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Chemical Strengthening of Soda-Lime Glasses via Ion Exchange Method

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Abstract: The aim of this study is to improve the mechanical properties of glasses by the chemical strengthening method via the ion-exchange technique. For this purpose, KNO_3 salt baths were utilized for commercial soda-lime glasses. The diffusion-controlled strengthening mechanism is based on creating the compressive stress on the surface of glass by displacing the larger potassium ions with sodium ions. SEM-EDS line scan and XRF analysis, four-point bending, and Vickers hardness tests were performed for the structural and mechanical characterization of ion-exchanged glasses. The optimization of parameters led to a treatment duration of 24 hours at 400°C, resulting in a penetration depth of K^+ ions reaching 85 µm. After ion exchange process, the improvement in the hardness, fracture toughness as well as bending strength values of the glasses was observed. The strengthened glasses exhibited notable enhancements in mechanical properties, specifically, hardness increased from 517 HV to 612 HV, and the fracture toughness increased to 3.14 MPa.m$^{1/2}$ compared to the untreated glass, which displayed the fracture toughness of 1.09 MPa.m$^{1/2}$. Furthermore, the bending strength of treated specimens significantly improved to 421.6 MPa, representing a five-fold increase over the untreated sample's bending strength of 79 MPa.

Keywords: Chemical tempering, ion exchange, mechanical properties, soda-lime glass, strength

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1. INTRODUCTION

The concept of glass describes in everyday life, as a material that is transparent solids having a hard and brittle structure. With a more technical definition, glass is a high-viscosity, inorganic liquid that does not have a crystalline structure or a definite melting point (1). Compared to other types of materials, glasses have features that meet the needs both technically and decoratively in many areas for centuries. However, its hard and brittle structure limits these usage areas. Today, glass is strengthened in many industries via different thermal and chemical strengthening methods to overcome its natural weakness and bring out its inherent superior properties (2–6).

Compared to the traditional thermal and chemical procedures (i.e., etching, flame polishing, tempering, etc.) the ion exchange, principally in the category of chemical strengthening method, provides many practical advantages especially diverse shape applicability including thin cross-sectional applications such as 2 mm and less (7-9). The ion exchange process, as stated in Equation 1, is based on the ion movement-diffusion mechanism occurring between the glass and salt bath where the process is performed (10). These ions are primarily monovalent alkali metals situated within the Si-O network structure of the glass and the molten salt bath (11-13).

$$A_{glass} + B_{salt} = A_{salt} + B_{glass} \quad \textbf{(1)}$$

Monovalent ions embedded in the glass networks embody the mechanical weak points in the glass and have the tendency of moving through an electric potential difference or concentration gradient with the help of thermal driving forces. Therefore, the monovalent ions located at the interface of the glass surface and molten salt bath displace their locations mutually. When ions with larger diameters settle in the gaps of glass networks, the compressive stresses form at the surface and accordingly tensile stresses occur in the inner parts to balance forces. In addition to the compressive stress formations, the surface

chemistry of glass changes depending on penetration depth and amounts which causes the alteration of its refractive index value (14–16).

The main scope of the study is to improve the mechanical properties of soda-lime glasses by applying the ion exchange process and to examine the effects of process parameters on strength of soda-lime glasses systematically. The ion exchange method was applied in molten KNO_3 salt at various temperatures and times. The process temperatures were selected based on the glass transition temperature (T_g) of the samples and the melting temperature of KNO_3 salt and three different values were investigated. Likewise, considering routine process duration applications, four different time parameters were determined and examined. SEM-EDS line scan and XRF analysis techniques were utilized for the structural characterizations. The mechanical performance investigations were carried out via 4-point bending tests and Vickers hardness measurements. Moreover, the fracture toughness values of processed samples were determined.

2. EXPERIMENTAL SECTION

Experimental studies were carried out with commercial soda-lime glasses with the thickness of 2.1 mm and 2 cm x 6 cm dimensions, supplied by Kutaş (Tamcam) Group. The chemical structure of the samples is stated as (% wt.) 71.9 SiO_2, 14.3 Na_2O, 7.9 CaO, 4 MgO, 0.4 K_2O, 1.2 Al_2O_3 and 0.3 others. Soda-lime glass samples with a thickness of 2.1 mm and 2 cm x 6 cm dimensions were used for experimental studies. To minimize surface pollution and increase the efficiency of the ion exchange process, the glasses were cleaned in an ultrasonic cleaner using acetone and then dried using distilled water and alcohol.

