

Enhancement of mechanical properties of alkali aluminosilicate glasses by chemical tempering

Inês Maria Carreiro Pinho

ines.maria.carreiro.pinho@tecnico.ulisboa.pt

Instituto Superior Técnico, Universidade de Lisboa, Portugal

January 2021

Abstract

Chemically treated glasses have several applications, namely for smartphones screens, because with this treatment their mechanical properties are improved. Starting from an alkaline aluminosilicate with high transmission in the visible region, its mechanical characterization was carried out (Young's modulus, Poisson's ratio, distortion modulus, Vickers hardness, equibiaxial flexion and fracture toughness). The results were compared with two commercial glasses: computer monitor glasses and glasses normally used in mobile phone screens (Gorilla Glass 5[®]) and it was concluded that this composition is suitable for the intended use, as it presented module values Young (82 ± 1 GPa) and fracture toughness ($1,6 \pm 0,1$ MPa.m^{1/2}) superior to commercial glass Gorilla Glass 5[®] (72 ± 1 GPa and $1,2 \pm 0,1$ Mpa.m^{1/2}, respectively).

Then, the effect of ion exchange on the composition was studied to optimize its mechanical properties. Exchange cycles in KNO₃ were carried out at two temperatures (420°C and 450°C) for several times (from 1h to 90h). These glasses were characterized by density, transmission, hardness and fracture toughness, in order to conclude which time and temperature allow the best compromise between hardness and transmission. There was an increase in the hardness of the glass with the time of exchange, obtaining an average value of 728HV for 30h at 420°C, 716HV for 12h at 450°C and 695HV for 9h at 450°C. The optimization of mechanical properties, maintenance of optical properties and optimization of the process is achieved with 9h of exchange at 450°C with KNO₃. In the exchanged glasses, the fracture toughness increased to $2,2 \pm 0,1$ Mpa.m^{1/2}, which allows estimating an optimization of the mechanical properties.

Keywords: Ion exchange, alkaline aluminosilicate glasses, Weibull statistics, mechanical properties, optical properties

1 Introduction

According to Shelby⁽¹⁾, glass can be defined as an "amorphous solid completely devoid of long-range periodic atomic structure and with a glass transition region". Given the definition of glass, it is not possible to fit this material into the classic states of matter, so it is necessary to create a fourth state of matter, the glassy state⁽²⁾. There are several types of glass, such as silicates, with lead oxide, tellurides, germanates... and depending on the chemical composition, the physical and chemical properties are different⁽²⁾. In addition to the chemical composition, heat and/or chemical treatments applied to glass also influence its properties.

Since the discovery of glass, a lot has evolved in production technology and glass applications, from material transport containers, windows, glass for cars and airplanes, optical fiber, glass for special applications (for electronics, cathode ray tubes, products fused silica, X-ray tubes, sintered glass, ceramic glass ...) and glass for cell phone screens, television, computers...⁽³⁾ One of the areas with significant research and progress is that of high mechanical resistance glass with potential application on mobile phone or monitor screens, for example.

Several processes allow changing the mechanical properties of glasses. One of them is thermal tempering, where the glass is heated to a certain temperature and then cooled quickly, leaving the glass surface to be compressed, which prevents the propagation of cracks and consequently allows the

glass to be loaded with higher loads, as this like many fragile materials, it is more resistant to compression than to traction⁽⁴⁾. Another process is chemical tempering where the surface compression is the result of a layer with a different composition than the chemical composition of the glass, which can be obtained by several processes such as 1) application of temperatures below the glass transition temperature, 2) application of a layer with a lower thermal expansion than the remaining glass or 3) exchange between of an ion present in the glass composition (such as lithium or sodium) by a larger ion (such as potassium), "tightening" the structure and thus reaching the desired compression.⁽⁴⁾

Therefore, the objective of this work is to optimize the mechanical properties of an alkaline aluminosilicate composition through chemical treatment. The time and temperature of the chemical treatment that yields the best compromise between hardness and transmission is selected. Having determined this commitment, the mechanical properties achieved are determined and compared with commercial glasses (glass monitor from a personal computer and glass Gorilla Glass 5[®] from Corning). Finally, the potassium layer after the chemical exchange is studied, using electron microscopy.

2 Experimental method

In this work, an alkaline aluminosilicate glass (GM3) composition was developed (Table 1), and characterized. The characterization of the samples was done by determining

density, optical properties (UV-Vis transmission and refractive index) and mechanical properties (Vickers hardness, Young's modulus, distortion modulus, Poisson's ratio, hardness, fracture toughness and fracture resistance). The results were compared with commercial glasses, namely with two computer monitor glasses (LG1 and LG2) and the "Gorilla Glass 5[®]" commercial glass (GG5). Furthermore, the GM3 composition was also chemically treated by two ion exchange cycles in potassium nitrate (KNO₃) at 420°C and 450°C at various times (1h, 3h, 6h, 9h, 12h, 18h, 24h, 30h, 36h and 90h) in order to determine which combination allows the best compromise between transmission and hardness. After the ion exchange treatment, the samples were studied again in order to evaluate the effect of the chemical treatment on the mass, density, UV-Vis transmission and hardness of the samples. The elastic constants (Young's modulus, distortion modulus, Poisson's coefficient) and fracture toughness were also measured and compared.

2.1 Glass production

The composition used in the glasses produced for this work is called GM3 and has SiO₂, Al₂O₃, Li₂O, MgO, ZnO, TiO₂ and ZrO₂. The composition is not indicated in this work as it may be patented.

The properties of the glasses result from the sum of properties provided by their constituents⁽⁵⁾: Silica (SiO₂) is the network former and was introduced as a fine powder in order to facilitate its "digestion", while aluminum oxide (Al₂O₃) provides greater stability as it decreases the tendency to crystallize and increases the chemical and mechanical resistance of glass. Magnesium oxide (MgO), a network modifier, and zinc oxide (ZnO), an intermediate oxide, improve the workability, while lithium oxide (Li₂O) not only improves the melting rate and influences the melt viscosity, but Li⁺ can be replaced by K⁺, yielding local compression during the chemical treatment. Titanium oxide (TiO₂) and zirconium oxide (ZrO₂) were added as nucleating agents, inserted for further enhancement of the mechanical properties.

The glass is produced in the laboratory using the oven cycle shown in the Figure 1. Stages at different temperatures are performed with the following functions:

- 300°C: removal of all water molecules that the constituents may have incorporated
- 900°C: decarbonation of lithium carbonate
- 1500°C: melting of the composition
- 1620°C: temperature at which the viscosity of the fluid allows easy casting

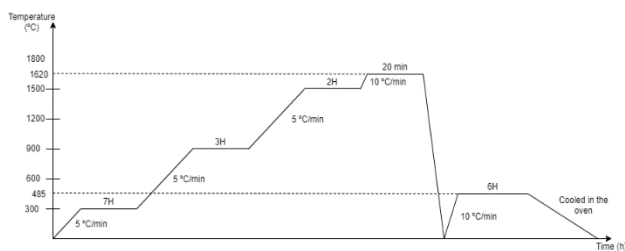


Figure 1: Programmed stages of the oven to produce annealed glass samples

In addition to the production of the glass Figure shows the annealing cycle, carried out after the pouring, in order to release the stresses introduced in the glass during the process but without changing properties such as transparency or coloring. Annealing was carried out for 6 hours at 485 °C and cooled in the oven, since this treatment has to be carried out below the temperature of glass transition (T_g) and below the temperature from which crystallization occurs, which would produce glass-ceramic, which is not the scope of this work.

