Effects of temperature and time of ion-exchange on the mechanical behavior of chemically toughened soda-lime glass

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Effects of temperature and time of ion-exchange on the mechanical behavior of chemically toughened soda-lime glass

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ABSTRACT

The effect of immersion time and heating temperature on the mechanical properties of chemically toughened glass was examined. The glass samples of 100 x 100 x 20mm were first immersed in 2M of NaNO₃ salt solution at 450°C for 4 hours to enrich the surface of glass samples with sodium ions then dipped in 2M KNO₃ solution each at different temperature and time of immersion. Mechanical tests such as hardness, impact strength and flexural strength were performed on the untreated and toughened glass samples. The results obtained show that glass C has the highest value of hardness 58.3HRC while glasses A, B, and D also display a better hardness value of 45.7, 57.5, and 55.2HRC respectively compared with un-treated glass with hardness 40.9HRC. The impact test also shows that glass C has the highest impact strength of 1.25 KJ/m; glass B has the least impact strength of 0.19 KJ/m while the untreated glass has 0.37 KJ/m. The microstructure examination shows that glasses B and C showed a structure in resemblance with lamella structure displayed by most composites while glasses C and D display the highest flexural strength of 144 and 135.5 MPa respectively.

Keywords: Ion exchange; chemically toughened glass; Hardness; Impact strength; Flexural strength; Microstructure
1. Introduction

In theory, glass is very strong and theoretically the estimated strength indicates the values of approximately 7000MPa (Donald, 1989). However, due to surface flaws and defects, glass fails in practice below their estimated theoretical strength value (Macrelli, 2001; Green et al., 2003). Since glass normally fails as a result of surface flaws, residual surface compression in term of ion exchange and thermal tempering can be used to increase fracture strength (Abram et al., 2003).

It is therefore possible to enhance the mechanical properties of glass in several ways, and which has been differently categorized by several researchers. Bartholomew and Garfinkel (1980) identified two major approaches for improving the strength property of glass, namely either producing glass devoid of any surface defects or by rendering the surface flaws dormant or inoperative. Fire polishing and etching are applications of the first option, but they only result in temporary increase in glass strength. Glass edge processing by CO₂ laser irradiation is another similar essential approach; the flexural strength and the thermal fracture strength of glasses with CO₂ laser processed edges has been found to be much higher than that of glass with other conventional dry polished or wet polished edges (Akamatsu et al., 2005). Bogart and Dilliard (1971) also describe the method of combining ion exchange strengthening and fire polishing in improving the strength of glass by rendering the surface flaws inoperative while another approach is to protect the surface of the glass by coating as stated by Bartholomew and Garfinkel (1980). Several methods have been devised for creating surface compressive stresses in line with Bartholomew and Garfinkel (1980) second approach. Surface compressive stresses can be generated by ion-exchange, thermal strengthening, and vitreous enameling or by cladding with a material of lower thermal expansion coefficient. The thermal strengthening or cladding methods result in a relatively thick compressive surface layer in comparison with the other methods according to Bousbaa
et al. (2003). Increase in strength is made possible because the compressive stresses at the surface have to be overcome before defects can be subjected to net tensile forces. In order to enhance greater strength, the depth of a compressive layer must generally be higher than the size of any severe flaws, that is, equal to or greater than 50µm as stated by Brungs and McCartney (1975) as most flaws size reach 1–10µm into the glass. Varshneya and Lacourse (2003) suggest that the compression layer on the glass surface should be about 30µm thick in order to provide an effective protection against cracking due to the surface flaws.

The two prominent mechanisms employed in chemical strengthening are ion exchange and differences in coefficient of thermal expansion between the surface and the subsurface regions of a glass as identified by Fine and Danielson (1988). The result however is a function of whether a high or lower temperature of ion exchange process is used as described by (McCartney, 1972). Meanwhile the differences in expansion coefficient can be achieved by overlaying a glass with low coefficient of expansion on a high expansion coefficient glass. The only disadvantage of the latter method is that excessive differences in thermal expansion usually lead to sharp stress gradient at the interface between the compositions of the two glasses and thus a risk of coating debonding (Bartholomew and Garfinkel, 1980).

Ion exchange is centered on the principle of exchange of ions present in the glass by ions of different size. The larger ion literally stiffens the surface when a larger ion is exchanged for a small ion in a glass, thereby putting the glass into compression with a balancing tensile stress in the interior (Fine and Danielson, 1988; Hill and Donald, 1989; Kellman, 1993). Ion exchange is a diffusion controlled process, thus it is dependent on temperature and time. The stresses generated when ion exchange is carried out at temperatures approaching or exceeding the glass transition are quickly relaxed or eliminated due to the glass viscous flow. Therefore,
for a given composition of glass, the maximum strength is obtained at the shorter treatment times with increasing temperature (Donald, 1989).

