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STRENGTH ENHANCEMENT OF SODA-LIME SILICA GLASS USING ION EXCHANGE PROCESS

REFORZAMIENTO DE UN VIDRIO SILICO SÓDICO CÁLCICO EMPLEANDO EL PROCESO DE INTERCAMBIO IÓNICO

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Abstract

This work presents brittleness reduction and flexural strength increase due to composition change on a soda lime silicate (SLS) glass and further improvement was achieved by chemical tempering process. It was possible to predict and prove the effect of composition variation on the index of brittleness through Vickers indentation technique. Some glasses were subjected to ion-exchange process where flexural strength was tested. A selected composition was evaluated varying the chemical strengthening time. Also, the result of a statistical topometric analysis of fracture surface of the selected glass composition with and without ionic exchange treatment is reported.

Keywords: ion-exchange, soda lime silica glass, surface enhancement, brittleness, scaling factor.

Resumen

Este trabajo presenta la reducción de fragilidad e incremento de la resistencia a la flexión debido a un cambio de la composición del vidrio calizo y por el proceso de templado químico. Fue posible predecir y demostrar el efecto de las variaciones en la composición del vidrio en el índice de fragilidad por indentación tipo Vicker. Además, el vidrio fue sometido a un proceso de intercambio iónico midiendo la resistencia a la flexión. Una composición seleccionada se evaluó el efecto del tiempo del proceso por temperado químico. Además, se reporta el resultado de un análisis estadístico topométrico de la superficie de fractura del vidrio seleccionado y su efecto con el tratamiento intercambio iónico.

Palabras clave: intercambio iónico, vidrio calizo, mejoramiento superficial, fragilidad, factor de escalamiento.

1 Introduction

Nowadays, the demand of lightweight glass is one of the glass industry priorities where many applications such as containers, automotive and structural glass are target markets. Lighter material is obtained by diminishing its thickness with overall detriment of its mechanical strength (Albarrán *et al.*, 2006). Although hardness and high scratch resistance places glass in advantage with respect to other materials, its brittleness and low flexural strength are crucial disadvantages for specific applications of this material. This is due to the unavoidable microcracks formed over its surface during glass manufacturing. If the energy exceeds balance of those cracks, they will propagate until fracture; this fact is explained by the Griffith criterion (Olagnon *et al.*, 2006). While it is very easy to eliminate those surface imperfections,

this effect is temporal because those defects appears again with the use, it is possible to improve glass performance by adding several kinds of additives and/or surface enhancers (Carturan *et al.*, 2007; Tartivel *et al.*, 2007).

As the crack tip is under a stress tension field, a compression stress field near the crack tip reduces its propagation; that is to say, to propagate the crack must overcome the compression field. A process that has been used to diminish glass brittleness is to introduce a strong compression layer on its surface. Two processes are currently used to obtain strengthening: a) physical tempering (Sglavo *et al.*, 2004), which consists in cooling the surface faster than its interior when glass still has certain viscosity, this is made by a specific airflow, and b) chemical tempering (Gy, 2008), where

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ions are replaced by different ones with a larger ionic radius, this process is called ion-exchange or chemical strengthening and it occurs from the surface to the interior. Physical method is best suited on glass samples thicker than 3 mm due to heat conduction coefficient of glass and chemical method is best for thinner samples because limited ion penetration; on the other hand, chemical strengthening can be successfully used in complicated geometries. In the ionic exchange, glass is soaked for a relatively long time inside a bath melt of KNO_3 at a temperature lesser than its glass softening point. LaCourse (Sinton *et al.*, 1999) performed a multivariate linear regression analysis on a SLS glass to observe the effect of composition with respect to the depth of K^+ ion-exchange and mechanical strengthening as well. Their work is quite significant because opens up wide possibilities to tailor glass formulations to achieve better mechanical strengthening.

On the other hand, Sehgal and Ito (Sehgal and Ito, 1998; Segal and Ito, 1999) presented a compositional study of brittleness effect of a SLS glass. They observe that when SiO_2 content increased, brittleness diminished since it favors rigid 3D structure formation with open spaces increasing network strength. Also, when Ca^{2+} ions were replaced by Mg^{2+} and when Na^+ ions by K^+ as well had a positive effect on glass strength. And later on, Ito (Ito, 2004) reported a brittleness relationship on glass density. Accordingly, there is a brittleness optimum value of around 2.4 g/cm^3 where lower values are dominated by high network strength but with lesser mechanical deformation and hence increasing brittleness.