Before the ion-exchange process, DSC/TGA of the glass samples was performed using a NETZSCH STA449 F3, from 30 °C to 650 °C with a heating rate of 10 °C /min under 50 mL/min flowing argon gas. As given in Figure 1, the glass transition onset temperature was determined as 582.1 °C from the DSC curve. T_g value was used in the determination of the maximum applicable process temperature so 450 °C was determined as the highest temperature for this study.

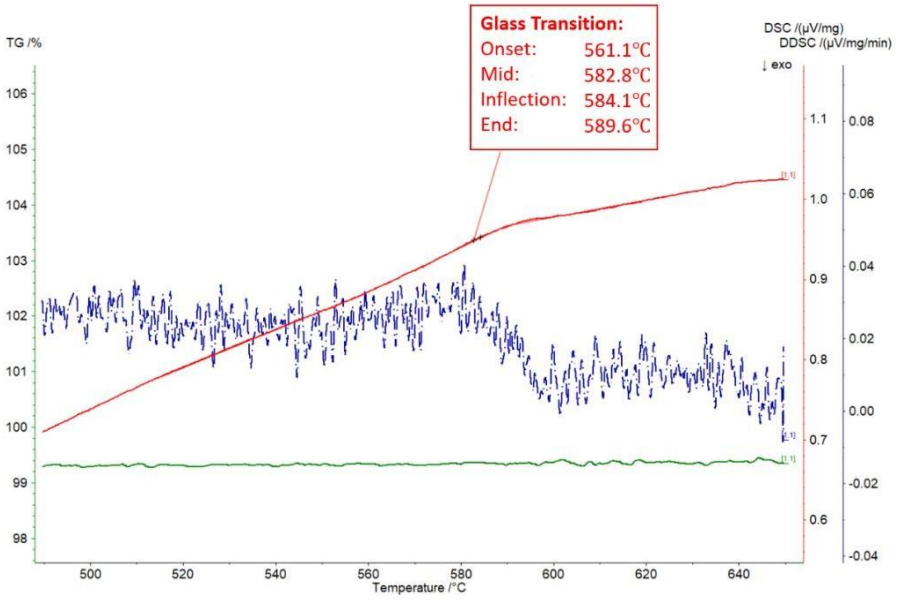

Figure 1. DSC Analysis Result of Samples.

Glass samples were subjected to an ion exchange process in a potassium nitrate salt bath (KNO_3) in the Nabertherm Controller B170 muffle furnace. The melting point of KNO_3 is 334 °C, so the experiments were carried out at 350 °C, 400 °C, and 450 °C for 4, 8, 12, and 24 hours. After the process, the surfaces of the glass samples were cleaned with distilled water to remove the salt bath residues.

The cross-sectional structural characterizations were carried out via SEM-EDS analyses (Scanning electron microscopy - Energy Dispersive X-ray spectroscopy-using JEOL™ JSM 5410 microscope) to determine the amounts of potassium-sodium replacements and the diffusion depth profile alterations. Likewise, relevant element amounts were determined and compared with Thermo Scientific – Niton XL3t GOLDD XRF analyzer before and after processing of glass samples.

The mechanical properties of processed samples were determined via a four-point bending test (AUTOGRAPH SHIMADZU AGS-J) to examine the bending strength variations and Vickers hardness instrument (TUKON™ 1102 instrument) under 500 g, 1000 g, and 2000 g loads for 10 seconds to measure the surface hardness alterations. Moreover, the fracture toughness values of processed samples were calculated according to Palmqvist Model.

3. RESULTS AND DISCUSSION

The XRF results of processed samples at different times and temperatures revealed that with increasing temperature K-Na replacements took place due to the thermal driving forces and concentration gradient effects. These substitutions became more obvious at longer process durations (16). For the treated samples for 12 hours and 24 hours, the potassium concentration in the samples increases steadily with increasing temperature which is consistent with REF (17).

