

# Influence of poly (ethylene) glycol used as organic template on the structure of calcium silicate bioactive glasses

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In this paper were prepared porous calcium silicate bioactive glasses by the sol-gel method using poly (ethylene) glycol (PEG) as an organic template. The structure of the glasses prepared was investigated by XRD, FTIR and SEM/EDS. The in vitro bioactivity of these glasses was carried out by immersing them in a stimulated body fluid (SBF) at 37 °C and pH 7.4 for a reaction time period of 14 days. The results show that the use of the PEG (as pore former) enables the synthesis of porous calcium silicate glasses with excellent bioactivity.

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*Keywords:* Bioceramics, Bioglasses, Sol-gel processing, FTIR, SBF

## 1. Introduction

Since the discovery of 45S5 Bioglass by Hench [1], the bioactive glasses and glass-ceramics have attracted significant attention in the area of orthopedics and dental implants. Their clinical success is due to the strong bonding at the bone- implant interface, through the formation of a biologically active carbonate apatite layer that is chemically and crystallographically equivalent to the mineral phase in the bone [2]. The recent development of bone tissue engineering has led the interest of many scientists in the design of Bioglass<sup>®</sup>-based scaffolds, i.e. porous systems able to drive and foster the bone tissue regrowth [3]. Ideal for an artificial bone substitute is to have a high porosity (300-500 µm) to allow bone ingrowth, nutrient delivery to the center of the regenerated tissue and vascularization [4, 5]. Bioglasses prepared via sol-gel method always have an interconnected mesoporous structure [6]. Porosity can be increased by adding polymer beads or other organic agents (porogens) such as gelatine, sucrose, that burn out during the sintering and leave pores [7].

The aim of this work is the synthesis, characterization and the bioactivity study of porous bioactive glasses using the sol-gel method and PEG as an organic template. The PEG was used in order to change the mesoporous structure of the binary calcium silicate glasses and therefore their properties. PEG is a thermoplastic polymer widely used as additive in the sol-gel method to increase the porosity and a well-known biomaterial used in cosmetics, biotechnology, pharmaceuticals, packaging, due to its excellent properties such as non-toxicity and

immunogenicity, water-solubility and protein resistance [8].

## 2. Experimental

The initial proportion of the raw materials was: SiO<sub>2</sub>/CaO=50/50 (mol/mol). The sol was prepared in a cylindrical container by mixing distilled water, HNO<sub>3</sub>, tetraethyl orthosilicate and calcium nitrate tetrahydrate, following this order. On completion of hydrolysis, the sol was aged in a drying oven at 60 °C to reach high viscosity near the gel point. Then, the polyethylene glycol (PEG) particles were ground and sieved in size <300 µm and added into the gel with strong stirring for ½ h. After aging for 1 day, the gel was dried in an environment containing of 50:50 % mixture of water/ethanol, and the temperature was increased to 120 °C and kept for 2 days. The dry gel was ground and sieved in size <63 µm and pressed into disks of 13 mm in diameter and 2 mm in thickness. The disks were thermally stabilized in an electric furnace in air atmosphere at 700 °C for 3 hours with a heating rate of 10 °C/min.

The structure of the bioactive glasses prepared was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy equipped with energy dispersive spectroscopy (SEM/EDS).

The in vitro bioactivity of these glasses was carried out by immersing them in a simulated body fluid (SBF) proposed by Kokubo [9], with ion concentrations nearly

equal to those of human blood plasma, at 37 °C and pH 7.4 for a reaction time period of 14 days.

FTIR spectra of the glasses were recorded using a Perkin Elmer Spectrum 2000, on discs prepared by mixing of the sample powder and KBr.

XRD measurements were performed with a Siemens D5000 X-Ray Diffraction.

The morphology of the glasses was examined before and after immersion in SBF in a FEI Quanta 200 Scanning Electron Microscope (SEM) and simultaneously their elemental analysis was determined by Energy Dispersive Spectroscopy (EDS).