At this point we wonder if it is possible to find a SLS glass composition suitable for ion exchange with low brittleness. However, any change on glass formulation must be taken wisely, especially on fast drawing production lines as glass containers for instance (Mallik and Holand, 2005). Then, care must be taken as well to keep any alternative formulation with similar rheological parameters. To achieve this goal it is necessary to determinate the viscosity as a function of temperature. This process is time consuming and it quite expensive since it needs a variety of analytical apparatus to complete a full spectra of viscosity vs. temperature. Therefore, it is admissible to calculate viscosity at three important temperatures: “flow point”, “working point” and “melting point”. Those are associated with the necessary temperature to achieve viscosities in the order of 10^5 , 10^4 and 10^2 poises respectively and are also known on the industry argot as “Log5”, “Log4”

and “Log2”. The first two parameters are important on the glass production design since are then related with the melt transportation and gob molding. The later is related with the necessary temperature to melt raw materials and have economical implications to observe.

In 2008 J. L. Sánchez-López *et al.*, studied the hydrodynamics of a reactor using model theory, this model can be accurately used to enhance the analysis of the contraction of glass once has been enhanced by ionic exchange, actually, they studied the contraction in the emulated bed of reactors. It is important to enhanced the mechanical properties of a substrate to support high stresses; for instance, in 2014 M. A. Soto-Borbón, reported the characterization of a screen printing film formed by TiO_2 and alginate, supported on glass substrate, this material can be optimized if the glass where previously strengthened by ionic exchange method.

Duygu Guldiren *et al.* in 2016, investigate the ion exchanged soda lime glasses in terms of their physical and mechanical properties, using AgNO_3 - KNO_2 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, they found that silver colored slightly by the sylver, and the ratio of silver/potassium salts that enhances the mechanical properties was 1 to 4 respectively. The maximum hardness was of 6.19 GPa at 420°C and 240 min. Finally, Marek Patschger and Christian Tüssel, used a salt coating to obtain the ion exchange. They has been design a continuous process for chemical strengthening of glass below the T_g , in which a spray coating of the glass with a potassium containing salt solution which is a mixture of KNO_3 - KCl - K_2SO_4 . They have been found a lower diffusion coefficient for the ion exchange of K^+ . They found an activation energy of 122 kJ/mol at 455°C in a salt in which every salt is equal in proportion.

The objective of this work is to investigate a number of alternative compositions suitable for chemical tempering with the smaller brittleness possible. Also, those new formulations must be restricted in its composition to avoid make sensible changes on the rheological properties of glass. In this work eight compositions were proposed, prepared, tested and the most promising composition was subjected to ion-exchange treatment at several

processing times and compositional effects are discussed. Also, it is studied the effect of the change in the stress field due to the collective behavior of the ion-exchange process over the self-affine parameters.

2 Experimental

A typical transparent glass container formulation was selected as base composition. And eight compositions were proposed to be tested. Each one of the individual components was properly weighed (SiO_2 , MgCO_3 , CaCO_3 , Na_2CO_3 , K_2CO_3 and Al_2O_3) to obtain batches of 100 g. General precautions were taken to dry all raw materials to insure stoichiometric compositions on each case. After, they were dry-mixed for about 15 minutes and later were transferred into a high temperature furnace (CM FurnacesTM). In order to eliminate carbon dioxide, power batches were heated up to 800°C during 30 minutes, then the samples were melted at 1550°C for 3 hours, followed by refining at 1450°C for 1 hour. Each melt was poured and splashed-in between of a couple of stainless steel plates at room temperature and they were immediately annealed at 600°C for 1 h and finally were slowly cooled down until room temperature inside the furnace. Parts of the glasses were cut to obtain flat samples of 2 mm × 3 cm × 3 cm. The rest of the pieces were saved for alternative testing. For mechanical and ion exchange test a large number of rods were fabricated by slow drawing technique at 600-700°C. Temperature was controlled by a custom made vertical cylindrical open furnace. All rods were made of around 1 mm diameter and exact measurement was performed by a micrometer. Also, after every glass was annealed and cooled down to room temperature all samples were keep inside a desiccator to control humidity levels on every sample, even after rod drawing the samples were immediately returned to dry conditions. All glass samples were analyzed by Differential Thermal Analysis (DTA-50 ShimadzuTM).

