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Synthesis and characterization of a calcium silicate bioactive glass

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Over the last three decades the bioactive ceramics including bioglasses, glass-ceramics, sintered hydroxyapatite, become one of the major fields in biomaterials, due to their intimate bond with living bone through the formation of a biologically active carbonate apatite interface layer. The purpose of the work was to examine the structure of a calcium silicate bioactive glass prepared by the sol-gel method. The samples were characterized by thermogravimetric and differential thermal analysis (TG/DTA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). No traces of organic matter or nitrates in the stabilized material were found according to FTIR and TG/DTA measurements. The materials produced are amorphous even after stabilization at 700 ^{o}C up to about 850 ^{o}C. However, the materials sinterized at 1000^{0}C for 1 hour reveal crystalline phase and indeed that of $CaSiO_3$ (wollastonite). Thus, the materials prepared by the sol-gel method are homogeneous with high purity and after their stabilization below their crystallization temperature, they are amorphous. These characteristics allow their application in the area of orthopedic and dental implants as a bone substitute biomaterial.

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1. Introduction

Over the last three decades the bioactive ceramics including bioglasses, glass-ceramics, sintered hydroxyapatite, become one of the major fields in biomaterials, due to their intimate bond with living bone through the formation of a biologically active carbonate apatite interface layer [1], chemically and cristallographically equivalent to the mineral phase in the bone [2]. During the first stage, an amorphous calcium phosphate layer is formed which, upon nucleation and growth of an apatite-like phase, becomes crystalline, giving rise to nanocrystals of hydroxycarbonate apatite (HCA), similar to those formed by the bone. These nanocrystals, combined with collagen fibers, form the layer that bonds the bioactive material with both soft and hard tissues [3].The main application of these bioactive ceramics in the clinical field is the filling of osseous cavities, manufacture of small parts for middle ear bone replacement and maxillofacial reconstruction and dental applications [4].

The sol-gel process is a chemical synthesis technique for the preparation of glasses, ceramics, glass-ceramics and composites. The chemistry involved in this process is based on inorganic polymerization reactions of metal alkoxide precursors $M(OR)_n$, where M represents the network forming element such as Si and R the alkyl group C_xH_{2x+1} [5]. These precursors undergo hydrolysis and condensation reactions to form a three-dimensional metal oxide network. Applying the sol-gel method, it is possible to manufacture ceramic or glass materials in a wide variety of forms: ultra fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials [6]. The major advantages of this method in comparison with conventional melting technique are the homogeneity in atomic level of the material produced and the relatively low temperature of their processing.

2. Experimental

The initial proportion of the raw materials was: SiO_2/CaO=50/50 (mol/mol). The procedure was similar to that of Hench and Saravanapavan [5, 7]. Fig. 1 schematically illustrates all the stages of the sol-gel process to obtain the glass. The sol was prepared by mixing distilled water, HNO_3, tetraethyl orthosilicate and calcium nitrate tetrahydrate, following this order. The sol was cast in cylindrical containers hermetically sealed and left to gel at room temperature for 4 days. The containers were transferred without their lids to an oven for the aging of the gel and were heated at 60 ^{o}C, for 3 days. Then, the drying followed at 150 ^{o}C for two 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 ^{o}C for 3 hours and then sintered at 1000 ^{o}C for 1 h with a heating rate of 10 ^{o}C/min.

TG/DTA curves were recorded under He atmosphere at a heating rate of 5 ^{o}C/min from room temperature to 1300 ^{o}C. An SETARAM (Labsys TG) thermobalance model was used with Al_2O_3 as the reference material.

