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# Strengthening Dental Porcelains by Ion Exchange Process

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Additional information is available at the end of the chapter

## Abstract

Porcelains have been used in dentistry for many decades because of their excellent aesthetic qualities, besides other favorable characteristics. Despite these desirable characteristics, porcelain restorations may fail in the oral environment due to fracture. Studies on the clinical success rate of porcelain onlays, inlays and veneers have shown that their fracture rate is relatively high and is among the main reasons for failure of these restorations. The fracture of dental porcelains is a consequence of its brittle nature and low fracture toughness. Porcelains are also highly susceptible to weakening during their lifetime in the oral environment, because the sizes of defects tend to increase by the slow crack growth phenomenon. Therefore, in order to increase the lifetime of porcelain restorations, it is necessary to enhance their overall resistance to crack propagation. Among the methods proposed to strengthen glasses and ceramics, a potential method to improve the mechanical properties of dental porcelains is the chemical strengthening or tempering by the ion exchange process. In this chapter, the effects of chemical tempering on mechanical behavior of dental porcelains are reviewed. Dental porcelains are based on alkali-containing aluminosilicate glass compositions and can have leucite ($KAlSi_2O_6$) crystalline particles dispersed in the glassy matrix. The ion exchange process can be carried out by the paste method using $KNO_3$ salt at a temperature that is 80% of glass transition temperature ($T_g$) of porcelain during a short time (15 to 30 min). In this treatment, the small $Na^+$ ions in the glassy matrix are exchanged by larger $K^+$ ions from the salt, resulting in a $K^+$ concentration profile that results in a steep gradient of residual compressive stress by the ion stuffing effect at the surface region of the porcelain. No significant variations in strengthening have been observed when temperature and time varied around the above indicated

values, since the increase in these parameters enhanced the stress relaxation process, which hinders the effect of higher ion interdiffusion. Although few porcelains with high leucite content have no strengthening response to ion exchange process, most dental porcelains can be strengthened and significant increases in fracture toughness (up to around 150%) have been reported. The same level of increase in flexural strength has been observed, but the variability of fracture stress also increases due to the relative small thickness of compressive layer and the decreasing resistance curve effect. The lower reliability is counterbalanced by significant increases of the resistance to slow crack growth phenomenon, leading to higher strength retention after long lifetimes even at low levels of fracture probability. Therefore, it is expected that the application of chemical tempering (strengthening by ion exchange) can improve the lifetime of dental porcelain restorations.

**Keywords:** Bioceramics, dental porcelain, ion exchange, chemical tempering, strength, toughening, lifetime

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# 1. Introduction

Dental porcelains have been used in dental restorations due to their good qualities, including high color stability, high resistance to stain, good biocompatibility, low thermal conductivity, high wear resistance, and capacity to mimic dental structures [1–3]. Notwithstanding, disadvantages of these restorations include high susceptibility to fracture, risk of debonding, and microleakage [4–6]. For feldspathic porcelain onlays placed in posterior teeth after 6 years, the observed cumulative survival rate was ~60%, with bulk fracture in 16% of the restorations [7]. The reported clinical success rate for maxillary anterior porcelain veneers after 10 years was 64%, and main reasons for failure were fracture (11%) and large marginal defects (20%) [2]. Similar behavior was also observed for posterior feldspathic porcelain inlays, and marginal defects and fracture were 22% and 11% of the restorations, respectively, after an 8-year period of clinical assessment [8].

The high susceptibility to fracture of porcelain restorations is caused by their brittle nature, that is, their low capability to absorb strain energy due to an external loading before fast crack propagation occurs. The resistance to crack propagation can be quantified by the fracture toughness ($K_{Ic}$) which is given by [9,10]:

$$K_{Ic} = Y \cdot \sigma_f \cdot \sqrt{c} \tag{1}$$

where, $Y$ is a geometrical constant, $\sigma_f$ is fracture stress, and c is crack size that results in fracture. From Griffith's energy failure criterion, the term $\sigma_f \cdot c^{1/2}$ is constant, which implies that strength ($\sigma_f$) is not constant and varies inversely with the square root of critical flaw size ($c^{1/2}$). Further-

more, Equation 1 also shows that the porcelain strength is directly related with its fracture toughness, $K_{Ic}$.

Dental porcelains have relatively low values of $K_{Ic}$ (around 0.6 to 1.2 MPa.m$^{1/2}$) [11,12], especially when compared to metals, which have $K_{Ic}$ higher than around 30 MPa.m$^{1/2}$ [13]. As a consequence, porcelains have low strength values usually in the range of 40 to 120 MPa [14, 15]. Moreover, the strength of porcelain restorations can decrease during their lifetimes in the oral environment, since a weakening effect known as subcritical crack growth causes the flaw sizes to increase slowly over time [16,17]. Therefore, it is important to develop processing methods that can enhance the overall resistance to crack propagation, particularly strength and fracture toughness, in order to increase the lifetime of porcelain restorations.

Different methods have been proposed to strengthen dental porcelains, including addition of reinforcing phases, like ceramic fibers or phase transformable tetragonal zirconia particles, and incorporating a compressive surface layer, which can be achieved by thermal tempering, glazing with a glassy material having lower thermal expansion coefficient, or chemical tempering [18–20]. Among these, chemical strengthening by ion exchange is a promising method to significantly enhance the mechanical behavior of dental porcelain restorations.

## 2. Chemical tempering

Chemical tempering is a strengthening or toughening treatment by ion exchange process that introduces a residual compressive stress layer on the surface of glassy materials that hinders the crack propagation and increases the material resistance to fracture. In this treatment, alkali ions of the glass are removed and exchanged by other larger alkali ions from an external source at a temperature sufficiently high to promote ion interdiffusion. Figure 1 shows the sizes of different alkali ions. The most applied alkali ion pair for strengthening is the $Na^+/K^+$, but other pairs are also exchangeable, like $Li^+$ by $Na^+$ and $K^+$ by $Rb^+$, depending on the glass composition [21,22].
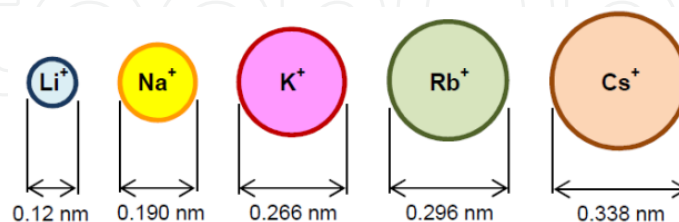


**Figure 1.** Pauling's calculated ionic diameters for alkali metals. Data from [21]

An usual practice is to make an ion exchange treatment in sodium-containing aluminosilicate glasses with a melt of $KNO_3$ salt, at a temperature between the melting point of salt and the glass transition temperature ($T_g$) of the glass. During the process, $Na^+$ ions diffuse out from the glass into the salt and simultaneously the diffusion of $K^+$ ions from the salt into the glass takes

place, with equal and coupled counterdiffusing ion fluxes ($J_{Na+} = J_{K+}$) to maintain the eletro-neutrality (Figure 2) [23].
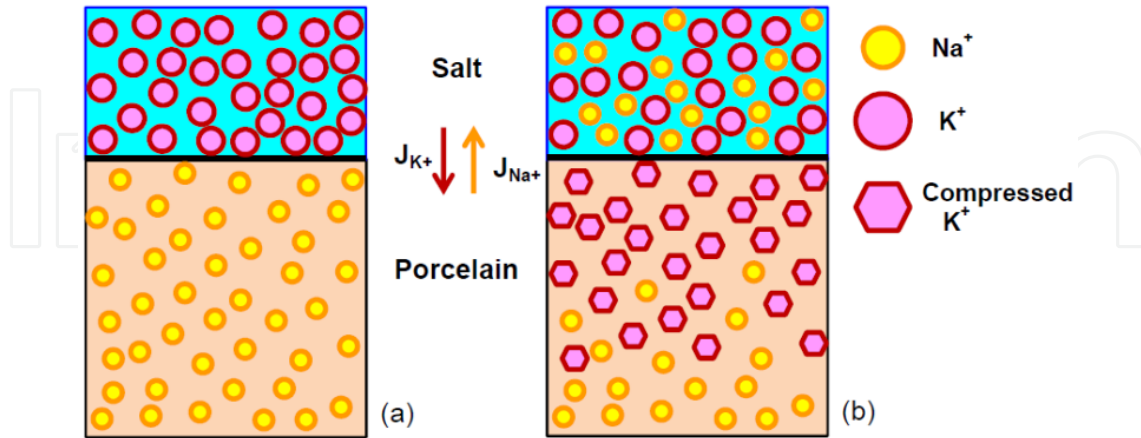


