Compositional optimization for molding of bioactive glasses in the SiO\textsubscript{2}-Na\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5} system

Otimização da composição para moldagem de vidros bioativos no sistema SiO\textsubscript{2}-Na\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5}

ABSTRACT
This paper shows the determination of the most energy efficient composition for molding of bioactive glasses in the SiO\textsubscript{2}-Na\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5} system. Ten compositions were formulated in the range where the glass has a bioactivity index greater than 8 and the curves of viscosity as a function of temperature were drawn using the Vogel-Fulcher-Tammann (VFT) equation. Analyzing the curves, the composition 43SiO\textsubscript{2}-30CaO-21Na\textsubscript{2}O-6P\textsubscript{2}O\textsubscript{5} has the lowest viscosity over the entire working temperature range, requiring less heat to be molded and consequently consuming less energy in the ovens.

Keywords: bioactive glasses, Vogel-Fulcher-Tammann, vitreous conformation, biomaterials.

RESUMO
Este documento mostra a determinação da composição de maior eficiência energética para moldagem de biogás no sistema SiO\textsubscript{2}-Na\textsubscript{2}O-CaO-P\textsubscript{2}O\textsubscript{5}. Dez composições foram formuladas na faixa onde o vidro tem um índice de bioatividade maior que 8 e as curvas de viscosidade em função da temperatura foram desenhadas usando a equação Vogel-Fulcher-Tammann (VFT). Analisando as curvas, a composição 43SiO\textsubscript{2}-30CaO-21Na\textsubscript{2}O-6P\textsubscript{2}O\textsubscript{5} tem a viscosidade mais baixa em toda a faixa de temperatura de trabalho, exigindo menos calor para ser moldado e consequentemente consumindo menos energia nos fornos.

Palavras-chave: vidros bioativos, Vogel-Fulcher-Tammann, conformação vítrea, biomateriais.
1 INTRODUCTION

Bioactive glasses and glass-ceramics have been developed to solve a wide range of medical problems, including bone repair, cancer therapy, soft tissue repair and dental restorations (KAUR, 2017).

To be molded into a product, a vitreous material must have its viscosity lowered by heating. The viscosity at a given temperature depends on the chemical composition of the material, so it is interesting to determine which composition achieves a lower viscosity at a lower temperature, so that the energy consumption of the ovens is as low as possible (VARSHNEYA and MAURO, 2019).

Bioglasses

In the early 1970s, hydroxyapatite, a natural ceramic and the main mineral constituent of bones, was the only synthetic material considered to be entirely compatible with the body. In the search for greater biocompatibility, Professor Larry L. Hench has developed a glass that can be mixed with other ingredients, such as calcium, to join fractured bones (KRISHNAN and LAKSHMI, 2013).

This new vitreous material, when dissolving in a normal physiological environment, activates genes that control osteogenesis, producing bone with the same quality as the natural (XYNOS et al., 2000).

The surface of a bioglass implant, when subjected to an aqueous solution (body fluids), converts into a layer of silica gel rich in CaO and P₂O₅ that mineralizes to hydroxycarbonate in a matter of hours (Fig. 1). This gel layer is so similar to the hydroxyapatite matrix that the osteoblasts differentiate forming a bone layer (ANDERSSON et al., 1990; WALLACE et al. 1999).

Figure 1 – Formation of bone tissue on the surface of a bioglass.

Source: Velez (2016)
The original bioactive glass, called Bioglass 45S5, has the following mass composition: 45% SiO$_2$, 24.5% CaO, 24.5% Na$_2$O and 6% P$_2$O$_5$. It is composed of minerals that occur naturally in the body and the molecular proportions of calcium and phosphorus oxides are similar to those of bones (XYNOS et al., 2000).

**Bioactivity**

Professor Hench used the term "bioactivity" to describe the osteogenesis created by his glass (HENCH and WEST, 1996). The concept was then extended to other materials, being defined as those that provoke a specific biological response at the interface with the body, resulting in the formation of a bond with the living tissue (RATNER et al., 1996).

