

Influence of Molten KNO_3 Flow Conditions on Mechanical Properties during Fabrication of Chemically-Toughened Glass

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ABSTRACT

In this study, we examined the influence of molten KNO_3 flow on mechanical properties and their deviation when a chemical toughening process was applied to soda lime silicate glass ($\text{Na}_2\text{O-CaO-SiO}_2$). KNO_3 melt flow was controlled using three methods: (1) glass tray rotation, (2) impeller stirring, and (3) natural convection. DOL and hardness were found to be enhanced by tray rotation because this rotation was able to maintain the concentration around the glass surface, in contrast to other methods. However, there did not appear to be a statistically significant difference in the 3-point bending strength for the three flow conditions due to the ground edge condition.

Key words : Ion exchange, Chemically-strengthened glass melt flow, Deviation, Soda lime silicate glass

1. Introduction

Ion-exchanged glass, which is called chemically-strengthened or toughened glass, has been applied widely to mobile devices because of its excellent mechanical properties of high strength and surface hardness. In the chemical strengthening process, sodium-containing glasses are immersed in molten KNO_3 below the glass transition temperature and Na^+ in the glass is mutually exchanged with K^+ in it.¹⁾ Since K^+ ions are larger than Na^+ ions, a compressive stress can be induced on the glass surface and this stress can enhance the mechanical properties of the glass.

Many studies have shown that the mechanical properties of ion-exchanged glass depend on temperature, time, and melt composition.²⁻⁷⁾ However, the quality of ion-exchanged glass products has been found to be unsatisfactory by many customers because of the fluctuation of the glass mechanical properties from several reasons; for example, micro-flaws exist in the ground edge and the inhomogeneous composition on the glass surface needs to be strengthened. In order to improve the strength weakness from edge grinding, chemical treatment using HF and organic acids is suggested.⁸⁾ It is speculated that the inhomogeneous composition on the glass surface could be derived from stagnant molten alkali salt. Commercially, a large bath and stirring system are used to make chemically strengthened glasses. However, it is difficult to sustain a concentration gradient around the glass because many glass pieces are put into unmovable trays, of which the size is similar to that of the

bath. Thus, the exchange between Na^+ and K^+ at the glass surface occurs in a nearly static state.

Considering the above, we had an idea as follows: if KNO_3 melt flow between the melt and the glass were retained dynamically during glass ion exchange, it might be possible to maintain the concentration gradient around the glasses and improve the quality of the chemically-strengthened glass. Three methods were applied to make ion-exchanged glasses; differences of mechanical properties were estimated statistically according to the methods.

2. Experimental Procedure

Soda lime glasses with dimensions of $50 \times 100 \times 0.7 \text{ mm}^3$ were made for mobile phones by Asahi Glass Co. LTD. Ten glass sheets were ion-exchanged at 400°C for 6 h in accordance with the results of preliminary experiments under three flow conditions: two dynamic conditions, which were tray rotation and extra impeller stirring, and one static condition. These experimental conditions are shown in the schematic diagram in Fig. 1. The DOL and CS of the glasses were measured using a surface stress meter (Hankooklab, FSM-6000LE, Korea). The 3-point bending strength and hardness were tested using a universal testing machine (R&B, 302ML, Korea) and a micro-Vickers hardness tester (Shimadzu, HMV 2T, Japan), respectively. Minitab14 was used for statistical analysis.

3. Results and Discussion

Figure 2 ~ 5 show the results of DOL, CS, hardness, and strength. In the case of DOL (Fig. 2), compared to the other results, the highest average and the narrowest deviation appeared in the case of tray rotation. Considering the laws

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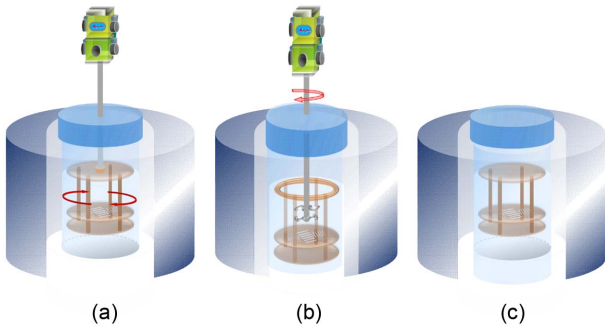


Fig. 1. Schematic diagrams of the 3-methods of ion exchange: (a) tray rotation, (b) impeller stirring, (c) no stirring (natural convection).