Since longer process treatments at higher temperatures caused more potassium penetrations, the cross-sectional SEM-EDS line scan analyses of processed samples at 350 °C- 450 °C for 12-24 hours were further investigated to see the diffusion profile as presented in Figure 3 and given in Figure 4. With increasing temperature, K+ - Na+ replacements became deeper, and the highest diffusing depth was observed at approximately 132 µm at the sample treated 450 °C for 24 hours.

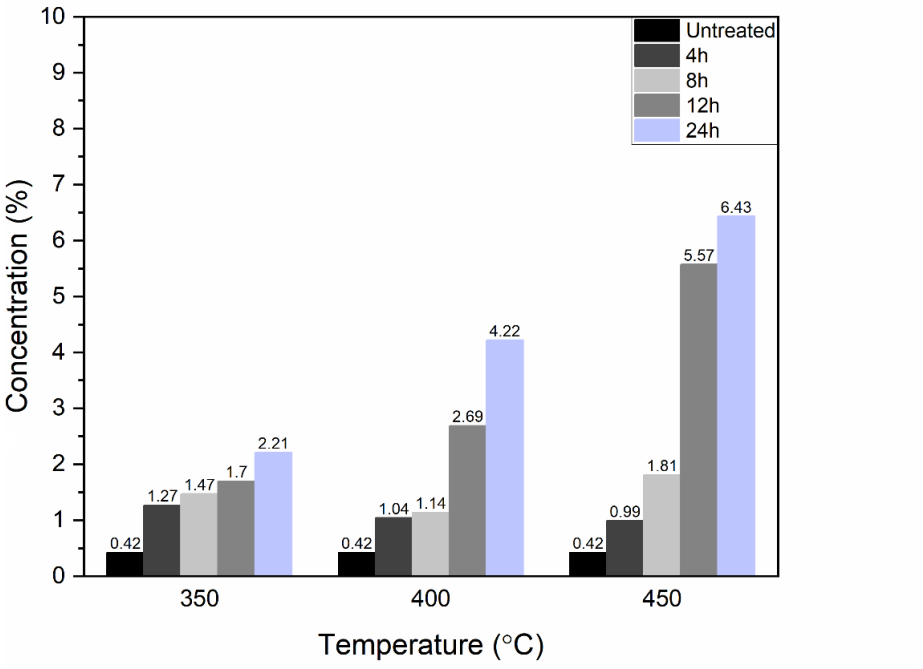

Figure 2. Concentration change of potassium in the sample.

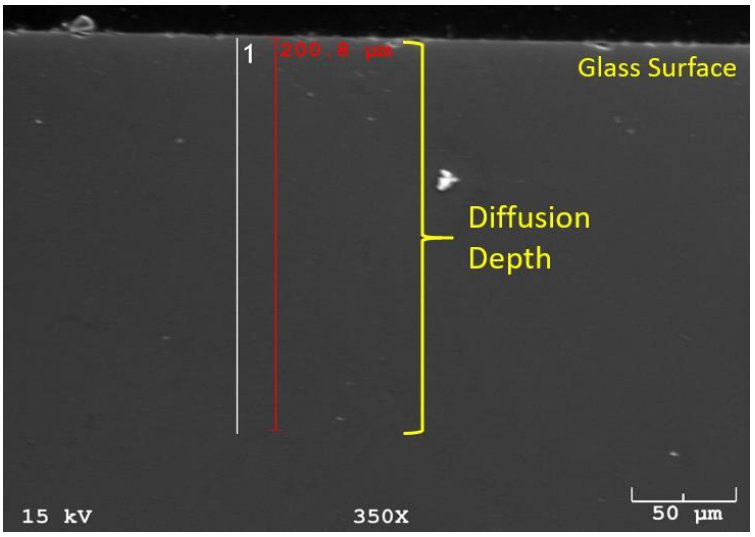

Figure 3. EDS line scan analysis image of sample treated at 350 °C for 12 hours.