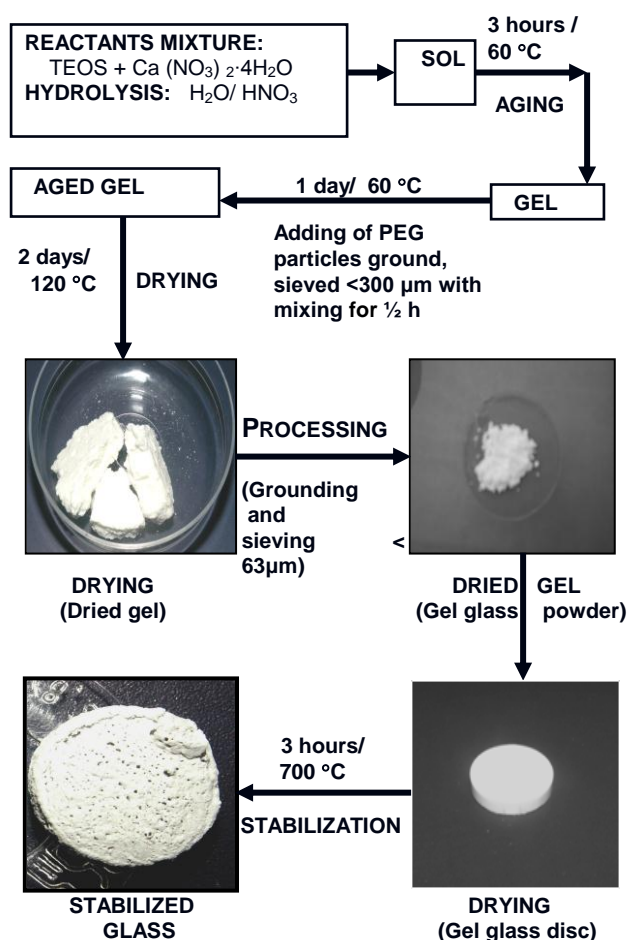


Fig. 1. Schematic illustration of the sol-gel process for the manufacture of the glass.

### 3. Results and discussion

#### FTIR

Table 1 presents the groups and their wavenumbers of the FTIR spectra of the glass.

Table 1. FTIR results.

Group	Wavenumbers (cm <sup>-1</sup> )*	Wavenumbers (cm <sup>-1</sup> )**
Si-O-Si and O-Si-O	460	450
O-Si-O	800	818
Si-O-Ca	950	945
Si-O-Si	1080	1066
(NO <sub>3</sub> ) <sup>-</sup>	1380	1384
H <sub>2</sub> O	1630	1632
(CO <sub>3</sub> ) <sup>2-</sup>	1410-1490	1419

\*: wavenumber (cm<sup>-1</sup>) region for the corresponding peak according to the literature

\*\* : wavenumber (cm<sup>-1</sup>) determined from the FTIR spectra of the glass

Table 2 presents the groups and wavenumbers of HA based on its FTIR-spectrum.

Table 2. FTIR results.

Group	Wavenumbers (cm <sup>-1</sup> )*	Wavenumbers (cm <sup>-1</sup> )**
(P-O) vibrational mode of an amorphous phosphate	568 and 1035	564 and 1052
(CO <sub>3</sub> ) <sup>2-</sup> carbonate group	1419, 1489 and 871	1406, 1480 and 873

\*: wavenumber (cm<sup>-1</sup>) region for the corresponding peak according to the literature

\*\* : wavenumber (cm<sup>-1</sup>) determined from the FTIR spectra of the glass

Fig. 2 shows the FTIR spectra of the glass after aging, drying and stabilization (a) and the FTIR spectra of the glass after 14 days immersion in SBF (b).

According to Fig. 2 (a), after the aging at 60 °C the peak at 450 cm<sup>-1</sup> is assigned to the bending modes of the Si-O-Si and O-Si-O bonds [10, 12]. The peak at 818 cm<sup>-1</sup> corresponds to the stretching mode of the O-Si-O bond [10, 11, 12]. The peak at 945 cm<sup>-1</sup> corresponds to the Si-O-Ca bonds containing non-bridging oxygen [10, 13]. The peak at 1066 cm<sup>-1</sup> is attributed to the symmetric stretching vibration of the Si-O-Si bonds [10, 11]. The peak at 1384 cm<sup>-1</sup> is assigned to the vibration of ionic (NO<sub>3</sub>)<sup>-</sup> [10, 11, 12]. The vibration of H<sub>2</sub>O (vibration due to the OH bond) is at 1632 cm<sup>-1</sup> [10, 11]. No peaks assigned to organic matter have been observed.

