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A study on ion-exchanged, soda-lime glass's residual stress relationship with K$^+$/Na$^+$ concentration

Huan Sun [ID] | Roberto Dugnani

University of Michigan – Shanghai Jiao Tong University Joint Institute, Shanghai, China

Correspondence
Roberto Dugnani, University of Michigan – Shanghai Jiao Tong University Joint Institute, Shanghai 200240, China.
Email: roberto.dugnani@sjtu.edu.cn

Abstract

In the past, studies have shown that the chemical composition within the exchanged layer could influence both the stress build-up magnitude and the stress relaxation rate. In this work, a novel approach was proposed to estimate the relationship between the stress relaxation parameters, the dilation coefficient, and the relative K$^+$/Na$^+$ concentration. The proposed method required knowledge of the residual stress profiles, the molten salt bath's temperature and soaking time, and the bath's composition. Based on the analyses performed on various residual stress profiles in ion-exchanged soda-lime glass, both the dilation coefficient and the magnitudes of the relaxation time constants were found to consistently decrease with K$_2$O concentration.

KEYWORDS
chemical strengthening, dilation coefficient, ion-exchange, residual stress, soda-lime glass, stress relaxation

1 | INTRODUCTION

In chemically strengthened glasses, residual compressive stresses are introduced near the surface during the ion-exchange process. In the course of the exchange process, the glasses are heat-treated below the glass transition temperature, T_g, in molten salt baths containing alkali ions larger than the ones originally present.[1] Although the molten salt bath's high temperature promotes ions diffusion and produces deeper exchanged layers, it could also affect negatively the strength of glasses by facilitating stress relaxation.[2]

Understanding the stress relaxation behavior and its relationship with the glass's composition is crucial to optimizing the chemical strengthening process and it is the subject of ongoing research. The stress relaxation behavior is both temperature and time-dependent, but the glass composition has also been shown to be a significant factor.[3] The dependence of soda-lime glass's (SLG) stress relaxation on the molten salt bath's temperature has been extensively studied for fixed chemical compositions and temperatures below the glass transition (ie, $T = 385°C–550°C$).[4–6] In the past, equivalent temperature-induced time shifts were utilized to adjust the stress relaxation's "master curve" function and account

for temperature variations near the T_g.[7–9] Mills and Sievert[7] proposed using a "shift factor" (log a_T) to shift the relaxation function along the logarithmic timescale. If the heat-treated material had a single relaxation time obeying an Arrhenius-type relation, the shift factor could be expressed as follows:

$$\log a_T = \frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \quad (1)$$

For SLG, when $T > T_g$, a variation of Equation(1) known as the Williams-Landel-Ferry (WLF) Equation [10] is generally used:

$$\log a_T = \frac{-C_1\left(T - T_{ref}\right)}{C_2 + \left(T - T_{ref}\right)} \quad (2)$$

In Equation(2), C_1 and C_2 are material constants, and T_{ref} the reference temperature. Regretfully, the WLF equation could compensate for temperature effects, but not for the local chemical composition.

Recently, Zheng and Mauro[11] used topological constraint theory to construct viscosity models for silicate

glasses and showed that the viscosity of various organic and inorganic glasses was a function of the composition of the glass-forming liquids. However, a simple model for the relaxation function could not be established due to the complexity of the glass-forming systems and the nonlinearity of the viscosity.

Burggraaf[12] presented various residual stress profiles for ion-exchanged, alkali-aluminosilicate glasses (ASG) induced by different treatment times. Burggraaf assumed that the relaxation time constants, τ_i, were functions of both the K_2O concentration and treatment time. Based on analyses of available stress profiles, Burggraaf concluded that the relaxation times in alkali-ASG decreased with K_2O concentration.

Shen and Green[3] studied the viscosity and the stress relaxation behavior of mixed-alkali lime-silicate glass (0.01 mol% ~15.5 mol% K_2O, $K_2O + Na_2O \approx 14.3$ mol%) below $T_g = 580°C$. The viscoelastic response was estimated by three-point bending in the temperature range 450°C-550°C, and by uniaxial, compressive stress relaxation tests at 550°C. The viscosity of the "as-melted" glasses was reported to increase with K_2O concentration for K_2O in the range 1.9-15.5 mol%.

Yu et al[13] generated molecular dynamics (MD) simulations to estimate the dynamics of relaxation in ASG with different alkali concentrations at room temperature and pointed out that the relaxation behavior was strongly affected by the chemical composition. ASG containing 8 mol% K_2O and 8 mol% Na_2O showed more volume relaxation than potassium-free sodium glass (16 mol% Na_2O).

Recently, Ragoen et al[14] provided direct evidence that the stress relaxation in silicate glasses was affected by the concentration of the exchanged potassium. Nuclear magnetic resonance was used to study the structure of ion-exchanged silicate glass (binary Na-silicate and ternary Na, Mg-, Na, Ba-, and Na, Ca-silicate), and it was found that by increasing the exchanged potassium content, the distance of Na–O bonds decreased and the Si–O bond angle increased. Ragoen et al suggested that both the contraction of Na–O and the opening of the Si–O bond angle could better accommodate the K^+ and hence induce stress relaxation.

Although various studies in the literature indicated that the chemical composition of exchanged silicate glasses could influence the stress relaxation behavior, no direct method to establish such compositional effects presently exists. Currently, the compositional effects are either inferred through MD simulations[13] or estimated by stress relaxation tests in "as-melted" materials.[3] In this work, a novel approach to estimate the relationship among the glasses' local, chemical compositions, and both the relaxation time constants and the dilation coefficient in ion-exchanged glasses is presented. The method requires knowledge of the residual stress profile, the molten salt bath's temperature and soak time, and the bath's composition.

1.1 | Residual stress profile

A commonly used expression to describe the residual stresses induced by the ion-exchange process is Sane and Cooper's[4] equation:

$$\sigma(x,t) = -\int_0^t \left(\frac{E}{1-v}\right) R(t-t') \frac{\partial}{\partial t'} \{B \cdot (C(x,t') - \langle C(t')\rangle)\} dt' \quad (3)$$

In Equation(3), $C(x, t')$ is the ionic concentration near the surface, $\langle C(t')\rangle$ is the average cross-sectional ionic concentration, $R(t)$ is the material's stress relaxation function, B the dilation coefficient, E the Young's modulus, and v the Poisson ratio. B, E, and v are often assumed constant, although variations of these parameters with compositions should be expected. For SLG, the ionic concentration, $C(\alpha)$, is well approximated by the expression:

$$C(\alpha) = \Delta C \cdot erfc(\alpha) + C_0; \quad \alpha \equiv \frac{x}{\sqrt{4Dt}} \quad (4)$$

C_0 is the ionic concentration of the untreated glass, ΔC to the difference between the surface's K_2O concentration and C_0, x the depth from the surface, t the soaking time, and D the effective ionic inter-diffusion coefficient. The inter-diffusion coefficient, D, was assumed to follow an Arrhenius relationship, hence:

$$\ln(D) = \ln(D_0) - \frac{E_a}{RT} \quad (5)$$

where $D_0 \, (m^2/s)$ is a material constant, E_a (J/mol), the activation energy, R (8.314 J mol^{-1} K^{-1}) the universal gas constant, and T (K) the temperature of the molten salt bath.

