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Influence of silver and potassium ion exchange on physical and mechanical properties of soda lime glass

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ABSTRACT

This study aims to investigate the ion exchanged soda lime glasses in terms of their physical and mechanical properties. By the motivation of preparing mechanically strengthened glass also representing antimicrobial property, commercial soda lime glass was subjected to ion exchange treatment using $AgNO_3$—KNO_3 mixed salt bath. Ion exchange treatment was performed using different salt bath concentrations at varying temperatures and time. After the ion exchange treatment, glass samples were examined by considering the amount of incorporated silver and potassium into the glass, density changes and the variation of the transmittance in the visible region. Treated glasses were further investigated by means of their surface and mechanical properties such as wettability, indentation behaviors including hardness and resistance to indentation cracking, scratch resistance and bending strength. The transmission of the treated glasses showed a decrease due to the coloring effect of silver. Wettability of the glass surface was reduced, while hydrophilicity was decreased after the ion exchange treatment. Almost 20% increase in the Vickers hardness values, substantial enhancement in the indentation crack resistance and scratch resistance as well as averagely 3.5–4 times higher bending strength were achieved for all of the treated glass samples compared to the untreated glass. This study addressed that the simultaneous incorporation of silver and potassium provided significant improvements on the mechanical properties of the soda lime glass.

1. Introduction

Glass has become essential material of the today's modern world with its use in many broad areas from the simple glass containers or bottles to the glass optical fibers carrying data all over the world. It can either be fragile or as strong as steel, can be shaped in many forms whether in bulk, fiber, film or powder. Its high chemical durability, hardness, transparency, forming ability and relatively low price makes it indispensable in many different applications [1–2].

Ion exchange in glass, which has been used for many years, is a convenient technique to modify the surface composition and properties of the glass surface without changing the bulk glass properties. Ion exchange technique is widely applied for altering the optical, mechanical, chemical and electrical properties, so it is used for many different applications such as strengthening of glass, fabrication of gradient index lenses and optical waveguides, coloration and decoration of glass. It is based on substitution of mobile monovalent ions (generally Na^+ or Li^+) in glass by the other ions generally from the molten salt bath e.g. K^+, Rb^+, Cs^+, Ag^+, Tl^+ or Cu^+/Cu^{2+}. Strengthening of glass takes place, when smaller ions in the glass exchange with the larger ions from the salt bath, due to the generated compressive stress on the glass surface [3–10]. Strengthening of glass using ion exchange technique was first applied by Kistler in 1962 to the soda lime silicate glass using KNO_3 bath [11–12]. Since then, many researchers worked on it to improve the surface and mechanical properties of glass. Ion exchange is based on diffusion of the ions. Many factors such as ion exchange temperature, ion exchange time, glass composition and the interface between the glass and salt have an effect on the efficiency of the process. In addition, usage of different metal ions and their varied salts and salt mixtures lead to change the efficiency [5]. All these parameters have considerable effects on the results. Therefore, numerous researches have been done about the ion exchange strengthening of glass since the first study executed; and it still continues to be studied [1–5,7–11].

Silver is the best known and the most commonly used metal ion for coloring the glass, fabrication of glasses for opto-electronics and waveguide technology, and synthesis of antimicrobial glass [13]. It is the first monovalent cation that was exchanged to examine the diffusion of silver in soda lime glass by Shülze in 1913 [3]. Silver ions are ideal for ion exchange treatment with their high mobility which lets them to be incorporated to the glass surface using different salts ($AgNO_3$, AgCl, Ag_2SO_4 etc.) as the ionic medium [14–15]. Silver ion exchange in glass is generally conducted to investigate the variations of optical properties of the glass in the literature. By using both silver and potassium, it is possible to develop glass which is mechanically strengthened, and at

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the same time exhibiting either color variations or strong antimicrobial property. However, there are fairly limited studies regarding the influence of silver ions on mechanical properties of the glass. Lee et al. [16] studied the ion exchange in soda lime silicate glass using $NaNO_3$, KNO_3 salt bath and their mixed salts with $AgNO_3$ by measuring the optical characteristics, electrical resistivity, hardness, bending strength and softening point of the glass.

On the basis of preparing mechanically strengthened glass showing also antimicrobial property, in this study, commercial soda lime glass was subjected to ion exchange treatment using $AgNO_3$—KNO_3 mixed salt bath at different concentrations for varying temperatures and time. By the use of silver and potassium in the same salt bath, it is possible to develop mechanical and surface properties and also antimicrobial activity of the glass surface in a single step process. The wt.% range of $AgNO_3$ used in this study was determined to be sufficient to make the glass surface antimicrobial, through the findings of an ongoing research on the investigation of antimicrobial properties of silver/potassium ion exchanged glass. This study aims to investigate the effect of concentration of the salt bath, ion exchange temperature and ion exchange time on the surface and mechanical properties of the glasses. The wetting ability, indentation cracking resistance and scratch resistance were described for the first time, along with the determination of the Vickers hardness and bending strength of the glass ion exchanged by using $AgNO_3$—KNO_3 mixed salt bath.

