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Chemical tempering of soda lime silicate glasses by ion exchange process for the improvement of surface and bulk mechanical strength

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ABSTRACT

The aim of this work is improving mechanical properties of soda-lime glass by imparting compression stress on the surface through ion exchange and investigate the effect of process parameters on chemical strengthening. KNO_3 salt bath was used for ionic exchange at varying temperatures and durations. Treated samples were investigated for their optical transmittance, surface potassium ionic concentrations and concentration profiles from surface to bulk using EDS and line scan EDS techniques. Effect of process temperature and time on the amount of mechanical strengthening was determined through the bending strengths (four-point), scratch resistances and indentation behaviors as micro hardness, crack formation load limit and cracking probability. Results were evaluated regarding ionic concentration variations. Transmittance decreased by 2% after the treatment. Surface potassium concentration increased with increasing temperature and was increased to become saturated in a short period. Potassium concentrations decreased from surface to bulk, and diffusion reached to deeper layers with increasing time and temperature. Ionic exchange improved micro hardness by 8–17%, threshold loads for indentation crack initiation 2–10 times, cracking probability down to 50%, strength up to 3.5–4 times and scratch resistance 2–4 times. Crack types changed between radial, median and lateral; depending on the degree of chemical tempering.

1. Introduction

With rapidly developing technology in our century, glass materials particularly started being used not only as housewares but also in many fields such as automotive, architecture, construction, aircraft, optical and aerospace industries, laboratories, energy generation [1–7]. Glass is the mostly preferred or the only choice for its esthetics and transparency, so to meet the needs of the sector and expand the use in different applications, glasses should be reliable materials with high strength [6]. Therefore, the development concerning mechanical properties of glass materials are of great importance, and today the efforts in this regard continue to rise [2,4,6].

Schneider et al. [8] defines glass as a brittle solid, behaving almost perfectly elastic. Mechanical properties, which are strictly related to the amount, depth and distribution of surface flaws, are the most important features of glass that determines its use. These surface micro cracks cause the glass to present poor mechanical behavior i.e. tensile strength varying within the tens of MPa, even though theoretically its structure enables up to thousands of MPa [3,8–12]. Studies on glass mechanical strengthening focuses on the suppression of these micro cracks by introducing compressive stresses to the glass surface, where stress limits the generation and propagation of cracks [1,7,10,11,13]. Besides other methods for inducing surface compression such as, thermal tempering, ion exchange, ion bombardment and surface crystallization and many more [3,11,14,15] chemical tempering has become the focus of studies in the last decades.

Ion exchange method used for chemical tempering is also applied for many years in production of optical waveguides, glass coloring and gaining antibacterial properties to glass [4]. In recent years, chemical tempering has become a popular choice for developing glass strength and improving the surface properties of glass. There are a variety of products and patents developed by different glass manufacturers in this regard; and still researches continue considering the effect of parameters on process efficiency such as temperature, time, glass composition and thickness, bath composition and concentration, exchanging pair of ions, specimen geometry, quality of glass surface etc. [4,5,11]. Since each parameter has numerous variables and affects the results to a great extent, each study carries its own authenticity. Chemical tempering is realized by the ionic exchange process of the alkali ions in the glass structure with the ions in a molten salt bath it is

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in contact with. The larger ions incorporated to the surface structure replacing the smaller ions cause local strains thus increase the strength of glass by forming a compressive stress [1,4,10–14,16]. This method can be applied easily to complex shaped and very thin (down to 0.5 mm) parts of varying sizes, the resulting product is suitable for machining and the process does not require expensive machinery or equipment [1,3,10]. The majority of the products commercialized by chemical tempering method use alkali aluminosilicate glass; developed products generally serve as electronic equipment panels and screens.

In the present study, it was aimed to improve the mechanical properties of soda-lime glass by chemical tempering and investigate the effect of ion exchange process parameters on strengthening. Ion exchange was applied using pure KNO_3 salt bath and soda-lime silicate glass at varying temperatures and durations. Samples were examined for their optical properties, hardness values and surface ionic concentrations using EDS technique. A process duration and a temperature was selected to investigate the effect of temperature and time on mechanical strengthening. Further characterizations as indentation crack formation behaviors, scratch resistances and bending strengths were realized on selected samples. The results were evaluated together with the surface and bulk ionic concentration variations.

Hardness, cracking probability, deformation zone and scratch resistance analysis give information about the mechanical response of only one surface of glass samples, which were but ion exchanged on both sides under presented experimental studies. Regarding the nature of bending test, the mechanical behavior is determined by both bulk and surface properties of the glass samples. Since both sides of the glass sample contain a certain level of compressive stress sustained by ion exchange, the correlations with surface mechanical properties must be handled carefully. The comparative interpretation of the mechanical test results examined from various angles are thought to be essential contributions to literature, as no studies were found including the mentioned characterization steps all at once.