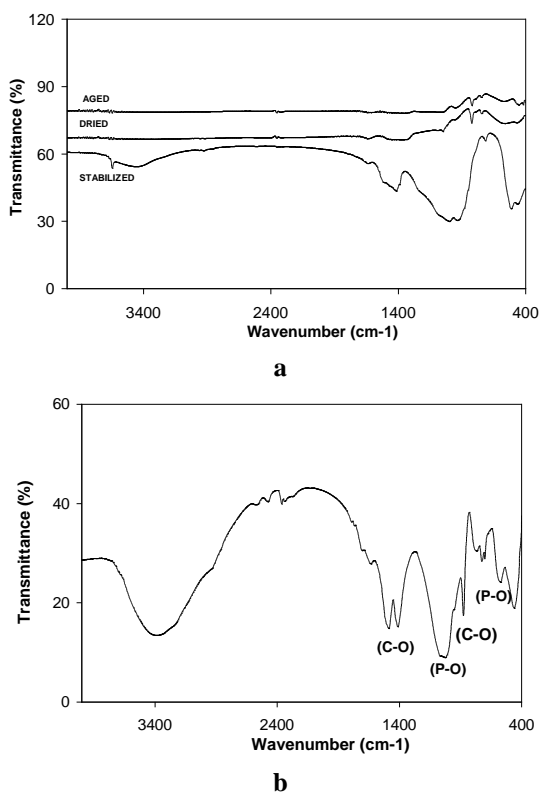


Fig. 2. FTIR spectra of the glass before (a) and after 14 days immersion in SBF (b).

The same bands are observed for the dried glass.

According to the Fig. 2 (a), after the stabilization at 700 °C, the material shows the peaks of H<sub>2</sub>O (vibration due to the OH bond), Si-O-Si and O-Si-O (bending modes), O-Si-O (stretching modes) and Si-O-Si (symmetric stretching modes). The peak at 1384 cm<sup>-1</sup> due to the vibration of ionic (NO<sub>3</sub>)<sup>-</sup> is disappeared [10, 11, 12]. The peak at 1410 cm<sup>-1</sup> corresponds to (CO<sub>3</sub>)<sup>2-</sup> groups [11]. The presence of carbonate is attributed to a carbonation process of the material due to the atmospheric CO<sub>2</sub> as a consequence of the high calcium content [11].

According to Fig. 2 (b), the peaks at 564 and 1052 cm<sup>-1</sup> are assigned to the (P-O) vibrational mode of an amorphous phosphate [12]. The peaks at 1406, 1480 and 873 cm<sup>-1</sup> correspond to (CO<sub>3</sub>)<sup>2-</sup> carbonate group [12].

### XRD

The XRD results of the materials that were stabilized at 700 °C, confirm the amorphous state as indicative of the internal disorder and glassy nature of this material.

Fig. 3 shows the XRD results of the glass after the thermal process at 700 °C.

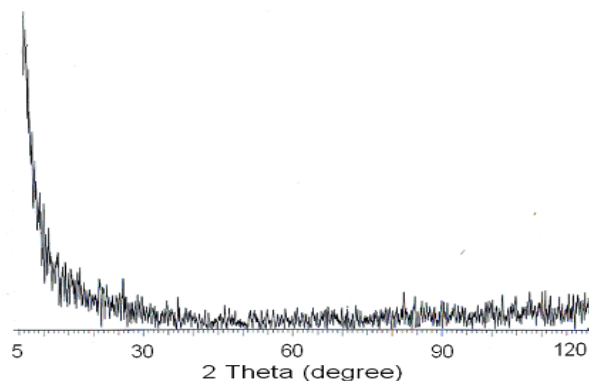
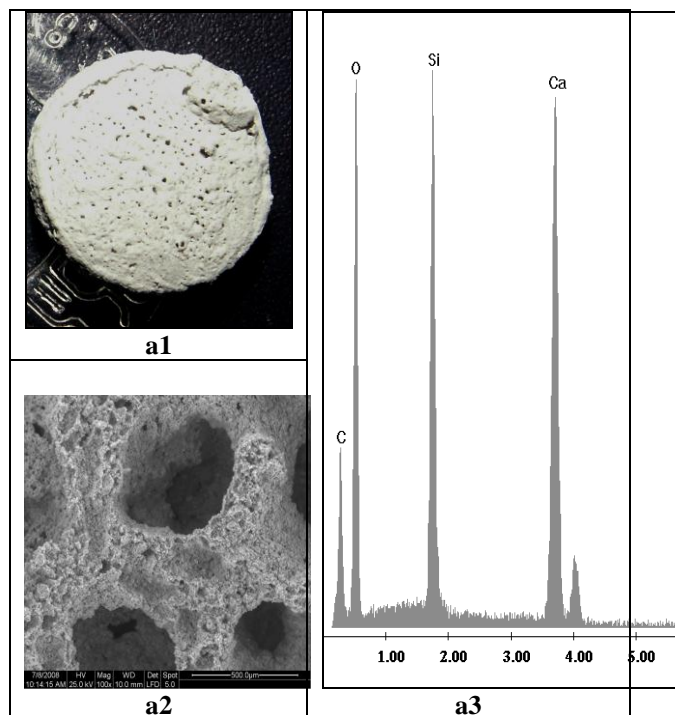


