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J Dent Res 92(5):467-471, 2013

ABSTRACT

We tested the hypotheses that glass-ceramic veneers and overglazes degrade by ion exchange in an acidic environment, and that they degrade by breakdown of the silica network in a basic environment. Disk specimens of glass-ceramic veneer and glaze were fabricated and immersed in pH 2, 7, or 10 buffer solutions, for 1, 3, 5, 10, 15, and 30 days. Each specimen was placed in a shaker bath containing de-ionized distilled water at 80°C. Concentrations of Al³⁺, Ca²⁺, Zn²⁺, Li²⁺, and Si⁴⁺ were analyzed by means of inductively coupled plasma atomic emission spectrometry (ICP/AES). Statistical analyses were performed by factorial ANOVA. Significant differences occurred among leached ion concentrations as a function of material type, solution pH, and exposure time. A substantial release of Si occurred at pH 10 over time, leading to a breakdown of the glass phase. At pH 2, dissolution was controlled by an ionic exchange mechanism. We conclude that ceramic veneers and glazes may be susceptible to considerable degradation in low- and high-pH buffer solutions.

KEY WORDS: dissolution, chemical stability, acidic pH, basic pH, ion release, surface degradation.

DOI: 10.1177/0022034513484332

Received October 19, 2012; Last revision January 29, 2013;
Accepted March 7, 2013

A supplemental appendix to this article is published electronically only at <http://jdr.sagepub.com/supplemental>.

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Surface Degradation of Dental Ceramics as a Function of Environmental pH

INTRODUCTION

In vitro studies have shown that ceramics are susceptible to corrosion in the range of oral fluid pH (Anusavice, 1992; Milleding *et al.*, 1999b, 2002; Butler *et al.*, 2004; Ccahuana *et al.*, 2010; Junpoom *et al.*, 2010; Kukiattrakoon *et al.*, 2010b, c). The dissolution potentials of ceramics in acidic liquids such as soda pop (pH 2.525-4.038 for common brands) (Jain *et al.*, 2007) and fruit juices (pH 2.0-5.50) differ considerably with the variation in buffering capacity of the patient's saliva and diet. Some basic substances, such as lima beans or soy beans (pH 12), spinach (pH 8.3), and antacids (pH 10-14), can also cause dissolution of glass-phase ceramics. ISO standard 6872 for dental ceramics requires evidence of minimal chemical solubility for dental ceramic materials that are exposed to a 4% HAc solution.

Dietary habits and the buffering capacity of saliva can have a significant effect on the pH of the oral environment (Bartlett *et al.*, 2011) and on the chemical durability of ceramic-based restorations. Moreover, ceramic corrosion can affect the fracture strength of these materials (Drummond *et al.*, 1991; Pinto *et al.*, 2008) and increase surface roughness (Milleding *et al.*, 1999a), which can affect the survival of restorations and damage to adjacent oral structures as a result of increased plaque accumulation. In addition, rougher surfaces are more susceptible to adhesive and abrasive wear from the opposing dentition. Moreover, humans experience discomfort when the roughness of restorations (Ra) is 0.50 μm or more (Jones *et al.*, 2004). The ceramic microstructure has been shown to influence the susceptibility of the prosthesis surface to pH changes, *i.e.*, reduced chemical durability (Anusavice and Zhang, 1997; Milleding *et al.*, 2003). Also, the cytotoxicity potential of leached ions increases during surface degradation (Mackert, 1992; Messer *et al.*, 2003).

Previous clinical studies reported by the authors revealed clinical degradation and roughening of ceramic surfaces between years 1 and 2 (Esquivel-Upshaw *et al.*, 2006, 2012, 2013). These crowns were made from a non-veneered (glazed) lithium disilicate glass-ceramic core ceramic and a lithium disilicate glass-ceramic core that was veneered with a glass-ceramic. The study participants reported this condition as "rough". Based on these clinical observations, we performed the present *in vitro* investigation to determine the cause of the roughening process and the mechanism of surface degradation.