For a fixed composition, a widely used model to describe the stress relaxation behavior is the generalized Maxwell's model[15]:

$$R(t) = \sum_{i=1}^N A_i e^{\frac{-t}{\tau_i}}; \quad \sum_{i=1}^N A_i = 1 \quad (6)$$

A_i are the weight factors, and τ_i the relaxation times. Both A_i and τ_i are functions of the chemical composition and temperature.

1.2 | Relaxation models and analytical solution

This section presents three methods described in the literature to estimate the residual stress profiles in silicate glasses. Shen and Green[16] evaluated Equation(3) numerically to estimate the residual stress profiles in ion-exchanged SLG. The viscosity of the glass was assumed to be linearly related to the K_2O concentration. Uniaxial, compressive stress relaxation

tests at various temperatures (450°C-550°C) were performed to generate the stress relaxation functions for the relevant glass compositions (K_2O concentration: 0.01-15.5 mol%). Based on stress relaxation tests, the approximate relationships between the relaxation time constants and the K_2O concentration for "as-melted" glasses were obtained.

Dugnani[17] solved analytically Sane and Cooper's integral equation hence allowing a more accurate estimation of residual stress profiles from empirical data. The dilation coefficient, B, was assumed constant and the stress relaxation function was described by the Prony series; composition-dependent relaxation time constants were considered. Dugnani's closed-form description of the residual stresses could be regressed to measured residual stress profiles and directly solve for the unknown parameters. Like in Shen and Green,[16] in Dugnani it was assumed that τ_i were linear functions of the chemical composition:

$$\tau_i(\alpha) = \tau_{0,i}\left[1 + \chi_{0,i} \cdot erfc(\alpha)\right] \tag{7}$$

$\tau_{0,i}$ referred to the relaxation times of the bulk glass, and $\chi_{0,i}$ were constants relating the relaxation times to the ionic concentration. In Dugnani, the residual stress profile for the concentration-dependent relaxation model, was approximated by:

$$\sigma(x,t) \approx \sigma(x,t)\big|_{\tau_{0,i}} + \Delta\sigma\left(\alpha, \xi_i, \chi_{0,i}\right) \tag{8}$$

The first term of the Equation(8) was the stress profile computed using the relaxation time constants corresponding to the chemical composition at the core of the glass:

$$\sigma(x,t)\big|_{\tau_{0,i}} \approx -\frac{B \cdot E}{1-v} \cdot \Delta C \cdot \sum_i A_i \cdot \exp\left(-\xi_i^2\right)\left\{\cos\left(2\alpha\xi_i\right)erfc(\alpha) + \frac{e^{-\alpha^2}}{\pi\alpha}\sin^2\left(\alpha\xi_i\right) + \frac{4}{\pi}\sum_{k=1}^N\frac{e^{-\left(\alpha^2+k^2/4\right)}}{k^2+4\alpha^2}\cdot\alpha\left[\cosh\left(k\xi_i\right) - \cos\left(2\alpha\xi_i\right)\right]\right\} \tag{9}$$

where $\xi_i = \sqrt{\frac{t}{\tau_{0,i}}}$. The second term in Equation(8), $\Delta\sigma$, was an adjustment to account for the variable ionic concentration within the exchanged layer:

$$\Delta\sigma\left(\alpha, \xi_i, \chi_{0,i}\right) \approx \begin{cases} -\frac{BE\Delta C}{1-v}A_i\frac{\chi_{0,i}}{2}e^{-\xi_i^2}\left\{e^{4\alpha^2\xi_i^2}\xi_i^2 + \alpha\xi_i\sqrt{\pi}\left(1-2\xi_i^2\right)erfi\left(2\alpha\xi_i\right)\right. & \\ \left. -\alpha\xi_i\left[2e^{\xi_i^2}\xi_i - \sqrt{\pi}\left(1-2\xi_i^2\right)erfi\left(\xi_i\right)\right]\right\} & \text{for } 0 \leq \alpha < 0.5 \\ 0 & \text{for } 0.5 \leq \alpha \end{cases} \tag{10}$$

Equation(8), was shown to estimate the stresses within 2.2% from the numerically computed solutions when the surface relaxation time $\tau_s \leq 3\tau_0$ (τ_s was the relaxation time constant at the glass's surface).

Seaman et al[1] computed the residual stress profiles in ion-exchanged SLG by assuming that the dilation coefficient, B, was constant and that the stress relaxation was a diffusion-controlled process aided by water vapor. Seaman et al analyzed Sane and Cooper's[4] set of 27 residual stress profiles obtained from direct, photoelastic measurements. The samples analyzed were SLG plates soaked for 0.25-288 hours in molten salt bath at temperatures in the range 385°C–490°C. The newly defined "stress relaxation diffusion coefficient", D_s, was introduced by Seaman et al and its magnitude estimated through the relationship $x_m = 2\sqrt{D_s t}$, where x_m was the depth of the compressive stress's peak, and t the treatment time. The stress relaxation was assumed to intensify with increasing water vapor-pressure though the relationship:

$$\tau_i = \tau_{0,i}\exp\left\{-C_{s_0}^*\,erfc\left(\frac{x}{\sqrt{4D_s t'}}\right)\right\} \tag{11}$$

$C_{s_0}^*$ referred the normalized water concentration at the surface of glass, and t' the time from when the strain contribution was imposed to the final treatment time. By combing the water concentration-dependent model to Equation(3), Seaman et al were able to reproduce the relevant features of the stress profiles reported by Sane and Cooper.

The objective of this study was to provide an effective methodology to estimate the relationship between the residual stress and the chemical composition in ion-exchanged SLG below the glass transition temperature. In the past, the task has been carried out through numerous stress relaxation mechanical tests on "as-melted" glasses of various compositions.[3] Since "as-melted" glasses often display physical properties that differ from ion-exchanged glasses with the same composition, this work attempted to directly derive such relationship by analyzing the stress profiles of the ion-exchanged glasses.

1.3 | Ion-exchanged material properties

When assuming E and B constant in Equation(3), undesirable errors might be introduced in the estimations of the residual stress profiles. Shen and Green[3] considered variations in the chemical composition of the Young's modulus using the Makishima and Meckenzie model[18] for "as melted" glasses and determined that a reduction in the Young's modulus of approximately 10% should be experienced during the

ion-exchange of SLG. More relevant experimental results by Puentes et al[19] using SAW waves on ion-exchanged SLG glass, suggested that the reduction in E only amounted to approximately 2.9%. Similarly, Kreski[20] compared the elastic moduli and Poisson's ratios of SLG 'host' and 'stuffed' glasses obtained thorough MD simulations and found that, after the K^+ ion-exchange, E decreased by 1.6% whereas ν was nearly unaffected.

The physical origin and magnitude of the network dilation coefficient, B, remain subjects of debate in the literature. The experimental work of Tsutsumi et al[21] on the swelling of Na^+-K^+ exchanged SLG waveguides suggested a relative constant value of B for KNO_3 bath temperatures in the range 350°C-440°C. Similarly, the experimental work conducted by Fu and Mauro[22] showed that in SLG, B marginally increased with K_2O diffusion. It should be noted that Fu et al's calculations used core glass values for E and ν to estimate B. Furthermore, Fu and Mauro estimated the compressive stress at the glass's surface using the FSM-6000 but no details on the ray-tracing assumptions made by the device's software to estimate the surface stress were provided. Mauro et al[23] showed that in some silicate glasses, B increased by as much as 15% during the Na^+-K^+ exchange yet no specific values for the concentration of the ionic species in the ion-exchanged glasses were provided. MD simulations by Kreski et al[24] and Tandia et al[25] on $x Na_2O \cdot (20-x) K_2O \cdot 80 SiO_2$ (mol%) binomial glasses, suggested that, B might increase with K_2O content. Finally, Shen and Green[16] studied ion-exchanged SLG by numerically fitting experimentally obtained, residual stress profiles and suggested that B should decrease with K_2O concentration.

