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Effect of Surface Acid Etching on the Biaxial Flexural Strength of Two Hot-Pressed Glass Ceramics

Tabassom Hooshmand, DDS, PhD, Shaghayegh Parvizi, DDS, & Alireza Keshvad, DDS, PhD

Research Center for Science and Technology in Medicine, School of Dentistry, Tehran University of Medical Sciences, Tehran, Iran

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Correspondence
Tabassom Hooshmand, DDS, PhD, Research Center for Science and Technology in Medicine, School of Dentistry, Tehran University of Medical Sciences, Ghods St., Tehran 14174, Iran. E-mail: hoshmand@sina.tums.ac.ir

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Abstract

Purpose: The purpose of this study was to assess the effect of surface acid etching on the biaxial flexural strength of two hot-pressed glass ceramics reinforced by leucite or lithium disilicate crystals.
Materials and Methods: Forty glass ceramic disks (14-mm diameter, 2-mm thick) consisting of 20 leucite-based ceramic disks (IPS Empress®) and 20 lithia disilicate-based ceramic (IPS Empress 2®) were produced by hot-pressing technique. All specimens were polished and then cleaned ultrasonically in distilled water. Ten specimens of each ceramic group were then etched with 9% hydrofluoric (HF) acid gel for 2 minutes and cleaned ultrasonically again. The biaxial flexural strength was measured by the piston-on-three-ball test in a universal testing machine. Data based on ten specimens in each group were analyzed by two-way ANOVA ($\alpha = 0.05$). Microstructure of ceramic surfaces before and after acid etching was also examined by a scanning electron microscope.
Results: The mean biaxial flexural strength values for each group tested were (in MPa): nonetched IPS Empress = 118.6 ± 25.5; etched IPS Empress = 102.9 ± 15.4; nonetched IPS Empress 2 = 283.0 ± 48.5; and etched IPS Empress 2 = 250.6 ± 34.6. The results showed that the etching process reduced the biaxial flexural strengths significantly for both ceramic types ($p = 0.025$). No significant interaction between the ceramic type and etching process was found ($p = 0.407$).
Conclusion: From the results, it was concluded that surface HF acid etching could have a weakening effect on hot-pressed leucite or lithia disilicate-based glass ceramic systems.

Dental ceramic restorations are widely used, because they are durable, esthetically appealing, and provide excellent biocompatibility. The invention of pressable glass ceramics reinforced by leucite or lithium disilicate crystals aimed at improving strength and durability over that of conventional dental ceramics.[1,2] IPS Empress is a leucite-reinforced glass ceramic that obtains its strength by finely dispersed leucite crystal reinforcement and was designed for restoring single units, including veneers, inlays, onlays, and crowns. IPS Empress 2 glass ceramic was developed to enable the fabrication of three-unit fixed partial dentures up to the second premolar. Its main crystalline content is primarily 60wt% lithium disilicate.[3] Resin composites are usually used to bond ceramic restorations to the tooth structure and also to repair fractured ceramic in repair systems. The establishment of the bond between ceramic and resin composite is usually created via micro-mechanical attachment by hydrofluoric (HF) acid etching and/or grit blasting, and chemical bonding by a silane coupling agent; however, a major concern exists about the use of HF acid etching due to its hazardous effects on health[4] and possible deleterious effects on ceramic strength.[5] It has been reported that etching the porcelain does not only provide the necessary surface roughness conducive to mechanical interlocking, but would appear to have a weakening effect on the feldspathic porcelain surfaces.[6] In a previously published study by Hooshmand et al,[7] it was concluded that a durable resin–ceramic bond could be obtained by using an appropriate silane application without the need for HF acid etching the ceramic surface, confirming the earlier observation.[8]

Mechanical strength is an important factor that controls the clinical success of dental restorations. Although numerous studies have established the increase in bond strength of resin to ceramic achieved by etching, there is little research in the dental literature to establish how this will affect the mechanical properties of hot-pressed glass ceramic systems.

Several studies have evaluated the effect of factors such as surface preparation methods, layering, casting conditions, and microstructure on the strength of some types of dental ceramics.[9–14] Controversy exists concerning the effect of surface acid etching on the ceramic materials. The industrial literature has shown the strengthening effect of acid etching on glass through the removal of surface flaws, thereby reducing stress concentration and increasing overall strength.[15,16] However, this might not apply to multicomponent glass systems consisting of one or more crystalline phases, such as those used in dentistry. In fact, a decrease in strength for some dental ceramics by surface acid etching has been found.[5,17]

With the introduction of hot-pressed glass ceramic systems, the effect of acid etching on the mechanical strength of these ceramics has not been fully investigated in the dental literature. The aim of the present study was to assess the effect of surface acid etching on the biaxial flexural strength of two hot-pressed glass ceramics reinforced by leucite or lithium disilicate crystals.