2.2 Ion exchange process

To carry out the ion exchange, a crucible with solid salt (potassium nitrate, KNO₃) is placed in the oven with a heating cycle of 10°C/min until reaching the temperature of the ion exchange (420°C or 450°C) in order to melt all the salt to be placed the sample that will undergo the ion exchange. The sample must be placed in an upright position to ensure that the ion exchange process takes place on both surfaces of the sample (Figure 2).

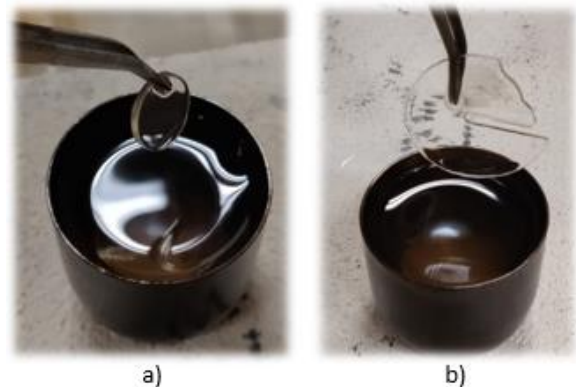


Figure 2: Sample and sample holder to be taken from the exchange salt

2.3 Samples characterization

2.3.1 Density

This characterization process must be carried out before and after the ion exchange process, having been carried out on a *Mettler Toledo AM50* scale together with an accessory for the determination of density by the Archimedes method, in distilled water.

2.3.2 Optical properties

2.3.2.1 UV-Vis transmission

This characterization method was carried out on a *Helios Gamma UV-Vis* spectrophotometer from Thermo Fisher Scientific, from 190 nm to 1100 nm. This process must be carried out before and after the ion exchange process.

2.3.2.2 Ellipsometry

This characterization method was carried out on a HORIBA UVISEL ellipsometer in the visible range. This process must be carried out before and after the ion exchange process. A

wavelength was defined to extract the refractive index values: 590nm, which corresponds to the sodium D-line.

2.3.3 Mechanical properties

2.3.3.1 Elastic Constants

The test for determining the Young's modulus (E), the distortion modulus (G) and the Poisson's ratio (ν) were performed according to the E1876-01⁽⁶⁾ standard on the IMCE nv professional RFDA equipment. The impact on the sample was performed using a polymeric stick with a steel ball at the end as a "hammer", whose vibration frequency is treated by the software, resulting in the constants.

2.3.3.2 Hardness

The characterization of the samples in relation to the hardness was done through Vickers microhardness, carried out on the Duramin Struers durometer with loads of 200 grams for 15 seconds. The hardness values shown are the result of an average of at least 15 hardness measurements.

2.3.3.3 Fracture toughness

The fracture toughness was determined using the Indentation-Fracture Method, as stipulated in the JIS R 1607(7) standard. Mitutoyo's AVK-C2 durometer was used with 5 kg loads for 15 seconds. From equation (1), assuming the experimental values of K_{IC} and the equibiaxial rupture stress (σ_f) and, according to standard C1322-05b⁽⁸⁾, $Y = 1.29$ (assuming that the rupture of the specimens occurs due to hemispherical surface defects of radius "a"), it is possible to estimate the size of critical defects.

$$K_{IC} = \sigma_f \sqrt{a} Y \quad (1)$$

2.3.3.4 Fracture resistance

For this test the *ring-on-ring* technique has been performed on a 5566 loading machine from INSTRON, with a crossbar speed of 5mm/minute. In the assembly used carried out it was defined that the diameter of the support ring (D_s) is 20,2mm and the diameter of the load ring (D_L) is 10,1mm. In this method, fracture resistance (σ_f) is obtained, which can then be analyzed by Weibull statistics.

2.3.4 Electron microscopy

The analysis of electron microscopy or SEM (Scanning Electron Microscope) was performed using the Hitachi S2400 equipment, and the analysis by EDS (Energy-dispersive X-ray spectroscopy) was obtained on Bruker's Quantax equipment. For this test it is necessary that the sample is conductive, which is not the case with glass samples, so the preparation of the samples for this analysis involves the deposition of a thin film of a conductive material such as gold and palladium, used in this case.

3 Results

3.1 GM3 samples

Through DTA analysis it is possible to determine the glass transition temperature, important for the definition of the annealing and ion exchange temperature to be applied to the GM3 composition. Figure 3 presents the result of the analyzes

made with powdered and bulk samples and it is possible to conclude that the glass transition temperature occurs around 525°C.

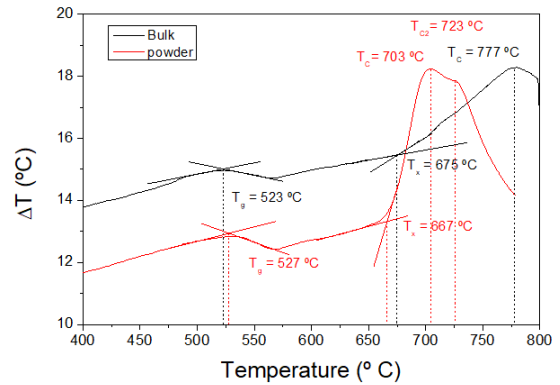


Figure 3: DTA analysis of the GM3 composition

Table 2 shows the characterization results performed for GM3 glasses, including not only those obtained in mechanical tests but also the Vickers hardness, density and Weibull modulus.

Table 1: Characterization of GM3 glasses

	ρ [g/cm ³]	Transm. (700-950nm) [%]	HV _{0.2}	n @590nm	E [GPa]	G [GPa]	$\sigma_{fracture}$ [MPa]				Weibull modulus			ν	K_{IC} [MPa.m ^{3/2}]	a [mm]
							group	$\bar{\sigma}$	σ_{lower}	σ_{upper}	m_{lower}	m_{upper}	$m_{Weibull}$			
GM3	2,49 ± 0,01	92	619 ± 10	1,54	82 ± 1	33 ± 1	128	120	112	6,89	5,50	3,88	0,24 ± 0,01	1,6 ± 0,1	107,62	

Given the final application, UV-Vis transmission must also be monitored. The transmission curves for commercial glass and GM3 composition are shown in Figure 4.

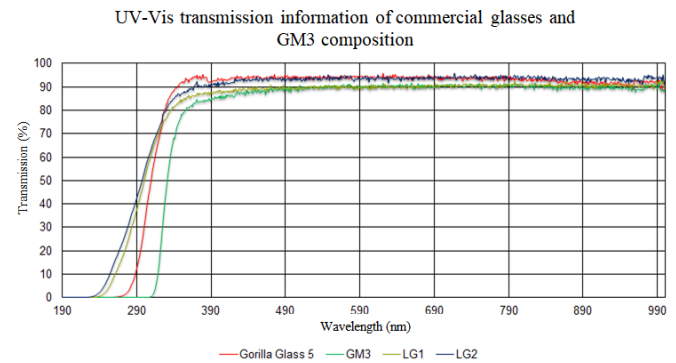


Figure 4: UV-Vis transmission of LG, Gorilla Glass 5[®] and GM3 glasses

3.2 Ion exchange GM3 samples

Two ion exchange temperatures were used: 420°C and 450°C. Exchange time of 1h, 3h, 6h, 9h, 12h, 18h, 24h, 30h and 36h were carried out at each temperature. The salt used was KNO₃ (potassium nitrate). The specimens were named according to the following formula: GM3-salt used-temperature-exchange time.

