Degradability of fluorapatite-leucite ceramics in naturally acidic agents

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This study was conducted to evaluate the titratable acidity and effect of naturally acidic agents on the surface microhardness, elemental composition, and surface morphology of fluorapatite-leucite ceramics. One hundred and ten ceramic disks (IPS d.SIGN), 12.0 mm in diameter and 2.0 mm in thickness, were fabricated. Before immersion, the baseline data of Vickers microhardness and elemental composition were recorded. Four groups were immersed in acidic agents (citrate buffer solution, green mango juice, and pineapple juice) and deionized water (control) at 37ºC for 168 hours, whereas one group was immersed in 4% acetic acid at 80ºC for 168 hours. After immersion, specimens were evaluated and data were analyzed using one-way repeated ANOVA and Tukey’s test (α=0.05). Microhardness values significantly decreased after immersion (p<0.05). In terms of elemental composition, the weight percentages of silicon, potassium, aluminum, and sodium also decreased after immersion (p<0.05). Results of this study showed that fluorapatite-leucite ceramics were affected by long-term immersion in acidic agents.

Keywords: Acidic agent, Degradability, Fluorapatite-leucite ceramic

INTRODUCTION

Dental ceramics have been used to fabricate a diverse range of restorations—inlays, onlays, veneers, crowns, and fixed prostheses. The principal attributes that fuel these extensive applications are their highly esthetic properties, biocompatibility, resistance to wear, and chemical inertness1-5. On being chemically inert, many factors play a role in bolstering the chemical durability of dental ceramics. These factors run the gamut from the composition and microstructure of the ceramic material to the chemical characters of both the ceramic material and the erosive or acidic agent, the exposure time and temperature5,6.

Previous studies have reported that corrosion or degradation of dental ceramics occurred when ceramics were exposed to aqueous solutions or acidic agents4-7. This phenomenon arises because of selective leaching of alkaline metal ions which are far less stable in the glass phase than in the crystalline phase3. Ceramic degradation causes the exposed surfaces to become roughened8,9, promotes plaque accumulation3,4,8,9 and wear of the opposing natural teeth or restorative materials, as well as discoloration of dental ceramics. Taken together, degradation of dental ceramics severely compromises the esthetic appearance of ceramic restorations8,9. IPS d.SIGN (Ivoclar Vivadent AG, Schaan, Liechtenstein) is a new type of feldspathic-based ceramic containing dispersed fluorapatite (Ca10(PO4)6F2) and leucite crystals (K2O·Al2O3·4SiO2) in a feldspathic glassy matrix10. It has become increasingly popular for the veneering of metal-ceramic restorations. Fluorapatite crystals, 2-5 µm in length and 0.3 µm in diameter of needle-like morphology, are known to be enclosed in natural bone and teeth. These very small crystals in dental microstructures result in very special optical properties such as translucence and opalescence. Hence, the presence of these crystals in IPS d.SIGN also imparts these special optical properties to fluorapatite-leucite ceramic restorations11.

As for the leucite crystals (less than 3 µm in diameter of flower-like morphology) also present in IPS d.SIGN ceramic, they contribute to the overall strength12. This is chiefly because a large mismatch between the coefficients of thermal expansion of leucite (22-25×10⁻⁶/ºC) and glass matrix (8×10⁻⁶/ºC) correlates with the displacive phase transformation of leucite from cubic to tetragonal, leading to development of tangential compressive stresses around the leucite-glass interface during cooling12-15. These residual stresses then obstruct the crack driving force and act as crack deflectors, thus bestowing the fluorapatite-leucite ceramic with improved strength or increased hardness16.

People who regularly consume acidic foods and sour fruits and drinks, or have diseases such as gastrointestinal reflux or anorexia and bulimia nervosa, are predisposed to dental erosion17,18. These predisposing factors exert their erosive effect on enamel by dissolving the surface apatite crystals18,19. However, little is known about their effect on fluorapatite-leucite ceramics which may have fluorapatite, like in enamel. Therefore, the aim of this in vitro study was to evaluate the changes in surface microhardness, elemental composition, and surface morphology of fluorapatite-leucite ceramics after being immersed in acidic agents (pineapple juice, green mango juice, citrate buffer solution, and 4% acetic acid). This study also included testing the titratable acidity of the acidic agents. The null hypothesis of this study was that there would be no differences in the microhardness and elemental
composition of the ceramics after immersion in the acidic agents.