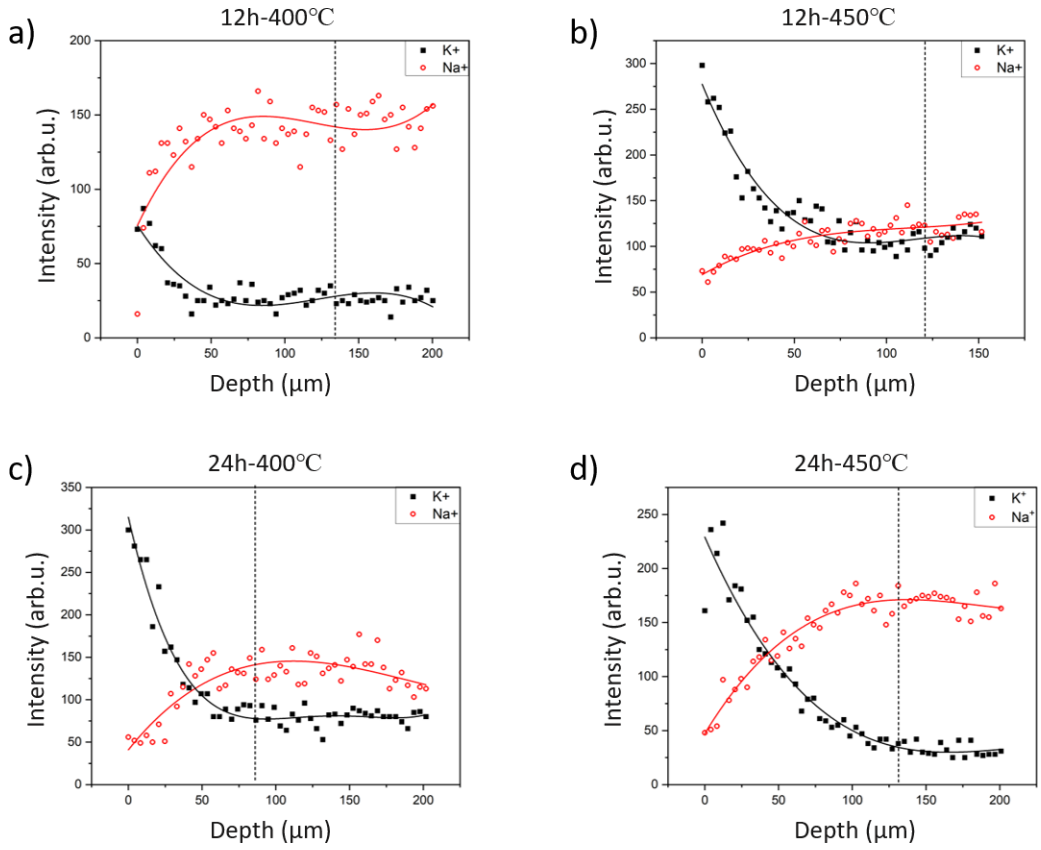

Figure 4. After a) 400 °C -12h, b) 450 °C -12h c) 400 °C -24h d) 450 °C -24h treatment, change of potassium composition according to depth after ion exchange.

For mechanical performance measurements, 4-point bending tests were performed to observe the change in bending strengths of treated samples for 12- 24 hours (Figure 5). The bending strength of the untreated sample is 79.5 MPa. So, after the treatment at 400 °C for 24 hours, the value increased to 421 MPa. Erdem et al. conducted ion exchange process for soda lime glasses and reported an increase in bending strength of soda-lime glasses from ~80 MPa to ~360 by ion-exchange method at 425 °C for 16 hours (16). The strength of the processed samples was improved with temperature until 450 °C then decreased which is probably because of that 450 °C is close to the strain point of this glass type. As mentioned in many literature studies, the effect of stress relaxation on the chemical strengthening of glasses is quite large. In a study by Macrelli (15), stress relaxation can become an effective parameter if the difference between the strain point of the glass and the temperature at which the ion exchange process is performed is less than 100 °C. In this case, in soda lime glasses where the strain point value is assumed to be around 514 °C, the 450 °C process temperature is a critical value for stress relaxation. According to literature, the specified temperature values may also be important after certain processing times such as 8 hours. As a result, the reason why no increase in strength and fracture toughness was observed at processing times of more than 12 hours and at processing temperatures higher than 400 °C can be interpreted as the stress relaxation becoming an effective parameter at the specified time and temperature values (15).