Microhardness test was performed by Vickers indentation test using a ShimadzuTM microdurometer with an applied load of 1 Kg during 45 seconds each test. Crack characteristics were determined employing an optical microscope (Nikon) supported by digital image analysis. Vickers Hardness (H_v) in GPa was calculated according to the classic equation (1):

$$H_v = 1.8544 \left(\frac{P}{a^2} \right) \quad (1)$$

where P is the applied load in kgf and a is the arithmetic mean (in mm) of the indentation diagonal length. Experimental glass brittleness was calculated according (Sehgal *et al.*, 1995) to the following equation (2):

$$B = \gamma P^{-1/4} \left(\frac{C}{a} \right)^{3/2} \quad (2)$$

where B is the brittleness index, γ is function of the Young's modulus and its value is $2.39 \text{ N}^{1/4}/\mu\text{m}^{1/2}$ for SLS glasses (Sehgal and Ito, 1998), C is the average characteristic crack produced during indentation process. P and a are the same parameters measured for H_v . In order to obtain average measurements of C and a , 25 indentations were made by duplicate for each glass composition.

Flexural strength test of each glass composition was tested using a classic three point bend test configuration in an Instron 4303 universal testing machine. An acting force causes tension on the surface opposed to the contact midpoint of a test rod and fracture initiates on this point. The formula used to calculate the stress fracture was eq. (3):

$$\sigma_f = \frac{8PL}{\pi D^3} \quad (3)$$

where σ_f is the fracture strength, P is the applied load at the point of fracture, L is the distance between both stand points and D is the test rod diameter. 25 samples were used on each determination. For ion exchange test, 25 glass rods were immersed in a melted KNO_3 bath at 400°C at different time periods. This temperature was selected because is commonly used in glass strengthening process at industrial level (Gy, 2008), beyond that point the salt is degraded.

Additionally, A2 glass sample was immersed on a bath of melted potassium salt (KNO_3) at 400°C during 24 h, after this treatment the slides are cooled at a rate of 17 °C/h. AFM (Park Scientific model Auto Probe CP) scans in contact mode allowed us to obtain the topography of the fracture surface as well as the topometric profiles. A force of 9 nN with a scanning frequency of 1 Hz was used. The statistical topometric analysis was performed using the variable bandwidth method applied to the AFM profiles. A profile of length L is divided into windows (also called bands) of width Δ indexed by the point X_0 which is the first is the first point of the band. The standard deviation of the height ω and the difference δ between the maximum and minimum height are computed on each band and then averaged over all possible bands, according to the

following algorithms:

$$\langle \omega(\Delta) \rangle_{X_0} \alpha \Delta^\zeta \quad \text{and} \quad \langle \delta \rangle_{X_0} \alpha \Delta^\zeta \quad (4)$$

It is important to note that the variable bandwidth method is only for values $\zeta \in [0, 1]$, and its values are independent of the scan size, which makes it ideal technique for the surface profiles.

3 Results and discussion

Table 1 summarizes details about calculated parameters of selected formulations. In general, the amount of network modifiers ($\text{RO} + \text{R}_2\text{O}$) and network formers ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) was kept within a certain range (24.0-26.2 mol% for the former and 73.8-76.0 mol% for the later). On the other hand, the relative amount of alkali-earth oxides to alkali oxides was tested on several ratios, generally was sought to lower this ratio. Furthermore, all alternative formulations increased the exchange of CaO for MgO and Na_2O for K_2O , predominantly. Viscosity and density calculations were performed using global statistical glass model recently developed (Fluegel, 2007; Fluegel, 2008) for predicting complete viscosity and room temperature density values for a wide variety of glass compositions with high reliability degree. We settled for up to 2-3% changes on flow and working points to avoid drastic changes on possible manufacturing conditions. Calculated densities had only minor changes and in general are very close to the “ideal” value of 2.4 g/cm^3 for SLS glasses reported by Ito (Ito, 2004).

