Theoretical calculus of the mechanical strength of binary oxide glasses

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Abstract. The mechanical strength of the glasses is determined by the strength of the established bonds between the different macro-anionic species, these bonds being the weaker compared to the covalent ones inside the macro-anionic species. In this paper is proposed a probabilistic relationship to calculate the theoretical mechanical strength of the SiO$_2$ glass and of some compositions in the Na$_2$O·SiO$_2$ system, in good agreement with literature data.

1. Introduction

A glass, both as a melt and in a solid state, is a system consisting of entities of different types and dimensions (so-called “macro-anionic” species), which can be determined based on some structural models. In a fundamental way, it is considered that the mechanical strength of a material is determined by the bonding forces made between the constituent ions (atoms). For the unary oxide glasses, such as SiO$_2$ glass, an attempt to calculate the theoretical mechanical resistance, $R_t$, was based on a Griffith-type equation, obtained from the energy balance related to a Si-O chemical bond break [1], the bond having the equilibrium length $d_e = d$:

$$R_t = \frac{4E\sigma}{\pi d}$$

where $E$ is the modulus of elasticity; $\sigma$ - surface energy.

The qualitative and quantitative evaluations that have been made so far in the literature on the structures and properties of the glasses [1-6] allow some clarifications on the way in which the structural particularities of the vitreous state determine the theoretical and practical values of the mechanical strength. A glass, both as a melt and in a solid state, is a system consisting of entities of different types and dimensions (so-called “macro-anionic” species), which gives the structure a nano- and micro-heterogeneous character. Based on some structural models, we can determine the weight (number) of the different macro-anionic species (distribution curve) knowing that between the structural entities the nature of the bonds is predominantly ionic (of the dipole-dipole type), and inside them the bonds are essentially of covalent nature. In this context, the mechanical strength of the glasses is determined by the strength of the bonds that are established between different macro-anionic species, these being the...
weaker compared to the covalent ones inside them. This raises the problem of establishing, qualitatively and quantitatively, the components of these interactions.

2. Mathematical approach
At a first structural level, the glass systems are made up of atoms (ions) of different nature, according to the chemical composition of the glass. This determines, depending on the dimensions of the system, both the number of components and their relative distribution.

A structural image of the Na$_2$O-SiO$_2$ glass at submicroscopic level is shown in figure 1 [7].

![Figure 1. Na$_2$O·SiO$_2$ glass structure obtained by molecular dynamics simulation [7].](image)

The SiO$_2$ structure is a three-dimensional one, consisting of [SiO$_4$] entities linked by corners. The steric characteristics of the structure are represented by the internuclear distance $d_{Si-O}$, the O-Si-O angle, the angle of Si-O-Si bridges and the type and weight of the cycles formed by several tetrahedrons.

In the case of crystalline SiO$_2$, for various polymorphic forms, in the ideal situation all these characteristics are strictly constant, in different elemental volumes of SiO$_2$. Even for real crystals, however, there is some distribution of values of these characteristics around an average value. For instance, in the table 1 [4], for various polymorphic forms of crystalline SiO$_2$, the range of values in which are placed the actual values for the Si-O internuclear distances, the O-Si-O and Si-O-Si angles (including the average values of them) are presented.

From the data presented in table 1 one can note that:
- even for polymorphic forms of crystalline SiO$_2$ the steric characteristics present fluctuations around the average values
- the values of the O-Si-O angles have a low variability around the average value of 109.5°, imposed by a sp$^3$ hybridization, typical for silicon with respect to oxygen
- Si-O-Si angles show a greater dispersion of values around average values
- there is a certain correlation between the internuclear distances Si-O, $d_{Si-O}$ and the $\Phi = Si-O-Si$ angles, meaning that for higher values of the $\Phi$ angle correspond smaller values for $d_{Si-O}$.

Considering for properties the average values for vitreous SiO$_2$ ($E = 7 \cdot 10^{10}$ N/m$^2$, $\sigma = 0.3$ N/m), for $d = d_e = 1.60 \cdot 10^{-10}$ m, for the theoretical mechanical resistance it results, according to the equation (1), the
value $R_t = 1.29\cdot10^{10} \text{ N/m}^2 [2]$. Assigning reasonable experimental values for the various sizes, a final form for the equation is obtained:

$$R_t = \frac{3.06}{\sqrt{d_e}} \cdot 10^5 \quad (2)$$

If in equation (2) it is considered - according to [3] - $d = d_e = 1.60\cdot10^{-10} \text{ m}$, $R_t = 2.42\cdot10^{10} \text{ N/m}^2$.

