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Effect of ion-exchange temperature on mechanical properties of a dental porcelain

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Abstract

The objective of this study was to determine the influence of different ion-exchange temperatures on the biaxial flexural strength (σ_f), hardness (HV) and indentation fracture resistance (K_{IF}) of a dental porcelain. Disk-shaped specimens were divided into five groups ($n = 10$) and submitted to an ion-exchange procedure using KNO_3 paste for 15 min in the following temperatures (°C); (I) 430; (II) 450; (III) 470; (IV) 490; (V) 510; and control (no ion exchange). The value of σ_f was determined in artificial saliva at 37 °C. The values of HV and K_{IF} were obtained using 3 Vickers indentations in each specimen (19.6 N). Results showed that ion exchange increases significantly the properties of the material as compared to the control and no significant differences were found among the temperatures tested for any of the properties studied.

Keywords: C. Fracture; C. Hardness; C. Mechanical properties; C. Strength

1. Introduction

Dental porcelains are used in dentistry due to interesting qualities such as high color stability, high chemical durability, good biocompatibility, low thermal conductivity and elevated wear resistance. Despite these desirable characteristics, porcelain restorations may fail in the oral environment due to microleakage, debonding or fracture. A cumulative survival rate of ~60% has been reported for feldspathic onlays without metal reinforcement placed in posterior teeth after 6 years, being bulk fracture reported in 16% of the restorations [1]. It has also been shown a clinical success rate of 64% for maxillary anterior veneers after 10 years. The main reasons for failure were fracture (11%) and large marginal defects (20%) [2]. For posterior feldspathic inlays, after an 8-year clinical assessment period, marginal and bulk fracture were reported in 22% and 11% of the restorations, respectively [3,4].

The fracture of ceramics is a consequence of its brittle nature, that is, its inability to suffer plastic deformation. The brittleness of ceramics is also a result of their low fracture toughness (K_{Ic}) which is a property related to the quantity of energy that can be absorbed before fast crack propagation occurs. Dental porcelains show relatively low values of K_{Ic} (around 0.7 MPa $m^{1/2}$) [5,6], especially when compared to zirconia toughened alumina (ZTA) with K_{Ic} of 7.0 MPa $m^{1/2}$ [7]. Porcelains are also highly susceptible to strength degradation during their lifetimes in oral environment, because the sizes of defects tend to increase due to the slow crack growth phenomenon [8–10]. Therefore, in order to increase the lifetime of porcelain restorations, it is necessary to enhance their overall resistance to crack propagation.

An effective method to improve the mechanical properties of porcelains is the so-called ion-exchange process which consists in the creation of a compressive skin on the surface of the material due to the exchange of smaller sodium ions for larger potassium ions from an external source, at a temperature lower than its glass transition temperature (T_g). This technique results

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in an increase in flexural strength for feldsphatic porcelains up to 150% [11]. Moreover, it was demonstrated that the fracture toughness of these materials may be increased by a factor of two [12,13] and the stress corrosion susceptibility coefficient can become from 52 to 124% higher [11,14] depending on the material and the test environment.

There are three factors that may affect diffusion processes such as the ion exchange: material composition, atomic radius of exchangeable ions and diffusion rate. The latter is strongly influenced by the binomial time/temperature, however one important aspect of such diffusion process is that no ion exchange occurs before a minimal time/temperature relation is reached [15]. Care should be taken when the exchange process is carried out because exposing the material to temperatures close to the T_g or to prolonged exchange times may cause stress relaxation due to the accommodation of exchanged ions in the glass network, by means of diffusion and viscous flow processes [16]. This effect will ultimately eliminate the compressive stresses at the surface. An ideal ion treatment temperature of 100 °C below the material's T_g has been suggested [17], however the dental literature often reports temperatures around 450 °C to perform the ion exchange [11,13,18] regardless of the material tested. Such predetermined temperature may not be the most appropriate for all materials, since each one has its own strain point and therefore ought to have its own optimal ion-exchange temperature.

The most applied method for strengthening dental porcelains by ion-exchange process is the so-called paste method. While in the conventional chemical strengthening method the material is immersed in a molten KNO_3 bath for a long soaking time (usually up to 24 h), in the paste method the material surface is covered by a KNO_3 paste and heat-treated for a short treatment time (up to 30 min) [14,19].

The objective of this study was to determine the effect of variations in the ion-exchange temperature using the paste method on hardness, indentation fracture resistance and flexural strength of a dental porcelain. The hypothesis to be tested is that temperature variations affect these mechanical properties.