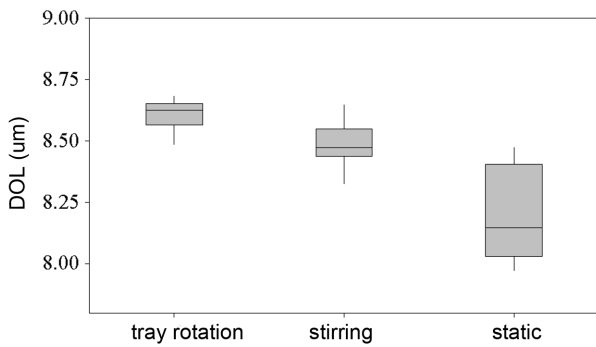


Fig. 2. The DOL of ion exchanged soda lime silicate glass with KNO_3 liquid flow conditions.

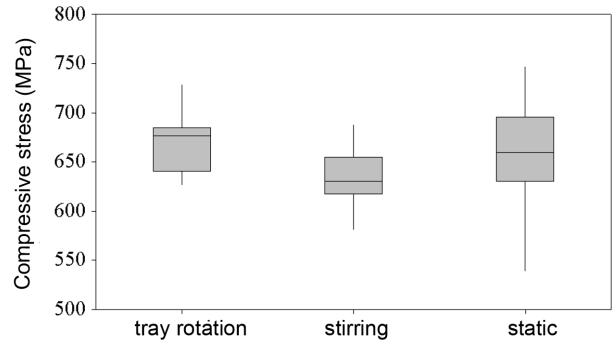


Fig. 3. Compressive stress with KNO_3 liquid flow conditions after ion exchange.

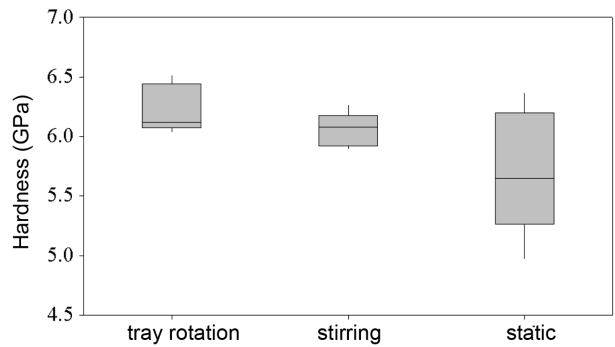


Fig. 4. Hardness of ion exchanged soda lime silicate glass with KNO_3 liquid flow methods.

of statistical probability, the situation becomes clearer. A significant difference in the average of DOL with respect to the KNO_3 flow conditions was determined by one way ANOVA (analysis of variance): 1) null hypothesis, there is no difference with other KNO_3 flow conditions (confidence level: 90%); 2) alternative hypothesis, there is a distinct difference with others. The results of the analysis are illustrated in Table 1. The p -value of DOL was less than 0.1. This means that the null hypothesis can be dismissed. KNO_3 melt flow around the glass surface can reduce the deviation and enhance the average of DOL.

Figure 3 shows the results of CS induced on the glass surface after ion-exchange. It seems that there is no distinction among melt flow methods. Especially, although the rotation and the static method showed obvious distinctions of DOL, CS in these methods showed little difference. So, we checked the statistical significance of the two methods. Significant differences in CS for tray rotation and static methods were

determined using a 2-sample t -test: 1) null hypothesis, there is no difference between the two KNO_3 flow conditions (confidence level: 90%); 2) alternative hypothesis, there is a distinct difference between the two flow conditions. The p -value between the two methods was 0.513; there was no difference between the two methods. The KNO_3 flow did not affect the CS, unlike the case of DOL.