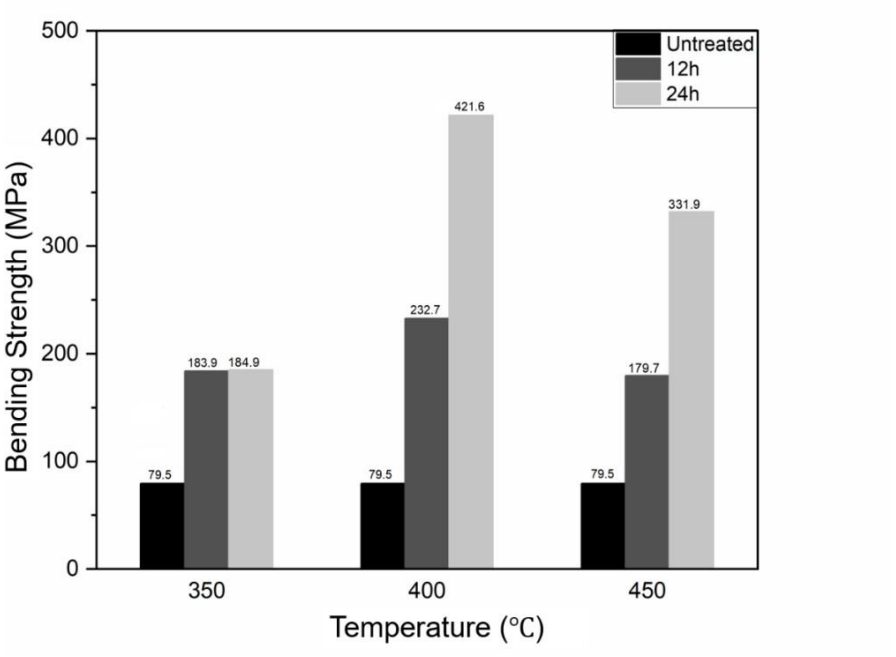

Figure 5. Bending strength values of glass samples that untreated and treated for 12 and 24 hours at 350 °C, 400 °C, 450 °C temperature values.

Figure 6 gives the Force-Displacement graphs were generated for the samples processed at 350 °C to 450 °C for 12 and 24 hours to compare with the untreated one. Apparently, the force and displacement values of untreated glasses are lower than treated glasses. Considering the process time effect, the strength values that the samples can withstand were higher at the sample treated longer. Glasses processed for 24 hours had the highest stress values for all temperature parameters (i.e., 826.3 N and 456 N for the sample treated at 400 °C for 24 hours and 12 hours, respectively. Likewise, 650.5 N and 352.3 N for the sample treated at 450 °C for 24 hours and 12 hours, respectively). Considering the effects of process temperatures, the strengths increased up to 400 °C, then the values decreased as a result of the softening of the glass samples treated close to the strain point (e.g., 362.5 N, 826.3 N, 650.5 N for the sample treated for 24 hours at 350 °C, 400 °C and 450 °C, respectively).