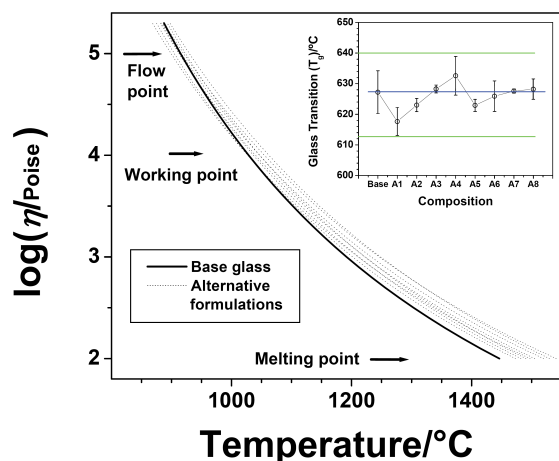


Fig. 1. Viscosity vs. temperature continue line is the base glass composition, dot lines are alternatives compositions from A1 to A8. Insert: glass transition temperature for each composition.

In Fig. 1 is showed the calculated viscosity vs. temperature of base and alternative glass compositions calculated from global statistical glass model of Fluegel (Fluegel, 2007; Fluegel, 2008). On this plot, we can observe a similar trend on all cases. There are only small differences on the flow-to-working point regime which is crucial on the design of glass processing lines, specifically in the drawing process. There is a trade-in because we predict a general increase (up to 6%) on melting point of all proposed formulations. We also evaluate glass transition temperature on all glass compositions, these results are showed in table 2 and plotted on right hand insert on Fig. 1. It is observed a minor deviations ($\pm 2^\circ\text{C}$) of T_g of all alternative glasses compared to base composition. This situation suggests that there are only small variations on the rheological behavior on the chosen glasses confirming the glass viscosity calculations.

Yamane and Mackenzie (Yamane and Mackenzie, 1974) analytically derived an equation for calculating the Vickers hardness of silicate glasses. They proposed that the resistance of a glass to permanent indentation is a combination of resistances to shear flow, elastic deformation, and densification. Accordingly, the resistance to shear flow is governed by the shear modulus and a relative bond strength factor, while that of elastic deformation by the bulk modulus. Their equation is as follows eq. (5):

$$H_v = 0.051E \left[\frac{\alpha}{(0.462 + 0.09V - V^2)} \right]^{1/2} \quad (5)$$

where E is the Young's modulus, V is the ionic volume fraction and α is the relative bond strength factor. The value of E on this work was calculated using *SciGlass*® software using the Priven-98 method. V was calculated according to eq. (6):

$$V = \frac{\rho}{\bar{M}} \sum_i \left(\frac{4}{3} \pi r_i^3 f_i \right) \quad (6)$$

where ρ and \bar{M} are the glass density and average molecular weight, respectively; r_i is the ionic radii and f_i is the number of cations in mole weight of glass (that is equal to the mole fraction times the Avogadro's number), respectively.

The relative bond strength factor α predicts decreased Vickers hardness with decrease of the elastic moduli and bond strength and is defined as the ratio of the average single bond strength to the Si-O

bond strength ε_{Si-O} , eq. (7):

$$\alpha = \frac{\sum_i (f_i n_i \varepsilon_i)}{\varepsilon_{Si-O} \sum_i (f_i n_i)} \quad (7)$$

where n_i is the coordination number and ε_i is the single-bond strength of the cation-to-oxygen bond. Excellent agreement between calculated and measured values was obtained by Yamane and Mackenzie on a wide range of glasses.

Vickers hardness obtained for each composition and is presented on Table 2. All alternative compositions had smaller H_v values than base composition. Calculated values from Yamane and Mackenzie (Yamane and Mackenzie, 1974) model are included and follow a similar trend as experimental values. This is quite significant since all formulations were aimed to reduce brittleness which was attained on all cases as well (see Fig. 4). In an attempt to explain these results we plotted on Fig. 3 the brittleness vs. alkali to alkali earth ratio (RO/R_2O), where we observe the highest level of B as the ratio approaches to 1. There is a significant decrease of brittleness as the amount of alkali increases and it appears that there is a minimum of B value at RO/R_2O ratio of 0.5 with an increase of brittleness at lower RO/R_2O ratios. To confirm this behavior, we construct a similar plot using experimental data from Ito's work (Sehgal and Ito, 1998; Segal and Ito, 1999; Ito, 2004; Sehgal *et al.*, 1995) and it is displayed on right insert at Fig. 3 and here there is minimum value of brittleness at 0.5.