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

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

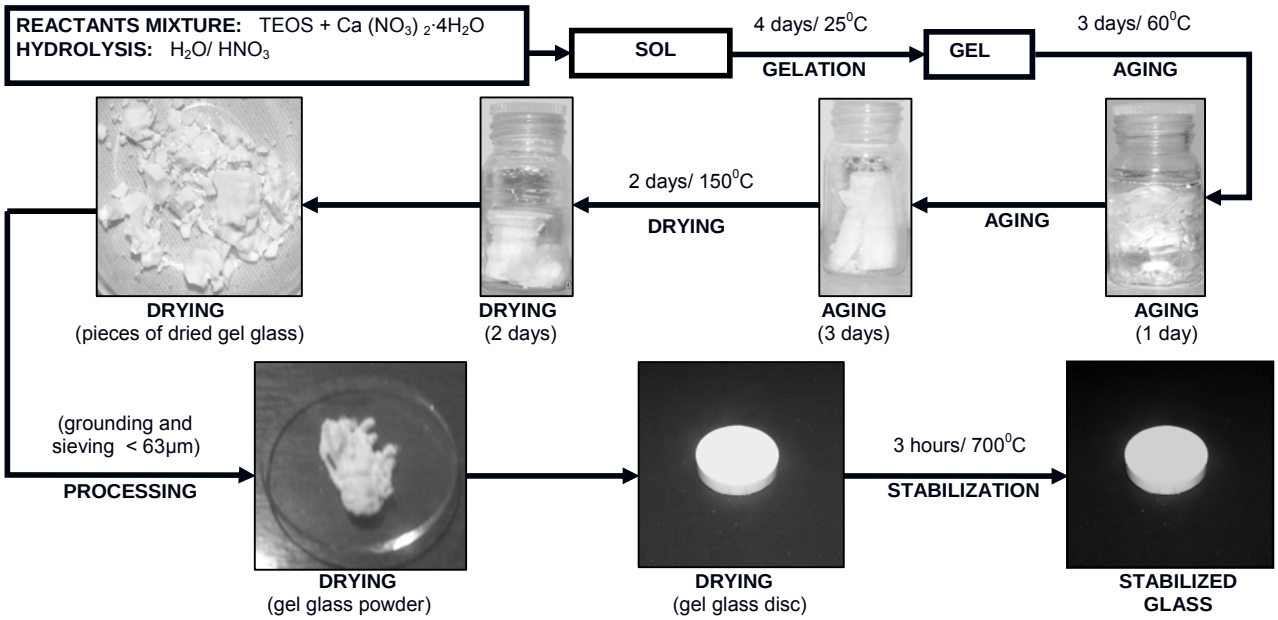

Fig. 1. Schematic illustration of the sol-gel process for the manufacture of the glass.

3. Results and discussion

TGA/DTA

Fig. 2 shows the TGA /DTA curves of the glasses after aging (a), drying (b), stabilization (c) and the TGA curves corresponding to the weight loss of the glasses (d).

Table 1 presents the DTA results at different stages of the glass processing. A DTA curve is a plot of specific heat changes of the glass versus temperature and is used to determine the temperatures at which phase transition occur. The TGA curve is a plot of the weight loss versus temperature.

Table 1. DTA results.

Peaks	Thermal Processes		
	Aging (60 °C)	Drying (150 °C)	Stabilization (700 °C)
The first endothermic process	137	115	-
The second endothermic process	528	535	-
Exothermic peak	895	897	860

The first endothermic peak of the aged (24.2 % weight loss) and dried gel (<6 % weight loss) is attributed to the loss of residual water and ethanol [5, 9]. The second endothermic peak of the aged (32.2 % weight loss) and dried gel (46.0 % weight loss) is due to the loss of organic (i.e. alkoxy group) and nitrates ($CaNO_3.4H_2O$ and HNO_3) used in the sol preparation [4, 9].The exothermic peak of the aged, dried and stabilized gel glass is due to the crystallization of $CaSiO_3$(wollastonite) [5, 9]. According to the Fig. 2(d) the stabilized glass at 700 °C reveals negligible weight loss by heating even up to 1300 °C. The TGA/DTA analysis is proper method to determine the optimal stabilization temperature (mainly at 700 °C, which temperature is above 600 °C and lower than 850 °C, whereas the crystallization begins).