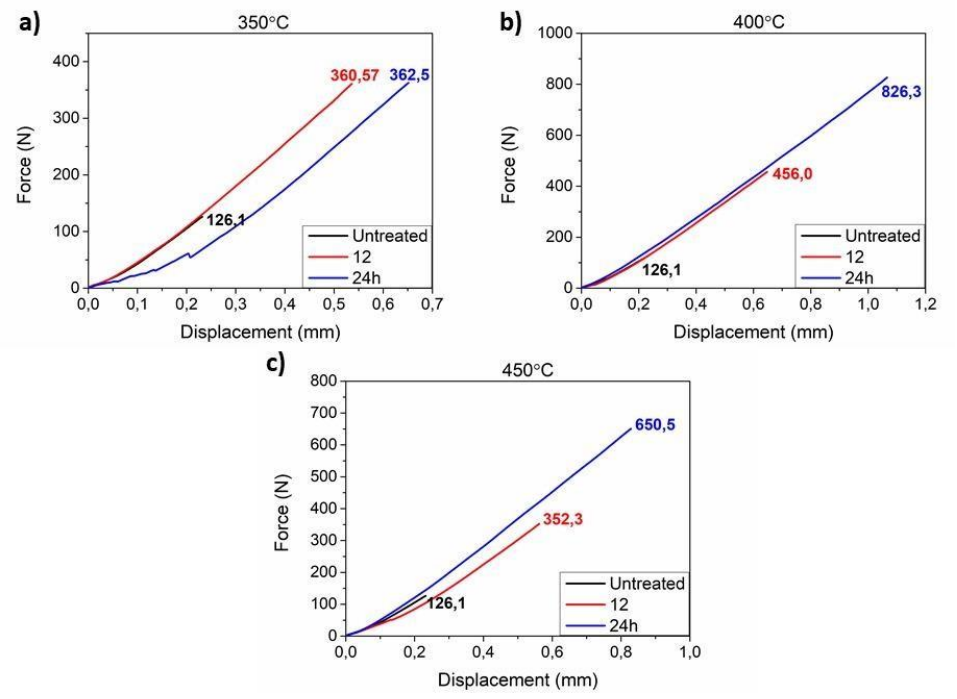

Figure 6. Force-displacement graph of untreated and ion-exchanged glasses at a) 350 °C b) 400 °C c) 450 °C for 12 and 24 hours.

Vickers hardness measurements were carried out at 500 g, 1000 g and 2000 g loads to evaluate the cracking resistances of processed glasses. The sample treated at 350 °C, 400 °C for 12 h had resisted up to 1000 g (Figure 6). However, the sample treated for 24 hours at 400 °C did not fail to 1000 g (Figure 7). All samples had severe crack formations at higher loads namely 2000 g.

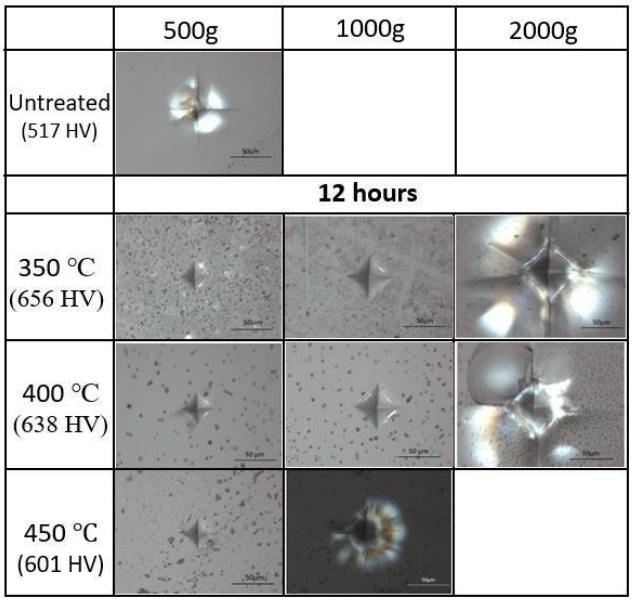

Figure 7. Optical microscope images of untreated and treated glasses at 350 °C, 400 °C, 450 °C for 12 hours.

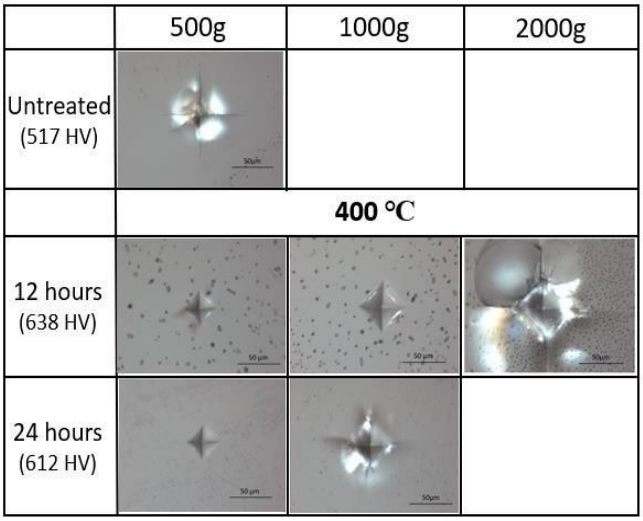

Figure 8. Optical microscope images of untreated and treated glass at 400 °C for 12 and 24 hours.