**Figure 2.** Schematics of (a) before and (b) after ion exchange process in dental glassy porcelain. J – ion flux

During the ion exchange process, concentration gradients of K$^+$ and Na$^+$ are formed at the region near the glass surface that can be described by the Fick's second law, given by [22–26]:

$$C_x = (C_S - C_0)\left[1 - erf\left(\frac{x}{2\sqrt{\tilde{D}\cdot t}}\right)\right] + C_0 \tag{2}$$

where, $C_x$ is the ion concentration at depth $x$ (from surface) after ion exchange time $t$, $C_0$ is the initial ion concentration in glass, erf(z) is the Gaussian error function, and $\check{D}$ is the interdiffusion coefficient given by:

$$\tilde{D} = \frac{D_{Na}\cdot D_K}{D_{Na}N_{Na} + D_K N_K} \tag{3}$$

where, $N_i$ is fractional concentration of alkali ion $i$ and $D_i$ is its self-diffusion coefficient in mixed-alkali glass compositions, which increases exponentially with temperature by:

$$D = D_0 \exp\left(-\frac{Q_d}{kT}\right) \tag{4}$$

where, $D_0$ is preexponential factor, $Q_d$ is activation energy for diffusion, $k$ is Boltzmann's constant and $T$ is temperature. Figure 3a shows examples of K$^+$ concentration profiles after ion exchange at different time or temperature.
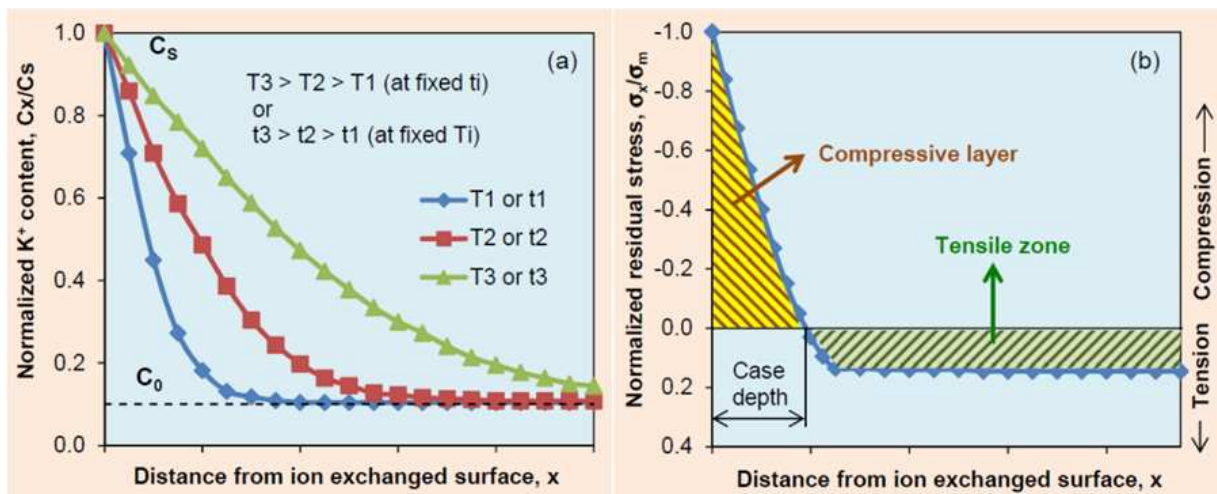
**Figure 3.** Normalized potassium concentration profiles (Equation 2) (a), and normalized residual stress profile (b) in dental glassy porcelain after ion exchange process

The bigger $K^+$ ions that replace $Na^+$ ions tend to cause material expansion (known as ion stuffing) in the exchanged surface layer, which is restricted by the non-ion exchanged glass region. This situation, when the ion exchange is carried out at a temperature lower than the $T_g$ of glass, generates a residual compressive stress field parallel to the surface in the K-rich layer. This layer has a gradient of compressive stress similar to the potassium concentration gradient, that is, the compressive stress is high at the surface and decreases with the increase in distance from surface. In order to counterbalance the net stress state, a residual tensile stress field is generated below the compressive layer (Figure 3b).

The residual compressive stress layer adds a toughening contribution, $K_{RC}$, which hinders crack propagation, leading to an increase in the fracture toughness in ion exchanged glass, $K_{Ic,IE}$, by:

$$K_{Ic,IE} = K_0 + K_{RC} \tag{5}$$

where, $K_0$ is the fracture toughness of unreinforced glass. The higher $K_{Ic}$ leads to a higher fracture stress, if a flaw size $c$ is unaltered (Equation 1). Therefore, the generation of a surface compressive layer by ion exchange can result in the increase in fracture toughness and strength of glasses and porcelains.

The toughening effect depends on the thickness of compressive layer, known as case depth (Figure 3b), especially when the glass contains deep surface flaws. Because of the relative slow ion exchange rate, the case depths varying from few tens to hundreds of micrometers have been reported, depending on the ion exchange parameters, including time (up to hundreds of hours of treatment have been reported), temperature, salt composition, exchangeable ionic pair, and glass composition [22,26,27].

An effect that can lower the strengthening rate by the ion exchange process is the stress relaxation that can occur during this process, leading to a reduction in the magnitude of

residual compressive stress [27]. Stress relaxation occurs by viscous flow of the glass and can be described by the Maxwell's model given by [28,29]:

$$\sigma = \sigma_0 \exp\left(\frac{G \cdot t}{\eta}\right) \tag{6}$$

where, $\sigma$ is the remaining stress at time $t$, $\sigma_0$ is initial stress, and $G$ and $\eta$ are shear modulus and viscosity of glass, respectively. Since $\eta$ decreases strongly with temperature, the rate of stress relaxation is more rapid with the increase in temperature.

The chemical tempering has been applied to strengthen cockpit windows for aircrafts, high speed train windshields, photocopier scanner glass, display windows in mobile personal electronic devices, compact disks for portable hard drives, high-end ophthalmic glasses, and glass items for drug delivery [22,26]. Advantageous characteristics of chemical tempering include: possibility to strengthen complex geometries and thin components (thickness of up to around 100 µm), which are difficult in thermal tempering; higher compressive stress level on the surface compared to thermal tempering; low level of internal residual tensile stress, with less fragmentation and explosion-like fracture propagation; and did not cause optical distortion. Disadvantageous characteristics include: limited to alkali-containing glasses; shallow depth of residual compressive stress layer (case depth); generation of corrosive alkali-containing salt residue; and high cost when long time of ion exchange is applied [22,26].

# 3. Dental porcelains

The feldspathic porcelain is a predominantly glassy material with variable crystalline content. Its basic structure has a network of silica with potassium, sodium, and other ions as network modifiers. In order to reduce the glass softening temperature and increase fluidity, metal oxide fluxes are added ($CaO$, $K_2O$, $Na_2O$), which decrease the softening temperature by reducing the amount of cross linking in the porcelain structure. The addition of alumina (between 8 and 20 wt%) is used for controlling the viscosity and decreasing the flow at high temperatures. When added, $B_2O_3$ in concentrations below 12 wt% also acts as a flux to form a less stable network of $BO_4/SiO_4$ [30–33].

Silica, soda, potash, and alumina are the constituents of mineral feldspar ($Na_2O/K_2O.Al_2O_3.6SiO_2$), the main raw material used in the manufacturing of dental porcelain [30]. Silica and alumina account for most of the feldspar, about 70 and 17 wt%, respectively. Feldspar porcelains are relatively pure and colorless, so pigments are added to produce shades of natural tooth [34]. In the process of obtaining porcelain, feldspar is mixed with fluxes, then heated to temperatures between 1150 and 1530°C, and rapidly cooled in water. With the thermal shock, the glass breaks into fragments called frits. Opacifiers ($TiO_2$, $ZrO_2$) and pigments ($Cr_2O_3$, $Fe_2O_3$) are also added to this glass [34]. Heating feldspar to high temperatures leads to an incongruent melting resulting in the formation of leucite and a liquid glass. The

leucite crystal is a mineral (potassium aluminum silicate) with high coefficient of thermal expansion compared to feldspathic glasses [30]. The porcelain structure after incongruent melting of feldspar has leucite ($K_2O.Al_2O_3.4SiO_2$) crystals involved in an aluminosilicate glassy matrix [32,33,35]. In general, the leucite ratio is governed by the $K_2O$ content of the frit and the time and temperature of the heat treatment; thus, the desired leucite content can be achieved by controlling the appropriate time and the crystallization temperature range [36].

The frits based on leucite are used in Dentistry since the early 60s [31]. However, feldspar is not essential as a precursor for the formation of leucite, and many dental porcelains do not use feldspar as the raw material. These materials are called feldspar-free porcelain and are synthesized in the laboratory by controlled addition of leucite instead of mineral processing. It has been suggested that porcelains with a large amount of leucite dispersed in the glass matrix are called leucite-based instead of feldspathic porcelains [30].

Feldspathic porcelains are usually presented as a liquid-powder system, in which the liquid (water with dispersant) is mixed with porcelain powder to form a slurry or paste that is applied to the refractory die or metal framework. After production of the green body, it is taken into an electric furnace for the firing cycle (Figure 4a) [3,37]. Chemical reactions between the porcelain powder components are completed during the process of obtaining the frits. Therefore, the main purpose of firing is sintering of particles, although some chemical reactions may occur during prolonged firing times or during multiple firing [30]. According to the firing (sintering) temperature, the porcelain used for restorations and bridges can be classified as being of high fusion (850 to 1100°C) and low fusion (below 850°C) [30]. The firing procedure involves high heating rates (around 60°C/min) under vacuum and few minutes at the maximum temperature. During this procedure, sintering process transforms the porous green body (Figure 4b) in a translucent and dense solid, almost pore free (Figure 4c), by means of densification mechanisms with mass transport by viscous flow [3,37]. Vacuum firing is a resource used to reduce the porosity of these materials [31]. At the end of the firing procedure, the porcelain can have three distinct phases: a crystalline phase (leucite), the glass matrix, and pores.