It is reported by (Ono, 1983) that the obtained compressive stress, which is directly proportional to the glass volume on which ion exchange, has occurred; this can be correlated to the square root of the treatment time. There is no risk of surface deformation as the ion exchange temperature is below the glass transformation point \( T_g \). There may be a alteration in the expansion coefficient of the glass surface as a result of exchange but this effect has been found to be relatively small as described by (Kadogawa and Yamate, 1971; Shen and Green, 2004) while (Tyagi and Varshneya, 1998; Kellman, 1987) states that introduction of any ion with different size from the original ions results in significant changes in the structure of the glass material and thus lead to increase in glass strength, resistance to thermal shock, and the sealing of surface micro-cracks. The two prominent systems generally investigated so far are the Soda-silica system in which the Sodium ions (\( \text{Na}^+ \)) are being replaced with Potassium ion (\( \text{K}^+ \)) and the Lithia-silica system in which Lithium ions (\( \text{Li}^+ \)) are being replaced by Sodium ions (\( \text{Na}^+ \)).

Several ion exchange treatments has been investigated and patented by different authors, including mixed multi-ion exchanges. Examples are exchange of \( \text{Na}^+ \) or \( \text{K}^+ \) for \( \text{Rb}^+ \), \( \text{Cs}^+ \), \( \text{Ag}^+ \), \( \text{Cd}^{2+} \), \( \text{Zn}^{2+} \) or \( \text{Cu}^+/\text{Cu}^{2+} \).

However, in this present work, the effects of temperature and time of ion exchange on the mechanical behaviour of chemically toughened soda-lime glass is investigated with the sole aim of determine the accurate temperature and time of ion exchange to obtain maximum mechanical properties as compare with untreated soda-lime glass.
2. Experimental Procedure

2.1. Glass Characteristics and Sample Preparation

The material used in this research is an ordinary soda-lime-silica glass (in sheet form) which was purchased in its as-received state with a 2 mm thickness. Its mean chemical composition as stated by Bousbaa et al. (2003) is given in Table 1. The as-received glass was first thoroughly rinsed with distilled water to remove any surface dirt and afterward dried. 15 glass samples of 100 x 100 x 2 mm were cut from the sheet glass and prepared for the chemical toughening procedures as shown in Table 2.

2.2. Salt Solution Preparation

Potassium Nitrate salt (KNO$_3$) and Sodium Nitrate salt (NaNO$_3$) were the two salts solution prepared in this research work. A Sodium Nitrate salt solution was first prepared for the initial toughening process to enrich the surface of the glass while a Potassium Nitrate salt solution was later prepared for the final ion exchange process. 2M each of KNO$_3$ and NaNO$_3$ was prepared by dissolving the appropriate amount of each salts in distilled water inside the salt bath.

2.3. Chemical Toughening Process

The chemical toughening process is carried out in two stages: first by immersion in sodium nitrate salt solution and heated to the appropriate temperature for specific number of hours to enrich the glass samples surface with sodium ions (Na$^+$); then immersion in potassium nitrate salt solution.

The prepared glass samples were placed initially inside the salt bath containing 2M NaNO$_3$ salt solutions and heated in an electric muffle furnace to a temperature of 450$^\circ$C for a holding period of 4 hours. This allows initial surface enrichment of the soda-lime-silica glass
samples with sodium ions (Na\(^{+}\)). The furnace was then shut down and the salt bath containing the sodium enriched surface sample glasses was brought out after cooling using a pair of tong.

The initial treated glasses with sodium nitrate salt solution were finally immersed inside another salt bath containing 2M KNO\(_3\) and placed inside electric muffle furnace for heating schedule at different temperature and holding time respectively as shown in Table 2.

2.4. Measurements

Measurement such as hardness, flexural strength, impact strength, and microstructure examination using optical micrograph were carried out and analyzed to assess the effects of temperature and holding time of ion exchange on the mechanical behavior of chemically toughened soda-lime glass.

2.4.1. Microstructure Examination

Light reflection microscope was used for the microstructure examination (morphology) while the micrograph was revealed and taken on the computer screen attached to the microscope for examination at magnification of 100. The microstructure examination was done for both control sample (untreated glass) and the chemically toughened glass samples as shown in Figures 1-5.

2.4.2. Hardness Test

The hardness test was carried out using Vicker’s micro hardness tester with Model LM-700AT and test load of 980.7mN according to ASTM E384. Both the treated samples and the untreated samples were mounted respectively on the micro hardness tester under the applied test load of 980.7 mN at 10 seconds dwelling time. Light was reflected to the sample
glasses and the micro hardness was detected through microscope. The average hardness results obtained is therefore shown in Table 3.

2.4.3. Impact Strength Test

The impact strength test was carried out using Ball Drop Impact Method. A ball mass 10g was dropped at different distance from the sample glasses respectively to make an impact. The average impact force at which breakage occurred was then calculated for each glass samples A, B, C, D, and the untreated samples respectively. The average impact energy obtained is shown in Table 4.