MATERIALS AND METHODS

Specimen preparation

One hundred and ten disk specimens (12.0 mm in diameter and 2.0 mm in thickness) of fluorapatite-leucite ceramic (IPS d.SIGN; Table 1) were prepared. The 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 ceramic mixture was condensed into a silicone mold (Provil, Heraeus Kulzer, Wehrheim, Germany), and a platinum foil and glass slide were placed over the filled mold. Excess liquid on the specimen surface was blotted dry with a piece of absorbent paper. After condensation, specimens were removed from their molds. Non-sintered test specimens were left on the platinum foil prior to the sintering process. The test specimens were then cured in a ceramic furnace (Progamat P700, Ivoclar Vivadent AG, Schaan, Liechtenstein) according to the manufacturer’s instructions (Table 2).

After curing, the specimens were polished (Phoenix 4000, Buehler GmbH, Düsseldorf, Germany) under running water on a rotating disk at 150 rotations per minute using 600- and 1,200-grit silicon carbide papers (3M ESPE, St. Paul, MN, USA). Then, the specimens were ultrasonically cleaned (PC3, L&R Manufacturing Co., Kearny, NJ, USA) in distilled water for 10 minutes. Finally, the specimens were subjected to glaze treatment according to manufacturer’s instructions (Table 2).

pH measurement

Four acidic agents were used in this study (Table 1): citrate buffer solution, green mango juice as prepared from fresh green mangoes, pineapple juice, and 4% acetic acid as diluted from 100% acetic acid. The initial

<table>
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<th>Table 1 Ceramic and acidic agents used in this study</th>
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<td>Ceramic and acidic agent</td>
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<tr>
<td>IPS d.SIGN</td>
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<tr>
<td>Citrate buffer solution</td>
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<tr>
<td>100% Pineapple juice</td>
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<tr>
<td>Green mango juice</td>
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<td>4% Acetic acid</td>
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wt%: weight percentage; vol%: volume percentage; ppm: parts per million

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<th>Table 2 Firing parameters of IPS d.SIGN ceramic</th>
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<td>Type of firing</td>
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pH value of each acidic agent was measured using a pH meter (900A, Orion Research Inc., Boston, MA, USA). Before each measurement session, the pH meter was calibrated using standard buffers of pH 4.0, 7.0, and 10.0 (Titrisol, Merck KGaA, Darmstadt, Germany). The pH value of 20 mL of each acidic agent was measured three times and calculated to give a mean initial pH value and standard deviation (SD).

Titratable acidity measurement
Twenty milliliters of each acidic agent was titrated with 0.1 N sodium hydroxide (NaOH). pH measurements were made throughout the titration using the pH meter until pH values of 5.5, 7.0, and 10.0 were reached to assess titratable acidity. Titrations were repeated 10 times to ensure reproducibility and to give a mean value and SD for each acidic agent.

Storage agent immersion and microhardness measurement
Fifty ceramic disks were divided into five groups (10 disks per group). All groups were subjected to microhardness measurement for baseline data and after immersion in storage agents. For microhardness measurement, disk specimens were measured with a microhardness tester (Micromet II, Buehler Ltd., Lake Bluff, IL, USA) using a Vickers diamond-tipped indenter under a 0.2 N indentation load for 15 seconds. Five indentations per specimen were performed on the top surface, and the mean baseline value of each specimen before immersion was calculated.

After baseline data measurement, four groups were immersed manually in 25 mL of three acidic agents (citrate buffer solution, pineapple juice, and green mango juice; Table 1) and deionized water (control) at 37°C for 168 hours. One group was immersed in 4% acetic acid at 80°C for 168 hours (as modified from ISO 6872). All specimens were immersed for 168 hours to simulate 22 years of immersion in artificial saliva at 22°C. This immersion duration is comparable to the clinical service life of metal-ceramic restorations; it is also longer than previous studies so as to evaluate the long-term effects. After the immersion regime was completed, the specimens were rinsed with distilled water for 5 minutes, dried, and fixed onto an aluminum cylinder of 13 mm diameter and 10 mm height. They were then sputter-coated with a gold-palladium alloy (SPI Module Sputter Coater, SPI Supplies, West Chester, PA, USA) for 8 minutes, resulting in a film thickness of about 100–300 nm, and examined under the SEM.