The Bioactivity Index ($I_B$) is measured by the time ($t_{0.5bb}$) it takes more than half of the interface to bind to the tissue:

$$I_B = \frac{100}{t_{0.5bb}}$$

(1)

any material with $I_B$ greater than 8, such as the Bioglass 45S5, will bind to soft and hard tissue. Materials such as synthetic hydroxyapatite, with an $I_B$ value smaller than 8 and greater than 0, will only bind to hard tissue (HENCH, 1990).

For bioglasses, $I_B$ varies depending on the composition, allowing its use in various applications. Figure 2 shows how this index varies with the components percentages:

**Figure 2** - Bioactivity index as a function of composition for bioglasses with 6%w of P$_2$O$_5$. 

Source: Hench (1990)
In Figure 2, region A is bioactive; in region B there is no bonding with living tissue because the reaction is very slow; in region C binding does not occur because the reaction is too fast; and in region D, bioactivity can occur, but the composition does not favor the formation of glasses (RAWLINGS, 1992).

2 METHODOLOGY

Composition intervals where the bioactivity index ($I_B$) is at least 8 were selected, as shown in Figure 3:

![Figure 3 – Determination of composition ranges where $I_B \geq 8$](image)

The composition ranges determined by Figure 3 are shown in Table 1:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>43 – 50</td>
</tr>
<tr>
<td>CaO</td>
<td>25 – 40</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>15 – 32</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>6</td>
</tr>
</tbody>
</table>

Source: based on Hench (1990)

Ten compositions were elaborated from the determined intervals and their viscosity curves were plotted as a function of temperature, using the Vogel-Fulcher-Tammann (VFT) equation (VOGEL, 1921):

$$\log \eta(T) = A + \frac{B}{T - T_0}$$

(2)
where \( A, B \) and \( T_0 \) are constants depending on the chemical composition of the material.

With the curves of each glass, the composition that requires less energy to be softened and, therefore, the most advantageous for manufacturing, was determined.

### 3 RESULTS AND DISCUSSIONS

The formulated materials are shown in Table 2 and the coefficients \( A, B \) and \( T_0 \) of the VFT equation were determined using the global statistical modeling of Fluegel (2007):

Table 2 - Compositions and coefficients of the VFT equation for bioglasses with \( I_B \geq 8 \) and 6\%w of \( \text{P}_2\text{O}_5 \)

<table>
<thead>
<tr>
<th>Composition code</th>
<th>Mass percentage</th>
<th>VFT equation coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{SiO}_2 )</td>
<td>( \text{CaO} )</td>
</tr>
<tr>
<td>Bioglass 45S5</td>
<td>45</td>
<td>24,5</td>
</tr>
<tr>
<td>C1</td>
<td>45</td>
<td>34</td>
</tr>
<tr>
<td>C2</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>C3</td>
<td>50</td>
<td>29</td>
</tr>
<tr>
<td>C4</td>
<td>43</td>
<td>30</td>
</tr>
<tr>
<td>C5</td>
<td>43</td>
<td>25</td>
</tr>
<tr>
<td>C6</td>
<td>43</td>
<td>36</td>
</tr>
<tr>
<td>C7</td>
<td>45</td>
<td>32</td>
</tr>
<tr>
<td>C8</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>C9</td>
<td>43</td>
<td>32</td>
</tr>
<tr>
<td>C10</td>
<td>47</td>
<td>32</td>
</tr>
</tbody>
</table>

Source: based on Krishnam and Lakshmi (2013) and Hench (1990)

With the coefficients in hand, the viscosity curves as a function of temperature were plotted:
Figure 4 shows that the glass of composition C4 (43SiO$_2$-30CaO-21Na$_2$O-6P$_2$O$_5$) has the lowest viscosity throughout the entire working range, requiring less energy to be softened and molded.

**4 FINAL CONSIDERATIONS**

The selected composition is different from commercial bioglasses, having lower viscosity, which facilitates its molding and reduces the energy consumption of the ovens. The results obtained open a range of research on the 43SiO$_2$-30CaO-21Na$_2$O-6P$_2$O$_5$ composition: *in vitro* cytotoxicity tests, biocompatibility studies among many other properties must be evaluated, such as tenacity, chemical stability and machinability, so that the material can be implemented in the biomedical market.
REFERENCES