Most dental porcelain developed for metal-ceramic restorations contain leucite ($KAlSi_2O_6$) as a main crystalline phase [38]. Leucite was first introduced so that the porcelain could reach a linear thermal expansion coefficient close to that of alloys used in metal-ceramic restorations. In this way, metal and porcelain have similar behavior when cooled together during the firing process, preventing the appearance of cracks in the porcelain [39]. Leucite is also the main crystalline constituent of most generations of porcelain for all-ceramic restorations [40]. In this case, leucite is not added with the aim of achieving thermal compatibility, but to increase the strength and fracture toughness of the material [32,41]. The amount, average crystal size, and crystal structure of leucite directly affect the thermal, optical, and mechanical properties of the final restoration [42]. One of the advantages having leucite as the crystalline phase is that the translucency of the porcelain is not lost, since the refractive index of this crystal is similar to that of the glassy matrix [43,44].
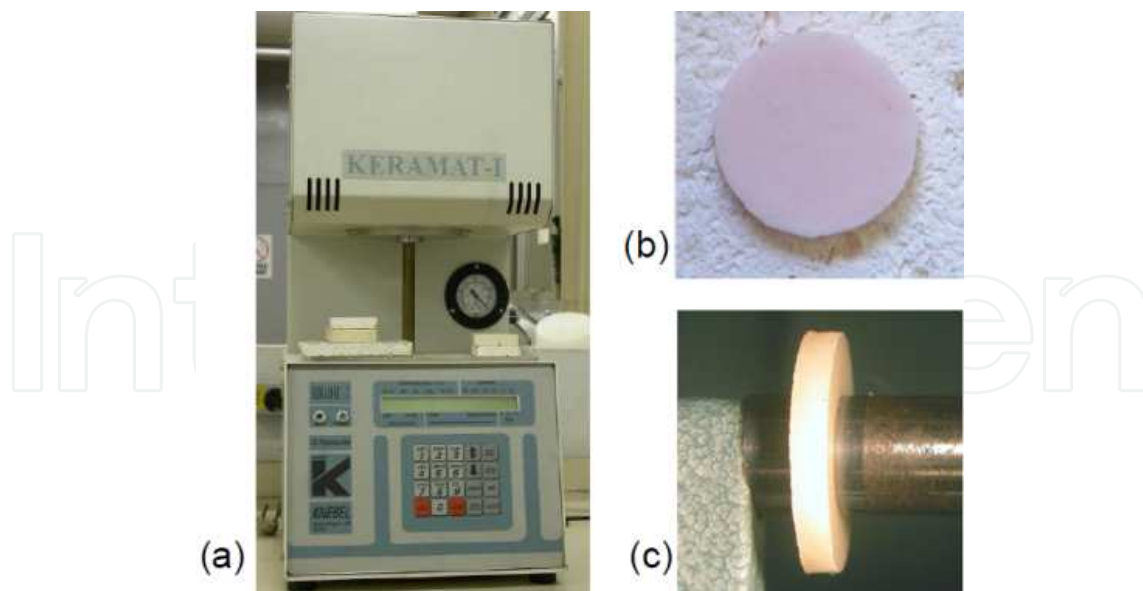
**Figure 4.** Dental porcelain furnace (a), green (b), and sintered (c) porcelain body [5]

The leucite crystal has a crystallographic polymorphic transformation (without change of composition) from tetragonal to cubic during heating. This transformation is displacive (martensitic) and accompanied by a marked change in the parameters of crystalline lattice with an increase of 1.2% by volume of the unit cell [38]. When a porcelain containing leucite is cooled from the firing temperature to room temperature, residual stresses arise in the material as a result of the large difference between the linear thermal expansion coefficients of the glass matrix (8.6 ppm °C$^{-1}$) and tetragonal leucite (22.3 ppm °C$^{-1}$). After cooling, tangential compressive stresses and radial tensile stresses appear in the glass matrix around the leucite particle and opposite stress fields in the tetragonal crystals [38,43]. The compressive stresses have a beneficial effect on the porcelains as they function as a mechanism for increasing the toughness, as opposed to the tensile stresses, which drive the cracks forward [45].

Figure 5 shows typical micrographs of dental porcelains containing leucite crystals. For porcelains with high leucite contents, the distribution of crystals usually is not homogeneous in the glassy matrix (Figure 5a), forming agglomerates of leucite particles (Figure 5b). In these micrographs, it is possible to see some circumferential cracks in the glass matrix surrounding leucite agglomerates, which reveal the radial tensile stresses generated during cooling [11]. The residual stress fields associated with the leucite crystals have significant effects on the fracture behavior of porcelain, since they change the propagation trajectory of a crack, driving it through the glassy matrix region with radial tensile stresses. The result is that a crack propagates bowing around leucite particles and agglomerates (Figure 5c). This effect is called crack deflection and is the main toughening mechanism caused by leucite crystals in dental porcelains. In fact, it has been observed that fracture toughness, $K_{Ic}$, increases with the increase of volume fraction of leucite [11].

The increase in porcelain's strength with the increase in leucite content has been observed experimentally. However, there is a tendency of this increase to achieve a maximum, because
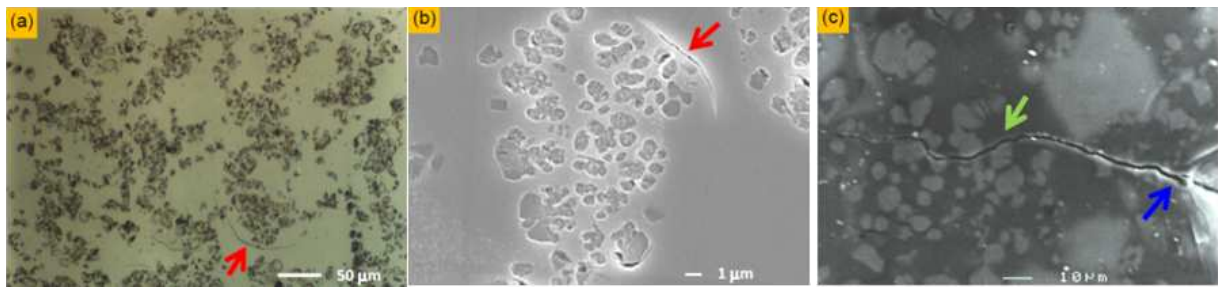
**Figure 5.** Micrographs (a – optical, b,c – scanning electron microscopy) of dental porcelains showing: (a) leucite (KAl-Si$_2$O$_6$) crystals dispersed in glassy matrix; (b) agglomerate of leucite particles; (c) radial crack emanated from Vickers indentation corner (blue arrow) deflecting among leucite particles (green arrow). In (a,b), red arrow indicates circumferential crack around leucite agglomerate generated by chemical etching with HF solution (also used to reveal leucite particles)

for porcelains with high leucite volume fraction spontaneous microcracks can be generated around big leucite agglomerates during cooling after sintering. These flaws have large size (c value in Equation 1) and limit the porcelain's strength, despite the increase in fracture toughness, K$_{Ic}$ [42,46]. Besides the quantity, the size, and distribution of the leucite particles also influences the mechanical properties of the porcelain [18,41].

# 4. Hardness and toughness of chemically strengthened dental porcelains

In this section, the effects of chemical strengthening using ion exchange by paste method on the hardness and fracture toughness of dental porcelains with different microstructures are shown. Table 1 shows descriptions of five porcelain powders used in this study, two recommended to be used as veneering materials for alumina cores (V and Cb) and three recommended for porcelain fused-to-metal restorations (C, D, and B), containing wide variation of leucite fraction (0 to 22 vol%).

Table 2 shows the chemical compositions of the porcelains measured by X-ray fluorescence spectroscopy (XRF 1500, Shimadzu), showing that all porcelains had aluminosilicate compositions with alkali and alkaline-earth metal oxides, besides other minor oxides. For porcelains containing leucite particles (C, D, and B), parts of SiO$_2$, Al$_2$O$_3$ and K$_2$O contents composed these particles. Considering the fraction and stoichiometry of leucite (KAlSi$_2$O$_6$ = K$_2$O.Al$_2$O$_3$.4SiO$_2$), the compositions of glassy matrix of these porcelains were calculated and are also shown in Table 2. Note that all porcelains had in the glassy matrix an initial K$_2$O content, and also potentially exchangeable Na$^+$ ions by K$^+$ ions from an external source.

Green specimens with bar shape (5 × 6 × 40 mm) were prepared by the vibration-condensation method, mixing the porcelain powder with distilled water and using a steel mold. Then, the specimens were vacuum sintered in a dental porcelain furnace (Keramat I, Knebel), following the firing schedules recommended by the manufacturers (sintering temperatures indicated in Table 1). After firing, the specimens were machined following the guidelines in ASTM C 1161 to the dimensions of 3 × 4 × 30 mm, and one of larger surfaces was mirror-polished using a

semi-automatic polishing machine (Ecomet 3, Buehler), with diamond suspensions of 45, 15, 6, and 1 μm. For each material, 10 specimens were prepared.

| Porcelain | Manufacturer / Brand Name | Manufacturer's Description | Leucite fraction (vol%) |
|---|---|---|---|
| V | VITA Zahnfabrik/Vitadur Alpha | Porcelain used with alumina frameworks. Sintering temperature: 960°C | 0 |
| Cb | Noritake/Cerabien | Porcelain used with alumina frameworks. Sintering temperature: 960°C | 0 |
| C | Dentsply/Ceramco Finesse | Leucite-based porcelain, used for metal-ceramic or all ceramic restorations, containing fine-grained leucite particles. Sintering temperature: 800°C | 6 |
| D | Ivoclar/d.Sign | Leucite-based porcelain, used for metal-ceramic or all ceramic restorations, containing leucite particles and crystals of fluorapatite. Sintering temperature: 875°C | 15 |
| B | Dentsply/Ceramco II | Leucite-based porcelain, used for metal-ceramic or all ceramic restorations, containing equiaxial leucite particles. Sintering temperature: 1000°C | 22 |

