



# Ion-exchange strengthening of borosilicate glass: Influence of salt impurities and treatment temperature



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## ABSTRACT

Two alkali borosilicate glass tubes, as used in pharmaceutical packaging, were subjected to chemical strengthening in four potassium nitrate salts, these mainly characterized by differing sodium and calcium content. The heat treatment was at 450 °C and 465 °C for 4 h. The mechanical strength of the tubes was measured by 4-point bending tests. The compressive stress build-up at the glass surface was checked by Vickers indentations. The composition of the glass surface after ion-exchange was studied by EDS analyses. The results show that treatment increases the strength to twice the initial value, and that this is similar in the two glasses. A greater sodium content in the salt slightly decreases the exchanged layer depth and, consequently, the bending strength. Conversely, even a very low calcium content in the salt dramatically decreases the efficiency of chemical strengthening: it is shown that calcium blocks the sodium-potassium exchange, this being attributed to the thermodynamically favoured Na-Ca exchange on the glass surface with respect to the expected Na-K.

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## 1. Introduction

Borosilicate glass is widely used in pharmaceutical packaging such as syringes, ampoules, and cartridges. This glass is durable and inert to drugs and chemicals [1]. Despite such advantages, the limited strength and scratch/contact resistance demand special care during handling, processing and final use.

Various techniques have been proposed to improve the mechanical resistance of glass, including polishing the surface to remove flaws, or polymer coating [2–4]. Physical tempering is widely employed for float glass, but cannot be used for reinforcing shaped articles or with low thermal expansion glass [5,6]. Chemical ion-exchange strengthening has been used to improve the mechanical properties of thin and complex (hollow) glass articles [5,7,8]. During the ion-exchange process, small alkali ions, such as lithium and sodium, representing typical “modifiers” in the glass, are replaced by the larger potassium ions in a molten salt, where the glass is held for a certain time. For this reason, chemical strengthening is limited to glasses containing alkali ions [2,3,9]. Type II borosilicate glass, typically used in pharmaceutical packaging, meets this requirement. Reports on ion-exchange strengthening of borosilicate glass are limited to a few papers and patents [8, 10–12]. Most of these focus on exchanging sodium with potassium in glasses containing many modifiers, while in practical applications, the glass has a limited sodium content [8,12,13].

One fundamental issue in industrial practice is contamination of the potassium nitrate salt typically used for the ion-exchange process [3–5, 8]. Various chemicals can contaminate the melt, such as alkalis or alkaline earth ions, silicon and aluminium oxides, iron, chromium or nickel from the glass, the environment or the vessel [14,15]. Some of the impurities are not involved in the process but others, such as monovalent and alkaline earth ions, can intervene in or even inhibit the ion-exchange process [14,16].

Several technical, economic and environmental issues relate to such contamination and the possible replacement of the salt [6,17,18]. Published papers describe the influence of salt impurities, mainly sodium poisoning, on the process performance, by considering the equilibrium condition between the salt and glass surface; however the systems studied often differ from the industrial practice [15,16,19–21].

The demand for ion-exchange of borosilicate glass is less frequent than for soda lime silicate glass. In industrial processes, refreshing the salt for chemical strengthening of borosilicate glass is a difficulty. The salts, used for chemical strengthening of soda lime silicate glasses, contain relatively large amount of sodium. The sodium concentration in the salt baths is not crucial for chemical strengthening of soda lime silicate glass; however the influence of sodium on chemical strengthening of alkali borosilicate glass is not clear. Knowledge of the salt impurities allows prediction of the renewal time and of the process efficiency trend in time.

In this work, type II borosilicate glasses from two industrial suppliers were subjected to ion-exchange using KNO<sub>3</sub> salts containing different amounts of sodium and calcium as main impurities. Our aim was to

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**Table 1**  
Chemical composition, wt%, and transition temperature ( $T_g$ ) of the glasses.

	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	other	$T_g$ (°C)
Fiolax - HC	7.0	<0.1	1.5	5.2	10.5	75.5	<0.3	565 °C
Nipro - LC	7.0	0.8	0.5	5.8	10.5	74.9	<0.5	540 °C

identify to the relative importance of these elements and of the process conditions, on the final mechanical performance.

## 2. Experimental procedure

In this work glass tubes of length 1.5 m, typical in pharmaceutical packaging, namely Fiolax clear-Schott (Germany) – HC and Nipro-Glass (Japan) – LC were used. The chemical compositions and the transition temperature of the glasses are as to Table 1.

Four commercial potassium nitrate salts, labelled N10, N16, N25 and C60<sup>1</sup> were considered for the ion-exchange process: the salts had been used in the lab for some previous chemical strengthening, with the exception of salt N25, this already used for at least 1000 h in Na-K ion-exchange processes. The chemical composition of the salts was first checked by ICP-OES (Spectro-Ciros, Kleve, Germany) and the melting point was measured by Differential Scanning Calorimetry (DSC) (DSC2010, TA Instruments, USA).

The original glass tubes, of 7 mm nominal diameter and 1 mm thickness, were cut into 50 mm samples. Ion-exchange was carried out in a semi-automatic furnace (TA 20, Lema, Italy) at 450 and 465 °C for 4 h, with a salt to glass weight ratio of 100:1. The samples were held over the salt bath for 20 min before and after immersion, as preheating and post cooling steps. The specimens were carefully rinsed with water after complete cooling.