Materials and methods

Each of the twenty glass ceramic specimens was made from the leucite-based core ceramic (IPS Empress ingots, Lot E 56830, Ivoclar–Vivadent, Schaan, Liechtenstein) and the lithia disilicate-based core ceramic (IPS Empress 2 ingots, Lot E 30883, Ivoclar–Vivadent) by the lost-wax and hot-pressed ceramic fabrication technique following the manufacturer's instructions.

Ceramic disk specimens were fabricated from wax patterns, approximately 14 mm in diameter and 2 mm thick. A mold of the wax disk pattern was produced by attaching it to a sprue former and placing a paper ring around it. Empress 2 special investment material (200 g), together with 31 ml of special investment liquid, and 13 ml of distilled water and IPS-Empress special investment material (200 g), together with 40 ml of special investment liquid and 10 ml of distilled water were mixed for 60 seconds under vacuum and poured into the ring. The paper ring and sprue former were removed after 1 hour. The molds were then transferred to a burn-out furnace, heated from room temperature to 250°C at a rate of 5°C/min, held at 250°C for 30 minutes, then further heated from 250 to 850°C at a rate of 5°C/min, and finally held at 850°C for 60 minutes. After completion of the heating cycles, the investment ring was removed from the heating furnace immediately, and the cold ingot was placed in the investment ring. The investment ring with the ingot and the alumina plunger were transferred to the preheated EP 600 pressing furnace at 700°C. This furnace has an automatic program, heated from 700 to 920°C at a rate of 59°C/min for the IPS Empress 2 ceramics and then held at 920°C for 20 minutes. For the IPS Empress ceramics, the furnace was heated from 700 to 1180°C. The ingot was subjected to a plunger pressure of 5 bar, as recommended by the manufacturer. Once cooled, the investment was divested from the specimen by sandblasting with 50 μm alumina particles at 5 bar pressure. The specimens were then cleansed by placing them in the Invex liquid (Ivoclar–Vivadent) for 20 minutes and were rinsed with water for 2 minutes.

The specimen surfaces were wet ground with 400-, 600-, and 800-grit silicon carbide paper on a grinding device. All specimens were then cleaned ultrasonically for 15 minutes in distilled water. Ten specimens from each ceramic group were etched with a 9% HF acid gel (Ultradent Products, Inc., South Jordan, UT) for 2 minutes, washed in running water, and then cleaned ultrasonically for 15 minutes in distilled water. The remaining ten specimens in each group served as unetched controls.

The piston-on-three-ball test (ASTM Standard F394-78)[17] was used to determine the biaxial flexural strength of ten disk specimens per test group. To more closely mimic dental restoration dimensions and make specimen fabrication realistic, a smaller specimen diameter than specified was adopted. Disk specimens were centered and supported on three steel spheres (3.18-mm diameter) positioned 120° apart on a 10-mm diameter circle. The load was applied to the specimen center by a right circular cylinder of hardened steel having a diameter of 1.58 mm with the flat end perpendicular to the axis. A thin plastic sheet was placed between the specimen surface and the flat-ended loading cylinder to distribute the load uniformly. The specimens were loaded in a universal testing machine (Zwick, Z100, Ulm, Germany) at a crosshead speed of 0.5 mm/min until fracture. Testing was performed at room conditions. The maximum tensile stress (MPa), which corresponded to the biaxial flexure strength, was calculated according to the equation suggested by the test standard (ASTM F394-78) as follows:[18]

$$\mathrm{S} = -0.2387\mathrm{P}(\mathrm{X} - \mathrm{Y})/\mathrm{d}^2,$$

where S is the maximum tensile stress (MPa), P is the load at fracture (N), and d is the specimen thickness (mm) at fracture origin. X and Y were determined as follows:

$$\mathrm{X} = (1+^{\nu}) \ln (^{\mathrm{B}}/_{\mathrm{C}})^2 + [(1 -^{\nu})/2](^{\mathrm{B}}/_{\mathrm{C}})^2,$$

$$\mathrm{Y} = (1+^{\nu})[1 + \ln(^{\mathrm{A}}/_{\mathrm{C}})^2] + (1 -^{\nu})(^{\mathrm{A}}/_{\mathrm{C}})^2,$$