In order to understand this reduction of brittleness and the appearance of a minimum at 0.5 RO/R_2O ratio we calculated the number of bridging oxygen atoms ($\#BO$) of all alternative compositions using the following eq. (8) (Deriano *et al.*, 2004):

$$\#BO = 4 - \frac{2(y + m + z + n - x)}{(w + 2x)} \quad (8)$$

where all variables are related to the stoichiometric composition $(SiO_2)_w(Al_2O_3)_x(CaO)_y(Na_2O)_z(MgO)_m(K_2O)_n$. The results are included in Table 2 and also showed on the left corner insert of Fig. 3. Here we observe an increase of $\#BO$ as the ratio approaches to 0.5. This is an indication that stiffness is favored as the amount of alkali earth ions are reduced compared to the amount of alkali ions and consequently, increasing the bridging oxygen atoms. Until this point samples A2, A5 and A7 show the lowest brittleness and have the highest $\#BO$ on the group. It is notorious that

sample A7 possesses the lowest Vickers hardness on the group and this composition contains the highest MgO content. This could be explained in terms of a more open structure formation as the amount of CaO is replaced allowing larger deformation upon indentation (Ito, 2004).

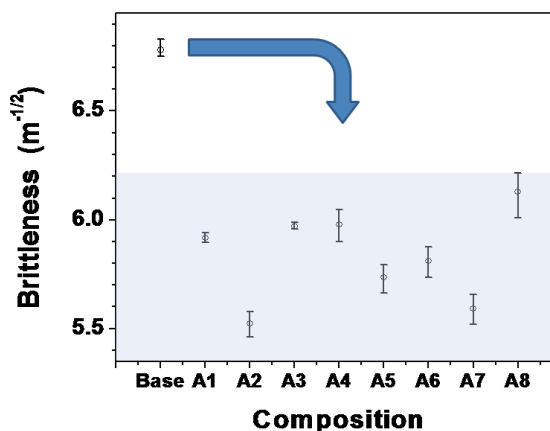


Fig. 2. Experimental brittleness (in $m^{-1/2}$) measured for each composition including the base glass. Vertical bars are the standard deviation. Here can be appreciate that the base composition has the highest brittleness.

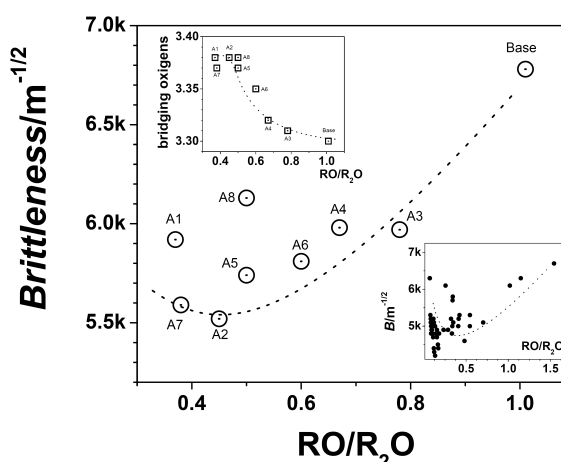


Fig. 3. Brittleness (in $m^{-1/2}$) vs. RO/R_2O ratio. \odot brittleness data from this work, \bullet are data from Ito's work (Sehgal and Ito, 1998; Segal and Ito, 1999; Ito, 2004; Sehgal *et al.*, 1995). \square number of bridging oxygens from this work. All dotted lines are guides to the eye.

Table 1. Alternative glass compositions along calculated properties.

