



Molecular dynamics simulations of ion-exchanged glass



K. Deenamma Vargheese, Adama Tandia, John C. Mauro*

Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA

ARTICLE INFO

Article history:

Received 10 June 2014

Received in revised form 14 July 2014

Available online 1 August 2014

Keywords:

Ion exchange;
Aluminosilicates;
Chemical strengthening;
Molecular dynamics;
Elastic moduli

ABSTRACT

Chemically strengthened glass is one of the key enablers of the modern consumer electronics industry. Molecular dynamics simulations offer an opportunity to build enhanced fundamental understanding of the ion exchange process used for chemical strengthening. In this work, we apply molecular modeling techniques to investigate several aspects of ion-exchanged glasses that are either inaccessible through experiment or too difficult to probe through experiments alone. In particular, we use atomistic modeling to study the dependence of the linear network dilation coefficient on the concentration of alkali ions exchanged. We also calculate the evolution of elastic moduli as a result of the ion exchange process. Both of these quantities—the network dilation coefficient and the Young's modulus—are critical parameters for determining the final compressive stress profile of the chemically strengthened glass. Finally, we revisit the issue of structural differences between as-melted and ion-exchanged glasses in terms of local atomic number density around alkali ions. The results of this work point to the unique structures attainable through ion exchange that cannot be achieved through melt-quenching alone.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Chemical strengthening of glass via the ion exchange process is a highly effective technique for increasing the practical strength of glass products [1–9]. Compared to other strengthening techniques such as thermal tempering, the ion exchange process offers a significantly higher degree of compressive stress. Ion exchange also enables the strengthening of thin glass sheets and glass products with complicated three-dimensional geometries.

The ion exchange process for chemical strengthening was originally developed by Kistler [6] in 1962. However, it has become a widespread industrial technique for strengthening commercial glass products only more recently. Today, chemically strengthened glass is truly ubiquitous, featured as an integral component of billions of personal electronic devices. One of the keys to this success has been the development of new glass compositions that are specially optimized for the ion exchange process [7–9]. Chemically strengthened glass is also finding its way into new applications such as high-strength substrates for organic electronics [10,11] and as anti-microbial substrates to help prevent the spread of infectious diseases [12].

The ion exchange process is based on immersing an alkali-containing glass in a molten salt bath containing larger alkali ions compared to what are found in the glass itself. During the ion exchange process, the smaller alkali ions from the glass are replaced by larger alkalis from the salt bath. By stuffing these larger alkali ions into sites

previously occupied by the smaller species in the glass, a compressive stress layer can be generated. This compressive stress provides a protective barrier that must be overcome before cracks can propagate in the glass [1,2].

The compressive stress profile generated through the ion exchange process is given by

$$\sigma(z) = -\frac{BE}{1-\nu} [C(z) - C_{\text{avg}}] \quad (1)$$

where E is the Young's modulus of the glass, ν is Poisson's ratio, and $C(z)$ is the local concentration of the substituting alkali ions at a penetration depth z in the glass. The prefactor $E/(1-\nu)$ converts the strain from the ion exchange process into a stress profile. In order for Eq. (1) to satisfy the force balance condition, the average concentration of the substituting cations, C_{avg} , is subtracted from $C(z)$ such that the integral of $\sigma(z)$ over the complete thickness of the glass is zero. In other words, the integrated negative (compressive) stress near the surface of the glass is exactly compensated by the integrated positive (tensile) stress in the interior so that the net force is zero [13–15]. Please note that Eq. (1) does not account for stress relaxation effects, which can act to reduce the magnitude of both compressive and tensile stresses at sufficiently high combinations of salt bath temperature and treatment time [16].

The quantity B in Eq. (1) is the linear network dilation coefficient (LNDC) [15–19], also sometimes called the “Cooper coefficient” in honor of A. R. Cooper, one of the pioneers in understanding the physics of chemically strengthened glass. The concept of the LNDC was originally proposed by Richmond et al. [20] in reference to the

* Corresponding author. Tel.: +1 607 974 2185.
E-mail address: mauroj@corning.com (J.C. Mauro).

stresses generated during the nitrogenation of metals. It can be considered as a property analogous to the thermal expansion coefficient of a material. While the thermal expansion coefficient defines the strain of a material per unit change in temperature, the LNDC gives the (linear) strain per unit change in alkali concentration, i.e., the strain per unit of alkali substitution during the ion exchange process [15]. Mathematically, the LNDC can be expressed as

$$B = \frac{1}{3} \left(\frac{1}{V} \frac{\partial V}{\partial C} \right) = \frac{1}{3} \frac{\partial \ln V}{\partial C} \quad (2)$$

where V is the molar volume of the glass.

One of the puzzling features related to the ion exchange process is the anomalous behavior of the LNDC. Specifically, when Eq. (2) is evaluated by measuring the difference in molar volume of as-melted (non-ion-exchanged) glasses between alkali end-member compositions, the value of B is always a factor of 2–4 higher than that deduced from ion-exchanged stress profiles using Eq. (1) together with measured values of E , ν , $\sigma(0)$, $C(0)$, and C_{avg} [2,19]. This so-called “network dilation anomaly” is found even in the limit of short-time salt bath treatments and therefore cannot be explained as an artifact of stress relaxation. From a technological perspective, the lower value of B for ion-exchanged glasses leads to a significantly lower compressive stress than what would be expected based on as-melted versions of the same glass compositions.