Fig. 3. XRD diffractogram of the glass after thermal process at 700 °C.

### SEM/EDS

After the elimination with combustion of the PEG particles [14] at 280 °C, the gel glass becomes more porous. According to the Fig. 4 (a1) and (a2), the SEM results indicate that the gel glasses have a macroporous network, containing pores mainly between 100 and 500 μm. After 14 day's immersion in SBF solution the surface has been covered by clear shaped spherical aggregated (HA) particles as shown in the Fig. 4 (b1) and (b2). According to the Fig. 4 (b3), the EDS results reveal the inclusion of the phosphorous in the composition of the newly formed layer. The crystallized apatite layer contains also minor components such as Na, Cl, and Mg and the Ca/P atomic ratio was 1.76, which was close to the theoretical value of 1.67 for apatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) [15].



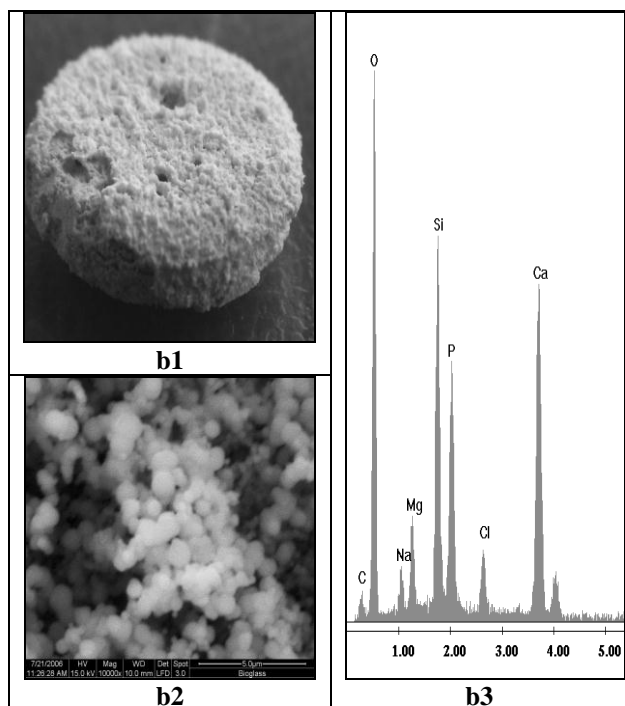


Fig. 4. (a1) Photograph image, (a2) SEM image and (a3) EDS spectrum of the glass discs, before the immersion in SBF solution and (b1) Photograph image, (b2) SEM image (clear shaped spherical aggregated HA particles) and (b3) EDS spectrum of the stabilized glass discs, after 14 days immersion in SBF.

According to literature, the use of the PEG modifies the mesoporous texture of the  $\text{SiO}_2\text{-CaO}$  glasses [16] and simultaneously it contributes to avoid the shrinkage and the crack occurrence during the manufacture. Moreover, a higher porosity has beneficial effect on apatite formation facilitating the transportation of ions through the liquid phase, thereby making it possible to achieve rapid transport nucleation [17].

#### 4. Conclusions

It can be concluded that the use of the PEG (as pore former) enables the synthesis of porous calcium silicate glasses with excellent bioactivity. This bioactive glass may be used as a biomaterial candidate.

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