Surface morphology analysis
To evaluate the effect of each immersion agent on surface morphology, three ceramic specimens from each group —before and after immersion (in each solution) at each time interval of 24, 96, and 168 hours— were examined. Prior to SEM analysis, the specimens were rinsed with distilled water for 5 minutes, dried, and fixed onto an aluminum cylinder of 13 mm diameter and 10 mm height. They were then sputter-coated with a gold-palladium alloy (SPI Module Sputter Coater, SPI Supplies, West Chester, PA, USA) for 8 minutes, resulting in a film thickness of about 100–300 nm, and examined under the SEM.

Statistical analysis
One-way analysis of variance (ANOVA) with repeated measurements was performed to assess the influence of different acidic agents on microhardness and elemental composition before and after immersion in acidic agents. Statistical differences among the storage agents were further analyzed with Tukey’s Honestly Significant Difference (HSD) test (α=0.05). Within each group, analysis was performed on microhardness and elemental composition data between baseline and each time point.

RESULTS
Titratable acidity
Table 3 shows the mean pH and SD values of each acidic agent tested, as well as the titratable acidity of each acidic agent. pH value was the lowest for green mango juice (2.36±0.02) and the highest for citrate buffer solution (4.99±0.01). Pineapple juice had the
lowest titratable acidity (22.45±1.12 mL), while 4% acetic acid had the highest titratable acidity (193.12±1.05 mL).

**Surface microhardness**
Table 4 shows the microhardness values of IPS d.SIGN ceramics before and after immersion in different storage agents. One-way repeated ANOVA revealed statistically significant differences among the different types of acidic agents (p<0.001). Before immersion, there were no statistically significant differences in microhardness among all the groups of IPS d.SIGN ceramics (p=0.86).

For the control group (deionized water), post hoc test after immersion revealed that there were no significant differences in mean microhardness at all immersion periods (p=0.82). For the acetic acid group, microhardness significantly decreased during the first 24 hours (p<0.001), while that of pineapple juice group decreased after 168 hours. For both green mango juice and citrate buffer solution groups, their microhardness significantly decreased during after 96 hours (p<0.001).

After 168 hours, the control group had the highest microhardness value among all the five storage agent groups and which was significant different from the others (p<0.001). Among the four acidic agents, there were no significant differences in microhardness (p=0.72).

**Elemental composition**
Table 5 shows the elemental compositions of IPS d. SIGN ceramics before and after immersion in different storage agents. Before immersion, the silicon element had the highest weight percentage (31.7±1.3 wt%) followed by oxygen (20.6±0.9 wt%). Magnesium ranked the lowest at 0.5±0.1 wt%.

After immersion, one-way repeated ANOVA revealed statistically significant differences in weight percentage for each of the nine elements among the different types of acidic agents (p<0.001 for all comparisons). A decrease in the elements' weight percentages (p<0.05) was observed for all the acidic agent groups as well as the control group. The weight percentage of titanium significantly decreased after immersion in 4% acetic acid (p<0.001). As for sodium, it showed no significant changes after immersion in deionized water and citrate buffer solution (p=0.76 and p=0.83, respectively). On the other hand, the weight percentages of oxygen and magnesium remained unchanged or even increased (p>0.05).
Surface morphology

Figures 1–6 show the SEM photomicrographs of IPS d.SIGN ceramics before and after immersion for 24, 96, and 168 hours. Before immersion (Fig. 1), the photomicrograph displayed a dense surface with a small amount of porosity. After immersion in different storage agents (Figs. 2–6), the common phenomenon was a gradual degradation of surface morphology whereby the extent of porosity increased with increase in immersion time, even with deionized water specimens. Notably in 4% acetic acid at 80°C, aggressive degradation of surface morphology visibly corresponded with increase in immersion time (Fig. 6).