where ν is the Poisson's ratio, A is the radius of the support circle (mm), B is the radius of the tip of the piston (mm), and C is the radius of the specimen (mm). Values for Poisson's ratio for the IPS Empress and IPS Empress 2 ceramics were assumed as 0.23 and 0.24, respectively.[3] Data based on ten specimens in each group were analyzed by two-way ANOVA at a significance level of $p < 0.05$, using the Statistical Package for Social Sciences (SPSS for Windows 11.5, SPSS, Inc., Chicago, IL). Microstructure of each glass ceramic was also analyzed before and after acid etching using a scanning electron microscope (XL30, Philips, Eindhoven, The Netherlands).

Results

The mean biaxial flexural strength values and the statistical analysis of the data for each group are presented in Tables 1 and 2, respectively. Two-way ANOVA showed that the type of material affected the biaxial flexural strength significantly ($p < 0.001$). The mean biaxial flexural strengths for the IPS Empress 2 ceramic in both groups (etched and non-etched) were significantly higher than that of the IPS Empress ceramic ($p < 0.001$).

Table 1 Mean biaxial flexural strengths for groups tested

Material	No.	Surface Treatment	Mean (MPa)	SD
IPS Empress	10	Etched	102.8710	15.39
	10	Nonetched	118.5930	25.55
IPS Empress 2	10	Etched	250.56	34.61
	10	Nonetched	283.97	48.52

SD = Standard deviation.

In addition, the etching process reduced the biaxial flexural strength significantly for the two types of ceramic materials ($p = 0.025$), but no significant interaction between the ceramic type and etching was found ($p = 0.407$). This indicates that the etching process reduced the biaxial flexural strength in both ceramics similarly.

Representative views of untreated and treated ceramic surfaces with HF acid etching are presented in the scanning electron microscope (SEM) images in Figures 1-4. SEM images show that the surfaces of polished IPS Empress and IPS Empress 2 ceramics became increasingly porous and irregular due to dissolution of the glass phase. As a consequence, elongated lithium disilicate crystals in IPS Empress 2 protruded from the glassy matrix (Fig 4).

Discussion

Mechanical strength is an important property that determines the performance of brittle materials. The optimum strength of any ceramic is dependent on the fabrication procedure and minimization of flaws.[19] Furthermore, several factors can also influence the definitive strength of ceramic materials, including dimension of specimens, test environment, polishing procedures, rate of stressing area of specimen subjected to the stresses, and testing methods.[3]

The measurement of the strength of brittle materials under biaxial flexure conditions rather than uniaxial flexure (3- or 4-point flexural tests) is often considered more reliable, because the maximum tensile stresses occur within the central loading area, and edge failures have no effect on specimen fracture.[20] This feature makes the method suitable for assessment of the effects of surface conditions on strength. Besides, the biaxial test is simpler to perform and provides a better simulation of clinically relevant sample size than that used for other strength tests.[20] Different methods have been developed for the biaxial flexural test, including the ring-on-ring,[21] ball-on-ring,[22] piston-on-ring,[23] and piston-on-three-ball tests.[24] In this study, the piston-on-three-ball test was used, because excellent results

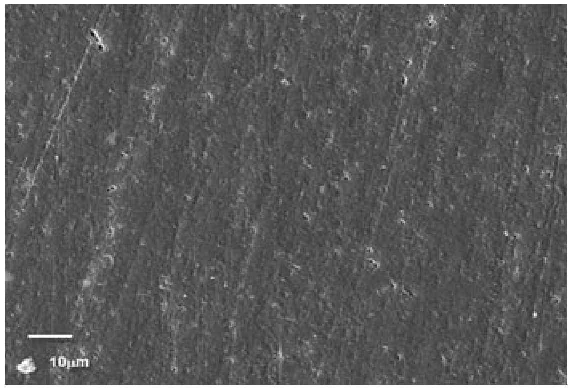

Figure 1 SEM micrograph of untreated IPS Empress ceramic (Mag. ×600).

by this method have been previously reported for brittle dental materials such as dental ceramics.[20]

Ever since HF acid etching was first suggested as a ceramic surface pretreatment for resin bonding, many different etching periods have been advocated and used. The manufacturer's recommended etching time for cementation of the IPS Empress ceramic restorations with a luting resin is 60 seconds and for IPS Empress 2 is 20 seconds; however, the most profound ceramic surface roughness and the highest bond strength data at the ceramic–resin interface have been obtained by 2-minute HF acid etching.[25] Manufacturers most commonly recommend an etching time of 1 to 2 minutes for 9% to 10% HF acid in ceramic repair systems. Other studies on the bond strength analysis of resin composite to ceramic have also applied a 2-minute HF acid etching for the IPS Empress and IPS Empress 2 ceramic surface treatments.[26,27] Thus, the effect of HF acid with an etching time of 2 minutes on the biaxial flexural strength of hot-pressed glass ceramics was assessed in the present study.