2. Experimental

2.1. Sample preparation

Experimental studies were conducted on Corning® 2947 soda-lime glass slides of 25 × 25 × 1(± 0.01) mm. As a result of chemical analysis of the glass realized by a Perkin Elmer Analyst 800 atomic absorption spectrometer with an error estimate of ± 2%, the composition was determined as (wt.%) 70.56 SiO_2, 14.54 Na_2O, 8.93 CaO, 3.41 MgO, 0.87 K_2O, 0.59 Al_2O_3 and 1.1 other.

Before the ion exchange process, thermal analysis of the unprocessed glass samples was performed using a PerkinElmer™ Diamond TG/DTA, in platinum pans with a specified weight of 25 mg, from room temperature to 800 °C with a heating rate of 10 °C/min under flowing (100 ml/min) argon gas. The obtained glass transition onset temperature (T_g) from the thermal analysis results was 549 °C. Ion exchange process temperatures were determined accordingly.

Glass samples were cleaned in an ultrasonic cleaner using deionized water and ethanol prior to ionic exchange process to maintain the contamination of the surface at a minimum, increase the contact area and improve the efficiency of ionic exchange process. Cleaning step of the samples were repeated after the ion exchange process in order to remove the salt bath residues from the sample surface.

Ion exchange process on glass samples was performed in a ProthermPLF 120/7 electrical furnace. Ionic exchange was conducted using 100% potassium nitrate salt bath (KNO_3, 99.0% purity, Alfa Aesar Company). Process was realized at temperatures 425 °C, 450 °C, 475 °C and 500 °C determined as being under the glass transition temperature (T_g) and for 0.5, 1, 2, 4, 8, 12, 16, 20 and 24 h. For narrative simplicity, samples were given notations representing the varying experimental parameters such as “425-1” representing the sample treated at 425 °C for 1 h.

Since the atomic weight of potassium ion is higher than sodium ion, an increase in sample weight was expected after the ion exchange process. A digital balance of 10^{-4} precision was used for the weight measurements of the ultrasonically cleaned samples before and after the ion exchange process.

2.2. Characterization methods

UV–Vis spectroscopy technique was used to investigate the effect of potassium ion exchange on the optical transmittance of the glasses in the visible region between 360 and 700 nm wavelengths, with a spectral bandwidth 0.1 nm. The investigations were realized using PG Instruments T80 + UV–Vis spectrophotometer, with a tungsten lamp and at room temperature.

The effect of ion exchange on micro hardness of glass samples were investigated through Vickers hardness measurements before and after the process. The indentations were realized under 0.49 N with a constant loading rate for 10 s dwell time using Schimadzu HMV-G21 Vickers micro hardness instrument capable of loading between 0.49 (50 g) to 19.61 N (2 kg). An optical microscope connected to a CCD camera and image analysis software aided for the measurements of the indent diagonals, to give the hardness values. An average value of 20 indentations was determined as the hardness of the sample. The tests were conducted at 23 ± 1 °C with 50–60% relative humidity.

Surface and cross section morphology were determined together with the amount of potassium incorporated to the surface by scanning electron microscopy technique by JEOL™ JCM-6000 Benchtop scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) technique using JEOL™ JSM 5410 microscope connected to Noran 2100 Freedom energy dispersive X-ray spectrometer. The concentrations of potassium and sodium ions on the glass surface after the ion exchange process were determined in weight percent. The diffusion depth of incorporated potassium ions after the ionic exchange were also determined using the same instrument by conducting a line scan EDS analysis on selected glass samples.

Schimadzu HMV-G21 Vickers micro hardness instrument was also used to examine the variations of indentation crack resistance of the selected glass samples after ion exchange through determining the variations in threshold loads for indentation crack initiation (TLICI), crack sizes and cracking probabilities, with methods inspired from former studies [9,12]. Applied loads on each of the sample were 0.49 N (50 g), 0.98 N (100 g), 1.96 N (200 g), 2.94 N (300 g), 4.90 N (500 g), 9.80 N (1 kg) and 19.61 N (2 kg) for 10 s dwell time. 20 indentations were realized per load and a crack was accepted to be initiated if at least two of the four corners had started to form cracks. Crack size was determined as the average length of the cracks formed and investigations were realized after 5 min to capture the delayed or slow growing cracks. Indent and crack images were taken under 40 × zoom for loads up to 4.90 N, and under 10 × zoom over that load to capture the full cracks. Cracking probabilities were determined in percentage per each load by calculating the number of indentations resulted in cracking out of the 20 indentations and comparisons were realized for identical loading conditions. Crack type and size comparisons were conducted under 19.61 N (2 kg) load where all selected samples had formed full cracks.

Scratch resistance of samples were examined using CSM nano-indentation and nano-scratch tester using a Rockwell diamond indenter with a 200 μm tip radius, resembling the studies of Bandyopadhyay et al. [17] and Petit et al. [18]. Each scratch test had a pre-scan phase carried at a very low load aiding to determine the sample surface topology, creating a baseline for the main scratching scan. Samples were cleaned with acetone and ethanol before the test. Scratch tests were applied at a constant speed of 0.02 mm/s with load raising gradually to 20 N over a length of 8 mm. Measurements were conducted at room