	Mol%								
	Base	A1	A2	A3	A4	A5	A6	A7	A8
SiO ₂	73.27	73.41	74.22	73.82	73.71	73.76	74.56	70.84	72.58
CaO	12.89	5.01	2.54	6.67	6.76	4.30	5.46	1.10	8.13
MgO	0.27	1.55	4.93	4.61	3.45	3.83	3.80	5.75	0.00
Na ₂ O	12.97	13.09	10.98	12.92	13.89	11.37	10.86	16.85	10.21
K ₂ O	0.08	4.50	5.58	1.46	1.35	4.86	4.48	1.26	5.98
Al ₂ O ₃	0.53	2.45	1.76	0.53	0.83	1.88	0.84	4.22	3.10
%RO	13.2	6.6	7.5	11.3	10.2	8.1	9.3	6.8	8.1
%R ₂ O	13.0	17.6	16.6	14.4	15.3	16.2	15.4	18.1	16.2
%network modifiers (RO+R ₂ O)	26.2	24.1	24.0	25.7	25.5	24.4	24.6	25.0	24.3
%network formers (SiO ₂ +Al ₂ O ₃)	73.8	75.9	76.0	74.3	74.5	75.6	75.4	75.1	75.7
%MgO in RO	2.0	23.6	66.0	40.8	33.8	47.1	41.0	84.0	0.0
%K ₂ O in R ₂ O	0.6	25.6	33.7	10.2	8.9	29.9	29.2	7.0	36.9
Calculated parameters:									
Working point Log4/°C	1029	1027	1055	1037	1027	1047	1040	1062	1047
Flow point Log5/°C	915	899	920	913	905	916	912	930	923
Density (g/cm ³)	2.506	2.458	2.436	2.464	2.466	2.449	2.453	2.445	2.478

Table 2. Glass transition, Vickers hardness, brittleness index of all glass compositions.

	RO R ₂ O	Experimental ^a <i>H_v</i> (GPa)	Standard deviation	Calculated ^b <i>H_v</i> (GPa)	Experimental ^c <i>B</i> (m ^{-1/2})	Standard deviation	# <i>BO</i> ^d	<i>T_g</i> (°C)
Base	1.01	5.63	0.114	4.98	6780	0.044	3.30	627
A1	0.37	5.30	0.053	4.95	5920	0.023	3.38	618
A2	0.45	5.05	0.092	4.82	5520	0.060	3.38	623
A3	0.78	4.73	0.085	4.88	5970	0.018	3.31	628
A4	0.67	5.00	0.215	4.93	5980	0.074	3.32	633
A5	0.50	4.86	0.027	4.86	5740	0.066	3.37	623
A6	0.60	4.68	0.081	4.80	5810	0.071	3.35	626
A7	0.38	4.58	0.188	5.13	5590	0.069	3.37	628
A8	0.50	4.89	0.059	4.94	6130	0.107	3.38	628

^aequation 1^bequation 5, 6 and 7^cequations 2^dequation 8

Flexural strengths from all glass compositions with and without ion-exchange process are shown on Table 3 and Fig. 4. The composition with the largest flexural strength without ion-exchange is A2 with a value of 228 MPa and the lowest one is A3 with 106 MPa. In several cases, there is a straight relationship between brittleness value and the flexural strength attained, as the case for A2 and A7 samples. Regarding ion-exchange results, the one that presents the greatest potential is A2 with a value of 400 MPa and the lower is A7 with 182.6 MPa (only a 4% increase for ion strengthening). This behavior could be explained in terms of high Al_2O_3 content on A7, as Kim (Kim, 1983) indicates its effect on reducing the rate of stress relaxation and therefore decreasing the ion exchange rate, this was also corroborated by Mattos (Mattos, 1999) as well. There is a similar situation on A6 sample, whose increase of flexural strength is only 12% on chemical strengthening treatment. Looking up at its composition we observe it has the largest SiO_2 content of the group and according to Sinton (Sinton *et al.*, 1999) this creates a closer and stiffer glass network and therefore reducing the K^+ ion exchange rate. On the other hand, A1 and A2 showed the highest increment on flexural strength upon chemical tempering. In both cases, there is a relative high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio where a presence of mixed-alkali effect favours the interdiffusion rate of K^+/Na^+ exchange (Sinton *et al.*, 1999). This model proposes that the increase of K^+ ions in the glass produces “K friendly sites”, lowering the activation energy. Moreover, A2 sample has a relative high MgO/CaO ratio which indeed decreases the activation energy of Na^+ diffusion and favouring indeed the interchange Na^+/K^+ rate (Pedone *et al.*, 2008). This situation places A2 composition with the largest flexural strength upon chemical strengthening and lower brittleness value.