DISCUSSION

In the oral cavity, ceramic restorative materials are exposed to harsh conditions arising from temperature...
changes and acid-base shifts by virtue of the foods and drinks consumed or due to diseases. This meant that ceramic restorative materials used in the mouth should be able to resist—or have only minimal—alterations under these conditions.

In the present study, the material under degradation investigation was fluorapatite-leucite ceramic. Changes in surface hardness, elemental composition, and surface morphology were evaluated via static immersion of this ceramic material in different naturally acidic agents over a period of 168 hours. The long immersion time of 168 hours was an
experimental strategy to evaluate the long-term effect of exposure to acidic agents on fluorapatite-leucite ceramic. On the other hand, this study had certain limitations. First, it was not within the scope of this study to examine the effects of attrition from chewing habits. Secondly, it was not within the scope of this study to compare degradation-related changes between fluorapatite-leucite ceramic and other types of ceramics. For this reason, this study did not use any control material such as a conventional feldspathic ceramic. Since its sole objective was to evaluate the degradation of a fluorapatite-leucite ceramic after immersion in

Fig. 4 SEM photomicrographs of IPS d.SIGN ceramics after immersion in green mango juice (×2000) at: (a) 24 hours; (b) 96 hours; and (c) 168 hours.

Fig. 5 SEM photomicrographs of IPS d.SIGN ceramics after immersion in pineapple juice (×2000) at: (a) 24 hours; (b) 96 hours; and (c) 168 hours.
naturally acidic agents, deionized water was employed as the control immersion medium or storage agent.

Results of the present study rejected the null hypothesis. After the immersion regime, it was revealed that the microhardness and elemental composition of IPS d.SIGN ceramic were affected by the acidic agents used: citrate buffer solution, green mango juice, pineapple juice, and 4% acetic acid. In particular, the 4% acetic acid resulted in the most aggressive degradation.

On the choice of acidic agents used in this study, green mangoes and pineapples were selected because they are the favorite sour fruits in tropical countries. For mangoes, citric acid, malic acid, ascorbic acid, and fumalic acid are the major organic acids. Similarly, citric acid and malic acid are the major acids in pineapples\(^{17-19,26}\). These acids might cause the degradation of fluorapatite-leucite ceramics due to their chelating effect\(^2\). As for acetic acid, it is used for chemical stability testing according to ISO standard 6872\(^{22}\). Besides, acetic acid is also fairly corrosive to glass or ceramics due to its chelating effect, although it is a weak organic acid.

On the measurement of titratable acidity, it was because this parameter is generally accepted as a better indicator of erosive potential than pH alone\(^{27,28}\). Results of the present study showed that acetic acid had the highest titratable acidity, which meant that it caused degradation to the ceramic material significantly more than the other storage media. Among the remaining three acidic agents (citrate buffer solution, green mango juice, and pineapple juice), titratable acidity results showed that green mango juice seemed to rank the highest in causing ceramic degradation — although there were no significant differences. Between pineapple juice and citrate buffer solution, pineapple juice should presumably result in more degradation than citrate buffer solution as it had a lower pH. However, contrary to expectation, pineapple juice had a lower titratable acidity than citrate buffer solution — which meant that it would result in less ceramic degradation than citrate buffer solution. It is probable that other components in pineapples may provide a protective effect against the erosive effect. To identify these components and their effects, further studies are required.

Another possible explanation for degradation by acidic agents could be the microstructure of fluorapatite-leucite ceramics. IPS d.SIGN, a feldspathic-based ceramic, is unique and distinct from other ceramics because its microstructure consists of fluorapatite and leucite crystal phases in a feldspathic glass matrix\(^{10}\). A large thermal contraction mismatch between leucite (22−25×10\(^{-6}\)/ºC) and the glass matrix (8×10\(^{-6}\)/ºC) could induce microcracks circumferential to the leucite particles\(^{29}\), resulting in increased susceptibility to acid-induced degradation of the ceramic\(^{30}\) from acidic agents. In addition, previous studies have reported that the size of the leucite particles in feldspathic-based ceramics increased during heat treatment within the normal ceramic firing range\(^{31,32}\), thereby further increasing the probability of microcracking\(^{33,34}\). On the effect of pH of storage media on slow crack growth of dental porcelains, Pinto et al.\(^{35}\) concluded that leucite-based ceramic (as opposed to ceramic without leucite particles) was more susceptible
to slow crack growth in acidic conditions compared to base and neutral conditions. This could thus explain why immersion in acidic agents had deleterious effects on IPS d.SIGN fluorapatite-leucite ceramic.