The objectives of this research were:

- (a) to test the hypothesis that glass-ceramic veneers and their respective overglazes degrade by ion exchange of protons for alkali ions and alkaline earth oxides in an acidic environment (pH 2); and

Figure 1. Mean weight change (weight loss) per area for glass-ceramic veneer (GCV) and glaze (GL) disk specimens ($\mu\text{g}/\text{mm}^2$).

- (b) to test the hypothesis that glass-ceramic veneers and their respective overglazes degrade by breakdown of the silica network by hydrolysis of Si-O-Si bonds in a basic environment (pH 10).

MATERIALS & METHODS

Thirty-six disks of glass-ceramic veneer (GCV) (IPS Eris for Empress 2 glass-ceramic core) and 36 disks of glaze (GL) (e.max® Ceram glaze, Ivoclar Vivadent, Schaan, Liechtenstein) were fabricated with a diameter of 12 mm and a thickness of 1.0 mm. Porcelain powder was mixed with the liquid recommended by the manufacturer and poured into a metal mold. The densities of randomly selected disks were measured to ensure structural consistency prior to immersion. A programmable dental furnace (Radiance Multi-Stage MSL Furnace, Jetrus International®, Melville, NY, USA) was used to sinter the specimens according to the manufacturer's recommendations.

The specimens were pre-dried for 7 min, dried for 2 min, heated to 403°C at a rate of 60°C/min under full vacuum, then to 724°C for 1.5 min, and subsequently cooled for 2 min. The GL and GCV specimens were processed identically, except that GL specimens were fired once and GCV specimens were fired twice. Specimens were polished after being fired through 600-grit abrasive, rinsed, and dried.

Each disk was washed 3 times in ethyl alcohol, dried, weighed (Mettler Toledo BB240, Toledo, OH, USA, precision 0.001 gm), and sealed in 15-mL polyethylene corrosion jars (Nalgene, Rochester, NY, USA) by means of 12.5-mm-wide Teflon tape. The disks were immersed in one of the following test solutions: pH 2, pH 7, and pH 10 buffer solutions for 1, 3, 5, 10, 15, and 30 days. The disks were placed vertically in the containers, allowing for exposure of both sides to the solution. Solution pH was measured before and after immersion (Mettler Toledo SevenMulti pH Conductivity Meter). The buffer solutions were certified as high purity (Fisher Scientific, Philadelphia, PA, USA; SB 108-500 Buffer Solution pH 7.00; SB96-500

Buffer Solution pH 2.00; SB116-500 Buffer Solution pH 10.00). The ratio of the specimen surface area to solution volume (A/V) was maintained at 2.333 to standardize corrosion rates. Each specimen was sealed in a polyethylene jar and placed in a shaker bath (Model 6300, Water Bath Shaker, Eberbach Corp., Ann Arbor, MI, USA) containing de-ionized-distilled water at a temperature of 80°C and a vibrating speed of 50 oscillations per min. The immersion process was performed at a temperature of 80°C in pH 2 or pH 10 buffer to accelerate degradation of the ceramic to simulate years of exposure *in vivo* at 37°C. This temperature is required to test the chemical durability of ceramics according to ISO 6872.

The disk surfaces were rinsed with ethyl alcohol and dried for 40 min at room temperature (25°C). Concentrations of

Al^{3+} , Ca^{2+} , Zn^{2+} , Li^{2+} , and Si^{4+} in the corrosion solutions were analyzed by means of an inductively coupled plasma atomic emission spectrometer (Perkin-Elmer 3200RL, Downers Grove, IL, USA). Prior to analysis, specific elements were tested against known concentrations of each element to determine the accuracy of elemental detection. The instrument was calibrated to an accuracy of 1.5 mg/L at 1 ppm. Each element was measured 5 times to ensure reproducibility of results. Disk surfaces that were exposed to the test solutions for 1, 3, 5, 10, 15, and 30 days were examined by scanning electron microscopy (JEOL JSM-6400 Scanning Electron Microscope, JEOL Ltd., Tokyo, Japan).