In order to characterize the exchanged GM3 glasses, measurements of mass, density, UV-Vis transmission and hardness were performed before and after ion exchange.

3.2.1 Ion exchange in KNO₃ at 420°C

In order to obtain statistically representative data on the effect of ion exchange, the tests were performed on more than one sample (two or three samples for each test condition). Table 3 shows the results obtained for each exchange time.

Table 3: Results obtained for ion-exchanged glasses at 420°C in KNO₃ at different times

Time (H)	Density (g/cm ³)		Transmission (%) (entre 700nm e 750nm)		Mass (g)		Hardness (HV)	
	Before	After	Before	After	Before	After	Before	After
1	2,48 ± 0,01	2,49 ± 0,01	88	87	0,75 ± 0,01	0,75 ± 0,01	619 ± 10	632 ± 14
3	2,50 ± 0,01	2,51 ± 0,01	91	91	0,43 ± 0,01	0,43 ± 0,01	619 ± 10	644 ± 9
6	2,48 ± 0,01	2,50 ± 0,01	88	87	0,58 ± 0,01	0,57 ± 0,01	619 ± 10	668 ± 12
12	2,49 ± 0,01	2,49 ± 0,01	89	88	0,59 ± 0,01	0,59 ± 0,01	619 ± 10	688 ± 11
18	2,49 ± 0,01	2,48 ± 0,01	88	88	0,61 ± 0,01	0,61 ± 0,01	619 ± 10	710 ± 10
24	2,49 ± 0,01	2,49 ± 0,01	84	80	0,66 ± 0,01	0,66 ± 0,01	619 ± 10	700 ± 18
30	2,51 ± 0,01	2,50 ± 0,01	85	85	0,54 ± 0,01	0,55 ± 0,01	619 ± 10	728 ± 12
36	2,49 ± 0,01	2,49 ± 0,01	83	86	0,66 ± 0,01	0,66 ± 0,01	619 ± 10	705 ± 12

Figure 5 shows the transmission curves before and after the exchange that obtained the highest hardness value (30 hours).

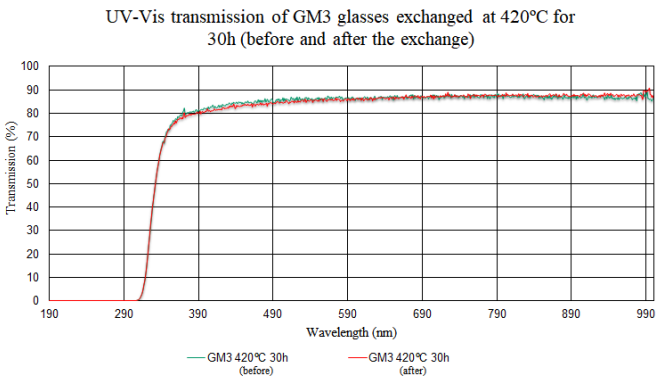


Figure 5: UV-Vis transmission of GM3 glasses exchanged at 420°C for 30h (before and after the exchange)

The variation of the refractive index with the exchange time was determined, with at least 3 measurements being made in each sample and the average values are shown in Table 4.

Table 4: Relationship between the refractive index and the exchange time at 420°C

Ion exchange at 420°C						
Ion exchange time (h)	1	12	18	24	30	36
n	1,52	1,53	1,52	1,52	1,53	1,50

For the 30h exchange, the elastic constants were determined, before and after the ion exchange, being indicated in Table 5.

Table 5: Elastic constants before and after ion exchange for 30h at 420°C

	E [GPa]		G [GPa]		ν	
	Before	After	Before	After	Before	After
GM3_KNO3_420_30_c	88 ± 1	87 ± 1	35 ± 1	36 ± 1	0,23 ± 0,1	0,23 ± 0,1
GM3_KNO3_420_30_d	85 ± 1	88 ± 1	34 ± 1	36 ± 1	0,23 ± 0,1	0,23 ± 0,1
GM3_KNO3_420_30_e	85 ± 1	89 ± 1	35 ± 1	36 ± 1	0,23 ± 0,1	0,23 ± 0,1
GM3_KNO3_420_30_f	84 ± 1	87 ± 1	34 ± 1	35 ± 1	0,23 ± 0,1	0,23 ± 0,1

Table 6 refers to the fracture toughness measured for 9h, 12h and 30h. The measurement for 30h is justified because it is the time where the greatest hardness is obtained and the others are the hardest times for the exchange at 450°C, in order to be able to infer if the K_{IC} change is related to time and/or temperature.

Table 6: Fracture toughness for ion exchange at 420°C (9h, 12h and 30h)

Ion exchange at 420°C			
Ion exchange time (h)	9	12	30
Young Modulus (GPa)	83	83	88
Fracture toughness (MPa.m ^{1/2})	2,2 ± 0,2	2,2 ± 0,1	2,2 ± 0,1

3.2.2 Ion exchange in KNO₃ at 450°C

For this temperature, a sample remained in the exchange bath for about 90h. This time served to study a much longer time and study the influence it has on the results.

The approach used to obtain results in KNO₃ exchanges at 450°C was the same as for results at 420°C: characterization through the measurement of mass, density, hardness and transmission before and after ion exchange to monitor the variation of these properties, the results of which are in the Table 7.

Table 7: Results obtained for ion-exchanged glasses at 450°C in KNO₃ at different times

Time (H)	Density (g/cm ³)		Transmission (%) (entre 700nm e 750nm)		Mass (g)		Hardness (HV)	
	Before	After	Before	After	Before	After	Before	After
1	2,48 ± 0,01	2,48 ± 0,01	87	83	0,67 ± 0,01	0,67 ± 0,01	619 ± 10	658 ± 25
3	2,47 ± 0,01	2,47 ± 0,01	87	87	0,59 ± 0,01	0,59 ± 0,01	619 ± 10	644 ± 11
6	2,49 ± 0,01	2,49 ± 0,01	88	84	0,60 ± 0,01	0,60 ± 0,01	619 ± 10	705 ± 12
9	2,49 ± 0,01	2,49 ± 0,01	84	81	0,69 ± 0,01	0,69 ± 0,01	619 ± 10	695 ± 13
12	2,49 ± 0,01	2,49 ± 0,01	84	81	0,69 ± 0,01	0,69 ± 0,01	619 ± 10	716 ± 13
18	2,50 ± 0,01	2,49 ± 0,01	87	86	0,64 ± 0,01	0,64 ± 0,01	619 ± 10	680 ± 14
24	2,49 ± 0,01	2,49 ± 0,01	86	85	0,67 ± 0,01	0,67 ± 0,01	619 ± 10	662 ± 23
30	2,50 ± 0,01	2,50 ± 0,01	89	88	0,62 ± 0,01	0,63 ± 0,01	619 ± 10	669 ± 10
36	2,48 ± 0,01	2,48 ± 0,01	83	83	0,64 ± 0,01	0,64 ± 0,01	619 ± 10	652 ± 12
90	2,48 ± 0,01	2,49 ± 0,01	87	84	0,62 ± 0,01	0,63 ± 0,01	619 ± 10	660 ± 10

Figure 6 shows the transmission curves before and after the exchanges that obtained the highest hardness value (9 and 12 hours).