In the present study, ceramic firing was performed only once during the firing process although it is usually done several times in clinical situations. It has been reported that multiple firings on ceramics affected their colors, thermal properties, and microcrack densities. However, little is known about the effect of multiple firings on hardness or elemental composition and the impact of combined effect with acidic agents. Therefore, to preclude any possible effect stemming from multiple firings, only one ceramic firing was performed in this study. Nonetheless, further studies are required to investigate the effect of multiple firings.

According to EDX analysis, immersion of fluorapatite-leucite ceramics in acidic agents caused the weight percentages of sodium, potassium, calcium, aluminum, and phosphorous elements to decrease — even in a neutral aqueous environment (deionized water group). This result was in accordance with previous studies, except for the decrease of silicon element. It should be noted that although dental ceramics were not simple sodium-silicate glasses, the materials were nonetheless dominated by the glass matrix. Consequently, the degradation process is principally controlled by reactions between the primary silica glass network and the surrounding aqueous environment. With sodium-silicate glasses such as dental ceramics, aqueous corrosion is generally ascribed to two dominant mechanisms. The first mechanism is the selective leaching of alkali metal ions; the second mechanism is the dissolution of the glass network (Si-O-Si). These mechanisms are controlled by the diffusion of hydrogen ions or hydronium ions (H$_3$O$^+$) from an aqueous solution into the glass coupled with the leaching of alkali ions from the glass surface to maintain electrical neutrality.

As highlighted above, there was an unexpected decrease in the silicon element after the immersion regime — a finding which was not consistent with previous studies. A possible explanation was the interruption of the Si-O-Si bond, thereby compromising the entire ceramic structure. Following the leaching out of the more easily released elements such as potassium and sodium, it was highly likely that pores or channels were created within the glass matrix. This then led to increased diffusion of water molecules and subsequent breaking of the Si-O-Si bonds. Another possible explanation might lie in the immersion time used. A prolonged immersion time period of 168 hours was used in the present study, which was substantially longer than that of previous studies. In light of the uncertainties pertaining to the decrease of silicon element, further studies are needed to confirm this result.

The most significant finding of this in vitro study was that fluorapatite-leucite ceramics could degrade in acidic agents (present in acidic foods and drinks) after a long period of immersion. However, it must be highlighted that the role of saliva was not taken into consideration in this study. During consumption, acidic foods or drinks come in contact with ceramic restorations only briefly before they are washed away by saliva. Moreover, the oral cavity presents an environment different from the current test environment due to the presence of water and differences in temperature change and pH level. Taking these environmental factors into consideration, ceramic restorations might be harshly affected in the oral cavity.

In the present study, only changes in hardness and elemental composition were used as parameters to evaluate the degradation of fluorapatite-leucite (IPS d.SIGN) ceramics. To further confirm the results of this study, additional methods such as depth analysis using cross-sections, roughness measurement, or analysis of elements released into acidic agents need to be employed. It should also be mentioned that the degradation of fluorapatite-leucite (IPS d.SIGN) ceramics was examined in vitro in this study. Therefore, further studies are required to elucidate the degradation effect on other dental ceramics or to examine the effect in vivo.

CONCLUSIONS

Within the limitations of this study, the following conclusions were drawn

1. The microhardness of fluorapatite-leucite ceramic was adversely affected by the acidic agents used: citrate buffer solution, green mango juice, pineapple juice, and 4% acetic acid at 80ºC.
2. On changes in the elemental composition, the weight percentages of silicon, potassium, calcium, aluminum, and sodium decreased after prolonged immersion in the acidic agents.
3. When fabricating restorations with fluorapatite-leucite ceramics for patients who consume acidic foods and drinks or with diseases that predispose them to dental erosion, these effects of acidic agents on the microhardness and elemental composition of fluorapatite-leucite ceramics should be taken into consideration.

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