2 | METHOD

"As-melted" glasses have been shown to display physical properties distinct from those of the ion-exchanged glass.[26] In this section, two methods are introduced to estimate the composition-dependent relaxation-constants and dilation coefficient by studying ion-exchanged residual stress profiles rather than by the direct mechanical testing of "as-melted" glasses with the same chemical composition. The relaxation-constants and dilation coefficient were first obtained by analyzing Sane and Cooper's[4] coarse yet extensive, experimental residual stress profiles and subsequently validated using the more detailed stress profiles for SLG reported by Shen and Green[16] and by Abrams.[27] The oxide compositions of the glasses considered in this work are summarized in Table 1.

The first method (referred to as the "master-curve approach") obtained the relationships between the dilation coefficient/time constants and the local chemical composition by regressing all the stress profiles (after shifting the value

TABLE 1 Oxide concentration (wt%) and T_g for the SLG samples analyzed

Oxide Components	Mills and Sievert[7]	Shen and Green[16]	Sane and Cooper[4]	Abrams[27]
SiO_2	71	71	74	72
Na_2O	15	14.7	12.9	13.9
Al_2O_3	1.5	0.1	1.8	0.7
CaO	8	11.8	6.8	11
MgO	4.5	1.7	4.5	0.1
SrO	—	0.3	—	0.1
Others	—	0.4	—	2.2
T_g(°C)	536	580[a]	520[b]	580[a]

[a]T_g = 580°C in Wereszczak and Anderson.[28]
[b]T_g = 520°C in Li et al.[29]

at T_{ref} = 450°C) for different K_2O concentration through the master relaxation function. The second method consisted in directly regressing the residual stress vs α profiles through a newly derived, analytical description of the stress relaxation behavior which considered both concentration-dependent B and τ_i.

2.1 | Master-curve approach (method I)

This section describes the steps undertaken to estimate the relationship between the ion-exchanged glass composition and the dilation coefficient/relaxation time constants. The method assumed that both the stress profiles and the molten salt bath's composition/temperature histories were known:

Step 1: Equation (5), was used to compute the interdiffusion coefficient, D, at the molten salt bath's temperature considered. The corresponding diffusion-depths, α, were then calculated for each stress profile at constant temperature.

Step 2: Approximate stress vs time curves were constructed from the residual stress vs α profiles in step 1, by considering discrete values of α (ie, α = 0, 0.25, 0.5, 0.75, 1, 1.25, and 1.5). In most cases, the residual stresses at the α of interest had to be interpolated from the available discrete data sets.

Step 3: For each α considered, master curves at the reference temperature (arbitrarily chosen as T_{ref} = 450°C) were constructed by applying the shift factor function, ie, Equation(13), to the stress relaxation data obtained in step 2. Subsequently, each master relaxation curve was regressed to Equation(16) and the stress relaxation time constants and dilation coefficient at selected K_2O concentrations were computed.

2.1.1 | Stress vs α

In this section, the methodology followed to estimate the interdiffusion coefficient, D, and the residual stress vs α profiles, is

described. Sane and Cooper[4] reported $D = 0.027$ μm^2/min at 400°C for SLG in a KNO_3 bath with 0.5% Na_2O. Regretfully, additional information was necessary to fully relate D to T. In this work, SLG glasses with similar compositions to the one used by Sane and Cooper were used to help establish the relationship between D and T.

Saggioro and Ziemath[30] estimated the K^+-diffusion coefficient ($D = 0.6$ μm^2/min) from the K_2O concentration profiles obtained for float glass soaked in molten KNO_3-bath at 565°C. Karlsson[31] provided the K^+-diffusion coefficients at different temperatures (460°C-520°C) for float glass in KNO_3/KCl mixture bath (coefficients calculated from concentration vs depth profiles). Patschger and Rüssel[32] measured the average K^+-diffusion coefficient ($D = 0.127$ μm^2/min) at 470°C from concentration profiles in SLG soaked in various KNO_3/$NaNO_3$ bath mixtures (KNO_3 range 50-100 mol%). Sinton et al[33] soaked SLG into a KNO_3 melt at 450°C and reported $D = 0.07$ μm^2/min form K^+ concentration profiles. Fu and Mauro[22] immersed SLG samples in 100% KNO_3 salt bath at 410°C for 8 hours, at 370°C for 16 hours, and at 450°C for 4 hours and measured D for each condition ($D = 5.3 \times 10^{-3} \mu m^2$/min at 370°C, $D = 0.027$ μm^2/min at 410°C, and $D = 0.082$ μm^2/min at 450°C). Gy[34] provided normalized K_2O concentration profiles for SLG soaked for 72 hours in KNO_3 salt bath at various temperatures (420°C, 460°C, and 490°C). In addition to the interdiffusion coefficients estimated from the literature, in this work D at $T = 385$°C was estimated from the residual stress profile ($t = 4$ hours) in Sane and Cooper[4] since for $T \ll T_g$ negligible stress relaxation was expected to occur:

$$\sigma(x,t) \approx -\frac{B \cdot E \cdot \Delta C}{1-v} erfc\left(\frac{x}{\sqrt{4Dt}}\right) \text{ for } T << T_g \quad (12)$$

Mauro et al[23] studied the temperature dependence of the mutual diffusivity for three compositions of silicate glasses and showed that in all cases the activation energy was nearly constant (ie, $E_a = 107.9$ kj/mol). Since the activation energy reported by Mauro et al's was similar to the values reported in the literature for SLG,[35–37] such value was adopted in this work and D_0 was subsequently estimated by regressing the data gathered from the literature. Once an approximate expression relating D to T was obtained, the non-dimensional diffusion depth, α, was evaluated based on Equation (4).

2.1.2 | Stress relaxation curves

In this section, the procedure used to obtain the stress relaxation function based on known stress profiles is described. Since $\alpha \equiv \frac{x}{\sqrt{4Dt}}$, when both α and T were constant and x was known, the soak-time, t, was the only unknown variable. The

residual stress vs α curves at constant temperature were first interpolated to obtain the stresses at arbitrarily chosen values of α (Figure 2). Subsequently, the stress vs time curves at T_{ref} (ie, the "master curve" for a fixed α) were constructed by applying the appropriate shift factor to all curves sharing the same α. Finally, each individual master curve was regressed to obtain the dilation coefficient and the stress relaxation constants as a function of α as described in the following section.