In the hardness values obtained as a result of the analysis, the glass samples belonging to the 400 °C parameters show higher results than the 450 °C (i.e., 638 HV for the sample treated at 400 °C for 12 hours and 601 HV for the sample treated at 450 °C for 12 hours, respectively) (Figure 7), which is consistent with the 4-point bending test in terms of temperature, while the samples belonging to the 12 hour processing time show higher values in terms of time at 400 °C (i.e., Likewise, 638 HV for the sample treated at 400 °C for 12 hours and 612 HV for the sample treated at 400 °C for 24 hours, respectively) (Figure 8). These findings are consistent with REF 16 in which the highest hardness was obtained 620 HV at 425 °C for 16 hours. Moreover, the fracture toughness values were calculated for the treated samples (Table 1). For these calculations, the Palmqvist model and equation (2) were utilized due to the c/a ratio (see Figure 8) where the Vickers indentation and crack length were a and c respectively (i.e., the Palmqvist model is used at $c/a < 2.5$, whereas the Half-Penny model is preferred when $c/a \geq 2.5$) (18).

Table 1. Fracture toughness values of glass samples.

Sample	Fracture Toughness (MPa.m$^{1/2}$)	Applied Load (g)
Untreated	1.09	500
12h – 350 °C	1.78	2000
12h – 400 °C	2.60	2000
12h – 450 °C	2.70	1000
24h – 400 °C	3.14	1000

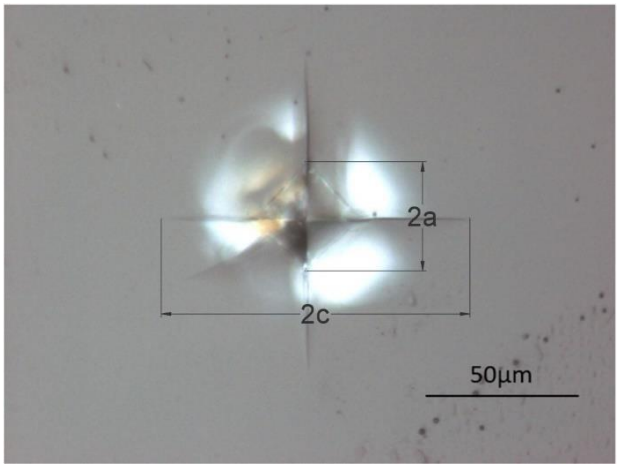

Figure 9. Vickers indentation and crack size

$$K_c = 0.079\frac{P}{a^{3/2}}\log\left(4.5\frac{a}{c}\right) \quad \textbf{(2)}$$

In general, the fracture toughness of the untreated soda-lime glass (1.09 MPa.m$^{1/2}$) increased with temperature up to 450 °C, however increase in treatment time to 24 hours at 400 °C yielded the highest fracture toughness of 3.14 MPa.m$^{1/2}$. Similarly, the rise in fracture toughness of soda-lime glasses (reported as 0.66-2.22 MPa.m$^{1/2}$ in REF 19) was stated at 425 °C for 16 hours of treatment in REF 16, but increasing treatment temperature demonstrated a negative effect on crack formation probability. Considering bending strengths and fracture toughness values, the optimum condition was found as 400 °C and 24 hours for ion exchange treatment of soda lime glass in KNO_3 bath.

4. CONCLUSION

The soda-lime glasses were strengthened via ion exchange-based chemical strengthening method. The process parameters were optimized as 24 hours and 400 °C. After the strengthening treatment with optimized parameters, the penetration depth of K ions was obtained as 85 µm. The mechanical properties were noticeably improved by means of this economical, green and fast process. The hardness value was increased from 517 HV to 612 HV, and the fracture toughness was reached to 3.14 MPa.m$^{1/2}$, while the untreated one shows 1.09 MPa.m$^{1/2}$. The bending strength of the treated specimens were enhanced to 421.6 MPa which is 5-fold higher than the bending strength of the untreated sample (79 MPa).

5. CONFLICT OF INTEREST

Authors declare that there is no conflict of interest with any person, institute, company, etc.

6. ACKNOWLEDGMENTS

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