**Table 1.** Si-O internuclear distances, O-Si-O and Si-O-Si angles for various polymorphic forms of crystalline SiO$_2$:

| Crystalline structure          | $d_{\text{Si-O}}$ (nm) | $<d_{\text{Si-O}}>$ nm | O-Si-O (°)     | Si-O-Si (°) | $<$Si-O-Si$>$ (°) |
|-------------------------------|-------------------------|-------------------------|----------------|-------------|------------------|
| α-quartz                      | 0.1607–0.1611           | 0.1609                  | 108.7–110.4    | 143.7       | 143.7            |
| B-quartz                      | 0.1591–0.1606           | 0.1598                  | 108.0–110.5    | 150.9       | 150.9            |
| α-tridymite monoclinic        | 0.1576–0.1622           | 0.1597                  | -              | 142.7–179.1 | 150.0            |
| α-tridymite triclinic         | 0.1585–0.1623           | 0.1606                  | 105.8–114.3    | 139.7–173.2 | 148.3            |
| B-tridymite                   | 0.5420–0.1563           | 0.1555                  | 105.9–111.9    | 165.2–178.7 | 171.7            |
| α-cristobalite                | 0.1600–0.1605           | 0.1602                  | 108.2–111.4    | 146.8       | 146.8            |
| B-cristobalite                | 0.1611                  | 0.1611                  | 107.8–112.8    | 146.7       | 146.7            |
| Keatite                       | 0.1562–0.1617           | 0.1590                  | 103.7–113.8    | 148.2–159.5 | 155.2            |
| Coesite                       | 0.1598–0.1631           | 0.1613                  | 108.3–111.0    | 136.1–180.0 | 148.4            |

Although different calculation methods lead to completely different results [1-3] - depending on the hypotheses of start, the considered simplifications and the actual values due to some physical or steric hindrances - two important conclusions can be drawn for the evaluation of the theoretical mechanical strength of the SiO$_2$ glass:

- its value is in the range of $1\cdot3\cdot10^{10} \text{ N/m}^2$, well above the values recorded in practice, but close to the performances obtained for a series of SiO$_2$ fibres subjected to special physico-chemical treatments
- whatever the calculation model proposed, in all cases, as well as in equations (1) and (2), a strong dependence between $R_t$ and the Si-O distance results, leading to the general equation:

$$R_t = \frac{C}{\sqrt{d}} \text{ [N/m}^2]\quad \text{(3)}$$

wherein $C$ is a physical constant that can be calculated from theoretical or experimental data, depending on the breakage model considered.

The main idea lies in the fact that the $R_t$ property was usually approached in a deterministic and not probabilistic conception. The probabilistic evaluation mode is supported by both the theoretical structural considerations and the principle equation (3). This is because the internuclear distance does not have a unique value, but has distributed values, even for the SiO$_2$ glass.

The mechanical strength of the SiO$_2$ glass has values distributed over a somewhat restricted range of values, 1.78–1.82·$10^{10} \text{ N/m}^2$, for values of $d_{(\text{Si-O})}$ length in the 0.160–0.166 nm range [2, 8].

The qualitative and quantitative assessments that have been made so far in the literature on the structure and properties of the glass [1-4] allow some clarification on how the structural particularities of the glass state determine the theoretical and practical values of the mechanical strength. This is based on the structural image with the characteristics considered so far, as well as the following:

- the number of coulombian bonds (between the macro-anionic species) formed per unit area, depends on the number (molar weight) of the different macro-anionic species (according to the distribution curve) and on their dimensions. In this way the number of contacts between microparticles with specified dimensions can be determined probabilistically;
- for glasses that are weak bases, macro-anionic species coexist with three-dimensional SiO$_2$ fragments.
On the other hand, it is expected that, if the SiO$_2$ weight is higher, the influence of the three-dimensional silica "blocks" on the properties will be prevalent. These components are:

- F$_0$ attraction force (of a Coulombian nature) between the microparticles;
- the tension due to the different expansion coefficients of the structural entities which are in contact (due to their different chemical compositions);
- the tension caused by different structural defects or/and by some particularities of the microstructure, for example, the separation of the microphases, the existence of superficial microcrystals.

The estimation of the theoretical mechanical strength of the glasses starts from establishing the R$_0$ value, which, in a first approximation, is proportional to the interaction force F$_0$ and with $n_0$, the number of ionic bonds per surface unit. Between the atoms (ions) of silicon, oxygen and sodium, physico-chemical bonds are made, mainly, which are:

- predominantly of covalent type, between silicon and oxygen; these may involve bridged oxygens O$_b$ (Si-O$_b$) or non-bridged oxygens O$_{nb}$ (Si-O$_{nb}$);
- predominantly of ionic type, between O$_{nb}$ and sodium ions (-O$_{nb}$... Na);
- dipole-dipole, which are present between the O$_{nb}$... Na bonds.