2.1.3 | Master stress relaxation function

In order to investigate the stress relaxation time constants, $\tau(\alpha)|_{T_{ref}}$, dependence on the K_2O concentration (and nominally eliminating the effects of temperature), the master relaxation curves had to be obtained at $T_{ref} = 450$°C. This task was accomplished by following the methodology outlined by Mills and Sievert[7] and Eisenberg and Takahashi.[8] Although for $T > T_g$ the shift factor, $log_{10} a_T$, was accurately described by the WLF Equation,[10] for $T < T_g$, a modified equation has been shown to be more appropriate:[38]

$$log_{10} a_T = -0.0244\Delta T + 0.697 \quad \text{for } 0.7 < \frac{T}{T_g} < 0.9 \quad (13)$$

The temperature in Equation (13) was expressed in °C and $\Delta T \equiv T - T_g$. The residual stress vs time curves at different temperature (385°C–490°C) were used to construct one individual stress relaxation master curve at the reference temperature for all the α considered. Two-terms, Prony series were chosen to describe the stress relaxation in SLG, as also in Dugnani[17] and Shen and Green:[5]

$$R(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (14)$$

The relationship could be further simplified as for small changes in the glass's chemical composition at constant temperature, the ratio τ_2/τ_1 has been shown to be nearly constant:[38]

$$\frac{\tau_2}{\tau_1} = \frac{\tau_{0,2}}{\tau_{0,1}} = \frac{\tau_{0,2}\left(1+\chi_2 erfc(\alpha)\right)}{\tau_{0,1}\left(1+\chi_1 erfc(\alpha)\right)} = k \quad (15)$$

It followed that the proportionality constants describing the relationship between the time constants and the concentration were nearly identical, that is, $\chi_1 = \chi_2$. Sun et al[38] estimated that at 450°C $A_1 = 0.23$; $A_2 = 0.77$; $k = 0.03$. By indicating as, σ_0, the hypothetical residual stress in the absence of relaxation, and combining Equation(14), Equation(15), and the values of A_1, A_2, and k, from Sun et al,[38] the stress relaxation function for ion-exchanged SLG at 450°C was obtained:

$$\sigma(t) = \sigma_0(\alpha) \cdot \left(0.23 e^{-\frac{t}{\tau_1(\alpha,450°C)}} + 0.77 e^{-\frac{t}{0.03\tau_1(\alpha,450°C)}}\right) \quad (16)$$

The values of τ_1, τ_2, and σ_0 were estimated for selected $\alpha's$ by regressing the master stress relaxation curve at T_{ref}, through Equation(16). Although A_1, A_2, and k were assumed constant,[38] $\sigma_0 = \frac{B(\alpha) \cdot E}{1-\nu} \cdot \Delta C$ was a function of α. Assuming both E and ν as approximately constants[19,20] (ie, $E = 65.1$ Gpa, $\nu = 0.22^5$), then $B(\alpha)$ could be easily estimated.

2.2 | Direct regression (method II)

The second method to obtain the dilation coefficient and the time constants consisted in regressing the stress vs α profiles (or stress vs x) through a newly derived analytical solution based on Dugnani's equation, that is, Equation(8), but improved by considering the concentration depend-ent, $B(\alpha)$. In Dugnani's work, the residual stress profile generated by the composition-varying time constants, that is, Equation(8), consisted of two terms: the first term de-scribed the solution to a composition-invariant relaxation time constant, $\sigma(x,t)|_{\tau_{0,i}}$, and the second (approximate) term accounted for the effects of variable chemical-composi-tion, $\Delta\sigma(\alpha, \xi_i, \chi_{0,i})$. Like for method I, $A_1 = 0.23$, $A_2 = 0.77$, and $k = 0.03$ were also assumed. For simplicity, $B(\alpha)$ was assumed to linearly depend on the exchanged K_2O concentra-tion, ie, $B(\alpha) = B_0 \{(1 + k_B \cdot \Delta C \cdot erfc(\alpha)\}$, where B_0 refers to the linear network dilation coefficient at the bulk of the ion-exchanged SLG. Combining Equation(3) and Equation(4) with the assumed expression for $B(\alpha)$:

$$\sigma(x,t) = -\int_0^t \left(\frac{EB_0\Delta C}{1-\nu}\right) R(t-t') \frac{\partial\{erfc(\alpha)\}}{\partial t'} dt'$$
$$-k_B\Delta C \int_0^t \left(\frac{EB_0\Delta C}{1-\nu}\right) R(t-t') \frac{\partial\{erfc(\alpha)^2\}}{\partial t'} dt' \quad (17)$$

The approximation $erfc(\alpha)^2 \approx erfc(1.7\alpha)$ was used to sim-plify Equation(17), which could then be integrated analyti-cally (see Appendix):

$$\sigma(x,t) \approx \sigma(x,t)|_{\tau_{0,i}} + \Delta\sigma(\alpha, \xi_i, \chi_{0,i})$$
$$+ k_B\Delta C \{\sigma(1.7\alpha)|_{\tau_{0,i}} + \Delta\sigma(1.7\alpha, \xi_i, \chi_{0,i})\} \quad (18)$$

For the direct regression method, the residual stress vs α curves for six soaking-times ($1hr$-$48hrs$) at 450°C reported by Sane and Cooper were considered. Each stress profile was individually regressed to Equation(18), where $\Delta\sigma$ was calcu-lated using Equation (A.6) and the optimal k_B, $\chi_{0,i}$ and $\tau_{0,1}$, were obtained for each soaking-time.

2.3 | Method I validation

The validation of Method I could only be carried out in-directly by comparing the behaviors of the predicted and corresponding experimental stress profiles. First, the ex-pected residual stress profiles for various soak-time and temperatures presented in the literature were computed

using the parameters optimized through Sane and Cooper's reported data, and subsequently qualitatively compared to the experimental stress profiles found in the literature for the same conditions. Three residual stress vs α (soak-ing time 1 and 48 hours) reported in the work of Shen and Green[16] and Abrams[27] were used in the comparisons. Detailed results of the comparison are shown in the fol-lowing section.

3 | RESULTS

In the first part of this section, an approximate equation de-scribing the interdiffusion coefficient, D, for SLG, is pre-sented and used to generate the residual stress vs α profiles for Sane and Cooper's residual stress data. In the second part, the approximate relaxation master curves for SLG at 450°C are obtained and both the dilation coefficients and the relaxation times vs K_2O estimated. Finally, the pre-dicted stress profiles using the time constants obtained in method I are validated by directly comparing them to various experimentally determined residual stress profiles from the literature.

3.1 | D and residual stresses

Figure 1 shows $ln(D)$ vs $1/T$ for various SLG cases reported in the literature.[4,22,30,32–34,39] The figure also shows the ex-pected trend obtained through regression analysis:

$$\ln(D) = -\frac{13000}{(T+273)} + 15.3 \quad (19)$$

In Equation (19) $D_0 = 4.4 \times 10^6 \ \mu m^2/min$; D was ex-pressed in μm²/min, and the temperature in °C.
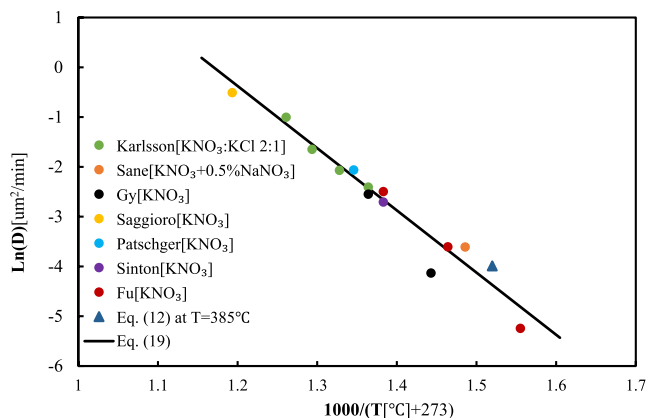