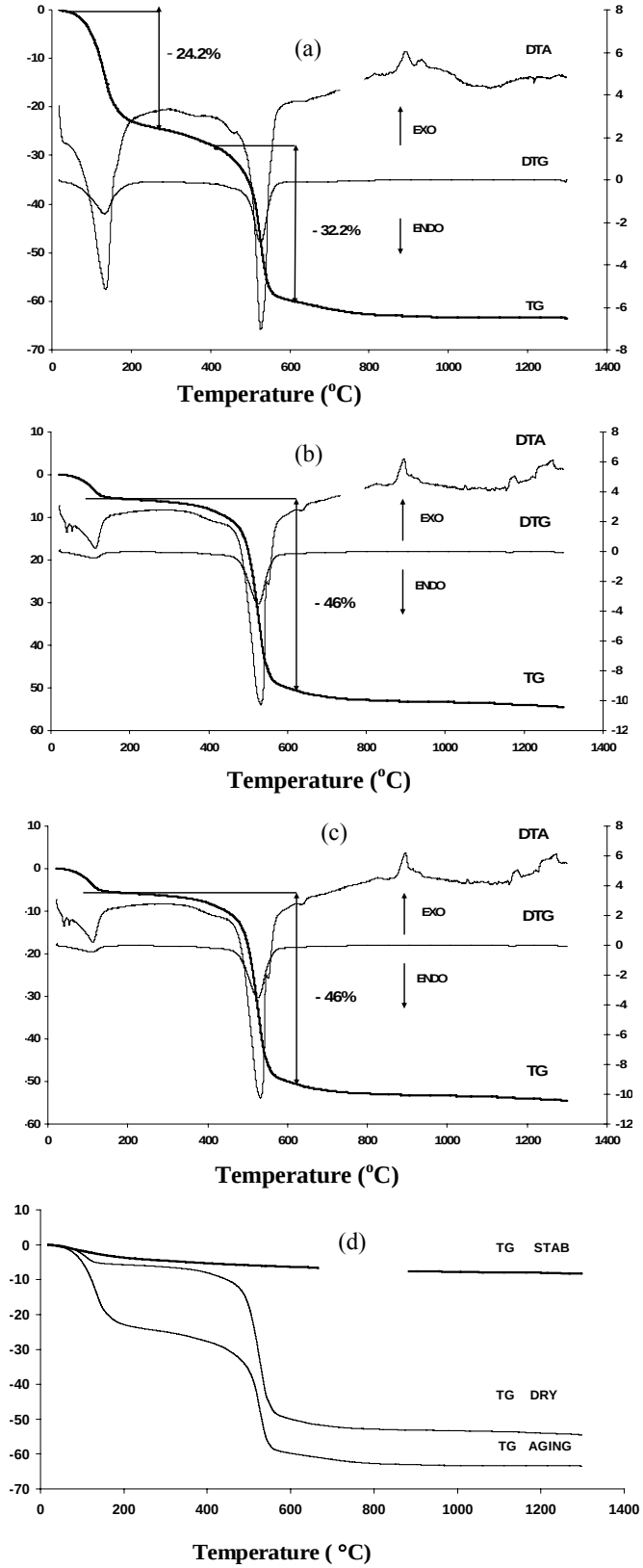

Fig. 2. TG/DTA curves of the glass after aging (a), drying (b), stabilization (c) and TGA curves corresponding with the weight loss (d).

XRD

Fig. 3 shows the XRD results of the glass after the thermal process at 700 °C (a) and 1000 °C (b). After the stabilization process at 700 °C, the XRD results confirm the amorphous state of the glass (Fig. 3 a). According to the literature [5], the crystalline phase of $CaSiO_3$ (wollastonite) reveals after the sintering process of the glass at 1000 °C (Fig. 3 b).