Both by their number (relative to the surface unit) and by the value of the interaction force, the first two types of bonds are more important and have a decisive contribution to estimate the average theoretical value of the mechanical strength, $\overline{R_0}$.

For a composition represented by the chemical formula mNa$_2$O·SiO$_2$, m = 0…2, if the ratio O/Si is noted with R it results:

- R = O/Si = m + 2
- Number of bridged oxygens: O$_b$ = 8 – 2R = 4 – 2m
- Number of non-bridged oxygens (equal to the number of O$_{nb}$...Na bonds): O$_{nb}$ = 2R – 4 – 2m = 4 – O$_b$ = 2m

Similar to SiO$_2$, it results:
The number of bridged bonds per surface unit and each oxygen, $n_1$, is

$$n_1 = \frac{4-2m}{4V_0^{2/3}} = \frac{1-0.5m}{V_0^{2/3}}$$

(4)

analogous, for non-bridged bonds

$$n_2 = \frac{2m}{4V_0^{2/3}} = \frac{0.5m}{V_0^{2/3}}$$

(5)

In equations (4) and (5), the coordination 4 of Si with respect to O was taken into account and, if $V_0$ is the volume of the oxygen atom in the glass, the equivalent surface can be considered $V_0^{2/3}$. The volume $V_0$ can be calculated based on the chemical composition and density, $\rho$, of the glass, with the equation:

$$V_0 = \frac{M/\rho - (n_{Na}V_{Na}+n_{Si}V_{Si})}{n_0}$$

(6)

wherein M is the molecular mass of the glass, n and V - the number and the ionic volume, respectively, for the atomic components of the glass.

The force required to break a chemical bond and, consequently, to separate two interacting atoms, F$_i$, is given by the equation:

$$F_i \approx \frac{E_i}{d_i} = k \frac{E_i}{d_i}$$

(7)

wherein E is the energy consumed to bring the interacting particles to the separation distance $d_i$ (i = 1 for the Si-O$_b$ bond; i = 2 for the O$_{nb}$...Na bond); k - constant.
Taking into account the equations 1 to 7, for the average theoretical resistance, $R_0$, it follows:

$$ R_0 \approx k \left( E_0 \frac{1-0.5m}{d_0 \sqrt{v_0^3}} + 0.5 \frac{m E_2}{d_2 v_0^2} \right) $$

Considering that the fundamental equation (7) is valid also for the SiO$_2$ glass, which has the average theoretical resistance $R_0$, and based on the equation (8), it results:

$$ R_0 = \frac{R_0 \left( E_0 \frac{1-0.5m}{d_0 \sqrt{v_0^3}} + 0.5 \frac{E_2}{d_2 v_0^2} \right)}{d_0 v_0} $$

wherein the index 0 refers to the SiO$_2$ glass.

### Table 2. Theoretical mechanical strength of the mNa$_2$O·SiO$_2$ glass

| m | %mol SiO$_2$ | M g/mol | $\rho$ g/cm$^3$ | $V_0$ cm$^3$ | d(Si-Ob) nm | $R_0 \cdot 10^9$ N/m$^2$ |
|---|---|---|---|---|---|---|
| 0 | 100 | 60 | 2.203 | 13.6 | 0.162 | 42.7 |
| 0.25 | 80 | 75.5 | 2.41 | 13.9 | 0.163 | 38.2 |
| 0.5 | 66.7 | 91 | 2.51 | 14.2 | 0.163 | 33.7 |
| 1 | 50 | 122 | 2.562 | 16.2 | 0.164 | 25.4 |
| 2 | 33.3 | 184 | 2.66 | 16.7 | 0.167 | 6.1 |
| 2 | 33.3 | 184 | 2.66 | 16.7 | 0.167 | 6.1 |

**Figure 2.** The influence of the Na$_2$O percentage on the theoretical mechanical strength of the Na$_2$O·SiO$_2$ glass.

Table 2 presents the calculations for the theoretical mechanical strength and figure 2 shows the influence of the Na$_2$O percentage on the theoretical mechanical strength of the Na$_2$O·SiO$_2$ glass.