FIGURE 1 *Ln(D)* vs the reciprocal of the molten bath-temperature, *1/T*, in SLG based on values reported in the literature[4,22,30,32–34,39] and regressed through equation Equation (19) (solid line) [Color figure can be viewed at wileyonlinelibrary.com]
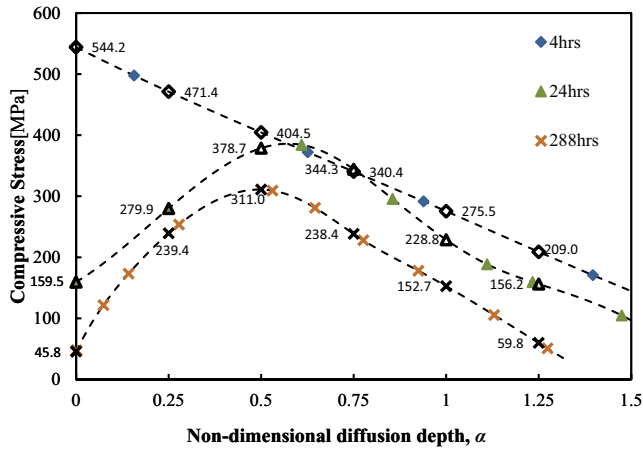
FIGURE 2 Residual compressive stress vs α in SLG for three ion-exchange times (4, 24, and 288hrs); $T = 425°C$; hollow marks: interpolated values [Color figure can be viewed at wileyonlinelibrary.com]

Figure 2 shows an example of residual stress vs α at 425°C based on Figure1C from Sane and Cooper.[4] The residual-stresses corresponding to $\alpha = 0$, 0.25, 0.5, 0.75, 1, 1.25 and 1.5

were approximated by interpolating the experimental values provided in the reference (hollow black-markers). Similarly, for other ion-exchanged temperatures (385°C–490°C), the residual stresses corresponding to the α's of interest were obtained by interpolation (not shown).

3.2 | Master curves

In this section, the master relaxation curves at 450°C for the SLG stress profiles considered are presented. The residual stress vs time from Sane and Cooper (after applying the appropriate time-shifts) and the corresponding regressed curves, that is, Equation(16), are displayed in Figure 3A through (F) for $\alpha = 0$, 0.25, 0.5, 0.75, 1, and 1.25.

3.3 | Concentration-dependent relaxation

In this section, the stress relaxation time constants, τ_i, obtained through the master-curve approach (method I) and through direct regression (method II) are qualitatively compared to the values obtained by Seaman et al's model. Table
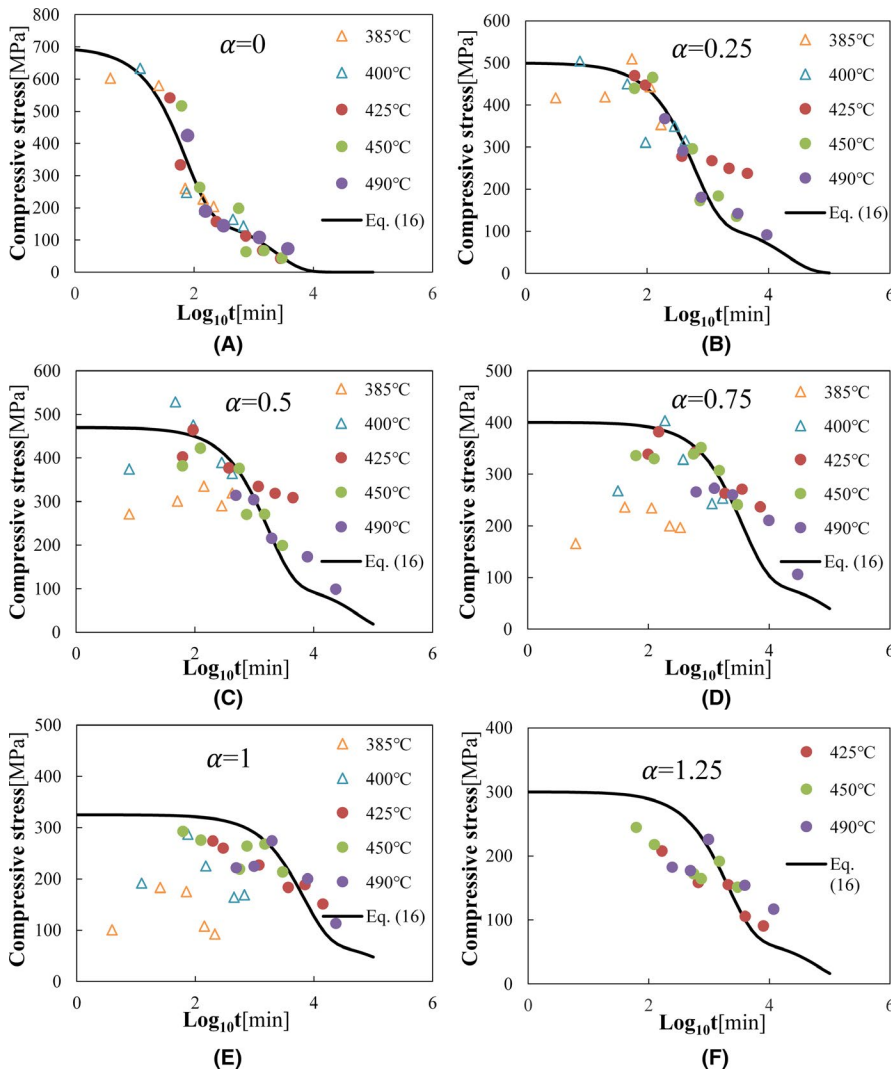

FIGURE 3 Residual compressive stress vs $Log(t)$ (after applying the appropriate shift factors) from Sane and Cooper,[4] and master stress relaxation functions at 450°C for (A) $\alpha = 0$, (B) $\alpha = 0.25$, (C) $\alpha = 0.5$, (D) $\alpha = 0.75$, (E) $\alpha = 1$, (F) $\alpha = 1.25$ [Color figure can be viewed at wileyonlinelibrary.com]
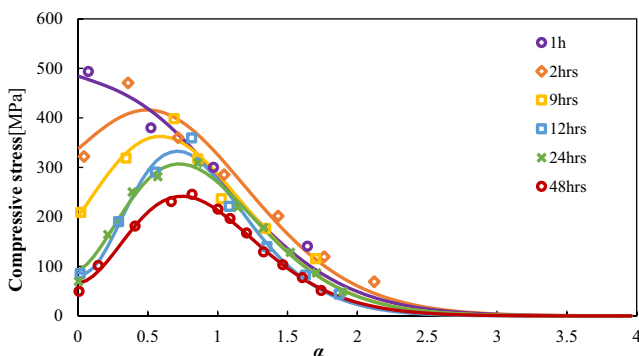
TABLE 2 Time constant, τ_1, and dilation coefficient, B, vs α (T = 450°C, method I)

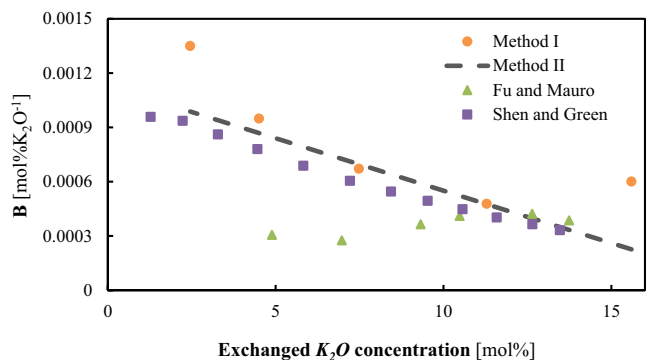| α	0	0.25	0.5	0.75	1
τ_1 (min)	2400	20 000	71 000	57 000	120 000
B (mol% K_2O^{-1})	0.00060	0.00048	0.00067	0.00095	0.00135

2 summaries the relaxation time, τ_1, and B obtained by regressing the master stress relaxation curves derived from Sane and Cooper[4] at 450°C as described in the previous section (method I).