2.4.4. Flexural Strength Test

Flexural strength test was carried out using universal Testing Machine (Instron 3369, 50KN Load Capacity) with strain/load rate of 5mm/min. The glass samples were placed on the two supporting rods of the machine one after the other in such a way that the projecting ribs of the samples had equal distance from the two supporting rods. Load was applied on the samples in such a way as to obtain a rate of increase of stress of 0.2N/mm per seconds. Load was applied to the sample until it fractured and the force at the point of fracture was noted. The flexural strength of each sample was calculated using the relation. The flexural strength test results obtained is shown in figure 6.

\[
\text{Flexural Strength} = \frac{3FL}{2bd^2}
\]

Where; F is breaking force in Newton

L is the distance between lower tension rods which the specimen is placed in mm

b is Breadth of specimen in mm
d is the thickness of the sample in mm

3. Results and Discussion

3.1. Microstructure Examination.

Figure 1 shows the optical micrograph of control sample (untreated soda-lime glass) with plate-like lines and non-uniform while Figures 2, 3, 4, and 5 show the optical micrograph of the treated glasses A, B, C, and D at 350°C for 5hrs, 400°C for 4hrs, 450°C for 3hrs, and 500°C for 2hrs respectively. Glass sample A shows a well dispersed coarse-like grains throughout the glass surface probably due to diffusion of bigger K⁺ replacing the smaller Na⁺ but at a lower temperature compare with the other treated samples. Glasses B and C show a more uniform fine textural consistency while glass sample D shows a resemblance to glass sample A but in a more uniform distribution.

3.2. Hardness

From Table 3, the untreated soda-lime glass has the least vicker’s hardness value of 420.7HV while samples B and C has the highest hardness value of 647.4 and 663.3 HV respectively while glass D has the hardness of 559.7 HV and glass A has 455.8HV. The superior hardness values displayed by the glasses B and C might be as a result of their fine uniform grain microstructure while glass A with coarse grain microstructure has the lowest hardness value of 455.8HV compared to other treated glass samples B, C, and D.

3.3. Impact Strength

Table 4 shows the results of the obtained impact strength values for the untreated and all the treated soda-lime glass samples. The untreated soda-lime glass sample has the impact strength of 0.37 KJ/m while glass C displayed better impact strength compared to other treated samples which might be as a result of its superior hardness.
3.4. Flexural Strength

Figure 6 shows the flexural strength of both the untreated (control sample) soda-lime glass and the treated glass samples A, B, C, and D respectively. The untreated sample has the flexural strength of 73.77 MPa while the treated glass samples A and B has the least flexural strength of 61.05 MPa and 60 MPa respectively while glass samples C and D has the superior flexural strength of 144.1 MPa and 135.5 MPa respectively. The superior flexural strength displayed by samples C and D might be as a result of their better elastic modulus.

4. Conclusion

The following conclusion can be drawn from the limit of this research:

- Hardness values increases as soaking temperature increases
- Better microstructure is obtainable at elevated temperature and time
- Impact values improve with temperature and time
- Maximum mechanical performance is obtainable at 450°C for 3 hours which is displayed by glass C from all the test results.
References


Figure 1. Showing the micrograph of the untreated soda-lime glass (x 200)

Figure 2. Showing the micrograph of glass A chemically treated at 350°C for 5 hrs (x 100)

Figure 3. Showing the micrograph of glass B chemically treated at 400°C for 4 hrs (x 100)
Figure 4. Showing micrograph of chemically treated glass C at 450°C for 3 hrs (x 100)

Figure 5. Showing the micrograph of chemically treated glass D at 500°C for 2 hrs (x 100)

Figure 6. Showing the flexural strength values of the control sample and the chemically treated samples.
Table 1. Mean Chemical Composition of the Soda-lime-silica glass used

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<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
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<td>Mass(%)</td>
<td>71.56</td>
<td>7.93</td>
<td>13.73</td>
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<td>1.32</td>
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Table 2. Samples Preparation for Chemical Toughening at various Temperature and Time

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<th>Time (Hours)</th>
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<tr>
<td>A</td>
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<td>5</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>400</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>450</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>500</td>
<td>2</td>
<td>3</td>
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<tr>
<td>Untreated glass</td>
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<td>-</td>
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Table 3. Hardness test results for the control sample (untreated glass) and treated soda-lime glass samples

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<td>HRC</td>
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<td>2</td>
<td>B</td>
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<td>Glass Designations</td>
<td>Impact Strength Values (KJ/m)</td>
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<tr>
<td>CTR Sample (untreated glass)</td>
<td>0.37</td>
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<tr>
<td>A</td>
<td>0.39</td>
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<tr>
<td>B</td>
<td>0.19</td>
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<tr>
<td>C</td>
<td>1.25</td>
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<td>D</td>
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Table 4. Impact test results of the control sample (untreated glass) and treated soda-lime glass samples