We select A2 composition for an ion exchange time study where test rods were treated in a molten KNO_3 bath at 400°C and 25 samples were extracted at 3 hours treatment, 25 samples more at 6, 12 and 24 hours, respectively. After proper cleaning of the samples, they were placed under flexural strength test. The results are displayed on Fig. 5. Here, we immediately notice an exponential increase of the σ_f upon interchange time. On right hand insert we have included a plot of flexural strength vs. \sqrt{t} with a linear correlation value of 0.97 which is interpreted as

a proper interdiffusion behavior of K^+ ion exchange (Gy, 2008). With this, we were able to find a soda-lime silica glass composition capable to have low brittleness, high flexural strength and possibility to increase up to 2.5 times fold upon a 2 hours ion exchange treatment. A2 composition has a relatively high composition of K_2O , this indeed may preclude its potential application on glass containers due to chemical degradability upon acid conditions. This ion exchange material has a potential application as protector of touch screens when is laminated over the screen.

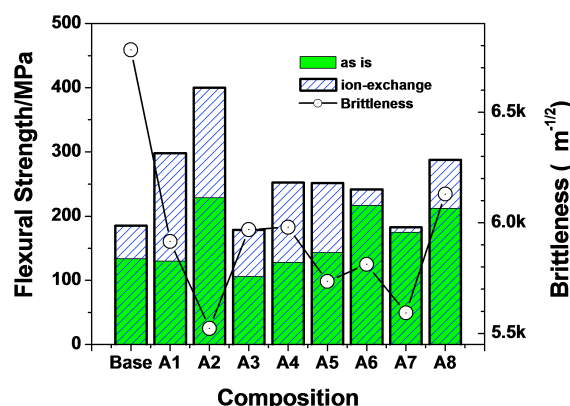


Fig. 4. Flexural strength of glass samples with and without ion-exchange along brittleness values of untreated glasses.

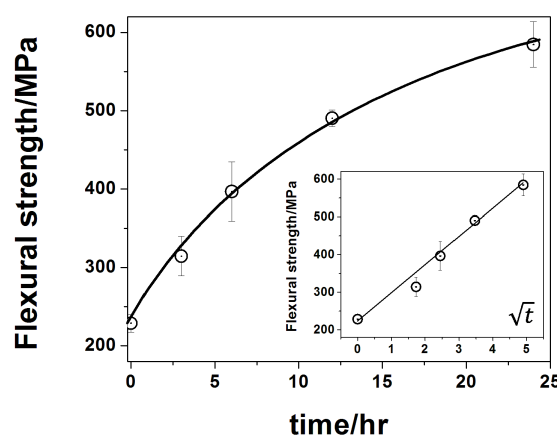


Fig. 5. Flexural strength on A2 sample vs. ion exchange time.

Table 3. Flexural strength of glasses without and with ion-exchange.

Composition	σ_f without ion exchange (MPa)	Standard deviation	σ_f with ion exchange (MPa)	Standard deviation
Base	133.4	13.6	185.2	54.3
A1	130.0	12.6	298.0	41.3
A2	228.7	23.2	400.0	20.4
A3	106.3	22.9	178.6	26.9
A4	127.9	22.7	252.3	17.8
A5	143.3	35.3	251.5	38.3
A6	216.4	13.6	241.6	14.3
A7	175.0	11.3	182.6	45.9
A8	212.0	16.9	287.4	14.1