**Table 1.** Description of five dental porcelains. Data from [47]

| Oxide | V | Cb | C | D | B |
|---|---|---|---|---|---|
| $SiO_2$ | 75.9 | 82.9 | 70.1 (69.9) | 67.6 (66.7) | 72.0 (71.9) |
| $Al_2O_3$ | 10.0 | 5.6 | 6.4 (5.7) | 9.0 (7.6) | 9.5 (7.5) |
| $K_2O$ | 7.1 | 4.6 | 8.7 (8.6) | 8.1 (7.7) | 9.2 (8.8) |
| $Na_2O$ | 3.6 | 3.6 | 5.5 (5.8) | 4.9 (5.8) | 3.8 (4.9) |
| CaO | 3.0 | 1.1 | 3.8 (4.0) | 3.7 (4.4) | 3.9 (5.0) |
| Others | 0.3 $ZrO_2$ | 0.8 $ZrO_2$<br>0.7 MgO<br>0.3 CeO | 5.0 (5.3) MgO<br>0.4 (0.5) $Tb_4O_7$ | 3.0 (3.5) ZnO<br>1.3 (1.6) $ZrO_2$<br>1.2 (1.4) BaO<br>0.6 (0.7) $TiO_2$<br>0.4 (0.5) $P_2O_2$ | 0.7 (0.9) BaO<br>0.6 (0.7) CeO |
| Traces (<0.2%) | Fe, Ni, Ti, Rb, Sr, Pb | Fe, Ni, Zn, Ti, Cr, Hf, V, I | Fe, Ni, Zr, Rb, Sr, Re, Cl | Fe, Ni, Cr, Hf | Fe, Ni, Rb, Sr, Cs, Tb, Cl |

**Table 2.** Overall chemical composition (mol%) of dental porcelains. The calculated compositions of glassy matrix for porcelains containing leucite particles are given in parenthesis. Data from [48]

Later, the polished surfaces were subjected to an ion exchange treatment. First, the surface of the specimen was coated with a layer of a paste composed of distilled water mixed with potassium nitrate ($KNO_3$). The amount of paste placed on each specimen was controlled by mass measurement. Then, the specimens coated with the paste were heat treated in an electric furnace (FP32, Yamato). The ion exchange cycle was conducted at a heating rate of 5°C/min with a first step of drying at 150°C for 20 min to remove the water from the paste, followed by a step of melting of $KNO_3$ and ion exchange at 450°C for 30 min, and then cooled inside the furnace to room temperature. The $KNO_3$ paste residue was easily detached and removed with a wet piece of cotton and the ion exchange treatment did not affect the superficial appearance of the specimens.

The contents of $K_2O$ and $Na_2O$ on the polished surfaces before and after ion exchange were determined by energy dispersive spectroscopy (EDS, Noram) coupled in a scanning electron microscopy (SEM, JSM 6300, Jeol). This analysis showed that the $KNO_3$ paste method caused the decrease of $Na_2O$ content with the increase of $K_2O$ content in all porcelains (Figure 6), indicating that the $Na^+$ ions from the glassy matrix were successfully exchanged by $K^+$ ions from the paste. The porcelains Cb and B (with 0 and 22% of leucite, respectively) had the highest relative increase in $K_2O$ content of around 35%.
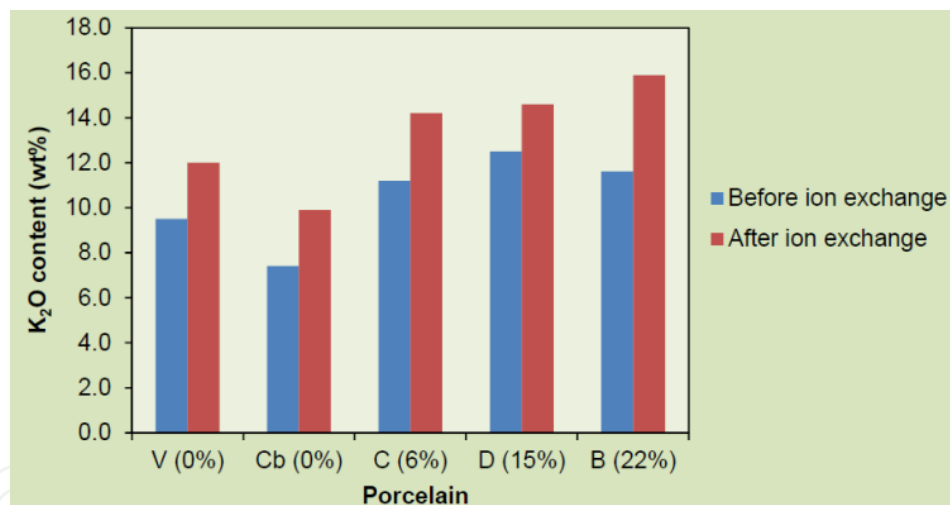


**Figure 6.** $K_2O$ content on the surface of dental porcelains before and after ion exchange process (value in parenthesis is the volume fraction of leucite crystal). Data from [47]

Vickers hardness and fracture toughness by indentation fracture (IF) method were evaluated on the polished surface before and after ion exchange. These properties were measured using a Vickers microhardness tester (MVK-H-3, Mitutoyo) with load of 9.8 N and dwell time of 20 s. The diagonal of hardness impression and the length of radial crack emanated from the corner of hardness impression were measured using an optical microscope (Zeiss) under magnification of 200 times, within 30 s after indentation to minimize the slow crack growth phenomenon [16]. Vickers hardness, HV, and fracture toughness, $K_{Ic}$, were calculated according to the following equations [16,49]:

$$HV = \frac{1.8544 \cdot P}{(2a)^2} \tag{7}$$

$$K_{Ic} = 0.016 \left(\frac{E}{H}\right)^{1/2} \left(\frac{P}{c^{3/2}}\right) \tag{8}$$

where, $P$ is the indentation load, $a$ and $c$ is the half-size of diagonal of the indentation or radial/median crack, respectively (Figure 7), $E$ is the elastic modulus, and $H$ is the material's hardness [defined as $H = P/(2a^2)$]. The elastic modulus of each porcelain was determined by the ultrasonic pulse-echo method [50].
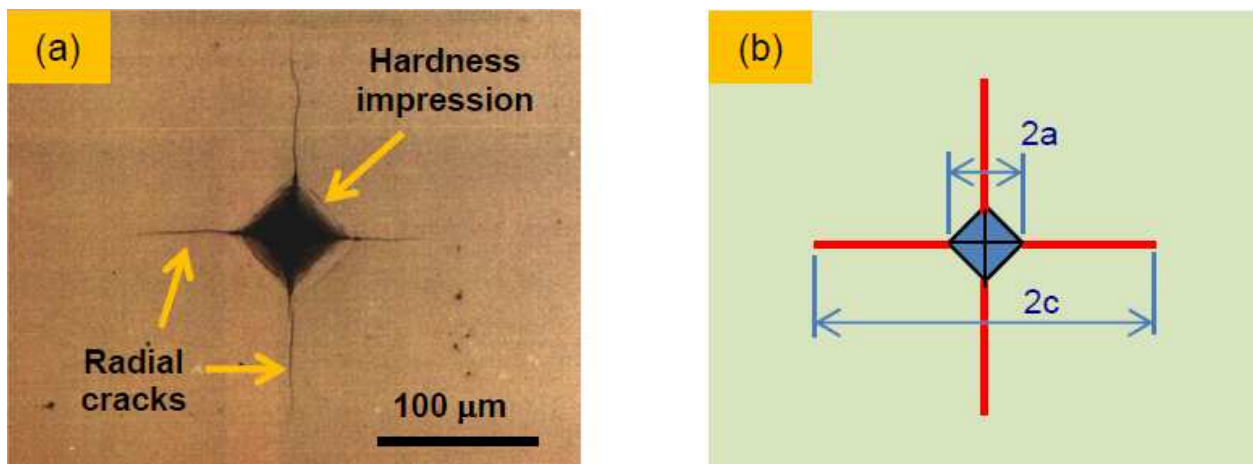


**Figure 7.** Optical micrograph of a Vickers hardness impression and the radial/median cracks generated on the corners of impression on the polished surface of a dental porcelain (a), and schematic image showing the dimensions a and c used to calculate the hardness, HV, and fracture toughness, $K_{Ic}$, by indentation fracture (IF) method

Figure 8a shows that ion exchange process increased significantly the fracture toughness, $K_{Ic}$, of most of the tested dental porcelains, with the increase in this property achieving up to around 150% (variation from 0.61 to 1.56 MPa.m$^{1/2}$ in porcelain C). However, there was also one porcelain (B with highest leucite content) that had no positive response to this toughening treatment. In general, the increase in $K_{Ic}$ was higher for the porcelains with lower leucite content. The variation in Vickers hardness, $HV$, followed similar tendency as $K_{Ic}$ (Figure 8b), but with lower relative increases that achieved up to around 70% (variation from 7.6 to 12.7 GPa in porcelain Cb).

Another work also observed beneficial effects of applying ion exchange (with K-containing compound at 450°C for 30 min) to increase the fracture toughness of dental porcelains. For eight dental porcelains, $K_{Ic}$ increased between 39% and 116%, but no significant differences in hardness values were observed [51].
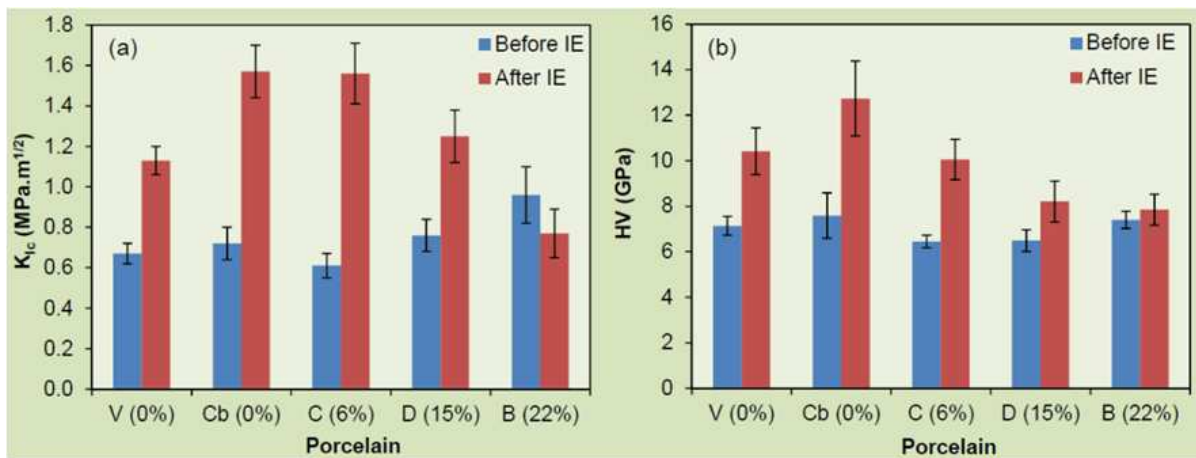
**Figure 8.** Fracture toughness, $K_{Ic}$ (a), and Vickers hardness, $HV$ (b), of dental porcelains before and after ion exchange (IE) process (in parenthesis the vol% of leucite crystal). Data from [47]