The biaxial flexural strength value for the nonetched IPS Empress ceramic reported by Cattell et al[1] was 120 MPa, which is very close to the value obtained in this study (118 MPa). Similar biaxial flexural strength for the IPS Empress 2 ceramic with that obtained in the present study has been also reported;[28]

Table 2 Two-way ANOVA analysis ($\alpha = 0.05$)

Source	df	Mean Square	F-value	P-value
Material	1	245044.585	220.749	0.000
Etching	1	6035.375	5.437	0.025
Materials & etching	1	782.340	0.705	0.407

df = degree of freedom.

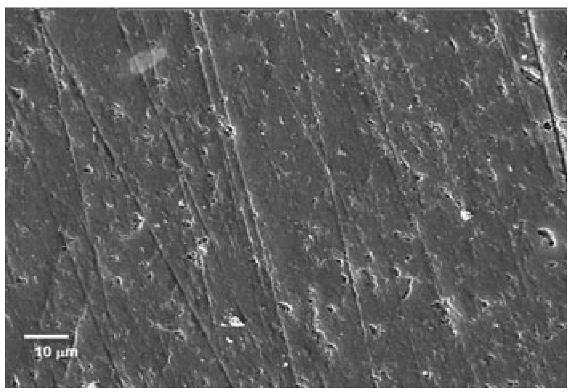

Figure 2 SEM micrograph of untreated IPS Empress 2 ceramic (Mag. ×600).

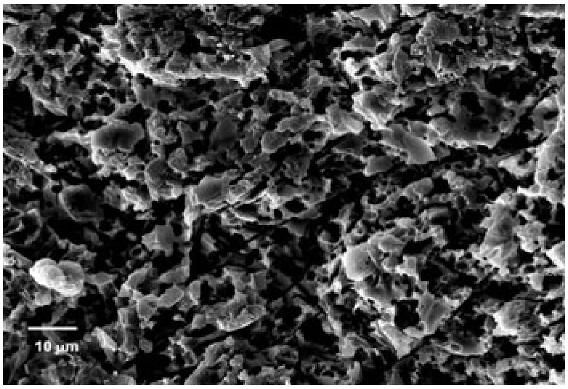

Figure 3 SEM micrograph of etched (HF for 2 minutes) IPS Empress ceramic (Mag. ×600).

however, in a study by Albakry et al[3] a much higher biaxial flexural strength for the IPS Empress (175 MPa) and IPS Empress 2 ceramics (407 MPa) was found. They suggested that a possible explanation for such a difference could be ascribed to the test design. Other studies reporting lower biaxial flexural strength values have used piston-tip diameters ranging from 1.3 to 1.6 mm,[1,29–31] (1.58-mm diameter was used in the present study), whereas Albakry et al[3] adopted a smaller piston-tip diameter of 0.75 mm. This may have improved the strength values, because a smaller area of the specimen was subjected to the maximum tensile stresses. Thus, there was subsequently less chance of the specimen having a critical flaw in that area, which led to the improved strength.[32] Other studies using a three-point bending test have also reported different flexural strength values for the IPS Empress and IPS Empress 2 ceramics.[33–35]

In this study, the IPS Empress 2 ceramic had significantly higher biaxial flexural strength values than that of IPS Empress in either etched or nonetched groups. Considering the same fabrication technique for both glass ceramic systems, the microstructural feature, which refers to the nature, size, shape, quantity, and distribution of the crystalline phases, has a profound effect on mechanical properties.[36] The fiber-like elongated lithium disilicate crystals embedding homogenously in a glass matrix in the IPS Empress 2 would act as an interlocking structure. This could prevent crack propagation and therefore enhance the flexural strength and fracture toughness.[35]

Figure 4 SEM micrograph of etched (HF for 2 minutes) IPS Empress 2 ceramic (Mag. ×600).