To obtain the ratio of ions leached from the ceramic specimens, we placed one disk each of GCV and GL ceramic in 10% hydrofluoric acid until totally dissolved. The solutions were analyzed under ICP for concentration of analytes.

Statistical Analysis

Statistical analyses were performed with an SAS statistical software program (V 9.2) for factorial analysis of variance (ANOVA). The natural log of elemental concentration (Al^{3+} , Ca^{2+} , Zn^{2+} , Li^{2+} , and Si^{4+}) was chosen as our response variable. Material type (GCV or GL), pH level (2, 7, or 10), and number of days (1, 3, 5, 10, 15, or 30), and all two-way interactions among them, were chosen as fixed factors.

RESULTS

Weight Change

There was no change in the pH of the solution before and after immersion of specimens. There were significant effects of material and pH on the weight change of the disks (Fig. 1). Weight differences after exposure for GCV were greater across all days and pH levels, particularly at pH 7 and 10. Also, the higher the pH level, the greater the pre- and post-weight differences across all days and both groups. This was particularly significant at pH = 10. Although the effect of exposure time was not significant,

Figure 2. (A) Ions leached from glass-ceramic veneer (GCV) for 'network former to modifier' ratio as a function of pH and time. (B) Ions leached over time from glaze (GL) for 'network former to modifier' ratio as a function of pH and time.

there was a significant overall effect of material ($p = .004$), a marginally significant overall effect of days ($p = .089$), and a significant effect of pH ($p = .003$).

Ions in Solution

These results reveal that there was a significant difference in release rates among the material type, solution pH, and exposure time. These results suggest that, at a pH of 10, there is a substantial release of Si over time (see Appendix), leading to a breakdown of the glass phase. At the low pH, analysis of the data suggests that the release of ions is similar to an ionic exchange mechanism or selective leaching of ions.

Total dissolution of both disks was calculated for the ratio of network former to network modifier [Si/(Li+Ca+Zn)]. The ratio for GCV was 1.6, and the ratio for GL was 8.0. Comparable ratios were found for the concentrations of ions at different pH levels and time periods (Figs. 2A, 2B).

SEM Analysis

After exposure to pH 10 buffer solution, the GCV specimens exhibited significant pitting and loss of surface structure, which suggests a breakdown of the glass phase (Fig. 3). At the low pH for the same time period, SEM images revealed some pitting but at isolated areas, which suggests a release of ions occurred in a manner similar to an ionic exchange mechanism (Fig. 4).

DISCUSSION

This study focused on disks made of GCV and GL that were weighed and examined after immersion, and the types and concentrations of ions leached into the buffering solutions were determined. Network modifiers (Ca, Zn, Li) and network formers

Figure 3. SEM backscattered image of glass-ceramic veneer (GCV) and pH 10, 30 days.

(Si, Al) were measured to determine the mechanism involved in leaching at different pH levels.

Based on the weight change data, the weight loss in the GCV group was, on average, 4.8 times greater than that of the GL group (95% CI = [1.7, 8.0]). The effect of pH ($p = .003$) was significant, as evidenced by an increase in weight loss across both groups and all days by 0.75 for each unit increase in pH (CI = 0.271, 1.22). The overall effect of exposure time in days ($p = 0.089$) was marginal, and there was an estimated weight loss of 0.14 mg increase per day (CI = -0.022, 0.30) from both groups at each pH. This weight loss was confirmed by the quantity of ions released in the solutions. At all times and for each pH, there was a significantly greater ion release from GCV than from GL, often an order of magnitude more. This included both network modifiers (Ca, Zn, Li) as well as Si^{+4} , the primary network former.