The increase in $K_{Ic}$ value is indicative of the operation of ion stuffing mechanism by ion exchange of smaller Na$^+$ by larger K$^+$ in the glassy matrix, which introduced residual compressive stress fields on the surface region of the porcelain. The compressive stresses hinder the radial/median crack propagation generated by the Vickers indentation (Figure 9), decreasing the ratio c/a (ratio between the sizes of radial/median crack and indentation diagonal) and increasing fracture toughness. This behavior is highly desirable since the compressive surface layer may decrease or even inhibit the generation of large and deep cracks on the surface of a dental porcelain restoration during mastication. Since surface cracks are deleterious to the mechanical strength of porcelains, decreasing its size results in lower strength degradation.
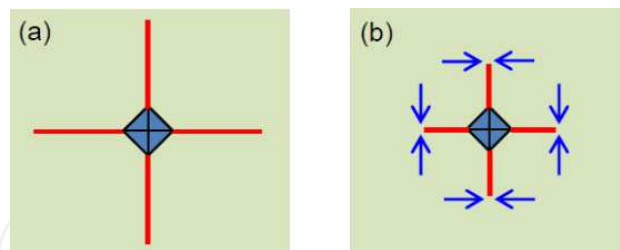


**Figure 9.** Schematic images of radial/median cracks generated at the corners of Vickers impression: (a) before ion exchange, without residual stresses and (b) after ion exchange, indicating the shortening of the cracks due to the residual compressive stress fields (indicated by arrows)

The residual stress (MPa) introduced by ion exchange was calculated according to the following equation [47]:

$$\sigma_r = \frac{K_{Ic,b} - K_{Ic,a}}{2\left(\dfrac{c}{\pi}\right)^{1/2}}$$

(9)

where, $K_{Ic,b}$ and $K_{Ic,a}$ are the fracture toughness measured before and after ion exchange, respectively. Figure 10 shows the calculated residual compressive stress values. It can be seen that ion exchange by paste method can generate significant compressive stresses, up to around 90 MPa, on the surface of dental porcelains.
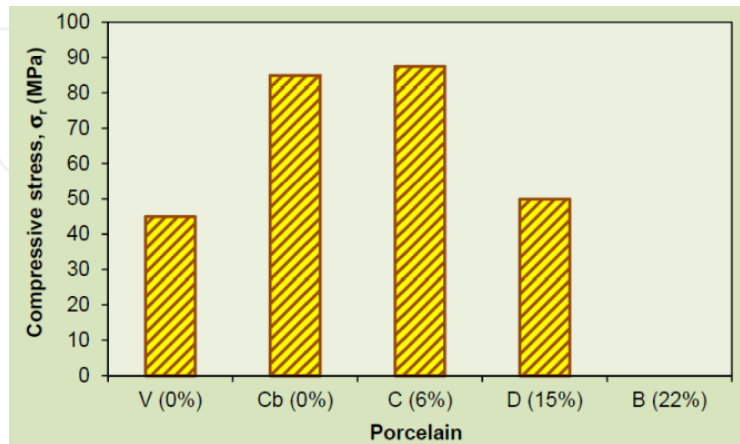


**Figure 10.** Residual compressive stress generated on the surface of dental porcelains by ion exchange process. Data from [47]

For porcelain B, which had the highest leucite fraction (22%), however, there was no introduction of residual compressive stress, although significant increase in $K_2O$ content after ion exchange have been detected (Figure 6). A possible explanation could be the occurrence of stress relaxation caused by the viscoplasticity of glassy matrix during the heat treatment of ion exchange process. The temperature used for ion exchange (450°C), however, seemed to be sufficiently lower than the glass transition temperatures, $T_g$, for all porcelains, as indicated by their annealing point (Table 3). This point is defined as the temperature at which the glass viscosity is $10^{14}$ Pa.s and most of the internal stresses are reduced within about 15 min [52]. The annealing point was determined by calculating the viscosity curve as a function of temperature from the chemical composition using the program SciGlass (SciGlass v.7.7, MDL Information Systems) [53].

| Porcelain | V | Cb | C | D | B |
|---|---|---|---|---|---|
| T (°C) at $\eta = 10^{14}$ Pa.s | 708 | 673 | 564 | 641 | 659 |

**Table 3.** Calculated annealing point (temperature) of dental porcelains

The overall and glassy matrix chemical compositions (Table 2) of porcelain B, compared to the other porcelains, did not justify the ineffectiveness of ion exchange to improve the mechanical properties in the porcelain B. The tendency that the relative increases in fracture toughness and hardness decreases with the increase in leucite content (Figure 8) suggests that the beneficial effects of ion exchange are counterbalanced by the toughening effect of leucite particles. It is possible that the ion exchanged $K^+$ ions could preferentially occupy the sites

under the tensile residual stressed regions around leucite particles and agglomerates, which could be energetically more favorable causing less increase in residual stresses. The chemistry of the glassy matrix also affected the response to ion exchange treatment, as can be seen from the results of both completely glassy porcelains (V and Cb, Figure 8). Both porcelains had the same initial $Na_2O$ content (3.6 mol%, Table 2), but in porcelain Cb higher residual compressive stress was generated (Figure 10). It is difficult to predict the interactive effects of different ions present in the glassy matrix in the ion exchange process between $Na^+$ and $K^+$ ions, since even low concentrations of some elements can have strong effects [26].

## 5. Ion exchange on strength, reliability, and lifetime of dental porcelains

In this section, the effects of chemical toughening using ion exchange by the paste method on the strength and lifetime of dental porcelains are shown. In this study, a feldspathic porcelain (Ultropaline Super Transparent, Jen Dental – UST) recommended for metal-ceramic or all ceramic restorations was used. The chemical composition of this porcelain is shown in Table 4.

| $SiO_2$ | $Al_2O_3$ | $K_2O$ | $Na_2O$ | CaO | MgO | Traces |
|---|---|---|---|---|---|---|
| 70.2 (69.9) | 10.4 (9.6) | 10.6 (10.7) | 4.1 (4.6) | 3.1 (3.5) | 1.3 (1.5) | Ti, Fe, Zr, Ni |

**Table 4.** Chemical composition (mol%) measured by XRF spectroscopy and calculated glassy matrix composition (in parenthesis) of Ultropaline Super Transparent (UST) dental porcelain (containing 12 vol% leucite particles)

Disc-shaped green specimens were prepared by vibration-condensation method and then sintered at 930°C following the firing schedule recommended by the manufacturer. After firing, the specimens were machined and mirror-polished with diamond suspensions down to 1 μm. For each test condition at least 10 specimens (12.5 mm in diameter and 1 mm in thickness) were prepared.

For the chemical tempering, a paste was prepared by mixing 10 g of $KNO_3$ powder (Merck) with 4 mL of deionized water. Porcelain discs, containing 0.4 g of this paste on the polished surface, were subjected to the ion exchange treatment in an electric furnace (FP-32, Yamato) with a heating rate of 5°C/min at 470°C (or other specified temperature) during 15 min, after an intermediate step at 150°C for 20 min for drying. After the treatment, the paste residue was easily removed with sprayed water.

The porcelain's strength was determined in biaxial flexural mode, which is an adequate loading condition for thin specimens, like the dental restorations. The biaxial flexure strength ($\sigma_f$) was determined using a piston-on-three-balls loading device in a universal mechanical testing machine (Syntech 5G, MTS) at a constant stress rate of 10 MPa/s (or other specified rate), with the specimen immersed in artificial saliva (Table 5) heated to 37°C (Figure 11). Flexural test performed in artificial saliva at 37°C is more severe (strength tends to be lower) than in usual laboratory environment, but these conditions are more clinically relevant, since they are closer to the oral environmental conditions.

| KH$_2$PO$_4$ (2.5 mM) | Na$_2$HPO$_4$ (2.4 mM) | KHCO$_3$ (1.5 mM) | NaCl (1.0 mM) | MgCl$_2$ (0.15 mM) | CaCl$_2$ (1.5 mM) | Citric acid (0.002 mM) |
|---|---|---|---|---|---|---|
| 100 mL | 100 mL | 100 mL | 100 mL | 100 mL | 100 mL | 6 mL |

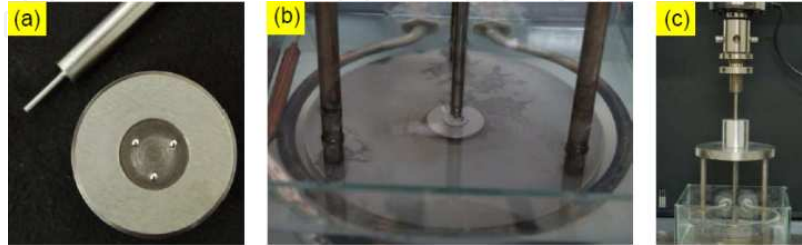**Table 5.** Composition of artificial saliva [5,54]



**Figure 11.** Images of biaxial flexural device: (a) loading piston and three-ball support; (b) disc specimen positioned in the flexural device and immersed in artificial saliva with heating element; (c) general view of the biaxial flexural loading device [5]

The biaxial flexural strength ($\sigma_f$) was calculated using the following equation [5,55]:

$$\sigma_f = \frac{0.2387 \cdot F}{w^2}\left\{(1+\upsilon)\left[1-2\ln\left(\frac{B}{A}\right)\right]+(1-\upsilon)\left[\left(\frac{A}{C}\right)^2-\frac{1}{2}\left(\frac{B}{C}\right)^2\right]\right\} \tag{10}$$

where, $F$ is the load at fracture, $w$ is the specimen thickness, $A$ is the radius of the support circle (4 mm), $B$ is the radius of the piston (0.85 mm), $C$ is the radius of the specimen, and $\upsilon$ is the Poisson's ratio (determined by ultrasonic pulse-echo method [56]).