2. Material and methods

The specimens of leucite-reinforced porcelain powder with leucite content of 12 vol% (Ultropaline Super Transparent, Jen Dental, Kiev, Ukraine – UST) were prepared by mixing 1 g of the porcelain powder with 0.4 mL of deionized water in order to form a slurry that was poured into a metal mold to obtain disc-shaped specimens (15 mm in diameter and 3 mm in thickness). Specimens were vacuum-fired in a porcelain furnace (Keramat I, Knebel, Porto Alegre, Brazil) according to manufacturer's instructions (maximum temperature of 930 °C, vacuum sintering time of 2 min, and heating rate of 60 °C/min). After sintering, the specimens now measuring 12.5 mm in diameter and 2.4 mm in thickness were machined in a surface-grinding device (MSG-600, Mitutoyo, São Paulo, Brazil) following the guidelines in ASTM C 1161 [20] to obtain parallel surfaces and to reduce thickness to 1.3 mm. Then, one surface was mirror-polished using a polishing machine (Ecomet 2, Buehler, Lake Bluff, USA) with diamond suspensions up to 1 μm to obtain the final thickness of 1.0 (±0.1) mm.

The chemical analysis of the UST powder was determined using X-ray fluorescence spectroscopy (Shimadzu XRF-1500, Shimadzu Co., Kyoto, Japan). The glass transition temperature, T_g, of the porcelain was determined by means of differential thermal analysis (DTA, Netzsch 404S, Netzsch-Gerätebau GmbH, Bayern, Germany) using 200 mg of the porcelain powder and a heating rate of 5 °C/min in air atmosphere. Fig. 1 shows the DTA curve for UST porcelain. Since the value of T_g was around 575 °C, it was determined that the "ideal" temperature for the ion-exchange process to be used in the present study should be 470 °C, that is ~100 °C below the T_g. The other temperatures of the experiment were chosen in order to produce small temperature variations above and below the "ideal" ion-exchange temperature of 470 °C.

The paste used on the ion-exchange treatment was prepared by mixing 10 g of KNO_3 (Merck, Damstadt, Germany) with 4 mL of deionized water. Then, 0.4 g of this paste was deposited on the polished surface of each porcelain disc and then the sets were subjected to the ion treatment in an electric furnace (FP-32, Yamato, Tokyo, Japan) in two steps with constant heating rate of 5 °C/min as follows: (i) from 25 to 150 °C and a holding time of 20 min for paste drying; (ii) from 150 °C up to the ion treatment temperature and a holding time of 15 min to promote the ion-exchange process. Six groups ($n = 10$) were prepared according to the ion-exchange temperature used: control (no ion exchange), 430, 450, 470, 490 and 510 °C.

Another set of experiments of ion exchange was carried out for determining the sodium concentration that was exchanged for potassium. For this purpose two porcelain discs were placed on one platinum crucible and then each one was covered with 0.4 g of KNO_3 paste. The samples on the crucible were submitted to the same ion-exchange heat treatment described above. After cooling, the discs were rinsed inside the crucible with 40 mL of deionized water and then they were removed from it. The resulting solutions were analyzed by atomic absorption spectroscopy (AA-670, Shimadzu Co., Kyoto, Japan) for determining the concentration of sodium that was exchanged by potassium. The analyses were carried out in

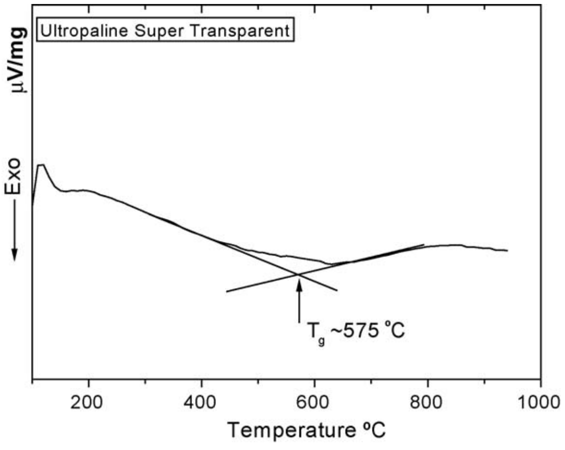

Fig. 1. DTA curve of UST porcelain.

duplicate and samples with only 0.4 g KNO3 paste, were used as blank.