Figure 4. SEM backscattered image of glass-ceramic veneer (GCV) after exposure to pH 2 buffer solution for 30 days.

SEM micrographs of the 2 material surfaces revealed a more generalized dissolution for GL and a rougher topography for GCV, which likely occurred as glass dissolution released crystals. These observations have resulted in a reformulation of the composition of GCV by the manufacturer by adding a network former to reduce ion release (personal communication, P. Oehri, October, 2011).

The ion release rate for Ca, Li, Zn, and Si from the glaze was the greatest for all time periods at pH 10. The concentrations of Li, Zn, and Si released from the glaze were similar at both pH 2 and pH 7. The release of Ca from the glaze did not follow this trend. In fact, the release rate of Ca at a pH of 2 was comparable with the release rate of Si.

The release rate trends from GCV were not as consistent as those from the glaze, with 2 exceptions. Ion release from GCV was at a maximum at a pH of 10. Also, the amount of ion release from GCV at all times and pH levels was considerably higher than that from the glaze.

The corrosion of silicate-based glasses can occur either by selective leaching or complete dissolution, but it usually involves a combination of the 2 mechanisms. In general, the process leads to the formation of a thin film or gel on the exposed glass surface, with the composition of the gel being significantly different from that of the non-corroded glass (Pantano *et al.*, 1974; Clark, 1975; Clark *et al.*, 1976). The composition and profile of the gel layer are usually a direct measure of the durability of the glass. Studies of binary soda-silica and lithia-silica glasses have established that the corrosion resistance is maximized when the reactions at the glass surface form a thin gel with a high surface silica concentration (Hench and Clark, 1978). In an acidic environment, the predominant reaction is an ion exchange between the protons in solution and network modifiers in the bulk. In a basic environment, the hydroxyl ions in solution attack the glass structure, breaking silicon-oxygen-silicon bonds, thereby resulting in generalized dissolution. At a neutral pH, a combination of the 2 reactions occurs. Corrosion of glass-ceramics is more complex since both glassy and crystalline phases are present. Glass dissolution leads to release of crystals into solution, which affects the kinetics of ion release.

Several *in vitro* studies (Milleding *et al.*, 2002, 2003; Kukiattrakoon *et al.*, 2010a, 2011) have analyzed ion release and surface compositional and roughness changes that occurred as a function of time, temperature, and pH. Most of these studies were limited to acidic conditions. With the high silica and alumina content of many of these materials, basic conditions (high hydroxyl content) will present a more severe environment, producing hydrolysis of the silica network and the resulting breakdown of the entire structure. The results of this study support this hypothesis. Ion release for all measured ions (both network formers and network modifiers) is greater at all time periods at a pH of 10 compared with a pH of 7 or 2.

This study confirms that exposure times at various pH levels in saliva is likely to affect ion release as well as surface changes. Furthermore, occlusal interactions between ceramic materials and natural tooth structure will also play a role in the degradation process. Further research is recommended to analyze leaching effects by cycling the exposure at both high- and low-pH levels, as occurs in the oral cavity, with longer intermittent periods at the neutral pH. This approach should more closely mimic *in vivo* conditions and monitor material stability.

This study investigated the mechanisms of ceramic degradation as a function of time and pH levels. Exposure in a basic pH buffer resulted in a complete breakdown of the silica network as compared with exposure to an acidic pH buffer, which resulted in selective ionic leaching of the glass matrix. Future studies should include cyclic events of exposure over a variable pH range to mimic the chemical durability of different materials under simulated intra-oral conditions.

ACKNOWLEDGMENTS

This study was supported by the University of Florida Office of Research and by NIH/NIDCR Grants K23 DE018414 and R01 DE06672. Ceramic materials were provided by Ivoclar (Ivoclar, Vivadent, Schaan, Liechtenstein). The authors declare no potential conflicts of interest with respect to the authorship and/or publication of this article.

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