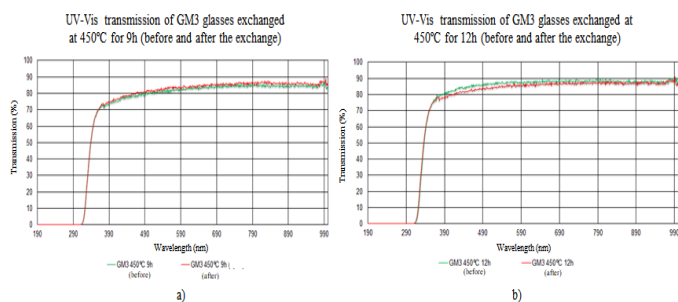


Figure 6: Graphics of UV-Vis transmission: a) Exchange at 450° for 9h, b) Exchange at 450°C for 12h

As in the case of exchanges at 420°C, in this case, the variation of the refractive index with the exchange time, shown in Table 8, was also determined.

Table 8: Relationship between the refractive index and the exchange time at 450°C

Ion exchange at 450°C					
Ion exchange time (h)	3	12	18	24	36
n	1,52	1,52	1,53	1,52	1,49

For the 9h and 12h exchanges, the elastic constants were determined, before and after the ion exchange, being indicated in Table 9.

Table 9: Elastic constants before and after ion exchange for 9h and 12h at 450°C

	E [GPa]		G [GPa]		ν	
	Before	After	Before	After	Before	After
	GM3_KNO3_450_9_b	86 ± 1	86 ± 1	35 ± 1	35 ± 1	0,23 ± 0,1
GM3_KNO3_450_9_c	86 ± 1	89 ± 1	35 ± 1	36 ± 1	0,24 ± 0,1	0,24 ± 0,1
GM3_KNO3_450_9_d	87 ± 1	87 ± 1	36 ± 1	35 ± 1	0,23 ± 0,1	0,24 ± 0,1
GM3_KNO3_450_12_b	87 ± 1	87 ± 1	35 ± 1	35 ± 1	0,23 ± 0,1	0,24 ± 0,1
GM3_KNO3_450_12_c	85 ± 1	84 ± 1	34 ± 1	34 ± 1	0,23 ± 0,1	0,23 ± 0,1
GM3_KNO3_450_12_d	85 ± 1	85 ± 1	35 ± 1	35 ± 1	0,23 ± 0,1	0,23 ± 0,1
GM3_KNO3_450_12_e	86 ± 1	86 ± 1	35 ± 1	35 ± 1	0,23 ± 0,1	0,23 ± 0,1

Also in this case, fracture toughness values for ion exchanges of 9h and 12h were determined (Table 10).

Table 10: Fracture toughness for ion exchange at 450°C (9h and 12h)

Ion exchange at 450°C			
Ion exchange time (h)	9	12	30
Young Modulus (GPa)	87	86	83
Fracture toughness (MPa.m ^{1/2})	2,1 ± 0,1	2,2 ± 0,1	Not measured

Figure 7 shows a diffractogram of a GM3 sample ion-exchanged at 450°C for 36h and a GM3 sample without exchange, to infer if the chemical treatment promotes the crystallization of the sample.

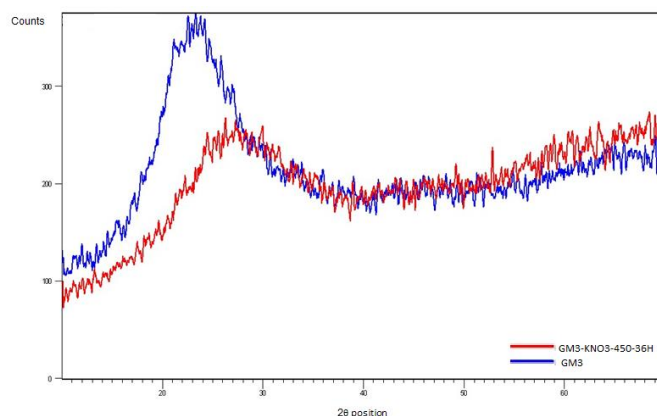


Figure 7: Diffracture of sample with 36h of exchange at 450°C and of a sample without exchange

3.2.3 Electron microscopy analysis

The thickness of the potassium layer over the specimens was analysed by SEM/EDS. The thickness of the potassium layer (Table 11) was determined by two methods: using the count graph provided by the equipment and with the measurement of the layer using the *ImageJ* software. These methods are not exact, as measurements are made manually, but several images were taken, in different areas of the samples, and the average was taken.

Table 11: Determination of the potassium layer caused by ion exchange

Ion Exchange at 420°C									
Exchange time (h)	1	3	6	12	18	24	30	36	
Measure source	Map	1,46 ± 0,028	2,44 ± 0,080	3,80 ± 0,051	5,78 ± 0,043	7,02 ± 0,023	7,88 ± 0,000	9,50 ± 0,020	9,63 ± 0,021
	Graphic	3,46	3,38	5,38	8,82	8,60	12,37	10,19	10,92
Average (µm)	2,46	2,91	4,59	7,30	7,81	10,13	9,85	10,28	

Ion Exchange at 450°C										
Exchange time (h)	1	3	6	12	18	24	30	36	90	
Measure source	Map	2,79 ± 0,028	5,35 ± 0,069	6,71 ± 0,000	8,84 ± 0,028	14,53 ± 0,023	13,01 ± 0,000	16,64 ± 0,000	21,38 ± 0,043	28,88 ± 0,030
	Graphic	4,92	6,32	7,10	9,20	13,63	13,57	17,55	23,04	31,94
Average (µm)	3,86	5,84	6,91	9,02	14,10	13,29	17,10	22,21	30,41	

3.3 Comercial glasses

The commercial glasses analyzed in this work were removed from unused computer monitors, the screen being disassembled and the outer glass cut and analyzed to obtain results and comparison with the GM3 glasses produced. These samples were named LG, Laptop Glass. Using EDS, the approximate composition of the two types of LG glass that were analyzed was determined (Table 12).

Table 12: Approximate composition of LG glasses

	% wt													
	SiO ₂	Al ₂ O ₃	Li ₂ O	MgO	ZnO	TiO ₂	ZrO ₂	Na ₂ O	CaO	As ₂ O ₃	SrO	BaO	P ₂ O ₅	K ₂ O
LG 1	58,84	17,12	n.a	n.a	1,03	n.a	n.a	0,05	9,19	2,05	8,40	3,31	n.a	n.a
LG 2	69,70	12,51	n.a	n.a	0,40	n.a	n.a	n.a	14,19	1,60	1,60	n.a	n.a	n.a

These glasses were characterized in terms of density, hardness (HV₀₂), elastic constants, fracture resistance and fracture toughness (HV₅), the results of which are described in Table 13.

Table 13: Characterization of LG glasses

	ρ [g/cm ³]	Transm. (700-750nm) [%T]	HV _{0.2}	E [GPa]	G [GPa]	$\sigma_{fracture}$ [MPa]			Weibull modulus			v	K _{IC} [MPa.m ^{1/2}]	a [μ m]
						σ_{upper}	$\bar{\sigma}$	σ_{lower}	\hat{m}_{upper}	\hat{m}_{corr}	\hat{m}_{lower}			
LG 1	2,50 ± 0,01	92	636 ± 16	65 ± 1	26 ± 1	142	132	123	5,21	4,31	3,28	0,25 ± 0,01	0,8 ± 0,1	23,67
LG 2	2,37 ± 0,01	96	611 ± 6	67 ± 1	27 ± 1	144	133	122	4,61	3,78	2,83	0,24 ± 0,01	1,0 ± 0,1	32,86

3.4 Gorilla Glass 5[®] samples

To promote a comparison between the properties presented by the GM3 composition (developed in this work) and by industrially produced glasses, samples of Gorilla Glass 5[®] (type of glass launched in 2016) were purchased, whose properties are specified in the technical sheet provided by the producer(9).