In this study, the biaxial flexural strength values obtained from the acid-etched specimens with 9% HF in both ceramic systems showed statistically significant differences with that of nonetched groups. In other words, the etching process reduced the biaxial flexural strength significantly for the two types of glass ceramics ($p = 0.025$), but no significant interaction between the ceramic type and etching was found ($p = 0.407$). In the present study, the weakening effect of surface acid etching for the two hot-pressed glass ceramics with different crystalline structures and composition supports similar findings by other studies on the other types of dental ceramic systems, such as aluminous or feldspathic ceramics.[5,6,17] The weakening effect of HF on leucite-based glass ceramic (IPS Empress) has also been confirmed by the fracture surfaces and bond strength data obtained from other studies.[26,27] On the other hand, other investigators have reported no significant difference in the flexural strengths between the etched and nonetched surfaces for both feldspathic and castable glass ceramics (Dicor, Dentsply, York, PA).[12,13] There is no comparative data in the literature on the lithia disilicate-based glass ceramic system used in this study.

SEM photomicrographs of etched ceramic surfaces from this study revealed that HF acid had an invasive effect, creating an irregular pattern and substantial surface disruption on both glass ceramics, very similar to those in the previous studies.[27,37] Preferential attack of HF on the grain boundaries at the interface of leucite crystals and the glass phase and its weakening effect have been reported for the leucite-based glass ceramics.[26,27] The main crystal phase of IPS Empress 2 glass ceramic is formed by elongated crystals of lithium disilicate. A second phase is composed of lithium orthophosphate. A glass matrix surrounds both crystalline phases. HF acid is able to remove the glass matrix and the second crystalline phase, thus creating irregularities within the lithium disilicate crystals.[35] Luo et al have shown increased surface roughness of IPS Empress 2 ceramic with etching time, using SEM and atomic force microscopy (AFM).[38] Preferential dissolution of glass matrix and protrusion of elongated crystals from the glassy matrix were demonstrated in their study. This is similar to the observations of SEM images in this study.

It should be noted that there are some limitations to this study. First, the biaxial flexural strengths reported will not reflect the actual fracture strengths in the clinical situation because of different environmental and loading conditions. Second, once ceramic restorations are bonded to tooth, their strengths improve. Third, the results obtained in this study would apply to treatment of the glass ceramic surfaces with 9% HF acid for 2 minutes. Future studies evaluating the effect of different acid concentration or etching time on the mechanical or fracture strength of the glass ceramic systems tested in this study in vitro and in vivo are required. Considering the hazardous and possible weakening effects of HF acid, the need for further investigation on optimizing the chemical bond at the resin–ceramic interface is also suggested.

Conclusion

Within the limitations of the present in vitro study, it can be concluded that surface HF acid etching could have a weakening effect on the hot-pressed leucite or lithia disilicate-based glass ceramic systems.

