Preparation of Bioactive Glasses with Different Silicon Content and Study of Their Properties

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Abstract

Bone is the second most commonly transplanted tissue worldwide, with more than 4 million surgeries performed annually using bone grafts or bone substitute materials to treat bone defects. However, significant limitations affect current treatment options and the clinical need for bone grafting continues to rise due to trauma, cancer, infection and arthritis. Bioactive glass can be implanted in the body and gradually degrade with the formation of new bone, thus eliminating the need for a second surgery to remove it. This paper focuses on the degradation properties of bioactive glass with different silica content.

Keywords

1. Introduction

Bioactive glass has two preparation methods, a more traditional is prepared by melting method, this kind of glass has good densification and mechanical properties, but high temperature leads to impurity adulteration and part of the ingredients volatilized ultimately Si content is too high, biological activity is very low, is not conducive to the use of clinical, the other method is the sol-gel method, this method can be very good preservation of the material, the error is small, and the production of the biological activity of the glass Biological properties are excellent.[1-4].

The first bioactive glass was invented by Hench of the University of Florida in 1969.[5] The professor made a biodegradable glass in the Na_2O-CaO-SiO_2-P_2O_5 system with a high calcium content and a composition close to ternary eutectic in the Na_2O-CaO-SiO_2 diagram. The bioglass 45S5 bonded rapidly to bone and also stimulated bone growth away from the bone-implant interface. The mechanism of bone adhesion is attributed to the hydroxycarbonate apatite (HCA) layer that is generated on the glass surface as the glass dissolves. HCA is similar to bone mineral and is able to interact with collagen fibers to integrate (bond) with host bone. The osteogenic properties of glass (often referred to as osteoinduction) are thought to be due to the dissolution products of glass, i.e., soluble silica and calcium ions, which stimulate osteoblasts to produce bone matrix. The HCA layer is formed by solution-mediated dissolution of the glass by a mechanism that is very similar to conventional glass etching. Accumulation of dissolution products leads to changes in the chemical composition and pH of the solution, providing surface sites and pH values that favor HCA nucleation. In body fluids in vivo or simulated body fluids (SBF) in vitro, there are five stages of HCA formation as shown in Figure 1.1.[6].

(1) Cation exchange, especially $Na+$ and $Ca2+$ within the bioactive glass, where H^+ is in solution; (2) erosion of Si bonds within the BG by hydroxyl ions and dissolution of soluble silica in solution as $Si(OH)_4$; (3) formation of an amorphous silica-rich layer as hydroxyls coalesce with each other; and (4) Ca^{2+} and phosphate (PO_4^{3-}) ion diffusion to form an amorphous calcium phosphate film; and (5) formation of a hydroxycarbonate apatite layer on the implant surface.
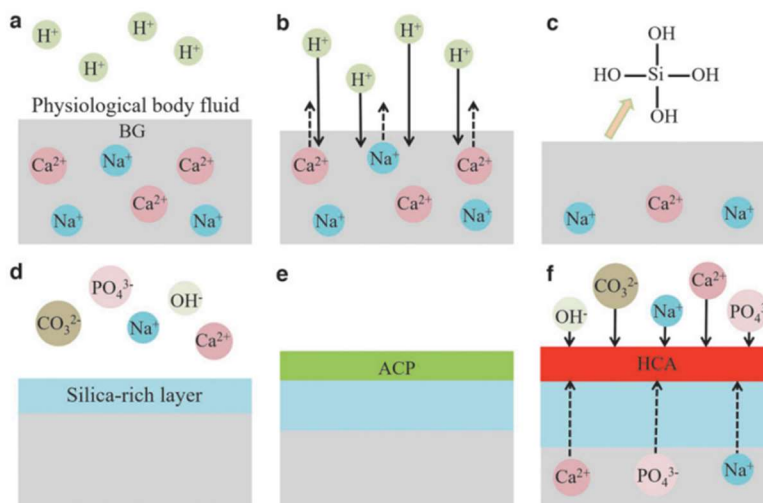
Figure 1. The formation process of HCA[6]

The ease of modifying glass compositions and inserting virtually any type of element in an amorphous network opens up a variety of possibilities for researchers to experiment with and customize the properties of bioactive glasses [7-9]. As a result, countless types of glasses have been synthesized and investigated to tailor specific properties or improve them in desired ways by changing the preoxides/modified oxides, molar ratios or adding new elements. All these efforts have led to the development of three main classes of bioactive glasses sorted by pre-oxides, namely silicate, phosphate and borate glasses, creating materials that exhibit highly attractive therapeutic properties related to killing of bacteria, angiogenesis (the ability to increase the formation of new blood vessels) and cancer therapy. However, phosphate degradation is too fast for generating a stable HCA layer, while the addition of boron exhibits some toxicity to some extent, which is not favorable for human use.