In a previous pair of studies [21,22], we performed molecular dynamics simulations of a series of alkali silicate and alkali aluminosilicate glasses to investigate the detailed atomistic origin of the network dilation anomaly. Our simulations showed that the anomalous behavior of the LNDC is a result of different local environments around alkali ions in as-melted versus ion-exchanged versions of the same glass composition. When a larger alkali ion is stuffed into a site previously occupied by a smaller alkali, the glass structure is not able to achieve its fully desired increase in molar volume, such as would occur in an as-melted version of the same composition. These results were confirmed by an independent molecular dynamics study due to Kreski et al. [23]. In our second investigation [22], we performed reverse ion exchange simulations to quantify the level of plasticity in the ion stuffing process. In these reverse ion exchange simulations, the invading alkali ions were swapped back to the original species, as in the as-melted glass. After this reverse exchange process was completed, we found that the original volume of the as-melted glass was fully recovered, indicating that strain induced by ion stuffing is entirely elastic in nature. In other words, the network dilation anomaly is the result of a failure to achieve the fully expected magnitude of elastic strain, and not a result of plasticity in the glass network as has been previously hypothesized [24–28]. Moreover, we showed that the elastic response of the glass to ion stuffing consists of instantaneous and delayed elastic contributions, both of which are fully reversible after substituting the original ions back into the ion-exchanged glass [22].

In the current paper, we extend our molecular dynamics simulations to explore three other features related to the fundamental physics of ion-exchanged glass. First, we consider the dependence of the LNDC on the concentration of alkali ions exchanged, showing that there can be a nonlinear scaling of strain as more alkali ions are exchanged. Second, we investigate the impact of ion exchange on the Young's modulus of the glass. We find that the modulus evolves non-monotonically as a result of the delayed elastic response of the glass following the initial ion substitution. This, of course, has a direct impact on the compressive stress values calculated through Eq. (1). Finally, we revisit the topic of structural differences between as-melted and ion-exchanged glasses of the same composition. In particular, here we calculate the atomic number density of various species around alkali ions to show the intrinsic differences in local environment between alkali sites before and after ion exchange.

2. Simulation procedure

For our molecular dynamics simulations, we consider a series of alkali aluminosilicate glass compositions according to the formula $x\text{Na}_2\text{O} (20 - x)\text{K}_2\text{O} 20\text{Al}_2\text{O}_3 60\text{SiO}_2$ (mol %), where $x = 0, 2, 4, \dots, 20$. These compositions have been chosen to cover the full range of alkali concentrations from pure Na_2O to pure K_2O end members. We specifically choose alkali aluminosilicates for this study since the structural and topological environment around aluminum allows for high alkali mobility while maintaining a rigid glass network [29–35]. Hence, alkali aluminosilicate glasses are the preferred choice for commercial chemically strengthened glass products.

The procedure for calculating the as-melted glass structures is similar to that of our previous study [22]. The simulations begin by placing ~20,000 atoms at random positions in a cubic simulation cell with periodic boundary conditions. The initial dimensions of the simulation cell are chosen to match experimental data in literature [36]. The “as-melted” glass structures are obtained through a stepwise quenching starting at high temperature, with combined Metropolis Monte Carlo (MC) [37] and molecular dynamics (MD) [38] that run at each temperature step. The temperature begins at 4200 K and decreases in steps of 300 K down to 900 K. From here, a reduction of 200 K brings the glass to its final temperature of 700 K, which corresponds to a typical laboratory temperature for ion exchange. At each temperature step, the MC run consists of 100 million trial moves under isobaric conditions (i.e., NPT ensemble at atmospheric pressure). The MC runs are performed using our in-house code, Molsym [39–41] with a target acceptance ratio of 0.35 for both individual atomic displacements and cell volume changes. Equilibration during each MC run is determined based on relaxation of the potential energy and volume of the system.

The output structures from the MC runs are used as input for the MD simulations, which are conducted using GROMACS [42]. Each MD run is performed under constant volume (i.e., NVT) conditions for 600 ps using a time step of 1 fs. The output from these MD simulations is then used as input for the next round of simulations at the subsequent temperature. After reaching the final temperature of 700 K, we perform another MD simulation in the NPT ensemble for 8 ns to calculate the final glass structure and molar volume of the system. We have found that a combination of MC and MD runs such as this provides an efficient and accurate procedure for calculating glass structures through atomistic level simulation [43,44]. All of the simulations are performed using the Pedone set of interatomic potentials for silicate systems [45]. Electrostatic interactions are calculated using the Wolf method [46] in the MC simulations and using particle mesh Ewald (PME) [47] in the MD part of the calculation.

After the initial “as-melted” glass is equilibrated at 700 K, the “ion-exchanged” glasses are prepared by a direct substitution of y mol % of Na with K atoms, with $y = 2, 4, 6, 8, 10, 12, 14, 16, 18$, and 20. These substitutions are followed by an MD simulation for 6 ns in the NVT ensemble and an additional 8 ns of equilibration in the NPT ensemble. The temperature is held constant at 700 K since this corresponds to a typical salt bath temperature used during the experimental ion exchange process. The calculation of the LNDC is based on the system's final molar volume before and after the Na exchange with K. Calculated values of molar volume are accurate within roughly $\pm 1\%$. Young's modulus values are subsequently calculated using stress–strain analysis [48] at a temperature of 300 K by straining the glass uniaxially until the point of fracture, allowing the dimensions of the simulation cell parallel and orthogonal to the strain direction to vary independently.

3. Results and discussion

3.1. Concentration dependence of the network dilation coefficient

We first consider the question of whether there is a dependence of the LNDC on the evolving concentration of K^+ ions during the ion

Download English Version:

<https://daneshyari.com/en/article/7902023>

Download Persian Version:

<https://daneshyari.com/article/7902023>

[Daneshyari.com](https://daneshyari.com)