Figure 12 shows the effects of ion exchange temperature on biaxial flexural strength, $\sigma_f$, and fracture toughness, $K_{Ic}$, determined by the indentation fracture method. It can be seen that ion exchanged specimens had significantly higher $\sigma_f$ values (around 130 MPa) compared to the control sample – without chemical tempering (57 MPa). This substantial increase of around 130% in strength was directly related to the increase in material's resistance to crack propagation, that is, fracture toughness. This property increased from 1.3 MPa.m$^{1/2}$ in control sample to around 2.8 MPa.m$^{1/2}$ in chemically tempered samples (relative increase of around 120%) [57]. The ion exchange by the paste method although short in time results in significantly strengthening and toughening of dental porcelains. Other works also showed increases between 20 to 83% in flexural strength by applying this method for feldspathic porcelains [58,59], although there are also reports showing no significant increases in some dental porcelains [60], particularly those with high K$_2$O content [61].

No effects of ion exchange temperature on $\sigma_f$ and $K_{Ic}$ were observed when this treatment was carried out between 430 and 510°C (Figure 12), which corresponded to a range between 75 and 89% of the glass transition temperature (T$_g$) of UST porcelain. This temperature (T$_g$), determined by differential thermal analysis, DTA (404S, Netzsch), at a heating rate of 5°C/min in

air, was 575°C [57]. At this temperature range, one could expect a significant increase in the ion exchanged $K^+$ ions with the increase in temperature, since the kinetic of ion exchange by interdiffusion with $Na^+$ ions of the porcelain is exponentially dependent on the temperature (Equations 2–4). In fact, it was determined by XRF spectroscopy that the sodium content in the $KNO_3$ paste residue increased with the increase in temperature of ion exchange treatment (Figure 13). The increase in $K_2O$ content and reduction of $Na_2O$ content in porcelain were also confirmed by EDS analysis in SEM. In this case, it seems that the increase in ion exchange rate was counterbalanced by the stress relaxation with the increase in temperature (Equation 6), inhibiting further increase in residual compressive stress and increases in toughness and strength. Therefore, an appropriate temperature for making ion exchange in dental porcelains with $K^+$ ions exchanged by $Na^+$ ions by paste method seems to be around 80% of glass transition temperature ($T_g$), or around 100°C lower than $T_g$ (for UST porcelain at 470°C).
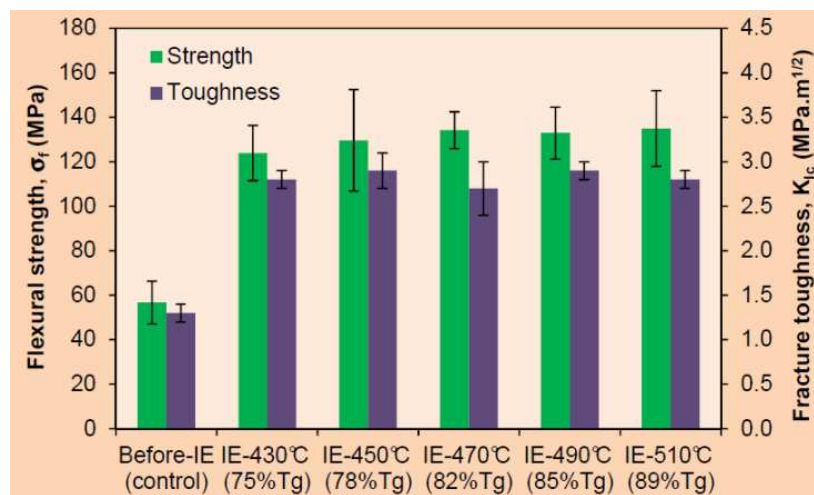


**Figure 12.** Biaxial flexural strength, $\sigma_f$, and fracture toughness, $K_{Ic}$, of UST dental porcelain before and after ion exchange (IE) at different temperature. In parenthesis is the temperature of IE relative to the glass transition temperature ($T_g = 575$°C). Data from [57]
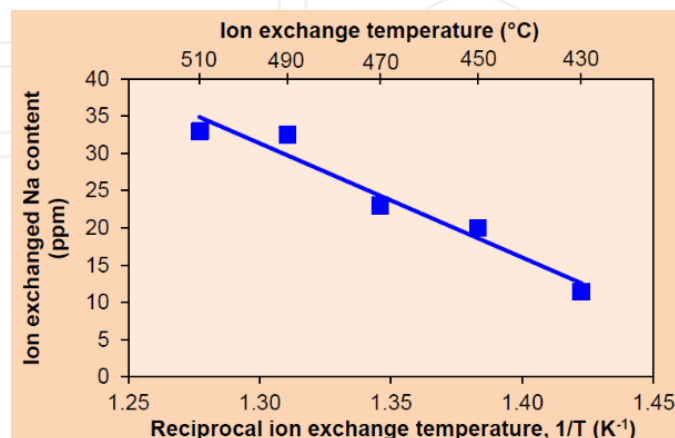


**Figure 13.** Sodium (Na) content in the $KNO_3$ paste residue after ion exchange treatment at different temperature for UST porcelain. Data from [57]

Small variations in flexural strength with varying ion exchange temperatures were also reported in another work. In general no significant differences were observed in strength when ion exchange with K-containing compound was applied to three dental porcelains between 300 and 600°C (for 30 min), although maximum values were observed at 450°C. Besides, small variations in strength with varying ion exchange time (10 to 90 min at 450°C) were also observed [62].

In order to evaluate the effects of the size of surface flaws on the strength of ion exchanged porcelain, the polished surface of specimens was indented with Vickers impression with increasing load from 2 to 49 N. In Figure 14a, it can be seen that the biaxial flexural strength, $\sigma_f$, of UST porcelain, without (control) and with ion exchange treatment (KNO$_3$, 470°C, 15 min), decreased with the increase in indentation load, since this increase causes the increase in radial/median crack size, $c$ (Figure 7b). However, the decrease in $\sigma_f$ was more accentuated in the ion exchanged specimens. These results showed that the beneficial effects of ion exchange are more pronounced for small surface cracks, and less effective for larger and deeper flaws. This behavior is related to the gradient of K$^+$ ion content introduced in the surface region, which results in a gradual decrease of residual compressive stress to the interior of porcelain. The positive effects of ion exchange disappear for flaws deeper than the thickness of compressive stress layer.
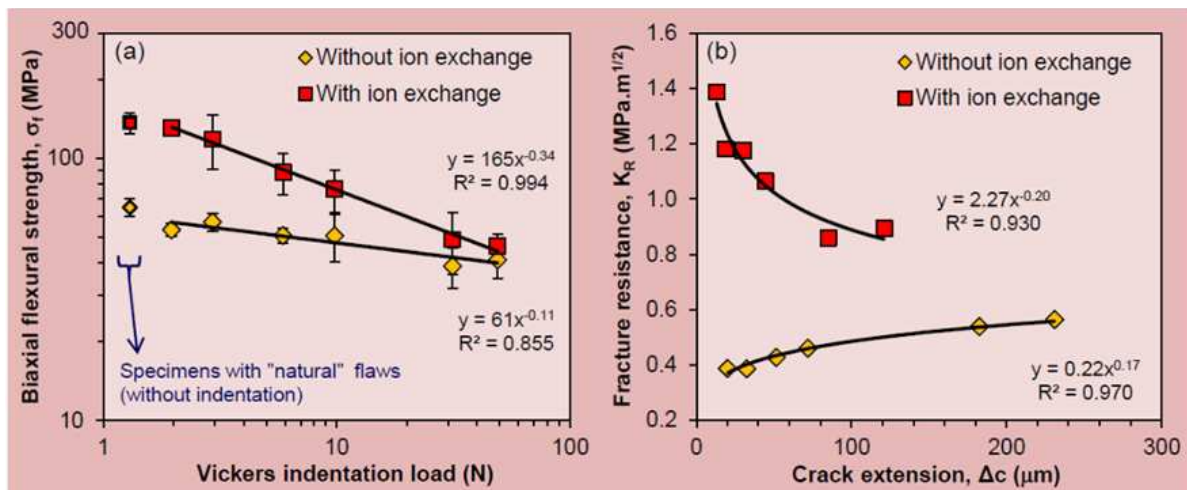


**Figure 14.** Biaxial flexural strength, $\sigma_f$, after a Vickers indentation at different loads (a) and fracture resistance, $K_R$, as a function of crack extension, $\Delta c$ (b), for UST dental porcelain with and without ion exchanges. Data from [63,64]

The fracture resistance, $K_R$, or $K_{Ic}$ as a function of crack extension, $\Delta c$, can be evaluated using the following equation [64–66]:

$$K_R = k \cdot \left( \Delta c \right)^q \qquad (11)$$

Where, the parameters $k$ and $q$ are determined using the data obtained by power law fits on the results of biaxial flexural strength, $\sigma_f$, as a function of indentation load, P, in Figure 14a.