Six residual stress profiles (soaking-time between 1 and 48hrs) at 450°C reported by Sane and Cooper[4] were directly regressed through Equation(18) to obtain the stress relaxation parameters at the same temperature as in method I. The fitting parameters were allowed to vary within a reasonable range estimated based on the limiting cases obtained by method I, ie, 5000 minutes $< \tau_{0,1} <$ 150 000 minutes, $-1 < \chi_{0,i} < -0.7$, 0.001 mol% $K_2O^{-1} < B_0 <$ 0.0015 mol% K_2O^{-1}, and -0.06 mol% $K_2O^{-1} < k_B < -0.03$ mol% K_2O^{-1}. Other unknowns such as D and k could vary within $\pm20\%$ from the nominal values to account for experimental errors, measuring errors, and glass composition variations among different sets. Figure 4 shows examples of residual stress vs α at 450°C for different soaking time (circular markers, 1-48hours) as well as the analytical solutions optimized by regression (solid lines). The values of α in the plot were obtained using $D = 0.07 \mu m^2/min$ for T = 450°C. The average values of regressed parameters were $\chi_{0,i} = -0.8$, $k_B = -0.05$ mol% K_2O^{-1}, $B_0 = 0.0011$ mol% K_2O^{-1}, and $\tau_{0,1} = 100 000$ minutes.

Although only approximately 90% of the K^+-ions are exchanged in SLG, in this work, for simplicity, it was assumed that K^+-ions replaced all Na^+ ions at the surface of the ion-exchanged glass. Hence by substituting $\Delta C = 15.6$ mol% and $C_0 = 0.6$ mol% into Equation(7), a function for $\tau_i(\alpha)$ was obtained. Figure 5 shows the normalized relaxation times, $\tau_i/\tau_{0,i}$ versus K_2O concentration at 450°C obtained by method I, by

method II, and by Seaman et al's model. For method I, the values of τ_1 appeared to decrease nearly linearly with K_2O concentration. For Seaman et al's model, $C^*_{(s_0)} = 2.3$, $D_s = 8.3 \times 10^{-12} cm^2/s$,[1] and $D = 1.3 \times 10^{-11}$ cm^2/s at T = 450°C (based on Equation(19)), and $\frac{\tau_i}{\tau_{0,i}} = \exp\{-2.3 erfc(1.2\alpha)\}$ according to Equation(11). Figure 6 shows the dilation coefficient, B vs K_2O concentration at
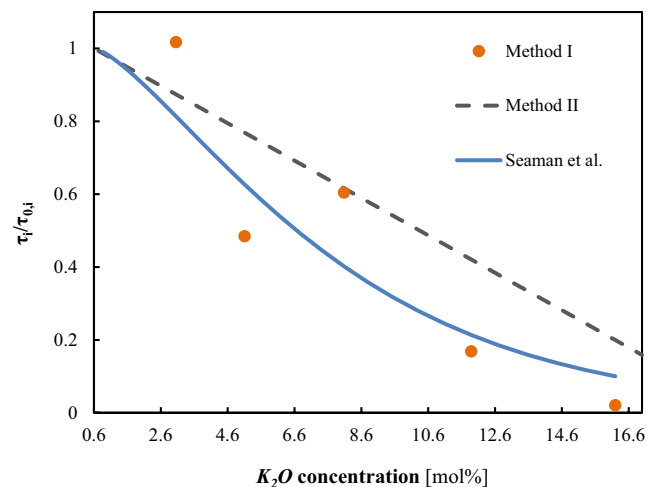
FIGURE 5 Normalized stress relaxation time constants vs K_2O concentration at $T = 450°C$ for Sane and Cooper's[4] ion-exchanged SLG, based on Method I (circular markers), Method II (dotted line), and Seaman et al's model[1] (solid line) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Residual compressive stress vs α at T = 450°C for Sane and Cooper[4] ion-exchanged SLG (1-48 h) and corresponding analytical solutions (solid lines) regressed though Equation (18) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 6 Dilation coefficient B vs K_2O concentration for ion-exchanged SLG based on the analyses of Sane and Cooper's stress profiles[4] at $T = 450°C$ (Method I, circular markers; Method II, dotted line); the experimental results of Shen and Green[16] ($T = 450°C$, square markers) and Fu and Mauro[22] ($T = 370-450°C$, triangular markers) are also shown [Color figure can be viewed at wileyonlinelibrary.com]

450°C estimated by method I and by method II. For comparison, in the figure are also shown B vs K_2O concentration in SLG as reported by Shen and Green[16] (after applying the appropriate change of units) and by Fu and Mauro.[22]

3.4 | Method I validation

The time constants obtained by the master-curve's approach (method I) analyzing Sane and Cooper's data were validated by comparing the predicted stress profiles to the experimentally determined stress profiles on SLG reported by Abrams[27] and Shen and Green.[16] When regressing the experimental data, the difference between the bath's temperature and the glass transition temperature, ΔT, was allowed to vary within $\pm 20°C$ from the nominal values obtained in method I, to account for inaccuracies in both T_{ref} and T_g. D was also allowed to vary within $\pm 20\%$ from the expected value obtained from the literature survey. Also $-1 < \chi_{0,i} < -0.7$ was estimated from the limiting cases obtained in method I, and similarly $5200\,minutes < \tau_{0,1} < 150\,000\,minutes$ was expected based on method I. The results of the regression analyses indicated $\Delta T = -110°C, \chi_{0,i} = -1, k_B = -0.03\,mol\,K_2O\%^{-1}, B_0 = 0.0011\,K_2O\,mol\%^{-1}$ and $\tau_{0,1} = 10\,000\,min$ best fitted Abram's[27] $48hrs$-soaking and Shen and Green's 48 hour-soaking stress profiles; $\Delta T = -140°C, \chi_{0,i} = -0.7, k_B = -0.04\,mol\,K_2O\%^{-1}, B_0 = 0.008\,mol\,K_2O\%^{-1}$, and $\tau_{0,1} = 15\,000\,minutes$ best fitted Shen and Green's[16] $1hr$-soaking. The expected ΔT for all samples was $-130°C$ based on $T_g = 580°C$.[28]

4 | DISCUSSION

In this work, the relationship between the residual stress profile and the K_2O concentration in ion-exchanged SLG was investigated by analyzing residual stress profiles through the master stress relaxation approach and direct analytical regression. In the proposed approaches, the material behavior was inferred directly from ion-exchanged SLG rather than from "as-melted" samples since the latter had been shown to display different properties than ion-exchanged glasses.[26] Moreover several mature and relatively accurate techniques exist to measure residual stress profiles in ion-exchanged SLG.[27,34,38,40]

To implement the proposed methods, the inter-diffusion coefficients, D, at all temperatures considered had to be known. Regretfully, the relationship between D and T was not fully established in the work of Sane and Cooper, hence in this work an approximate, working relationship was obtained from a broad literature survey.[4,22,30,32–34,39] Although Equation(19) fitted the available data reasonably well as shown in Figure 1, the use of "typical" values of D in the calculations was expected to introduce some systematic errors in the analysis.