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References

1. Cattell MJ, Knowles JC, Clarke RL, et al: The biaxial flexural strength of two pressable ceramic systems. J Dent 1999;27:183-196
2. Lawn BR, Dent Y, Thompson VP: Use of contact testing in the characterization and design of all ceramic crown-like layer structure: a review. J Prosthet Dent 2001;86:495-510
3. Albakry M, Guazzato M, Swain M: Biaxial flexural strength, elastic moduli and X-ray diffraction characterization of three pressable all-ceramic materials. J Prosthet Dent 2003;89:374-380
4. Meldrum M: Toxicology of hydrogen fluoride in relation to major accident hazards. Regul Toxicol Pharmacol 1999;30:110-116
5. Hussain MA, Bradford EW, Charlton G: Effect of etching on the strength of aluminous porcelain jacket crowns. Br Dent J 1979;147:89-90
6. Addison O, Fleming GJP: The influence of cement lute, thermocycling and surface preparation on the strength of a porcelain laminate veneering material. Dental Mater 2004;20:286-292
7. Hooshmand T, van Noort R, Keshvad A: Bond durability of the resin-bonded and silane treated ceramic surface. Dent Mater 2002;18:179-188
8. Aida M, Hayakawa T, Mizukuwa K: Adhesion of composite to porcelain with various surface conditions. J Prosthet Dent 1995;73:464-470
9. Johnson A, Shareef MY, van Noort R, et al: Effect of furnace type and ceramming heat treatment condition on the biaxial flexural strength of a canasite glass-ceramic. Dent Mater 2000;16:280-284
10. Kosmac T, Oblak C, Jevnicar P, et al: The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. Dent Mater 1999;15:426-433
11. Campbell SD, Kelly JR: The influence of surface preparation on the strength and surface microstructure of a cast dental ceramic. Int J Prosthodont 1989;2:459-466
12. Thompson JY, Anusavice KJ: Effect of surface etching on the flexure strength and fracture toughness of Dicor disks containing controlled flaws. J Dent Res 1994;73:505-510
13. Yen TW, Blackman RB, Baez RJ: Effect of acid etching on the flexural strength of feldspathic porcelain and a castable glass ceramic. J Prosthet Dent 1993;70:224-233
14. Shareef MY, van Noort R, Messer PF: The effect of microstructural features on the biaxial flexural strength of leucite reinforced glass-ceramics. J Mater Sci Mater Med 1994;5:113-118
15. Proctor B: The effects of hydrofluoric acid etching on the strength of glasses. Phy Chem Glasses 1962;3:7-27
16. Kobayashi K: Crystallized fused SiO_2 glass strength improvement by etching. Am Ceram Soc Bull 1987;66:807-809
17. Jones DW: The strength and strengthening mechanisms of dental ceramics, in Mclean JW (ed): Dental Ceramics. Proceedings of the First International Symposium on Ceramics. Chicago, IL, Quintessence, 1983, pp. 83-136
18. ASTM. F394-78. Standard test method for biaxial flexural strength (modulus of rupture) of ceramic substrates. 1996:1-5
19. Uctasli S, Wilson HJ: Influence of layer and stain firing on the fracture strength of heat-pressed ceramics. J Oral Rehabil 1996;23:170-174
20. Ban S, Anusavice KJ: Influence of test method on failure stress of brittle materials. J Dent Res 1990;12:1791-1799
21. Kao R, Perrone N, Capps W: Large-deflection solution of the coaxial-ring-circular-glass-plate flexure problem. J Am Ceram Soc 1971;54:566-571
22. McKinney KR, Herbert CM: Effect of surface finish on structural ceramic failure. J Am Ceram Soc 1970;53:513-516
23. Wilshaw TR: Measurement of tensile strength of ceramics. J Am Ceram Soc 1968;51:111-112
24. Kirstein AF, Woolley RM: Symmetrical bending of thin circular elastic plates of equally spaced point supports. J Res Natl Bur Stds 1967;71:1-10
25. Chen JH, Matsumara H, Atsuta M: Effect of different etching periods on the bond strength of a composite resin to a machinable porcelain. J Dent 1998;26:53-58
26. Della Bona A, Anusavice KJ, Shen C: Microtensile bond strength of composite bonded to hot-pressed ceramics. J Adhes Dent 2000;2:305-313
27. Della Bona A, Anusavice KJ, Mecholsky Jr. JJ: Failure analysis of resin composite bonded to ceramic. Dent Mater 2003;19:693-699
28. Cattell MJ, Palumbo RP, Knowles JC, et al: The effect of veneering and heat treatment on the flexural strength of Empress 2 ceramics. J Dent 2002;30:161-169
29. Cattell MJ, Clarke RL, Lynch EJ: The biaxial flexural strength and reliability of four dental ceramics- part II. J Dent 1997;25:409-414
30. Gorman CM, Mc Devitt WE, Hill RG: Comparison of two heat-pressed all ceramic dental materials. Dent Mater 2000;16:389-395
31. Wagner WC, Chu TM: Biaxial flexural strength and indentation fracture toughness of three new dental core ceramics. J Prosthet Dent 1996;76:140-144
32. Kelly JR: Perspectives on strength. Dent Mater 1995;11:103-110
33. Seghi RR, Sorensen JA: Relative flexural strength of six new ceramic materials. Int J Prosthodont 1995;8:239-246
34. Dong JK, Luthy H, Wohlwend A, et al: Heat-pressed ceramics: technology and strength. Int J Prosthodont 1992;5:9-16
35. Holand W, Schweiger M, Frank M, et al: A comparison of the microstructure and properties of the IPS Empress 2 and the IPS Empress glass-ceramics. J Biomed Mater Res 2000;53:297-303
36. Rahaman MN: Ceramic Processing and Sintering. New York, NY, Marcel Dekker, 1995
37. Della Bona A, Anusavice KJ: Microstructure, composition, and etching topography of dental ceramics. Int J Prosthodont 2002;15:159-167
38. Luo XP, Silikas N, Allaf M, Wilson NHF, Watts DC: AFM and SEM study of the effects of etching on IPS-Empress 2 dental ceramic. Appl Surface Sci 2001;491:388-394