2. Experimental

2.1. Sample preparation

Corning®2947 soda lime glass, which has a $1(\pm 0.01)$ mm nominal thickness, was used in the present study. The chemical composition of the glass was determined before the treatment. Powdered glass samples were dissolved in 5 vol.% HNO_3 and 10 vol.% HF water solution using a Teflon beaker; then the obtained solution was analyzed using a Perkin Elmer Analyst 800 atomic absorption spectrometer with an error estimate of $\pm 2\%$. Merck AAS standards were used for the quantification. The chemical composition of the glass was specified 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.

Thermal analysis of the samples before the ion exchange treatment was carried out using a PerkinElmer™ Diamond TG/DTA, with a constant sample weight of 25 mg, in platinum pans, from room temperature to 800 °C under a flowing (100 ml/min) argon gas with a heating rate of 10 °C/min. The glass transition onset temperature (T_g) was determined as 549 °C from the DTA curve.

Glass surfaces (2.5×2.5 cm size) were cleaned prior to use in order to remove any kind of contaminants, hindering the contact area between the glass surface and salt bath which is highly important for the efficient diffusion and ion exchange treatment. Cleaning was realized using ethanol and deionized water in an ultrasonic cleaner. The ionic medium was prepared using high purity powders of silver nitrate ($AgNO_3$, 99.9% purity, Alfa Aesar Company) and potassium nitrate (KNO_3, 99.0% purity, Alfa Aesar Company). Glass samples were treated in three compositions of salt mixture that $AgNO_3$ concentration varies between 1 and 3 wt.%. Ion exchange was carried out in an electrical furnace for 60, 120 and 240 min. The temperatures of the treatment were determined as 380–420 °C, according to the glass transition temperature (T_g) of the glass. After the treatment, glasses were kept in deionized water in an ultrasonic cleaner to remove any residues from their surfaces. Treated samples were represented by a notation as to its varying experimental conditions without indicating the constant parameters in some certain parts.

2.2. Characterization methods

The amount of the incorporated silver and potassium were determined by energy dispersive X-ray spectroscopy (EDS) technique using JEOL™ JSM 5410 microscope connected to a Noran 2100 Freedom energy dispersive X-ray spectrometer, realized on gold coated surface of the glass samples. Five measurements were taken from the different regions of the glass surface to check the consistency. EDS line scan analysis were performed on the cross-section of the treated glass samples within 100 μm range to investigate the penetration depths of the silver and potassium ions into the glass matrix.

Density of the glass samples was measured by the Archimedes method at room temperature using ethanol as an immersion liquid and a digital balance of sensitivity 10^{-4} g. Density values were recorded after three repeated measurements showed an error of 0.1%.

UV–vis spectroscopy technique was used to investigate the effect of the incorporated silver on the optical properties of the glasses. Transmission spectra of the treated glasses in the range of 360–700 nm wavelengths with a spectral bandwidth of 0.1 nm were examined by a PG Instruments T80 + UV–vis spectrophotometer at room temperature.

The wetting ability of the glass surfaces after the ion exchange treatment was evaluated by contact angle measurement technique using deionized water. Samples were cleaned in an ultrasonic cleaner with ethanol and deionized water before the measurement. Each glass sample was tested for several times by applying 5 μm droplets on different areas of the surface, and then the average contact angle values were calculated.

The Vickers hardness of the glass samples were measured before and after the ion exchange treatment using a Vickers microhardness tester (Shimadzu HMV-G21) with 0.49 N indentation load for 10 s dwell time. Measurements of the indentation diagonals were realized by an optical microscope connected with CCD camera and image analysis software. Ten indentations were performed for each glass sample in a thermally controlled environment at 24 ± 1 °C with 50–60% relative humidity.

Vickers indentations were carried out at various indentation loads ranging from 0.49 to 19.6 N at a constant loading rate for 10 s dwell time to investigate the indentation cracking resistance of the glass samples. Crack resistance was evaluated in terms of threshold load for crack initiation and indentation crack size. For this purpose, ten indentations were applied at each indentation load which was increased gradually. The probability of crack initiation was determined for each indentation load by counting the indentations that have at least two cracks formed from the corners of the indentation. Radial cracks which were generated from the corners of the indentation were considered. Threshold load for crack initiation was defined as the load where the probability of the crack initiation is equal to 50%. The indentation crack size was calculated by averaging the two crack sizes of each indentation which were located as the diagonals of the indentation. The measurements were recorded within 1 min after the indentation.

Scratch resistance of the glass samples was determined using CSM nano-indentation and a nano-scratch tester equipped with Rockwell diamond indenter having 200 μm tip radius. For each scratch test, prescan was carried out at a very low load to determine the sample profile, and then the second scan was performed for analysis. Surface of the glass samples was cleaned with acetone and ethanol before testing. Tests were carried out at load raised up to 30 N with a constant speed of 0.02 mm/s over 12 mm scratch length. All measurements were done at room temperature with a dry air.

The strength of the ion exchanged glass samples was determined through a four point bending test (with inner and outer spans of 10 and 20 mm, respectively) using a Shimadzu Universal Testing Instrument. Glass samples ($75 \times 25 \times 1$ mm^3) were subjected to bending test with approximately 0.5 mm/min displacement rate at room temperature with a dry air. Strength data were analyzed using Weibull distribution to calculate the failure probability as a function of strength. The following equation is used:

$$F = (i - 0.5)/n \quad (1)$$