The calculated fracture resistance, $K_R$, values as a function of crack extension, $\Delta c$, are shown in Figure 14b. For the non-treated porcelain, $K_R$ increased with the increase in crack size, the so-called rising R-curve behavior (crack growth resistance curve). This behavior is observed in leucite-containing porcelains and is caused by the friction between rough crack surfaces caused by crack deflection around leucite agglomerates [11]. Since this mechanical grip acts in the crack wake, the shielding effect at the crack tip is intensified with the increase in crack extension [67]. Rising R-curve effect is a desirable material behavior since it is necessary additional energy to propagate the crack, besides that needed at the crack tip [65,66]. For the ion exchanged porcelain, an opposite result was observed, with the decrease in $K_R$ as the crack size increased. The decreasing residual compressive stress from the ion exchanged surface cancelled the rising R-curve effect of porcelain microstructure and in addition, resulted in a decreasing R-curve effect. This behavior makes the strength of ion exchanged porcelain more sensitive to the size of flaws.

The variability of strength in ceramic materials is closely related to its flaw population, since fracture is a probabilistic event due to a random-like distribution of the strength-limiting flaws [68]. The strength variability of ceramic materials can be evaluated using Weibull statistic, which is based on the weakest-link theory, where the more severe flaw results in fracture propagation and determine the strength [69]. The Weibull two-parameter distribution is given by [14]:

$$P_{f,i} = 1 - \exp\left[ -\left( \frac{\sigma_{f,i}}{\sigma_0} \right)^m \right]$$

(12)

where, $P_{f,i}$ is the probability of fracture of ith specimen, $i$ is order number of $\sigma_{f,i}$ (fracture stress of ith specimen, ranked in ascending order of values), $\sigma_0$ is the characteristic strength (scale factor, defined for $P_f = 63.2\%$), and $m$ is the Weibull modulus (shape factor; the lower this value, the higher is variability). For this analysis, 30 specimens of UST porcelain for each condition (without and with ion exchange treatment – KNO$_3$, 470°C, 15 min) were tested in biaxial flexural mode at a stress rate of 1 MPa/s (in artificial saliva at 37°C). The Weibull parameters ($\sigma_0$ and $m$) were calculated based on the maximum likelihood method [70] and the results are shown in Figure 15.

It can be seen in Figure 15 that the ion exchange treatment increased more than 100% the characteristic strength, $\sigma_0$, but it also caused larger variability in fracture stress, reducing around 50% the Weibull modulus, $m$. Higher variability means lower reliability in the strength of porcelain, which was caused by the decreasing R-curve behavior in ion exchanged porcelain (Figure 14b), since shallow cracks were significantly toughened by high residual compressive stress level near the surface, but deeper surface cracks were less shielded by the decreasing resistance to crack growth. Therefore, strongest specimens in non-treated porcelain were strengthened more than the weakest ones. Clinically, it is more relevant to consider the fracture stress in an acceptable fracture probability, for example, at $P_f = 5\%$. Although strengthening is not so high as compared to the $\sigma_0$ value ($P_f = 63.2\%$), even at this low level of $P_{f,5\%}$ a significant
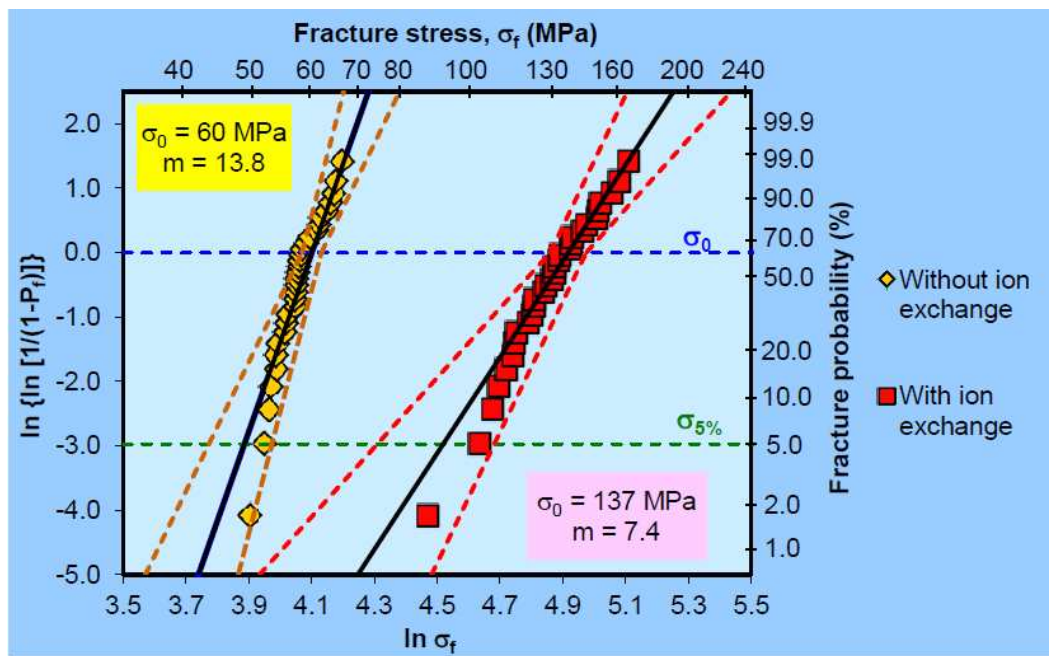
**Figure 15.** Weibull plot of biaxial flexural strength data, $\sigma_f$, for UST dental porcelain with and without ion exchange. Dotted lines are 95% confidence interval; $m$ is Weibull modulus, $\sigma_0$ is characteristic strength, and $\sigma_{5\%}$ is fracture stress at 5% fracture probability. Data from [71]

strengthening effect (at 95% confidence interval) is observed (Figure 15). In practice, the strengthening effect could be even higher than for $P_f$ = 5%, since clinical studies of inlays constructed with feldspathic porcelains have shown high fracture rates, up to 48% in evaluation periods of up to 3 years [72,73]. Therefore, although ion exchange reduces the mechanical reliability of dental porcelain, the strengthening effect is still significant even for low levels of fracture probability.

Another relevant factor related to the lifetime of a porcelain restoration is the mechanical degradation over time. When a ceramic material is subjected to a stress level lower than the fracture stress, the flaws (cracks) can growth slowly in a stable manner up to the time at which loading comes to a halt, reducing the material's strength due to the increase in crack size, or when a flaw achieves a critical size, given by the Griffith-Irwin fracture criterion (Equation 1), that results in (fast) fracture. This phenomenon is known as slow (or subcritical) crack growth, SGC, and silicate glasses, like porcelains, usually are highly susceptible to this type of degradation [74–76]. SCG occurs mainly by a stress corrosion mechanism (Figure 16), in which water molecules diffuse and are adsorbed at the crack tip, and then cause bonding rupture of glass network yielding Si–OH groups on each fracture surface, resulting in crack growth, by [76,77]:

$$\text{Si}-\text{O}-\text{Si}+\text{H}_2\text{O} \rightarrow 2\,\text{Si}-\text{OH} \tag{13}$$

Since the oral environment is aggressive to porcelain restorations and has many characteristics that favor SCG (water from saliva and dentin tubules, masticatory stresses, temperature and
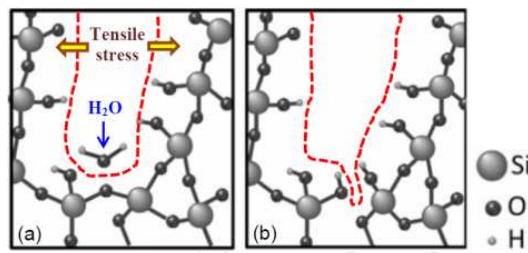
**Figure 16.** Schematic molecular images of slow crack growth (SCG) phenomenon in silicate glass: (a) diffusion of water molecule to the crack front (dotted line); (b) bonding breakage of $SiO_4^{4-}$ network causing increase in crack size

pH variations [67,78]), it is important to understand the response of strengthened porcelain to this phenomenon. The main method used to characterize the material's susceptibility to SCG is the dynamic fatigue method, in which specimens are tested in different stress rates and using the following equation [79–81]:

$$\log \sigma_f = \frac{1}{n+1} \log \dot{\sigma} + \log \sigma_{f0} \qquad (14)$$

where, $\sigma_f$ is the flexural strength, $\dot{\sigma}$ is the stress rate, $\sigma_{f0}$ the scaling parameter, and $n$ is the slow crack growth, SCG, susceptibility coefficient (the higher is $n$ value the lower is the susceptibility). Figure 17 shows the results of this test for UST porcelain, non-treated and ion exchanged ($KNO_3$, 470°C, 15 min). It can be seen that ion exchanged porcelain had significantly higher $n$ value (relative increase of around 50%), showing more resistance to SCG degradation. This effect is substantial and can impact the lifetime of a restoration.
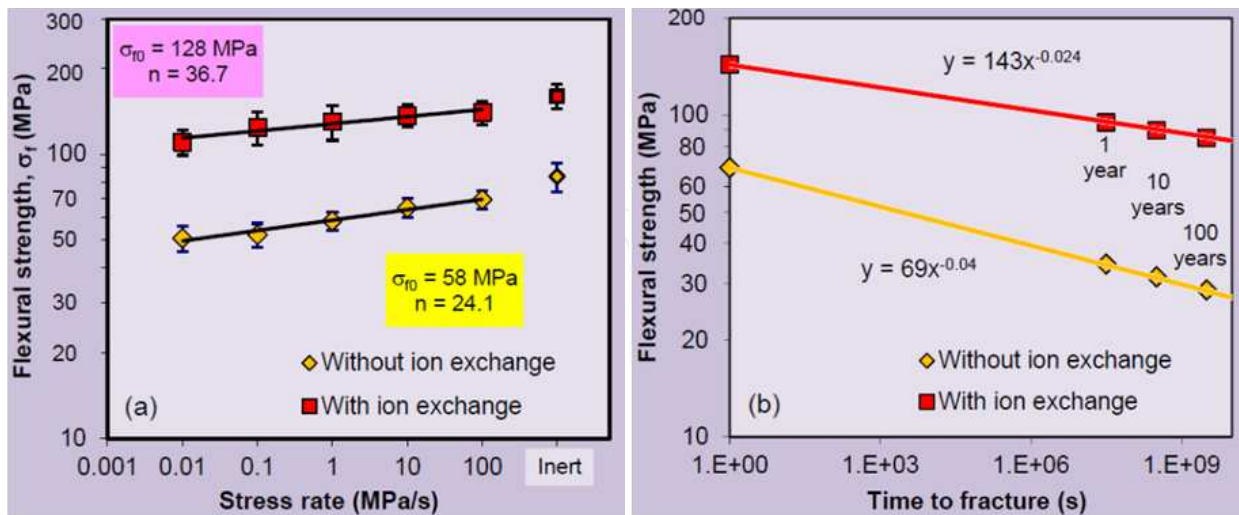