Method I required knowledge of the residual stress at specific α-values. To achieve this task, interpolation of the stress profiles was used as shown in Figure 2. This step was required as fixed α's were needed to obtain equivalent constant K_2O concentration curves. Then, for each fixed K_2O concentration curve, the master stress relaxation curves were constructed at the reference temperature ($T_{ref} = 450°C$) by applying the appropriate shift factors, that is, Equation(13). Notably, the shift factor approach would not be required if the stress profiles had been obtained at the reference temperature. Finally, the parameters describing the stress relaxation master curves were obtained by regressing the stress relaxation data through Equation(16).

As apparent from Figure 3, the residual stress measurements at the lower soaking bath temperatures (T = 385°C and 400°C) were inconsistent with the trends predicted at higher temperatures. The lack of consistency could be explained by the fact that, at low temperatures, the signal-to-noise ratio was very low. An alternative explanation could be that different tested batches might have had bath's chemical-concentrations deviating from the nominal values (or be poisoned by water as suggested by Seaman et al) thus affecting the magnitude of σ_0.

The main benefits of method I over direct regression were that a larger set of data could be concurrently used in the estimations and that no assumptions had to be made about the nature of the relationship between the relaxation time constants and the ionic concentration. Nonetheless, method I was found to be imprecise when considering low chemical concentrations of the exchanged species as the signal-to-noise ratio was low. Additionally, some inaccuracies might be introduced at high chemical concentrations due to the inherited difficulties in measuring the residual stresses near the free surface of the glass. The residual stress profiles of the ion-exchanged SLG in the work of Sane and Cooper,[4] which were analyzed in this work, were estimated by photoelasticity. Photoelasticity consisted in observing and measuring the location of fringes under a polariscope[41] and the method was expected to be relatively inaccurate near the free surface of the glass.[1]

Considering the limited accuracy and coarse description of the stress profiles in the work of Sane and Cooper,[4] the experimental residual stresses by Abrams[27] and Shen and Green[16] were used to indirectly validate the correctness of the parameters obtained in method I. A novel analytical equation considering both concentration-dependent B and τ, that is, Equation(18) was used to regress the residual stress profiles. In all cases the predicted and reported residual stress profiles were in excellent agreement, as shown in Figure 7 (solid lines) strongly suggesting that both the methodology and results obtained in this work were reasonably sound. The results also stress the importance of
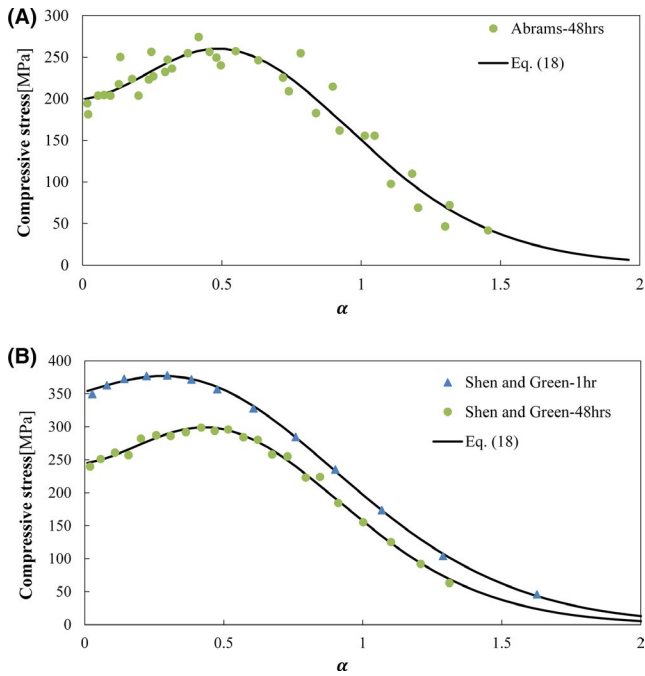
FIGURE 7 Predicted residual compressive stress vs α for SLG at T = 450°C based on Equation (18) (solid line) for (A) Abrams[27] 48 h-soaking, and (B) Shen and Green[16] 1 h and 48 h-soaking [Color figure can be viewed at wileyonlinelibrary.com]

considering non-constant B when estimating ion-exchanged SLG's stress profiles.

Method II estimated the relaxation function by direct regression of the residual stress-profile at 450°C reported by Sane and Cooper[4] as shown in Figure 4. The values of $\tau_{0,1}$, $\chi_{0,i}$, and k_B obtained from the stress profiles yielded marginally different results depending on the exchanged-time ($1hr$-$48hrs$). It was found that $\tau_{0,1}$ was between 40 000 and 150 000 minutes; also $-1 < \chi_{0,i} < -0.7$ and $-0.06\text{mol}\%$ $K_2O^{-1} < k_B < -0.03$ mol% K_2O^{-1} for the six stress profiles considered. The relatively large variations for the fitted parameters could be mostly attributed to the very coarse residual stress profiles reported in the work of Sane and Cooper. Although method II is simpler to implement, the regressions only had a few points to account for up to six unknowns, hence the accuracy of the results in this case was expected to be lower.

In addition to the methods proposed in this work, the approach described by Seaman et al[1] was used to estimate the relationship between the relaxation time constants and the chemical composition. Seaman et al evaluated numerically Sane and Cooper's integral equation (with constant B), ie, Equation(3), by assuming two, separate relaxation time constants: one independent of the ionic concentration, and one defined as a function of the moisture's concentration. Since Seaman's relaxation times were comprised of a constant term and a concentration-dependent relaxation time, it was mathematically analogous to the one described by

Equation(7) and Seaman et al's observations should also be applicable to the model presented in this work. It should be noted that a comparison between Seaman et al's model and the one in this work could only be carried out in a qualitative sense as Seaman et al did not describe the relaxation function by a two-term Prony series and did not allow B to vary with composition. Nonetheless, as it should be expected, the trends predicted in both the model presented in this paper and Seaman et al's were consistent with each other. Furthermore, both models were consistent with the conclusions reached experimentally by Burggraaf,[12] and though MD simulations by Yu et al.[13] Conversely, Shen and Green's mechanical testing[3] suggested that an opposite trend might subsist between the relaxation time constants and K_2O concentration for SLG at 550°C. The reasons for Shen and Green's discrepancies might be due to the fact that the mechanical behavior of "as-melted" glasses often differs from that of ion-exchanged glasses.[26]

Possible explanations for the observed, accelerated stress relaxation with increased K_2O concentration has been put forward in the past by various authors. Burggraaf's[12] study on ion-exchanged ASG indicated that the glass structure (Si-O skeleton) was more distorted as the K^+ concentration increased, and that the relaxation time of "distorted" glass was much shorter than that of the host glass. Varshneya et al[6] used MD simulation to study the stress relaxation of chemical strengthened SLG and suggested the existence of two stages in stress relaxation process: a fast delayed-elastic stress relaxation, and a slow irreversible stress relaxation. During the first stage, the alkali cations jumped from one ion cage into another with the net effect of relaxing the compressive stress. In the latter stage, the Si-O network topology changed as the K^+ stuffed, and more stress were relaxed. Ragoen et al[14] study on binary Na-silicate and ternary Na, Mg-, Na, Ba- and Na, Ca-silicate found that the distance of Na–O bond was shorter when increasing the exchanged potassium content and suggested that the contraction of Na–O could possibly increase the size of K–O coordinate shell and thus induce stress relaxation.

