SiO$_2$-CaO-Na$_2$O-P$_2$O$_5$ bioglasses prepared via sol gel method

Fields of use:
- Bones Substitutes
- Surgery

Plan
- Bioactivity definition
- Advantages of the Sol-Gel way
- Aim
- Bioglass Synthesis
- Characterizations
- Results and perspectives
Bioactivity definition

Carbonated Hydroxyapatite (HCA)

In vitro: Simulated Body Fluid

Calcium + Phosphorus

In vivo

Bioglass

- Similar to bones mineral phase
- Allow intimate chemical bond with living tissues
- Stable anchoring of the implant

Advantages of the Sol-Gel way

Classical synthesis of glasses by melting

low Si ratio  
high P ratio

glassceramics during the quench

bioactivity less interesting

TO REPLACE SYNTHESIS BY MELTING

SOL-GEL WAY ADVANTAGE

- Soft chemical, low temperature
- Larger composition areas
- Faster release of soluble silica.
- Higher surface area, rich in reactive silanol groups.
- Greater rates of resorption and bone formation.
- More bioactive, form the HCA layer faster.
**Aim**

Synthesize bioglass by sol-gel way & Control the resorption of the glass

- Slightly soluble ternary compound: $\text{SiO}_2 - \text{CaO} - \text{P}_2\text{O}_5$
- More soluble quaternary compound: $\text{SiO}_2 - \text{CaO} - \text{Na}_2\text{O} - \text{P}_2\text{O}_5$

- High melting temperature 1600°C: preparation by traditional method is more difficult.
- The sodium replaces a part of calcium

---

**Sol-gel way possibilities**

- Monolith
- Deposition on a substrate
- Impregnating a porous substrate
- Macroporous or composite with controlled porosity
- Film
- Sol
- Gel
**Sol-Gel synthesis:**

**Acid way**

- Ternary composition: $47\text{SiO}_2\ 48\text{CaO}\ 5\text{P}_2\text{O}_5$
- Quaternary composition: $47\text{SiO}_2\ 26.5\text{CaO}\ 21.5\text{Na}_2\text{O}\ 5\text{P}_2\text{O}_5$

**Basic way**

- Ternary notation: $47\text{SiP}_5\text{T}$
- Quaternary notation: $47\text{SiP}_5\text{Q}$

- It’s difficult for quaternary composition to include modifiers elements without crystallization during the drying acid process.
- After drying process (130°C - 24h), an aging thermal treatment permits to obtain the glass (temperature giving by TGA/DTA analysis).

**Acid hydrolysis reaction:**

- Average stability of the positive intermediate, which implies that the raw materials are never fully hydrolysed.
Basic hydrolysis reaction:

- Hydroxide ion replaces water as the nucleophile. It is more reactive, hydrolysis is accelerated.
- Good stability of the negative reactional intermediate, the hydrolysis reaction is rapid and complete.

Condensation reactions (valid for both ways):

Oxolation reaction:

And alcoxolation reaction:
Specific condensation reaction for ternary system in acid way (in investigation):

\[
\begin{align*}
\text{TEOS} & \quad & \text{Calcium alcoxide} & \quad & \text{inserting calcium in the grid} \\
\end{align*}
\]

Condensation reaction in for quaternary system in basic way:

Glycerol can make complexes with calcium ions, and can condense with the amorphous silicium grid in formation.

<table>
<thead>
<tr>
<th>Bioactivity definition</th>
<th>Advantages</th>
<th>Aim</th>
<th>Synthesis</th>
<th>Characterization</th>
<th>Results &amp; perspectives</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Characterization by Thermal Analysis

Thermogravimetric analysis: departure of water, methanol and ethanol
Thermal differential analysis: glass transition temperature and crystallization temperature

Aging of ternary gel over Tg (800°C) -> Glass

For quaternary gel, the TGA and DTA graphs are similar. To obtain the glass, the gel must be heated at about 550°C.
Characterization by X-ray diffraction

- The drying gel is amorphous.
- The crystalline phase is wollastonite (CaSiO$_3$). To retain the amorphous nature of the composition the gel heat treatment must not exceed 800°C.
- In case of quaternary composition, the gel treatment must not exceed 550°C.

Characterization by FTIR

- The spectrum of dried gel at 130°C is similar to that of a conventional silica gel.
- After treatment at 800°C, the appearance of a Si-O 2 NBO stretching vibration band 915 cm$^{-1}$ as well as the widening of the Si-O-Si angular bending band at 475 cm$^{-1}$ show the passage of the gel to a stabilized glass.
**Characterization of bioactivity**

- Observation of the HCA after 3 hours of immersion in SBF.
- The IR spectra exhibit the characteristic bands of the HCA at 3h. This ternary glass is bioactive.
- Results for quaternary system are quite the same.
Actual results:
- Preparation of two glasses has been successful
- Dip coating on classical glass with basic process.
  - Control of the drying process
  - Control of the thickness of the layer
- Cytotoxicity of glass obtained by basic process.
- Incorporation of more phosphorus

Perspectives:
- Impregnation of dense HA substrates
- Impregnation of porous HA substrates
- Study of the formed layer
- Study of the penetration and resorption

Composite or macroporous

Thank you for attention