2. Experimental

2.1 Materials

Tetraethyl orthosilicate, Triethyl phosphate, $Ca(NO_3)_2 \cdot 4H_2O$.

2.2 Preparation of Bioactive Glass

Table 1. Specimen number and formulation of bioactive glass (mol%)

Sample	SiO_2	CaO_2	P_2O_5
58S6P	58	32	6
60S4P	60	32	4
62S2P	62	32	2

Dissolve ethyl orthosilicate, triethyl phosphate, calcium nitrate tetrahydrate in 0.2M nitric acid solution in order, the time interval between additions is 1h, after the addition is complete, continue stirring for 1h, to obtain a transparent sol, the transparent sol is placed in a polytetrafluoroethylene bottle, and then sealed and left to stand for 3 days at 37 ℃, the hydrolysis products crosslinked each other through van der Waals force, hydrogen bonding and chemical bonding to obtain the gel; the gel is aged at 70 ℃ for 3 days; finally, it is placed in 120 ℃ and dried for 2 days to remove excess moisture, the dry gel is placed in a tube furnace and heated at a rate of 5 ℃/min and kept to 700 ℃. The gel was aged at 70℃ for 3 days; finally, it was dried at 120℃ for 2 days to remove excess water, and the dry gel was obtained. The dry gel was put into a tube furnace and heated to 700℃ at a heating

rate of 5°C/min, and kept for 3h, and then cooled naturally to obtain the bioactive glass.The sample numbers are shown in Table 1.

2.3 Degradation Performance Test

The bioactive glass powder was placed in SBF at a ratio of 1:100 and shaken at a constant temperature at 37°C. It was removed at 1,4,7 days and washed with acetone solution to stop the powder from further degradation, the powder was washed and dried, and the powder before and after degradation was subjected to material characterization.

3. Results and Discussion

3.1 Changes in PH

Simulated body fluids before and after degradation were measured using a PH meter, as shown in Figure 2, the PH increased rapidly over the course of 1 day, after which the PH continued to increase, but at a reduced rate. This is due to the precipitation of calcium ions and the rapid increase in PH, along with the formation of a large number of sites on the sample surface that facilitate non-homogeneous phase nucleation and crystallization. After the calcium ions phosphorus ions precipitation concentration increases, in the surface sites deposition formation of HA, reducing the contact surface of SBF with the glass, reducing the rate of precipitation of silica ions, and the rate of growth of the PH is then reduced.
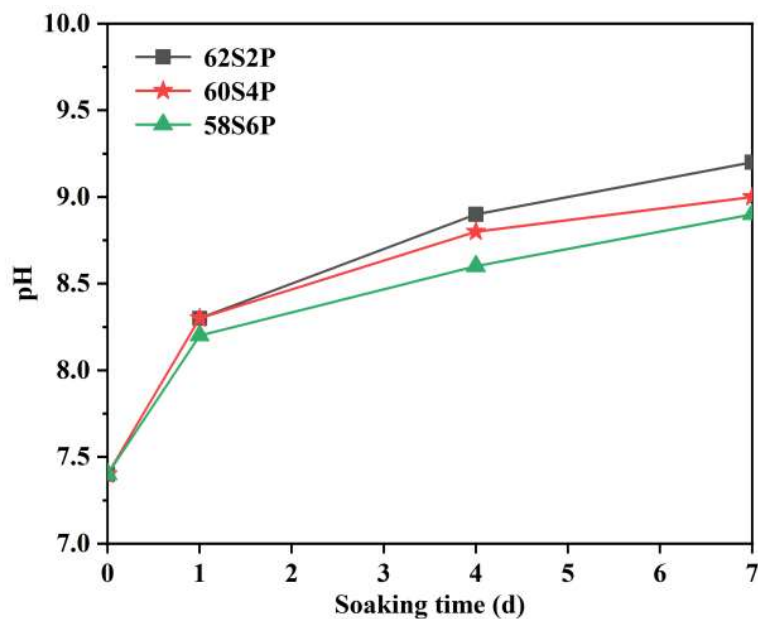

Figure 2. Changes in pH of SBF before and after degradation of three groups of glass powders immersed for 0,1,4,7 days