Vickers hardness (HV) and indentation fracture resistance (K_{IF}) were determined by making Vickers indentations with a load of 19.6 N and a dwell time of 20 s (MVK-H-3, Mitutoyo, São Paulo, Brazil) on the polished surface of 10 specimens in each experimental condition in air (22 °C, 60% RH). The length of the impression diagonals ($2a$) and the size of the radial cracks generated on the corners of the indentations ($2c$) were measured immediately after the Vickers impression. The value of HV was calculated according to following equation, where P is the indentation load [21]:

$$\mathrm{HV} = \frac{1.8544P}{(2a)^2} \tag{1}$$

The values of c/a relationship obtained for control group (no ion exchange) and ion-exchanged groups were 2.4 and 1.3, respectively. The largely applied Anstis et al. equation for median cracks can be used for the calculation of the K_{IF} value only for c/a values $\sim>2$ [22], since at low c/a ratios the radial cracks change to the Palmqvist type, and an specific equation for this range has been proposed [23]. Intending to use only one equation to evaluate the results of both groups, a "universal" equation applicable for both types of cracks was chosen to calculate the indentation fracture resistance, K_{IF} [24]:

$$K_{\mathrm{Ic}} = \frac{Ha^{0.5}}{\phi}\left(\frac{E\phi}{H}\right)^{0.4}\left\{14\left[1-8\left(\frac{4\nu-0.5}{1+\nu}\right)^{4}\right]\right\}^{-1}\left(\frac{c}{a}\right)^{(c/18a)-1.51} \tag{2}$$

where E is the Young's modulus (74.4 GPa), ν is the Poisson's ratio (0.22), ϕ is a constraint factor (3), and H is material's hardness ($H = 0.5P/a^2$) [25].

The biaxial flexure strength (σ_{f}) was determined using the piston-on-three-balls method (ASTM F394-78) [26] in a universal testing machine (Syntech 5G, MTS, São Paulo, Brazil) at a constant stress rate of 10 MPa/s with the specimen immersed in artificial saliva [27] heated and maintained constant at 37 °C. The biaxial flexural strength (σ_{f}) was calculated using Eq. (3):

$$\sigma_{\mathrm{f}} = -\frac{0.2387P(X-Y)}{d^2} \tag{3}$$

where σ_{f} is the maximum tensile stress, P is the load at fracture and d is the specimen thickness at fracture origin. X and Y were determined as follows:

$$X = (1+\nu)\ln\left(\frac{B}{C}\right)^2 + \left[\frac{(1-\nu)}{2}\right]\left(\frac{B}{C}\right)^2 \tag{4}$$

$$Y = (1+\nu)\left[1+\ln\left(\frac{A}{C}\right)^2\right] + (1-\nu)\left(\frac{A}{C}\right)^2 \tag{5}$$

where ν is the Poisson's ratio, A is the radius of the support circle, B is the radius of the tip of the piston and C is the radius of the specimen [26].

Indented samples were examined by scanning electron microscopy using a Quanta 3D high resolution, low vacuum SEM/FIB (FEI) microscope (JSM 6300, Jeol Inc., Peabody, USA), that allows the surface analysis without the need of gold sputtering. The same sample was observed before and after ion-exchange treatment (450 °C/15 min), in order to verify the effect of the ion exchange on the crack healing phenomenon.

3. Results

The results of chemical analysis are shown in Table 1, indicating that SiO_2, Al_2O_3, Na_2O, and K_2O were the main constituents of the porcelain studied. Fig. 2 shows how the sodium concentration varied as a function of the temperatures tested. It is possible to note that the sodium concentration increased significantly from ~12 to ~33 ppm when the ion-exchange temperature was increased from 430 to 490 °C. However, when the temperature changed from 490 to 510 °C, the sodium content remained approximately the same.

Mean values of HV, K_{IF} and σ_{f} as a function of the different ion-exchange temperatures are shown in Table 2. Statistical

Table 1
Chemical composition (wt%) of the porcelain UST.

SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	ZrO_2	Fe_2O_3
62.2	15.7	14.7	3.7	2.5	0.7	0.3	0.3	0.1

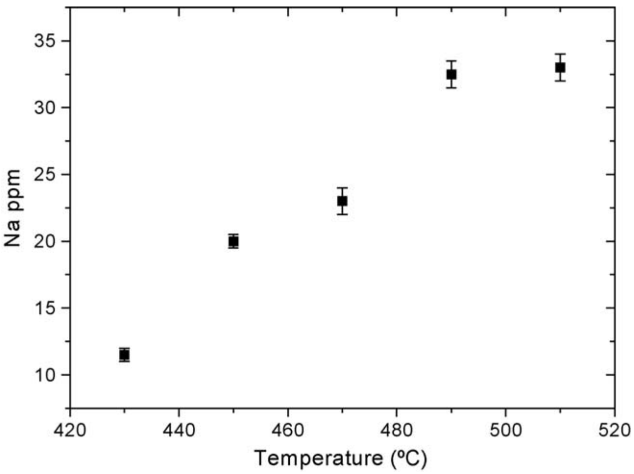

Fig. 2. Na concentration exchanged by K after ion-exchange treatment at different temperatures.

Table 2
Mean and standard-deviations of Vickers hardness (HV), indentation fracture resistance (K_{IF}) and biaxial flexural strength (σ_{f}) as a function of ion-exchange temperature. For each column, values followed by the same superscript are statistically similar ($p > 0.05$).

Group (temperature)	HV (GPa)	K_{IF} (MPa $\mathrm{m}^{1/2}$)	σ_{f} (MPa)
Control	$4.9 \pm 0.1^{\mathrm{b}}$	$1.3 \pm 0.1^{\mathrm{b}}$	$56.7 \pm 9.6^{\mathrm{b}}$
GI (430 °C)	$5.4 \pm 0.2^{\mathrm{a}}$	$2.8 \pm 0.1^{\mathrm{a}}$	$123.9 \pm 12.4^{\mathrm{a}}$
GII (450 °C)	$5.4 \pm 0.1^{\mathrm{a}}$	$2.9 \pm 0.2^{\mathrm{a}}$	$129.6 \pm 22.8^{\mathrm{a}}$
GIII (470 °C)	$5.4 \pm 0.2^{\mathrm{a}}$	$2.7 \pm 0.3^{\mathrm{a}}$	$134.2 \pm 8.3^{\mathrm{a}}$
GIV (490 °C)	$5.5 \pm 0.2^{\mathrm{a}}$	$2.9 \pm 0.1^{\mathrm{a}}$	$132.9 \pm 11.7^{\mathrm{a}}$
GV (510 °C)	$5.4 \pm 0.1^{\mathrm{a}}$	$2.8 \pm 0.1^{\mathrm{a}}$	$134.9 \pm 17.0^{\mathrm{a}}$

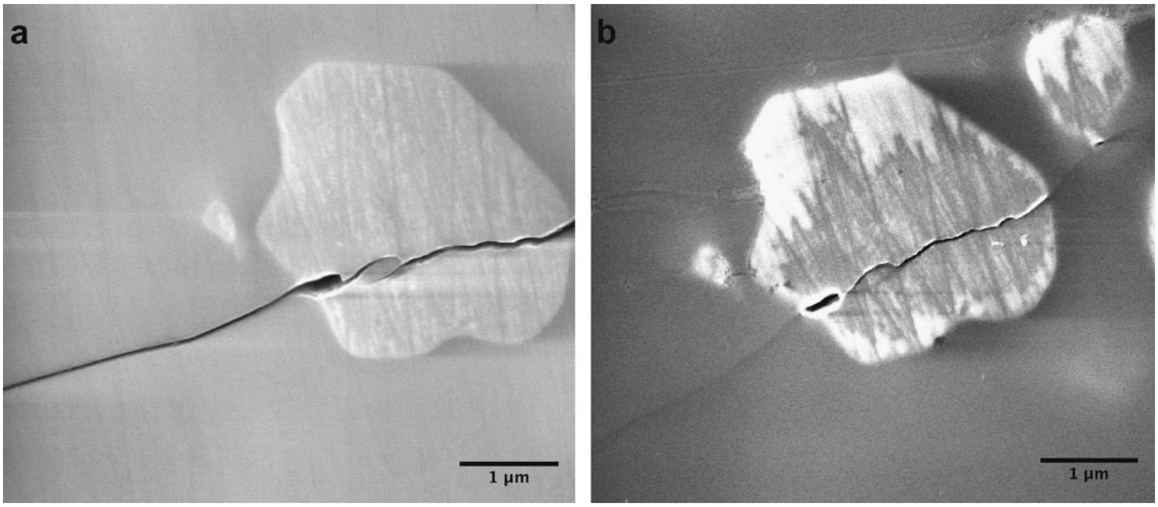

Fig. 3. FEG/SEM image of the UST porcelain: (a) before ion exchange and (b) after ion exchange at 450 °C for 15 min.

analysis revealed that ion exchange promoted a significant increase in all mechanical properties evaluated for all experimental groups compared to the control. For $\sigma_{f,}$ the ion exchange resulted in an increase of ~130% and for K_{IF} the treated groups showed values that were ~100% higher compared to the control group. For HV, the improvements obtained were ~9% higher. No statistical differences were observed among the values obtained in the different temperatures tested for any of the properties evaluated.