According to the above statements, we can write a calculus equation of the mechanical resistance $R_{0x}$ for a glass made by macro-anionic species of the xSiO$_2$·(2x-fx)Na$_2$O type.

$$ R_{0x} = F_{0x} n_{0x} \quad (10) $$
Taking into account (8) and considering $W_0 \sim E_0$ it results:

$$R \approx \frac{E_0 \cdot 1}{d_0^{2/3}} \frac{1}{\nu_0^{1/3}} \ [N/m^2]$$  \hspace{1cm} (11)

But, as the distance between the Si atoms of the two tetrahedra, $d_{(Si-Si)}$, is calculated, by simple geometrical considerations, with the equation:

$$d(Si-Si) = 2d(Si-O) \cdot sin(\Phi/2)$$  \hspace{1cm} (12)

at minimum values of $\Phi$, the distance $d_{(Si-O)}$ is changed, resulting in the end different values for $d_{(Si-Si)}$ in the cases of different modes of tetrahedron coupling. Considering the equations (11) and (12), the final calculus equation for $R_{ox}$ is obtained:

$$R_{ox} = R \frac{E_x}{E_o} \frac{d_0}{d_x} \left[ 1 - \frac{f_x}{2x} \right] \ [N/m^2]$$  \hspace{1cm} (13)

A check of the correctness of the equation (13) can be done considering the experimental data provided by the literature. Thus, for the activation energy of the viscous flow of SiO$_2$, quite scattered values are reported in the literature, between 443 kJ/mol and 669 kJ/mol. [1] For the glasses of the Na$_2$O-SiO$_2$ system the values are between 63 kJ/mol (more basic glasses) and 125 kJ/mol (more acid glasses) [1].

In relation (13) $d_0$ is basically the Si-O internuclear distance in the SiO$_2$ glass, so $d_0 = 0.162$ nm. For the atomic volume of oxygen $V_0$ in the SiO$_2$ glass and $V_x$ in glasses of the Na$_2$O-SiO$_2$ system, the following assessments can be made: $V_0 = 13.6$ cm$^3$, and $V_x$ varies between 13.8 and 15.1 cm$^3$ [1].

The calculation of some properties of the silicate glasses based on a macro-anions theory for different chemical compositions showed good agreement with the experimental data in the range of 50-80% mol SiO$_2$, after which some systematic deviations between the calculated and experimental values are recorded [2].

The next step of the calculation requires the determination of the number of bonds between the various macro-anionic species $i$ and $j$, as well as of the values $\sigma_{ij}$.

The tension $\sigma$ that appears between two macro-anionic species with different expansion coefficients is given by the known equation:

$$\sigma_{ij} = \frac{(\alpha_i - \alpha_j) \cdot E(\gamma_{i} - \gamma_{0})}{1 - \mu} \ [N/m^2]$$  \hspace{1cm} (14)

in which: $\alpha_i$ - the average expansion coefficient of microparticle $i$, determined over the temperature range $T_0 - T_{\gamma} \ [\text{grd}]$; $E$ - Young's module $[\text{N/m}^2]$; $T_{\gamma}$ - max $(T_{\beta i}, T_{\beta j})$, $T_{\beta i}$ - glass transition temperature of $i$ glass $[\text{grd}]$; $T_0$ - ambient temperature $[\text{grd}]$; $\mu$ - Poisson's coefficient.

A macro-anionic species $i$ may come into contact with another macro-anionic species $j$ (the total number of these contacts being $N_{ii} = C^2_{N_i}$) or with a macro-anionic species $j$ (the number of these pairs being $N_{ij} = C^2_{N_i} \cdot C^2_{N_j}$), where $C^p_m$ represents the combinations of $m$ objects taken as $p$. The total number of $N_i$ interactions is given by the equation:

$$N = \sum_{i=1}^{N} N_{ii} + \sum_{i=1}^{N} \sum_{j=2}^{N} C^2_{N_i} \cdot C^2_{N_j} = C^2_{N} = N(N - 1)/2$$  \hspace{1cm} (15)

From here, the frequency of occurrence $f$ of different interactions between entities of the same type and of different types is, respectively:

$$f_{ii} = \frac{C^2_{N_i}}{C^2_{N}} = \frac{n_i(n_i - 1)}{N(N - 1)}$$  \hspace{1cm} (16)

$$f_{ij} = \frac{C^2_{N_i} \cdot C^2_{N_j}}{C^2_{N}} = \frac{2n_i \cdot n_j}{N(N - 1)}$$  \hspace{1cm} (17)

For large values of $N$, the calculation of the values of $f_{ii}, f_{ij}, \alpha_i, \alpha_j$ is particularly laborious. For this reason, we illustrate here an application for a glass of sodium metasilicate composition for which the first 16 macro-anionic species are considered. The values for $n_i$ and $n_j$ are given by the molar percent $p_i$.
for the entities with $x$ silicon atoms, and $N = 100$. Following the calculations, one can observe that two distinct situations arise, in which the actual resistance of the glasses is differently determined:

- In a first situation, in which the frequency of occurrence of the different values for $R_0$ is made as a histogram, the values recorded for $R_0$ are always higher than the maximum stresses that appear between different macro-anionic species. In this case, the actual mechanical strength of the $R_0^{(1)}$ glass is:

$$R_0^{(1)} = R_{0_{min}} - \sigma_{max} \quad (18)$$

- A second possibility is to obtain a graph with the radial distribution of the theoretical mechanical strength of the glasses (surface with micro-cracks) [9]. It is observed that, in this case, a series of values of $\sigma$ exceed some values of $R_0$, which is equivalent to the breaking of bonds with the appearance of some cracks. Because the breakage of bonds occurs in the contact area of two microparticles, the size of the microcracks can be assimilated to the length of a circle arc (if we consider spherical microparticles) that can reach the maximum value of $\pi D$ (D - diameter of the macro-anionic species). In this situation the actual mechanical resistance $R_0^{(2)}$ of the glasses is calculated with Griffith's equation:

$$R_0^{(2)} = K \sqrt{\frac{E \gamma}{D}} [N/m^2] \quad (19)$$

in which: $K$ - factor that depends on the geometry of the microcracks; $E$ - modulus of elasticity [N/m²]; $\gamma$ - surface tension [N/m]; $D$ - characteristic dimension of the crack [m].

To check the relationships deduced from theoretical structural considerations, an application will be made for the case of a sodium metasilicate glass. The number of macro-anionic species considered for sodium metasilicate glass is $N = 16$, in which case their weight is over 0.7%. For this case, the situation in which $\sigma_{max} < R_{0_{min}}$ is more probable. In this way, the mechanical resistance $R_0^{(1)}$ is:

$$R_0^{(1)} = 98 \cdot 10^6 \ N/m^2$$

If, however, in the case of the glass of the same composition, about 40 macro-anionic species are taken into account - when the last macro-anionic species is present with a weight of about 0.1% - for $R_0$, the value of $68.7 \cdot 10^6 \ N/m^2$ results, $\Delta \sigma_0 = 310 \cdot 10^{-7} \ \text{grd}^{-1}$, and $\sigma_{0} = 88.3 \cdot 10^6 \ N/m^2$. Because $\sigma_{max} > R_{0_{min}}$, microcracks may occur due to breaking bonds. In the case of sodium metasilicate, the first 16 macro-anionic species have values between 0.5 and 1.2 nm [2], but when $x$ (the silicon atoms) increases, the diameter of the macro-anionic species increases to tens or even hundreds of nm and, therefore, in the same way but three times more, increases the length of the micro-cracks, this result being in accordance with experimental determinations. Table 3 shows for different values of $D$ [nm], the mechanical strength of the glasses, according to Griffith's equation.

| Microcrack dimension nm | 0.162 | 5 | 10 | 50 | 150 |
|-------------------------|-------|---|----|----|-----|
| mechanical strength $\cdot 10^{-7}$ N/m² | 216 | 19.4 | 13.7 | 6.1 | 3.5 |

We can observe from table 3 a somewhat surprising result that has been observed experimentally, also, [10] and is theoretically explainable through the statements made above: with the increase of the percentage of SiO₂ a decrease of the mechanical resistance takes place.
3. Conclusions
In this paper, the theoretical mechanical strength for Na₂O·SiO₂ and SiO₂ glasses was calculated, and the results were compared with the experimental values provided by the literature. The calculation of some properties of silicate glasses based on a macro-anions theory for different chemical compositions showed good agreement with the experimental data in the 50-80% mol. SiO₂ range, after which some systematic deviations between the calculated and the experimental values are recorded. In the case of sodium metasilicate, following the theoretical calculations it was observed that with the increase of the percentage of SiO₂ there is a decrease of the mechanical resistance, observed in experimental results, too.

Although mechanical resistance has been studied for so many years, it remains topical because the classical approaches lead to unique mean values, by considering the SiO₄ a perfect tetrahedron in respect to the internuclear angles and distances. Regardless of the calculation method used, the same conclusions are reached: there is a strong dependence between Rₜ and the distance Si-O, dₑ. It turns out that mechanical resistance must follow a probabilistic approach, taking into account the distribution of angles, chemical bonds, structural entities, internuclear distances that may have values with a certain probability (frequency of occurrence). This reality confirms the distributed mechanical strength values measured for the glasses.

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