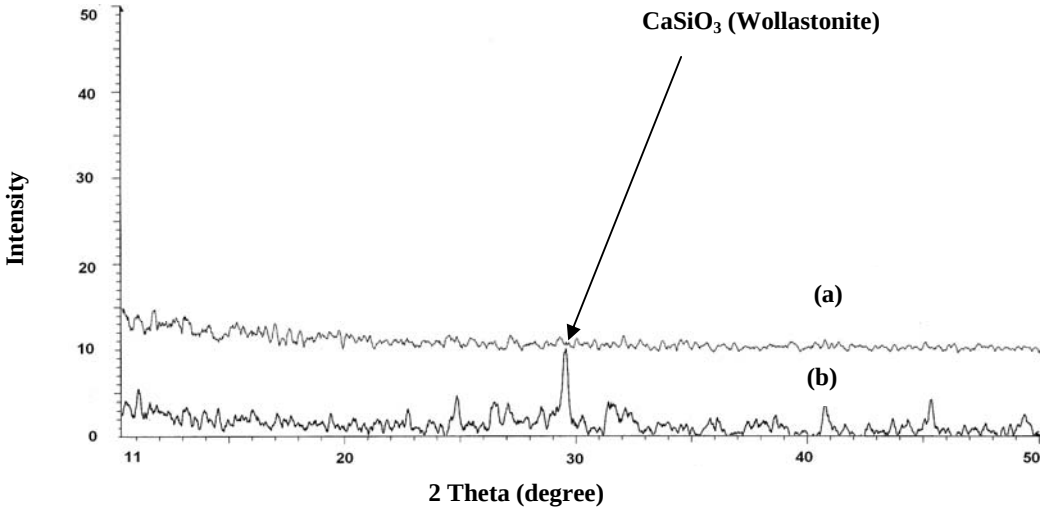

Fig. 3. XRD diagrams of the glass after thermal process at 700 ^{0}C (a) and 1000 ^{0}C (b).

FTIR

Fig. 4 shows the FTIR spectra of the glass after aging, drying and stabilization. Table 2 presents the groups and the corresponding wavenumbers according to the FTIR spectra of the glass.

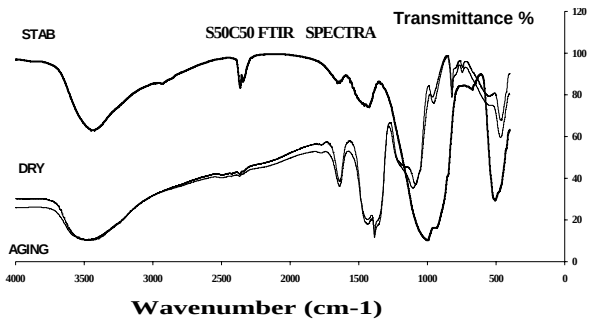

Fig. 4. FTIR spectra of the glass after aging, drying and stabilization.

Table 2. Groups and wavenumbers of the FTIR spectra of the glass.

Group	Wavenumbers (cm^{-1})*	Wavenumbers (cm^{-1})**
Si-O-Si and O-Si-O	460	458
O-Si-O	800	819
Si-O-Ca	950	950
Si-O-Si	1080	1080
(NO_3)	1380	1383
H_2O	1630	1635
$(CO_3)^{2-}$	1410-1490	1419

*: wavenumber (cm^{-1}) for the absorption peak according to the literature
**: wavenumber (cm^{-1}) determined from the FTIR spectra of the glass produced

According to the literature, the peak at 458 cm^{-1} is assigned to the bending modes of the Si-O-Si and O-Si-O bonds [5, 9]. The peak at 819 cm^{-1} corresponds to the stretching mode of the O-Si-O bond [5, 8, 9]. The peak at 950 cm^{-1} corresponds to the Si-O-Ca bonds containing non-bridging oxygen [5, 10]. The peak at 1080 cm^{-1} is attributed to the symmetric stretching vibration of the Si-O-Si bonds [5, 8]. The peak at 1383 cm^{-1} is assigned to the

vibration of ionic (NO_3). This peak is eliminated at 700 ^oC (Fig. 4) [5, 8, 9]. The vibration of H_2O is at 1635 cm^{-1} [5, 8]. According to the literature, the peak at 1419 cm^{-1} corresponds to CO_3^{2-} groups [8].

The materials produced are amorphous even after stabilization at 700 ^oC up to about 850 ^oC. No traces of organic matter or nitrates in the stabilized material were found according to FTIR and TG/DTA analysis. However, the materials sinterized at 1000 ^oC for 1 hour reveal crystalline phase and indeed that of $CaSiO_3$ (wollastonite).

4. Conclusions

The materials prepared by the sol-gel method are homogeneous with high purity and after their stabilization below their crystallization temperature, they are amorphous. These characteristics allow their application in the area of orthopedic and dental implants as a bone substitute biomaterial.

Acknowledgements

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