Figure 4 shows the hardness results after ion-exchange. The flow methods not only reduced deviation, but also improved the hardness of the surface. Statistical validation was performed to check the hardness under the same conditions as those used for DOL. A significant difference in the average of the hardness with respect to the KNO_3 flow conditions was determined by one way ANOVA (analysis of variance): 1) null hypothesis, there is no difference with other KNO_3 flow conditions (confidence level: 90%); 2) alternative hypothesis, there is a distinct difference with others. The ANOVA result for hardness was 0.086. The hardness increased with the strength of the fluctuation. The result for the hardness was correlated to DOL rather than induced by CS. Although it is not yet clear, it seems that the DOL caused the hardness to increase, despite this process's similarity with CS.

Figure 5 shows the results of 3-point bending strength testing after ion-exchange. In general, the strength of the ion exchanged glass was reinforced through the induction of CS on the surface. In contrast with the compressive stress

Table 1. Test Results for Statical Analysis According to KNO_3 Flow Methods

Group	p -value
DOL	0.001
Compressive stress	0.513
Hardness	0.086
3-point bending strength	0.377

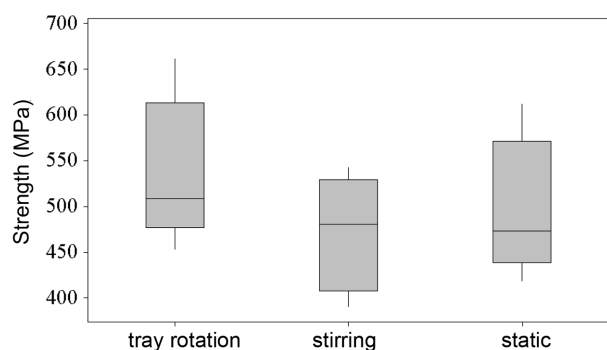


Fig. 5. Strength of ion exchanged soda lime silicate glass with KNO₃ liquid flow conditions.

results, the deviation of the strength was unaffected by the molten KNO₃ flow.

Fathi *et al.*, tried to maintain the concentration around the glass surface by using microwave and sonic-assist; they also had glasses with deeper DOL. However, the strength of the glasses was not improved and they explained this phenomena as stemming from stress relaxation and local atomic relation.⁹ According to Maeng *et al.*, the strength of the sodalime silicate glass was improved by the chemical treatment; it was confirmed that the main obstacle regarding strength reduction arose from cracks induced during grinding.⁸ It is difficult to verify the improvement of the 3-point bending strength because this study was conducted without additional treatment in the edge chamber. It can be inferred that the state of the abrasive edge chamber affected the strength and that Fathi's explanation is not a sensible deduction.

From previous results, it can be expected that the K⁺ concentration decreased gradually around the glasses and was not maintained at a constant level in the tank during ion exchange, even if there was natural convection. The potassium concentration around glass changed during the ion exchange process and it is hard to maintain the initial potassium concentration around the glass. Especially, when the impeller generated a flow of molten KNO₃, there is a slight improvement in the concentration of K⁺ ions in the surrounding glasses; however, it was not enough to improve the quality of strengthened glasses. The tray rotation was considered to be the best among the three methods for homogeneous ion exchange and for enhancing the mechanical properties. It is also thought that the complex structure of equipment prevents KNO₃ melt from flowing and maintaining the initial concentration around the glass.

So, in order to make deep DOL, reduce the deviation and

improve the mechanical properties of ion-exchanged glass, the KNO₃ melt has to be in a dynamic state. Because the ion exchange process is dominated by Fick's law, it is very important to maintain the initial concentration of the surrounding glasses.

4. Conclusion

Soda-lime glass, suitable for mobile devices, was subjected to ion exchange strengthening and the resulting mechanical properties were investigated as a function of KNO₃ melt flow conditions. It was statistically verified that there was a significant difference between the three flow conditions regarding the DOL and the hardness. It was found that there was no significant difference in the bending strength. Tray rotation was established as a better approach to reduce deviations in the quality using a simple impeller and natural convection, because tray rotation more effectively maintained a consistent concentration of K⁺ in the surrounding glass than did other methods.

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