from glass were much less stable in the glassy matrix phase than in the crystalline phase and, thus, would be leached more easily. Decreases in silicon may be the reason for the breakdown of the Si–O–Si bond, which impaired the entire ceramic structure. The leaching of the more easily released elements, such as potassium and sodium, possibly created pores or channels within the glassy matrix, resulting in increased diffusion of molecular water and the development of internal areas of localized Si–O–Si bond breakage [2].

The most significant finding in this in vitro study was that all types of ceramic could degrade in acidic agents or acidic food and drink. However, it must be noted that there were some limitations to this study. During consumption of acidic food or drink, the acidic agents used in this study contact for only a short time with ceramic restorations before they are washed away by saliva [24–26]. However, this study did not account for the role of saliva. Moreover, the oral cavity presents a different testing environment. For example, the presence of water, temperature changes and pH levels in the oral cavity may also considerably affect the properties of restorations. In addition, the present study evaluated an in vitro effect. Therefore, further studies are required to elaborate the effect of acidic agents or sour fruit juice on dental ceramics in vivo.

Conclusions

The chemical durability and microhardness of different types of dental ceramic were investigated in this study. Based on the results, it was possible to conclude that the acidic agents used in this study affected microhardness and elemental dissolution of four types of dental ceramic: feldspathic, aluminous, high-leucite and fluorapatite ceramics. The main element compositions of ceramics (silicon, aluminium and potassium) decreased after being immersed in acidic agents.

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