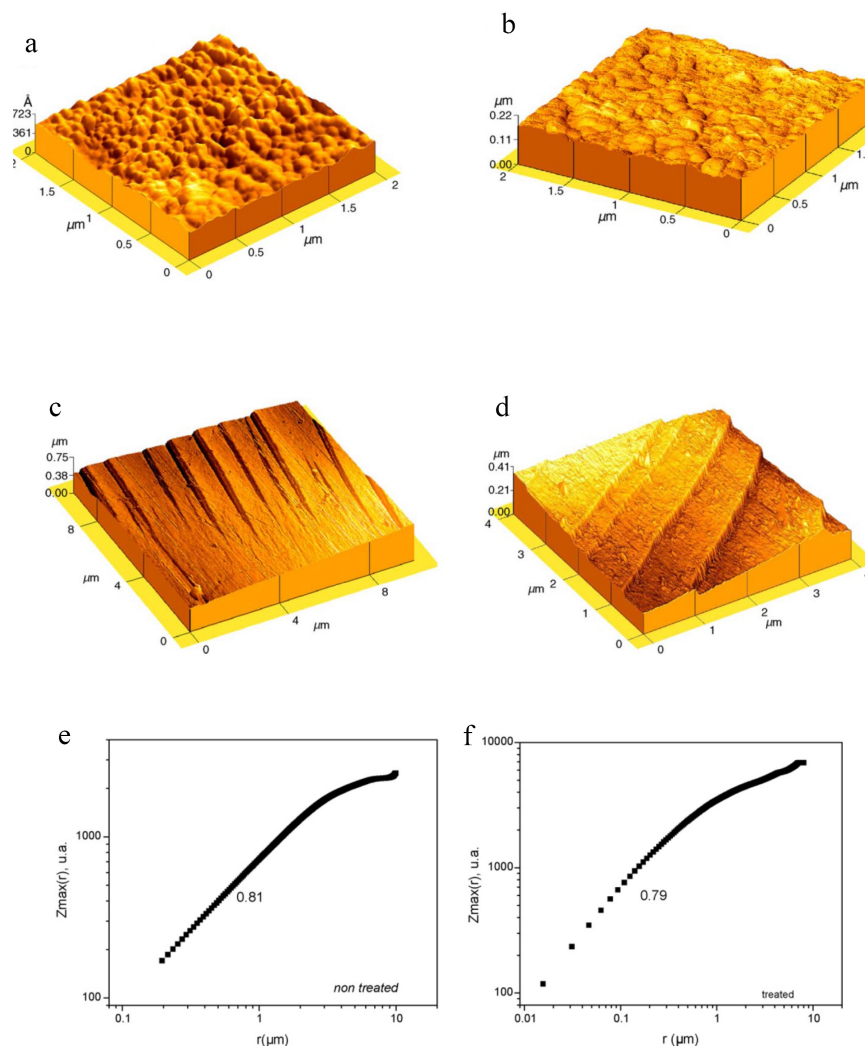


Fig. 6. A2 glass sample. AFM images: (a) mirror zone, untreated; (b) mirror zone, treated; (c) mist zone, treated and (d) hackle zone, treated. Self-affine curves: (e) untreated and (f) treated. Self-affinity log curves $\log(Z_{max})$ vs. $\log r$ in both value of its roughness exponent is close to 0.8. In non treated glass a value of correlation length of about 18 micrometers can be observed. While the treated glass has a correlation length of about 0.75 micrometers. Beyond the correlation length the surface is a flat object, below this value the surface is a fractal object.

The images of Figs. (6a)-(6b) show the topography of the mirror zone on the A2 sample without and with ionic exchange treatment, respectively. Even when both images exhibit roughness, their morphologies are different. Fig. 6c shows the topography from the mist zone and Fig. 6d shows the hackle zone, both on a treated sample. These results can be interpreted as a quantitative evidence of the self-affine character of the three fracture zones. The quantitative characterization of the self-affine parameters of the mirror zone is revealed variable bandwidth curves shown in Figs. (6e)-(6f), which corresponds to the non-treated and treated specimens, respectively. In both cases the roughness exponent has values consistent with the claimed universal value $\zeta \sim 0.8$ (Chavez and Garza, 2010). This implies that the ionic exchange treatment does not modify the exponent characterizing the self-affine regime. However, the curve corresponding to the treated samples suggest that the deviation from the power law occurs for lower values of compared to the non-treated case. This difference in the correlation length is directly related to the major heterogeneities in crystal and semi-crystal materials, but in the case of glass it can be related to the size of the stress field which varies from the treated and non-treated glass, this is what we propose to visualize as the collective behavior of the K^+ ions in the material, besides, apparently this is insignificant, because the penetration distance of the potassium ions to the thickness of the plates, however, by significantly increasing the bending stiffness, is shown what is known as a long distance effect.

Conclusions

On this study we were able to find a large combination of alternative glass compositions capable to attain large ion exchange diffusion and low brittleness values and selected the best eight candidates. After proper glass preparation, a series of mechanical test as Vickers hardness and three-point bend test were performed, and after chemical tempering treatment we find a new composition which indeed is suitable for strong glass applications as touch screen guards. Also, we were capable to find a relationship on the brittleness on RO/R₂O ratio and number of bridging oxygen atoms. The roughness exponent found for the mirror zone agrees well with universal value $\zeta \sim 0.8$ for both treated and non-treated glass, which is the value found for every material at high speed crack propagation fracture, thus the ionic exchange

treatment does not modify this parameter, but what is interesting and opens a new research opportunity is that the ion exchange does vary the correlation length, which means that the stress field can be equivalent to heterogeneities in polycrystalline materials.

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