The composition used in these glasses has some similarities with the composition developed for this work, as described in the patent US 9,387,651 B2(10). These glasses have undergone an optical polishing and finishing by CNC.

These glasses were characterized in terms of density, hardness (HV₀₂), elastic constants, fracture resistance and fracture toughness (HV₅) and the results obtained are described in Table 14.

Table 14: Characterization results for Gorilla Glass 5[®] glasses

	ρ [g/cm ³]	Transm. (700-750nm) [%T]	HV _{0.2}	n $\lambda=589nm$	E [GPa]	G [GPa]	$\sigma_{fracture}$ [MPa]			Weibull modulus			v	K _{IC} [MPa.m ^{1/2}]	a [μ m]
							σ_{upper}	$\bar{\sigma}$	σ_{lower}	\hat{m}_{upper}	\hat{m}_{corr}	\hat{m}_{lower}			
GG5	2,42 ± 0,01	96	579 ± 11	1,47	72 ± 1	30 ± 1	299	271	247	3,75	3,11	2,40	0,22 ± 0,00	1,2 ± 0,0	11,38

4 Discussion of results

4.1 GM3 glasses

Given the final application of all the glasses studied in this work, transmission is one of the properties that must be monitored. Figure shows a comparison between the UV-Vis transmission of the three commercial glasses (LG1, LG2 and Gorilla Glass 5[®]) and that of GM3 glasses. It is possible to conclude that the transmission in commercial glasses is slightly higher, which can be explained by the fact that GM3 glasses have a manual polishing, in contrast to the others. Another relevant fact is that the thickness of the GM3 samples is about twice the rest.

Table 15 shows a compilation of all the properties studied for the four types of glass.

Table 25: Results table of the four types of glass tested

	ρ [g/cm ³]	Transm. (700-750nm) [%T]	HV _{0.2}	n $\lambda=589nm$	E [GPa]	G [GPa]	$\sigma_{fracture}$ [MPa]			Weibull Modulus			v	K _{IC} [MPa.m ^{1/2}]	a [μ m]
							σ_{upper}	$\bar{\sigma}$	σ_{lower}	\hat{m}_{upper}	\hat{m}_{corr}	\hat{m}_{lower}			
GM3	2,49 ± 0,01	92	619 ± 10	1,54	82 ± 1	33 ± 1	128	120	112	6,89	5,50	3,88	0,24 ± 0,01	1,6 ± 0,1	107,62
LG 1	2,50 ± 0,01	92	636 ± 16	Não medido	65 ± 1	26 ± 1	142	132	123	5,21	4,31	3,28	0,25 ± 0,01	0,8 ± 0,1	23,67
LG 2	2,37 ± 0,01	96	611 ± 6	Não medido	67 ± 1	27 ± 1	144	133	122	4,61	3,78	2,83	0,24 ± 0,01	1,0 ± 0,1	32,86
GG5	2,42 ± 0,01	96	579 ± 11	1,47	72 ± 1	30 ± 1	299	271	247	3,75	3,11	2,40	0,22 ± 0,00	1,2 ± 0,0	11,38

According to Macrelli⁽¹¹⁾, Young's module for aluminosilicate glass is between 83000 MPa and 91000 MPa and the fracture toughness of the same glasses is between 0.85

MPa.m^{1/2} and 0.96 MPa.m^{1/2}, which compared with results obtained by GM3 glasses and it is possible to conclude that the properties of these glasses, are of the order of those portrayed in the literature. The fracture toughness obtained by the GM3 composition is higher than the values reported in the literature, which means that it is a promising composition for further optimization of its mechanical properties.

The GM3 composition has a Young modulus of 82 ± 1 GPa, a distortion modulus of 33 ± 1 GPa and a fracture toughness of 1.6 ± 0.1 MPa.m^{1/2}. Despite having higher values for the Weibull modulus, GM3 glasses have considerably lower fracture stresses compared to Gorilla Glass 5 glasses. Despite the results achieved for the Weibull module, GM3 glasses have considerably lower fracture stresses compared to Gorilla Glass 5 glasses. The presence of surface defects, very likely in test pieces with manual finishing, is a factor influencing the results obtained and which is evident in the size of the critical defect (a). It is therefore important to understand if the defects in the GM3 glasses were of the order of magnitude of the defects present in the Gorilla[®] glasses, what would be the rupture stress of the GM3. Using equation (1) and the procedure indicated in 2.3.3.3, replacing Y by 1.29, K_{IC} by 1.6 MPa.m^{1/2} and a by 11.38x10⁻⁶ m it is possible to obtain that the breaking tension of these glasses would rise to 367.9 MPa, a higher value than the glasses Gorilla Glass 5[®], which has already undergone chemical treatment, unlike GM3 glasses. For this reason, the GM3 samples produced after obtaining these results were subjected to optical polishing at a CNC, in order to have a finish similar to that of Gorilla Glass 5[®].

Regarding hardness, it can be seen that the GM3 composition has a value in line with the rest, although Gorilla Glass 5 glasses have already been subjected to ion exchange. According to US patent 9,387,651 B2⁽¹⁰⁾ these glasses are subjected to an annealing after the ion exchange treatment, which has the function of increasing the compressive layer and reducing the compressive and tensile stresses, which justifies the hardness obtained by samples of this type of glass. The application of ion exchange to GM3 glasses can introduce an optimization in their properties.

Weibull statistics make it possible to compare rupture stress results as long as the type of test performed is known (flexion in 3 points, 4 points or equibiaxial), the dimensions of the test crossings and test pieces and the stress obtained in the test to be compared. The comparison between Kulp⁽¹²⁾ (sodo-borosilicate glasses exchanged with KNO₃ for 30 minutes), Liu *et al.*⁽¹³⁾ (boron-aluminosilicate ceramic glasses nucleated at 825°C for 10h and crystallized at 930°C for 9h), Sun *et al.*⁽¹⁴⁾ (ceramic lithium disilicate glasses treated at 600°C for 1h) and the results obtained in this work is in the Table 16. It is possible to conclude that using the experimental value of rupture stress (119,6 MPa), the tension obtained if the same test described in the articles was performed is lower than that described, except for the case of lithium disilicate ceramic glasses.

Another data that is worth comparing with other works carried out is the value of fracture toughness. Comparing the values of K_{IC} between commercial glasses and GM3, it is possible to conclude that the latter has a higher value. Thus it

is possible to predict that the application of chemical treatment (ion exchange) to this composition optimizes the mechanical properties. To *et al.*⁽¹⁵⁾ made a comparison between the K_{IC} values of various compositions and, although the composition studied in this work is not similar to any of those presented in the referenced article, it is worth noting that the K_{IC} of ASA glass ($1,6 \pm 0,1 \text{ MPa}\cdot\text{m}^{1/2}$) is superior to all presented in (15), whose highest value is $0,73 \text{ MPa}\cdot\text{m}^{1/2}$, achieved by a composition with elements such as silica, sodium, calcium and magnesium.