The relationship between the normalized τ_i and the K_2O concentration obtained by method I were compared to both method II and Seaman et al's study.[1] The normalized trends for all the proposed methods shown in Figure 5 were found to be similar, as well as the magnitude of individual $\tau_{0,1}$ obtained by method I (Table 2) and by method II. The range of k_B obtained by method I and II (Figure 6) were also in good agreement (and in excellent agreement with Shen and Green's results at the same temperature) and suggested that the dilation coefficient in SLG decreased with exchanged K_2O content. The exact mechanisms relating B to changes in composition is still unclear but it has been suggested to be influenced by the base glass's composition.[16,21–25] A possible explanation for the concentration dependence of B was put forward by Shen and Green[16] who suggested that

the produced linear strain per mol% K_2O concentration decreased as the glass structure expanded slower with more K^+ ions stuffed.

5 | CONCLUSIONS

The stress profiles of chemically strengthened glasses could significantly affect the strength of silicate glasses. In the past, the effect of glass composition on the stress relaxation behavior has been established performing mechanical, stress relaxation tests on "as-melted" glasses which have a different physical behavior compared to ion-exchanged glasses. In this work, the relationship between K_2O concentration and the stress relaxation behavior was established by two, novel approaches which required knowledge of both the residual stress-profile in the ion-exchanged glass and the molten salt bath's temperature/composition. The proposed methods were used to obtain both the relaxation time constants and the dilation coefficient, B, based on the large set of residual stress profiles for SLG reported by the experimental work of Sane and Cooper. Both B and the relaxation times at different K_2O concentrations were estimated by regressing the residual stress vs time data sets through a master stress relaxation function at a reference temperature. A new analytical solution considering concentration-dependent B was also used to regress the stress profiles. Based on the analyses of the residual stress profiles in ion-exchanged SLG carried out in this work, it was found that:

- The estimated dilation coefficient and the time constants obtained from the measured stress profiles in the work of Sane and Cooper using the methodology proposed in this work, could accurately describe all other residual stress profiles for SLG available in the literature.
- Since nearly identical set of parameters (within 20% of each other) could accurately describe the residual stress profiles in SLG samples generated by various authors, it is unlikely that Sane and Cooper's data might have been 'poisoned by moisture' as previously suggested.
- Both the dilation coefficient and the stress relaxation time constants were found to decrease nearly linearly with K_2O concentrations.
- The method proposed in this work was able to reproduce accurately all the relevant features of the residual stress profile (DOL, peak stress) for one step, ion exchanged SLG.

To establish more precisely the relationship between the chemical composition and the dilation coefficient/relaxation time constants, precise residual stress profiles would have to be acquired in the future.

ORCID

Huan Sun https://orcid.org/0000-0003-2737-6123

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APPENDIX

This appendix describes a mathematical improvement in the evaluation of Equation B.9 in Dugnani.[17] In Dugnani's original work, the stress profile for concentration-dependent relaxation time was expressed as follows:

$$\sigma(x,t) \approx \sigma(x,t)\mid_{\tau_{0,i}} + \Delta\sigma(x,t,\chi_{0,i}),$$

$$\Delta\sigma(x,t,\chi_{0,i}) \equiv -\frac{BE}{1-\nu}\frac{\chi_{0,i}}{2\Delta C}\int_0^t R(t-t')\mid_{\tau_{0,i}}\left(\frac{t-t'}{\tau_{0,i}}\right)\frac{\partial}{\partial t'}C(\alpha)^2\,dt' \tag{A.1}$$

As Equation (A.1) could not be easily integrated when expressing the concentration, $C(\alpha)$, as the complementary error function, an approximate, piece-wise description for the concentration term in the integral's argument was used, namely:

$$C(\alpha)^2 \approx \begin{cases} \Delta C^2(1-2\alpha) & \text{for } 0 \leq \alpha < 0.5 \\ 0 & \text{for } 0.5 \leq \alpha \end{cases} \tag{A.2}$$

In this work, a continuous approximation (positive within the assumed range) was used to approximate $C(\alpha)^2$:

$$C(\alpha)^2 \approx \Delta C^2\left(1 - 0.51\alpha^3 + 1.89\alpha^2 - 2.36\alpha\right)$$
$$\text{for } 0 \leq \alpha \leq 1.4 \tag{A.3}$$

Substituting the relaxation function into Equation (A.1), led to:

$$\Delta\sigma \equiv \frac{BE\Delta C}{1-\nu}A_i\frac{\chi_{0,i}}{2\Delta C^2\tau_{0,i}}\int_0^t e^{-\frac{t-t'}{\tau_{0,i}}}\left(-1-\frac{t-t'}{\tau_{0,i}}\right)C(t,x)^2\,dt' \tag{A.4}$$

Like in Dugnani's work, a change of variables, ie, $s' = t'/\tau_{0,i}$, was implemented prior to the evaluation of the integral:

$$\Delta\sigma \approx \frac{BE\Delta C}{1-v} A_i \frac{\chi_{0,i}}{2} \int_{\frac{25}{196}s_0}^{s} e^{-(s-s')} (-1-s+s') \left(1-0.51\alpha^3 \left(\frac{s_0}{s'}\right)^{\frac{3}{2}}\right.$$

$$\left. +1.89\alpha^2 \frac{s_0}{s'} - 2.36\alpha\sqrt{\frac{s_0}{s'}}\right) ds'; \quad \text{with} \quad s_0 \equiv 4\alpha^2 s$$

(A.5)

Like in Dugnani, the lower limit of the integration in Equation A.5 was set as s_0 rather than 0, to enforce the condition $0 \leq \alpha \leq 1.14, s/s_0 \geq \frac{25}{196}$. Integration of Equation (A.5) yielded:

$$\Delta\sigma \left(\alpha, \xi_i, \chi_{0,i}\right) \approx -\frac{BE\Delta c}{1-v} A_i \frac{\chi_{0,i}}{2\alpha} e^{-\xi_i^2} \left\{ e^{0.51\alpha^2\xi_i^2} \left(0.14+0.71\xi_i^2\right) \xi_i^2\alpha^3 \right.$$

$$+\alpha \left\{\alpha\xi_i \left\{1.05-0.9\xi_i^4\alpha^2 + \xi_i^2 \left(-2.09+1.36\alpha^2\right)\right\} Erfi\left(\xi_i\right)\right.$$

$$+\xi_i\alpha \left\{1.05-0.9\xi_i^4\alpha^2 + \xi_i^2 \left(-2.09+1.36x\alpha^2\right)\right\} Erfi\left(0.71\xi_i\alpha\right)$$

$$+\xi_i^2 \left\{0.5e^{0.51\xi_i^2\alpha^2} - 1.18e^{\xi_i^2}\alpha + 0.94e^{\xi_i^2}\alpha^2 - 1.2e^{0.51\xi_i^2\alpha^2}\alpha^2 + 0.51e^{\xi_i^2}\alpha^3\right.$$

$$\left.\left.\left. -0.51e^{\xi_i^2}\xi_i^2\alpha^3 + 0.94\alpha^2\left(\xi_i^2-1\right)\left(Ei\left[0.51\xi_i^2\alpha^2\right] - Ei\left[\xi_i^2\right]\right)\right\}\right\}\right\}$$

(A.6)

Equation (A.6) was compared to the numerical evaluation of Equation (A.4) and the results were found to be within 0.5% in the interval $0 \leq \alpha \leq 1.4$.