**Figure 17.** Biaxial flexural strength, $\sigma_f$, as a function of stress rate (a) and predicted flexural strength as a function of time to fracture (b) for UST dental porcelain, with and without ion exchange, in artificial saliva at 37°C. In (a), $\sigma_{f0}$ is the scaling parameter and n is the slow crack growth, SCG, susceptibility coefficient. Inert strength was determined at 100 MPa/s in air with a drop of silicone oil on the tensile surface to inhibit the occurrence of SCG. In (b), the slope of fitted curve is related with $n$. Data from [63,71]

Using the results of the dynamic fatigue test, it is possible to extrapolate the strength decrease after long lifetimes, as shown in Figure 17b. For both conditions, the average strength decreases over time, and after 10 years the expected remaining strength drops to around 30 MPa for the non-treated porcelain, but it still remains high (around 90 MPa) for the ion exchanged porcelain [71]. The increase in the stress corrosion coefficient, $n$, is a significant effect, since the difference in strength between ion exchanged porcelain and non-treated one increases over time. Therefore, besides increasing the strength the compressive layer generated by ion exchange process also decreases the rate of strength degradation by slow crack growth phenomenon.

Using the results of Weibull distribution (Figure 15) and dynamic fatigue test (Figure 17a) it is possible to construct the strength-probability-time (SPT) diagram [79,82,83], as shown in Figure 18. This diagram makes possible the estimation of a fracture stress at any time during the lifetime of a dental restoration at any fracture probability level. For example, it is possible to verify that UST porcelain after ion exchange has at least twice the fracture stress than non-treated porcelain even at a fracture probability as low as 1% during long lifetimes (e.g., 100 years). Note that the difference in fracture stress increases over time, at any level of fracture probability.
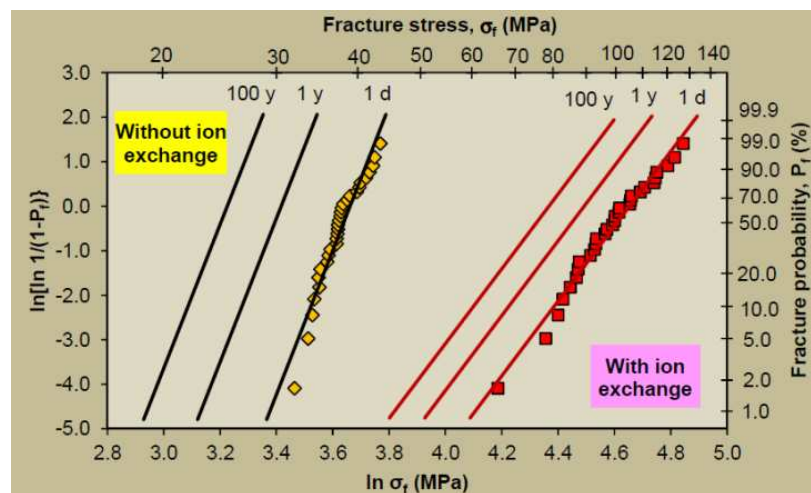


**Figure 18.** SPT (strength-probability-time) diagram for 1 day (1 d), 1 year (1 y), and 100 years (100 y) for UST dental porcelain, with and without ion exchange. Data from [63,71]

## 6. Two-step tempering processes

There are some two-step tempering methods proposed to overcome some limitations of the conventional (one step) ion exchange process. It was demonstrated that the application of ion exchange by the paste method after a thermal tempering treatment in a feldspathic porcelain resulted in an increase in the Weibull modulus ($m$ = 14.6) compared to only thermal tempered condition ($m$ = 8.7), with small decrease in average strength value [84]. Similar results were observed after applying a thermal tempering followed by a short-time chemical tempering in a silica-soda-lime glass dielectric, in which the reliability of thermal shock resistance was enhanced, with no change in the strength [85].

In order to increase the case depth, a two-step ion exchange was applied to a feldspathic porcelain. The specimens coated with a slurry containing 10 mol% LiCl and 90 mol% NaCl were heat treated at 750°C for 30 min and then cooled and heat treated at 450°C for 30 min. The first step was conducted above the melting temperature of chloride mixture and the second step below the glass transition temperature ($T_g$) of porcelain. The intent of first step was to exchange $Na^+$ ions and some $K^+$ ions in porcelain by smaller $Li^+$ ions from chloride mixture, considering that the high diffusivity at 750°C could result in a deeper exchanged layer. In the second step, some of $Li^+$ ions would be re-exchanged by bigger $Na^+$ ions, introducing a deep compressive layer. The determined thickness of ion exchanged layer was at least 140 μm [86].

Another two-step ion exchange method was proposed to introduce an engineered stress profile (ESP), in which a designed ion exchange stress profile with steep increase of the compression stress from the surface achieves a maximum at a predetermined depth and then decreases towards the interior of the glass. In the ESP glass, surface cracks growth in a stable manner up to the maximum compressive stress and are subsequently arrested, resulting in an uncommon surface crack pattern with a set of arrested cracks, before unstable fracture occurs. This behavior results in significant lower variability of fracture stress. The ESP is generated by a short second ion exchange process carried out for partial removal of the stuffing ion introduced in the first extended treatment [87,88]. This method was applied to a leucite-reinforced glass-ceramic prepared by heat-pressing method (Empress), using a $KNO_3$ bath in first step during 11 h at 450°C followed by a second step with a bath of 70 mol% $KNO_3$ and 30 mol% $NaNO_3$ at 400°C for 30 min (both temperature lower than $T_g$ of Empress). The two-step method resulted in increase in Weibull modulus ($m = 11.7$) in relation to the single-step ion exchange ($m = 5.1$) [89], and very high slow crack growth (SCG) susceptibility coefficient ($n = 107$) [90]. Figure 19 shows schematically the residual surface stress profiles from different ion exchange methods.
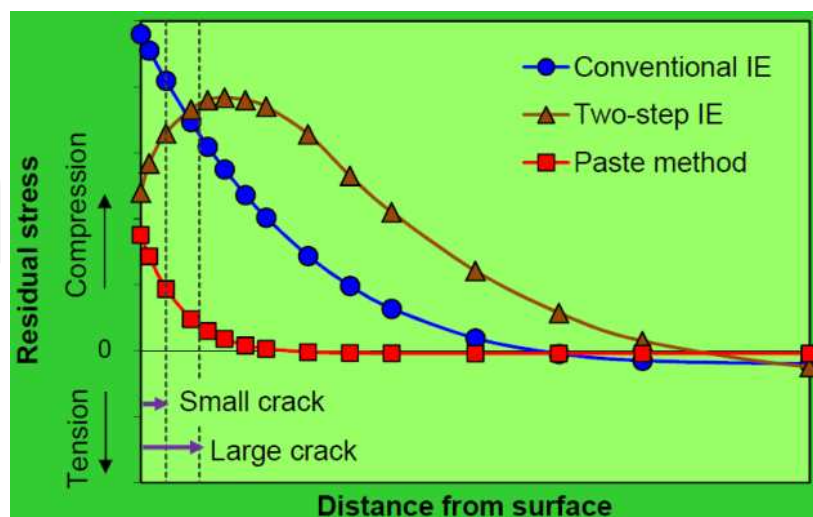


**Figure 19.** Residual surface stress profiles expected from different ion exchange (IE) methods: conventional extended (one-step) IE; two-step IE; and paste method (short IE treatment). Vertical dotted lines represent the depths of small and large surface crack. Data from [71]

## 7. Concluding remarks

Dental porcelains have been used for many decades because of their excellent aesthetic qualities, including the possibility to mimic natural teeth, besides other favorable characteristics. However, the low strength and fracture toughness, and high susceptibility to mechanical degradation by slow crack growth result in relatively low lifetimes in the oral environment. The introduction of a compressive surface layer by ion exchange is a promising process to enhance the mechanical behavior of dental porcelains. Exchanging small ions (e.g., $Na^+$) by larger ones (e.g., $K^+$) in the glassy matrix at temperatures lower than its glass transition temperature ($T_g$) can result in a steep gradient of residual compressive stress, which significantly increases the fracture toughness ($K_{Ic}$) in the porcelain surface. This increase leads to significant strengthening effects, even using the paste method, which is carried out in short times (less than 1 h). However, the strengthening is more pronounced for shallow surface flaws, because of the limited thickness of compressive layer and decreasing resistance curve (R-curve) behavior, which increases the variability of fracture stress and decreases the mechanical reliability (decreases the Weibull modulus, $m$). On the other hand, strengthening by ion exchange also significantly increases the resistance to slow crack growth phenomenon (stable crack propagation at low stresses intensified by water corrosion). This results in lower strength degradation over time and counterbalances the negative effect of decreasing reliability, leading to higher strength retention after long lifetimes (decades) even at a level of low fracture probability (e.g., 5%). The two-step ion exchange method has the advantage of increasing the material reliability, but at the expense of longer periods of treatment (above 10 h). In conclusion, it is expected that the application of chemical tempering (strengthening by ion exchange) can improve the lifetime of dental porcelain restorations.

## Acknowledgements

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