Table 16: Comparison table between results in the literature and those obtained in this work

	Glass type	Test type	Dimensions (mm)				$\sigma_{fracture\ estimated}$ (MPa)	$\sigma_{fracture}$ (MPa)	Difference (%) $\left(\frac{\sigma_{fracture} - \sigma_{fracture\ estimated}}{\sigma_{fracture\ estimated}} \times 100\right)$
			Assemble	b	h	r			
GM3	Alkali aluminosilicate	Ring-on-ring	$D_{support} = 20,2$ $D_{load} = 10,1$	12,5	119,6
Kulp [12]	Sodo-borosilicate	4-point	$L_{support} = 75$ $L_{load} = 22$	3	123,8	292	58
Liu et al [13]	Boro aluminosilicate ceramic	3-point	$L_3 = 20$	5	5	191,1	265	28
Sun et al [14]	Lithium disilicate ceramic	3-point	$L_3 = 16$	4	3	194,7	205,8	6

4.2 Ion exchanged GM3 glasses

Aaldenberg *et al.*⁽¹⁶⁾ carried out a work similar to this, in which a lithium aluminum glass with a composition similar to the GM3 composition was exchanged in KNO_3 . The authors propose a model that relates the mass gain per surface unit of the specimen as a function of the square root of the exchange time, indicating that the exchange process is controlled because the depth of the exchanged layer and the mass gain must increase proportionally with the root. square of the exchange time. The model has two components: a graph where it is possible to conclude if the relationship is linear (Figure 8) and another with calculations where it is possible to calculate the ion diffusion coefficient.

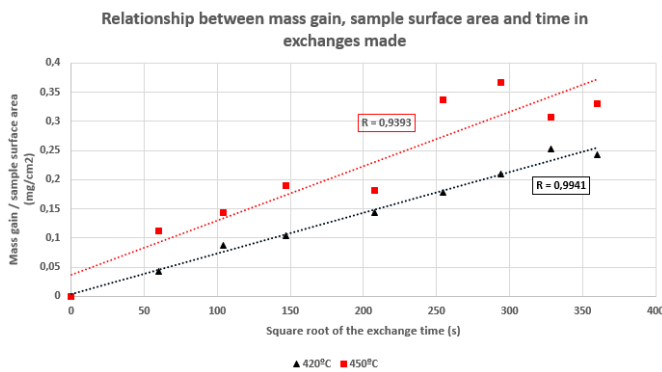


Figure 8: Verification of the ion exchange process control

The Figure 8 shows the relations for ionic exchanges at 420°C and 450°C and it is possible to conclude that the exchange processes developed in this work are controlled, according to what is referenced in (16).

From the calculations performed, it is possible to conclude that the ion diffusion coefficient is $(3,73 \pm 1,09) \times 10^{-13} \text{ cm}^2/\text{s}$ for the exchange of 420°C and $(1,29 \pm 0,81) \times 10^{-12} \text{ cm}^2/\text{s}$ for the exchange of 450°C, these values being the average and standard deviation of the result obtained for each variation of

mass and respective exchange time. As expected, the ion diffusion coefficient is higher for higher temperatures, according to the Arrhenius equation.

Figure 9 and Figure 10 show the relative variation of the monitored properties (density, transmission, mass and hardness) before and after the chemical process. As expected, the property that suffered the greatest relative variation was hardness, with the remaining variations being residual or due to causes external to the exchange:

- The slight variation in mass can be explained by the introduction of a "heavier" element in the structure.
- The reduced variation in density indicates that there were no significant structural change
- Changes in transmission may be due to the handling of samples and the introduction of scratches on the surface, not due to the exchange process itself.

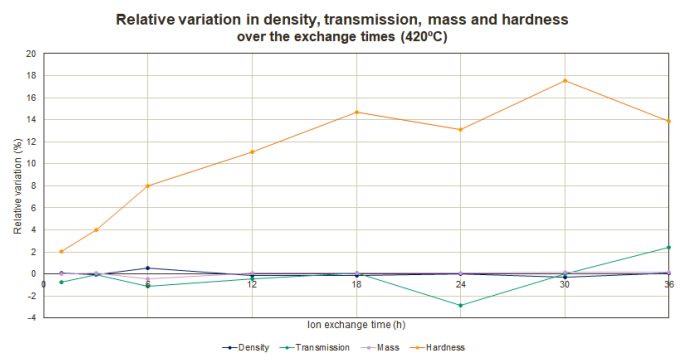


Figure 9: Relative variations due to ion exchange at 420°C

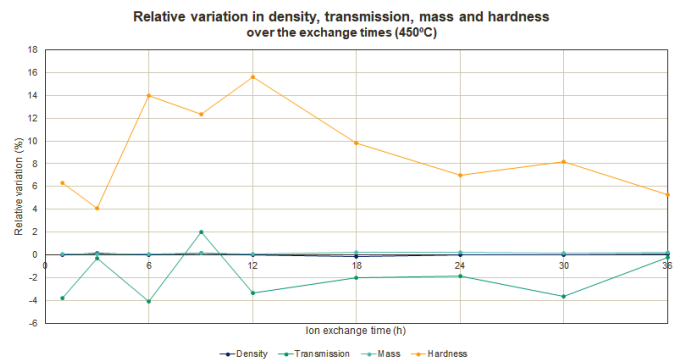


Figure 10: Relative variations due to ion exchange at 450°C

Regarding the refractive index, the variation between the value of the GM3 glasses (1,54) and the values after the exchanges (Table 4 and Table 8) is not significant, except for the ion exchange at 420°C for 30h and at 450°C 36h. According to Brocos *et al.*⁽¹⁷⁾, the refractive index (n) depends on the molar volume (V_m) through the Lorentz ratio indicated in equation (2), where R means molar refraction.

$$R = V_m \frac{n^2 - 1}{n^2 + 2} \Leftrightarrow n^2 - 1 = 3 \left(\frac{V_m}{R - 1} \right)^{-1} \quad (2)$$

Given that the molar volume of potassium, an element introduced into the structure with the exchanges, is higher than that of lithium, an exchanged element, it would be expected that the refractive index would decrease. This effect is noticed in the long-term exchange (30h and 36h), where the amount of potassium introduced is higher, even though the amount of potassium exchanged is reduced.

From Figure 11 it is possible to conclude that the highest hardness is obtained for 30h at 420°C and then for 12h and 9h at 450°C. According to Erdem *et al*⁽¹⁸⁾, with lower temperatures the hardness reaches higher values, while at higher temperatures there is a phenomenon of viscoelastic relaxation that causes a decrease in hardness for longer times. Gy⁽¹⁹⁾ stated that in addition to the phenomenon of viscoelastic relaxation, there is also a phenomenon of superficial structural relaxation that is evident at high temperatures and/or very long exchange times, which justifies the reduction of hardness at higher exchange times, more evident at the highest temperature (450°C).

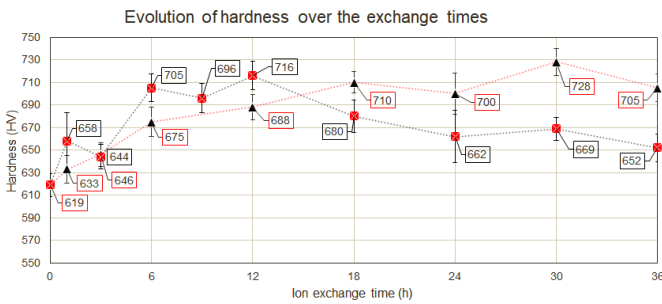


Figure 11: Evolution of hardness over the exchange times

Regarding the elastic constants, in the exchange of 30h at 420°C, three underwent changes in Young's modulus, on average of 3%. In the case of 9h (3 samples) and 12h (4 samples) exchanges, only one sample exchanged at 9h changed the value of Young's modulus, by 3%. Li et al⁽²⁰⁾ studied the effect of ion exchange on Young's modulus and also in that study there was an increase with ion exchange. According to Mackenzie and Wakaki⁽²¹⁾ this change is related to the contribution of the rotation of the SiO₄ tetrahedron, which can be explained through the semi-empirical law of the fourth power, considering the compacting or densification due to the ion exchange process. The remaining elastic constants did not change.