Fig. 3 shows a Vickers indentation crack propagating on the surface of the same sample before (Fig. 3a) and after ion treatment at 450 °C (Fig. 3b). A leucite particle is clearly noted on the material's surface and the crack is propagating right through it. By comparing these images it can be seen that both the length and depth of the microcrack were relatively smaller after the ion-exchange treatment.

4. Discussion

The null hypothesis of this study was rejected as the results showed that the temperature range tested (±40 °C around the ideal ion-exchange temperature) did not affect significantly any of mechanical properties tested.

The observed increases in the mechanical properties of the ion-exchanged samples compared to the control are a result of the creation of a compressive layer in the material's surface due to the exchange of small Na^+ ions for larger K^+ ions in the porcelain's glassy matrix [11,14,18]. This phenomenon creates a two-dimensional state of compression as a consequence of the increase in the molar volume that results in an expansion of the surface structure with concomitant restraint by the underlying bulk material. Hence, catastrophic failure only occurs in this case when the tensile stresses generated during loading are capable of overcoming the residual stresses induced by the compressive layer [14].

In Fig. 3, it can be observed a decrease in the length and depth of the microcrack after the ion exchange carried out at 450 °C, suggesting that a crack healing phenomenon may have occurred, resulting in the observed improvements in fracture strength after the ion exchange. Since this temperature is about 125 °C lower than the material's glass transition temperature (T_g) it is likely that the crack healing was due to the ion stuffing mechanism caused by the ion-exchange treatment rather than the viscous flow process as a consequence of heating.

By observing the results shown in Table 2, it is possible to note that the increases in apparent K_{IF} and flexural strength values of the experimental groups compared to their respective controls were very pronounced (at least twofold higher). Nevertheless, the increase in hardness values was somewhat modest (~9%) after the treatment. This small improvement in hardness is probably a consequence of an increase in the binding energy at the surface level due to the increase in residual compressive stresses that are a consequence of the higher potassium concentration [28]. However, it should be considered that this increase in binding energy will only reach its maximum after longer ion-exchange periods of 1.5–4 h [28]. Therefore, it is possible that the time frame used in this study (15 min) was too short to increase the binding energy up to its maximum, and this may have hindered any further improvement in hardness [13,28].

The above mentioned hypothesis (that changing the ion-exchange temperature would affect the mechanical properties of the porcelain) was formulated based on the fact that increasing the temperature would result in an increase in the kinetic energy of the ions in both the porcelain subsurface and within the KNO_3 paste, thus favoring the leaching of sodium and the uptake of potassium ions by the porcelain. Hence, it was initially speculated that the higher the temperature, the higher the strength, indentation fracture resistance and hardness of the porcelain after the ion exchange.

In fact, observation of Fig. 2 indicates that the increase in ion-exchange temperature gradually resulted in higher levels of sodium ions measured in the surrounding solution after the exchange process. This indicates that at least in part, higher temperatures increased the kinetic energy of the ions, inducing leaching of the sodium and concomitant potassium uptake. In this way, a positive effect of temperature increase in the mechanical properties would be expected at least up to 490 °C, however this effect was not observed in the present work.

One explanation for the lack of significant differences in the mechanical properties after varying the ion-exchange temperature is the fact that other phenomena are probably taking place during the ion-exchange treatment so as to counteract the compressive stresses generated by the incorporation of larger sodium ions. It is likely that increasing the temperature also leads to stress relaxation in the glass molecular network that will eventually decrease the residual compressive stresses that account for the improvements in the mechanical properties [16]. Furthermore, it is possible that there is a threshold concentration of potassium within the porcelain subsurface above which the compressive stresses generated due to the increase in molar volume do not translate into better mechanical properties. Additional studies are necessary to clarify this issue.

5. Conclusion

The results of this study indicated that the ion-exchange treatment increased significantly the properties of the material as compared to the control. Moreover, for the porcelain tested, a variation of ±40 °C around the ideal ion-exchange temperature of 470 °C did not affect the indentation fracture resistance, flexural strength and hardness of the tested porcelain.

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