The mechanical strength was measured by 4-point bending test, using inner and outer spans of 18.3 mm and 40 mm, respectively. The test was in lab air (temperature = 20 °C, relative humidity = 40%) with a constant load rate of 1.1 MPa s<sup>-1</sup>.

The presence of residual stress on the glass surface was indirectly checked by measuring the length of cracks generated by Vickers indentations, which were produced using maximum load from 3 N to 20 N and dwell time of 15 s. The measurement of the crack length in the as-received glass was also used as an estimate of the fracture toughness. In both cases, the crack length was measured within a few seconds of the indentation, to avoid any sub-critical growth phenomena.

Fragments from five different broken samples, randomly selected from each group of specimens, were collected. The fragments were fixed to an aluminium disc, with conductive adhesive tape, and coated with Au-Pd alloy. A scanning electron microscope - SEM (JSM 5500, Jeol, Japan) equipped with an energy dispersive X-ray spectrometer (EDS2000, IXRF System, USA) was used to check the chemical composition at the glass surface and the potassium concentration on a straight line from the external surface to a depth of about 100 μm. The concentration profiles were refined by applying a low pass filter and normalised to the silicon concentration, to remove fluctuations due to the non-perfectly flat surface. The chemical composition of the glass surface was determined in at least 10 different regions, 0.1 mm<sup>2</sup> area. Quantitative analysis of the elements followed the ZAF method, with standardless technique. The relative molar concentration of sodium and potassium was used to quantify the exchange process of sodium and potassium at the glass surface.

<sup>1</sup> The salts, with no reference to the reported order, were acquired from Sigma-Aldrich (ACS grade, ≥99.0%), Haifa – Eurochemicals (technical grade, ≥99.4%), Carlo Erba (ACS grade, ≥99.0%) and Lema, Parma - Italy (nominal purity ≥ 99.0%),

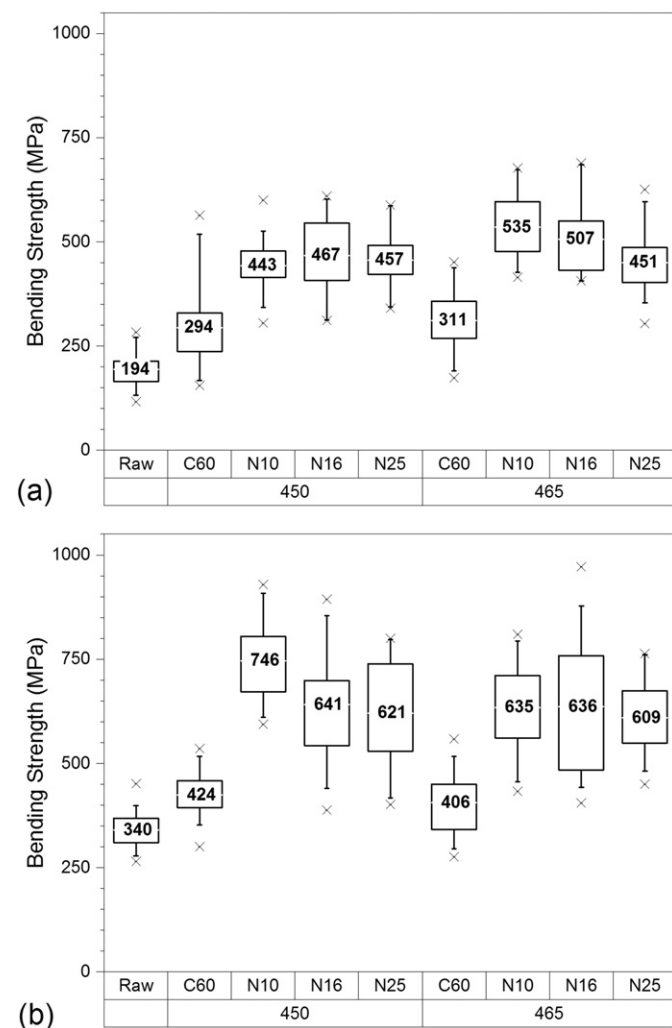
**Table 2**  
Fundamental impurities and melting temperature ( $T_m$ ) of the KNO<sub>3</sub> salts (ND = not detected).

	N10	N16	N25	C60
Sodium (ppm)	1039	1654	2431	769
Calcium (ppm)	ND	ND	ND	68
Magnesium (ppm)	5	5	5	5
Other elements	ND	ND	Li	S, Se
$T_m$ (°C)	330	324	322	327

## 3. Results and discussion

Table 2 shows the chemical composition of the KNO<sub>3</sub> used, in terms of fundamental foreign elements. Only one salt contained a significant amount of calcium in addition to the main impurity, sodium; traces (below 5 ppm) of other elements were also detected especially in salts N25 and C60. The principal impurity and its concentration were used to name the salts for easier reference. The presence of the reported contaminants accounts for the slightly different melting temperatures, always a few degrees lower than the thermodynamic melting point for pure KNO<sub>3</sub> (334 °C).

Fig. 1 shows the bending strength of LC and HC glass as a function of the salt used and of the treatment temperature. The mean bending strength, 25th and 75th percentiles and maximum and minimum values, are shown for each group of samples. The strength of HC raw



**Fig. 1.** Bending strength of (a) LC and (b) HC glass; mean value, 25th and 75th percentiles, maximum and minimum values are shown.

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