Figure 12 shows the evolution of fracture toughness values with time and temperature of exchange. It is possible to conclude that the exchange process increases this property, as expected, given that the introduction of a larger ion will “tighten” the network and, consequently, the cracks have greater propagation difficulties. Assuming the tenacity value of the exchange fracture at 9h 450°C (2,1MPa.m^{1/2}), the crack size calculated for the rupture of the ASA samples (107,63x10⁻⁶m) and Y = 1.29 it is possible to estimate the stress of rupture of the samples exchanged in these conditions through equation (1), equal to 159,9MPa, which translated into an increase of 25%. If the crack size of the Gorilla Glass 5[®] glasses (11.38x10⁻⁶m) is assumed, the

rupture tension would be equal to 482,6MPa, which translated into an increase of 75%.

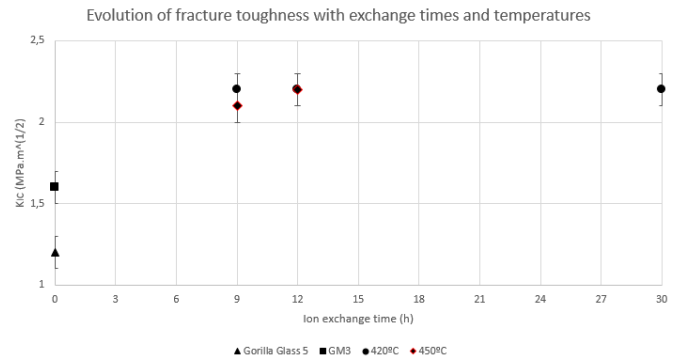


Figure 12: Evolution of fracture toughness with exchange times and temperatures

From the analysis of the Figure 7 it is possible to conclude that the exchange process does not promote the development of crystals, despite being a long exchange time, therefore, after the exchange the sample remains amorphous. It should be noted that the peak configuration differs between tests, but the swapped sample still has an amorphous structure.

The objective of this work is to define the best compromise between time and temperature of exchange that allows to optimize the mechanical properties of the glass without impairing the optical properties. Through the analysis of the results, three hypotheses are presented: 9 am to 450 ° C, 12 pm to 450 ° C and 30 h to 420 ° C, whose characterization results are found in the Table 17. All of the stated hypotheses allow a significant increase in hardness, and practically equivalent, an increase in the values of fracture toughness (equal to the exchange of 12h at 450°C and 30h at 420°C) and do not introduce changes in the optical properties. It is also important to analyze the optimization of the process that is achieved in the shortest possible time and temperature with good results, in order to reduce costs and allow a possible adaptation of this process industrially. That said, the optimization of mechanical properties, maintenance of optical properties and optimization of the process is achieved with 9h of exchange at 450°C with KNO₃.

Table 17: Ion exchange results at 450°C for 9h and 12h and 420°C for 30h

	ρ [g/cm ³]	Transm. (no-750nm) [%]	HV _{0.2}	E [GPa]	G [GPa]	σ _{fracture} [MPa]			Weibull modulus			ν	K _{IC} [MPa.m ^{1/2}]	a [μm]
						σ _{upper}	σ̄	σ _{lower}	m _{upper}	m _{corr}	m _{lower}			
9h 450°C	2,49 ± 0,01	81	695 ± 13	87 ± 2	35 ± 1	Not measured	Not measured	Not measured	not measured	not measured	not measured	0,23 ± 0,01	2,1 ± 0,1	not measured
12h 450°C	2,49 ± 0,01	81	716 ± 13	87 ± 1	35 ± 1	Not measured	Not measured	Not measured	not measured	not measured	not measured	0,23 ± 0,01	2,2 ± 0,1	not measured
30h 420°C	2,50 ± 0,01	85	728 ± 12	88 ± 1	36 ± 1	Not measured	Not measured	Not measured	not measured	not measured	not measured	0,23 ± 0,01	2,2 ± 0,1	not measured

It is possible to establish a relationship between the depth of the potassium layer and the hardness achieved (Figure 13), this relationship being explained by the phenomenon of viscoelastic relaxation already stated. In this type of treatment it must be decided whether, for the application, a large magnitude of superficial compression or a great thickness of the exchanged layer is desired⁽¹⁹⁾.

In Figure 14 it is possible to see the evolution of the thickness as a function of the exchange time and temperature, being possible to establish a trend line for each temperature, with the respective equation, which can allow estimating the potassium layer formed with exchanges not carried out in this study.

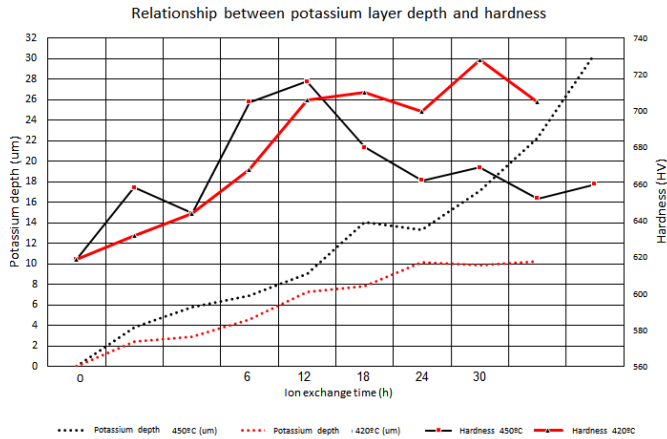


Figure 13: Relationship between potassium layer depth and hardness

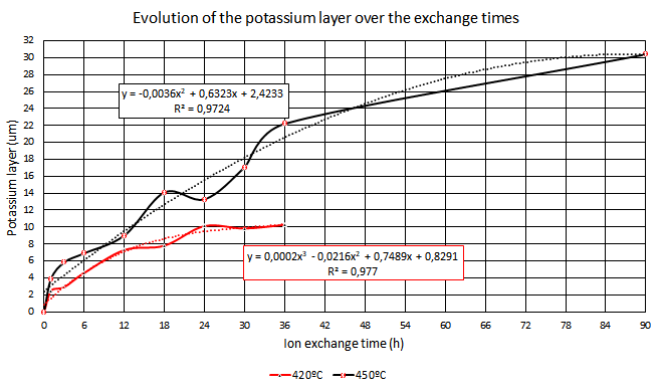


Figure 14: Evolution of the potassium layer over the exchange times

4.3 Comercial glasses

Although both types of glass were removed from “similar” monitors, it is possible to see in Table 12 that the determined composition presents some differences. The presence of lithium in the compositions is not possible to measure using the EDS technique given its low atomic weight. The biggest differences are found in zinc oxide (intermediate oxide) and sodium oxide, calcium oxide, strontium oxide and barium oxide (network modifying oxides). The intermediate oxides provide stability to the melt and the network modifying oxides reduce the viscosity of the glass as these elements “weaken” the network connections due to the increase in the ratio of oxygen to silicon that increases with the addition of these elements.⁽²²⁾ Therefore, differences in the composition of these elements mainly influence the production of these glasses. In

addition, the decrease in zinc oxide decreases the thermal expansion of the glass and increases the refractive index.⁽²³⁾

4.4 Gorilla Glass 5® glasses

The methods used by Corning® for the characterization presented in the technical sheet⁽⁹⁾ are not known but the comparison between the results obtained in the laboratory and those reported in the technical sheet indicate some differences, the most evident being the result of fracture toughness (Table 18).

Table 18: Comparison between the results obtained in the laboratory and those present in the technical sheet

	ρ [g/cm ³]	Hardness [GPa]	E [GPa]	G [GPa]	ν	K _{IC} (Mpa m ^{1/2})
Technical sheet	2,42	5,89	76,7	31,7	0,21	0,69
Measured	2,42 ± 0,00	5,68 ± 0,11	72,12 ± 0,67	29,47 ± 0,27	0,22 ± 0,00	1,06 ± 0,02

5 Conclusions

It is possible to conclude through the data indicated in the Table 15 that the chemical composition of the studied glasses presents excellent results of mechanical properties when compared with other commercial glasses. Preliminary results indicate that the ion exchange of these glasses allows maximizing the mechanical properties but, since there is still no experimental data of some of these properties in the exchanged GM3 glasses that prove this optimization, this point is missing to fully fulfill the purpose of this work.

It is, however, important to note that, if GM3 glasses had the same surface finish as Gorilla Glass 5® glasses, which would mean defects of the same order of magnitude, the rupture stresses reached by this glass would be higher. In order to provide the same finish as commercial glasses, GM3 glasses were sent to China for polishing, which is the reason why the mechanical data of the exchanged GM3 glasses was not reported.

The objective of this work is to determine the best compromise between time and temperature of ion exchange that allows to optimize the mechanical properties without impairing the optical properties. This commitment is reached at 9:00 am exchange at 450°C.

6 Future work

After all that has been described, it is evident that there are still some tests to be carried out in order to close this topic of study, namely the mechanical tests on GM3 glasses with 9h of ion exchange at 450°C.

There are other processes that should be explored in order to test a greater optimization of the mechanical properties of the glasses, maintaining the optical properties. These processes can undergo double ion exchange (Varshneya and Spinelli⁽²⁴⁾ prepared baths with potassium nitrate and sodium nitrate in different proportions; the K⁺ of the bath replaces the Na⁺ of the glass and the Na⁺ in the bath make the exchange with the Li⁺ of the glass⁽²⁵⁾), ion exchange in two steps, (ion exchange

assisted by electric field (accelerates the diffusion kinetics and decreases the time needed to obtain a superficially hardened glass⁽⁵⁾) and ion implantation. All of these processes must still be explored in ceramic glasses.

7 Acknowledgments

This work was supported by Fundação para a Ciência e Tecnologia (FCT), under the project *Glassmech - LISBOA-01-0145-FEDER-031192 | PTDC / CTM-CTM / 31192/2017*.

I am grateful for the indispensable help of the thesis advisors Professor Luís Santos and Professor Jorge Cruz Fernandes. And Doctor Bruno Nunes and André Dinis for the lab hours together.

References

1. SHELBY, J.E. *Introduction to Glass Science and Technology*. RSC advancing the chemical sciences, 2005.
2. BRILL, Robert H. A note on the scientist's definition of glass. *The Journal of Glass Studies*. 1962. Vol. 4, p. 127–138.
3. R., RAJARAMAKRISHNA and JAKRAPONG, Kaewkhao. Glass material and their advanced applications. *KnE Social Sciences*. 2019. Vol. 3, p. 796–807.
4. UHLMANN, D.R. and KREIDL, N.I. *Elasticity and Strength in Glasses*. 1980.
5. VARSHNEYA, ARUN AND MAURO, John C. *Fundamentals of Inorganic Glasses*. 3th. Elsevier, 2019.
6. ASTM E 1876 – 01: Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration. *American Society for Testing and Materials*. 2001. P. 1–16.
7. JIS R 1607: Testing methods for fracture toughness of high performance ceramics. *Japanese Industrial Standard*. 1990. P. 1–13.
8. C1322-05b: Standard Practice for fractography and characterization of fracture origins in advanced ceramics. *American Society for Testing and Materials*. 2005. P. 398–447.
9. Gorilla Glass 5[®] technical sheet. [online]. [Accessed 4 May 2020]. Available from: . www.corning.com/microsites/%0Aacsm/gorillaglass/PI_Sheets/Corning_Gorilla_Glass_5_PI_Sheet_RevB.pdf
10. INCORPORATED, Corning. Patent US 9,387,651 B2: Methods for producing ion exchanged glass and resulting apparatus. 2016.
11. MACRELLI, Guglielmo. *Chemical strengthening of glass by ion-exchange*. 2017.
12. KULP, Andrew. *Analysis of strength variation in glass due to ion exchange*. Virginia Polytechnic Institute and State University, 2012.
13. LIU, J., HAN, L., LUO, Z., HUANG, Q., HE, X., LIN, C., LU, A. Non-alkali glass substrate with improved mechanical properties for display devices. *Journal of Non-Crystalline Solids*. 2019. Vol. 524.
14. SUN, Y., MA, L., CUI, J., FENG, L., ZHANG, Z., YANG, Y., WANG, T. Effects of heat-treatment temperature and holding time on the microstructure and mechanical properties of lithium disilicate glass-ceramics. *Journal of Non-Crystalline Solids*. 2020.
15. TO, T., JENSEN, L. R., SMEDSKJAER, M. M. On the relation between fracture toughness and crack resistance in oxide glasses. *Journal of Non-Crystalline Solids*. 2020. Vol. 534.
16. AALDENBERG, E. M., LEZZI, P. J., SEAMAN, J. H., BLANCHET, T. A., TOMOZAWA, M. Ion-exchanged lithium aluminosilicate glass: Strength and dynamic fatigue. *Journal of the American Ceramic Society*. 2016. Vol. 99(8), p. 2645–2654.
17. BROCCOS, P., PIÑEIRO, A., BRAVO, R., AMIGO, A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. *Physical Chemistry Chemical Physics*. 2002. Vol. 5(3), p. 550–557.
18. ERDEM, I., GULDIREN, D., AYDIN, S. Chemical tempering of soda lime silicate glasses by ion exchange process for the improvement of surface and bulk mechanical strength. *Journal of Non Crystalline Solids*. 2017. Vol. 473, p. 170–178.
19. GY, R. Ion exchange for glass strengthening. *Materials Science and Engineering*. 2008. Vol. 149(2), p. 159–165.
20. LI, X., JIANG, L., LI, J., MOHAGHEGHIAN, I., DEAR J. P., LI, L., YAN, Y. Elastic-plastic deformation in ion-exchanged aluminosilicate glass by loading rate dependent nanoindentation. *Journal of Non-Crystalline Solids*. 2018. Vol. 491, p. 79–88.
21. MACKENZIE, J. D., WAKAKI, J. Effects of ion exchange on the young's modulus of glass. *Journal of Non-Crystalline Solids*. 1980. Vol. 38–39, p. 385–390.
22. AVANCINI, Tales. *Reciclagem de garrafas de vidro transparentes sob forma de frita cerâmica*. Universidade Federal do Rio Grande do Sul, 2016.
23. HURT, J.C., PHILLIPS, C.J. Structural Role of Zinc Oxide in Glasses in the System Na₂O-ZnO-SiO₂. *Journal of the American Ceramic Society*. 1970. Vol. 53(5), p. 269–273.
24. VARSHNEYA, ARUN, SPINELLI, Ian. High-strength, large-case-depth chemically strengthened lithium aluminosilicate glass. *American Ceramic Society Bulletin*. 2009. Vol. 88, p. 27–33.
25. VARSHNEYA, A. K. Chemical Strengthening of Glass: Lessons Learned and Yet To Be Learned. *International Journal of Applied Glass Science*. 2010. Vol. 1(2), p. 131–142.