3.2 Changes in Ion Concentration

Three groups of samples degradation process SBF solution Ca, P, Si ions concentration changes as shown in Figure 3, Ca, P ions 1 day concentration decreased, 1 day to 4 days the rate of concentration decrease increased, 4 days after the degradation rate tends to flatten out, it can be seen that a day within the 58S6P degradation is the slowest, 1-4 days of the 58S6P explanation of the fastest rate, this is due to the just degradation, P content of the sample degradation of the faster rate When hydroxyapatite did not cover the surface of the powder, the sample degradation rate is fast, and the P, Ca ions produced by degradation offset the amount consumed by the generation of hydroxyapatite.
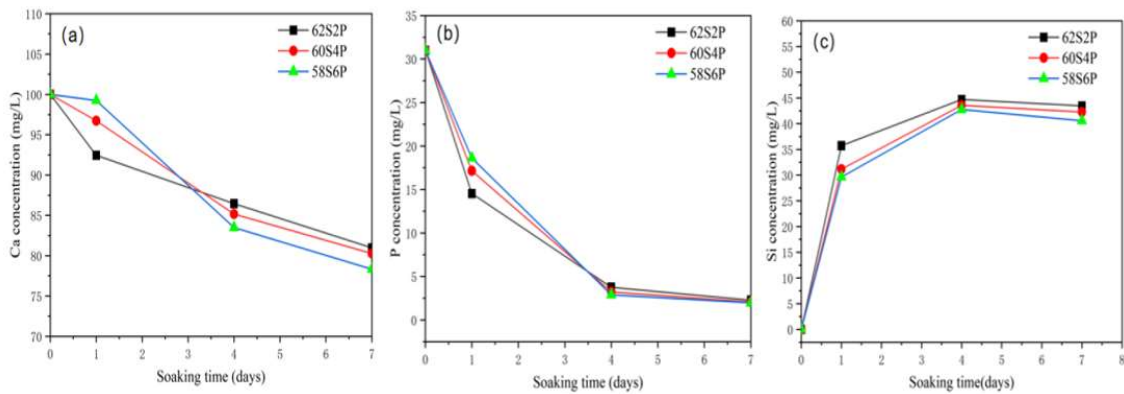
Figure 3. Changes in ion concentration during degradation of three groups of materials (a) Ca, (b) P, (c) Si

3.3 Change in Characteristic Peaks

Figure 4 shows the XRD patterns of 58S6P, 60S4P and 62S2P after SBF immersion, sharp diffraction peaks appeared at $2\theta=25°$ and $2\theta=32°$ after 1 day of immersion, they correspond to the (002) and (211) crystal planes of the characteristic peaks of HA, respectively. The intensity of the peaks corresponded to the abundance of the material, and with the increase of mineralization time, another peak appeared near 31.8°, which corresponded to the (300) crystal plane of HA, and the intensities of the peaks at (002) and (211) gradually became larger, indicating the increase of HA content.
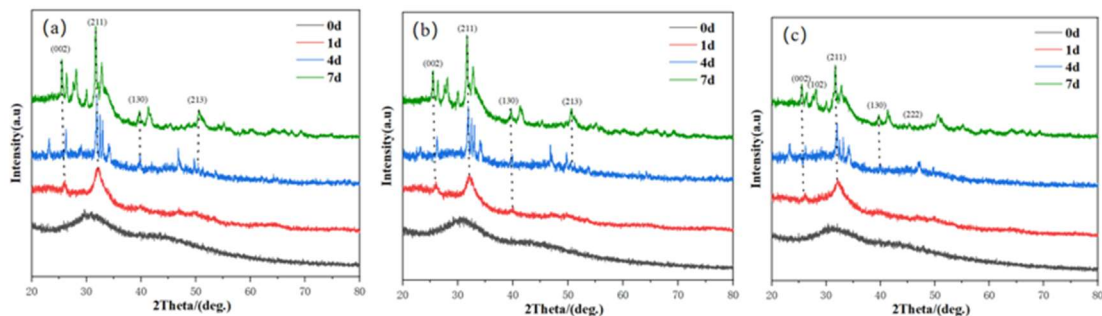

Figure 4. Xrd curves during degradation of three groups of materials (a) 58S6P (b) 60S4P (c) 62S2P

3.4 SEM

Figure 5 demonstrates the surface micromorphological structure of three groups of bioactive glass powders before and after immersion in SBF solution. To summarize, the amount of white deposited particles on the surface of all three groups of specimens increased with the extension of immersion time although the generation rate was not the same. Firstly, it was observed that the bioactive glass powders were irregularly shaped solid lumps with smooth surfaces and a large number of well-defined corners before immersion, whereas after one day of immersion, the surface of the specimens began to appear raised in localized areas or a small amount of white particles were formed, and their location was mainly concentrated at the corners, which was attributed to the large specific surface area and the presence of corners, and the formation of white particles was mainly concentrated at the corners. They are mainly concentrated at the corners, which is attributed to the large specific surface area, high surface energy and fast dissolution rate of active ions. In particular, more remarkable results were obtained for the S58P6 bioactive glass specimens with the addition of a loose network structure. After 4 days of immersion, the angularity of the surface of the specimen had disappeared considerably, and the white sedimentary particles gradually grew to spread to the surface planes and associate into layers, so that most or the whole glass surface was covered by them. At this stage, the glass samples still retained the high efficiency and continuity of the reaction, and finally, after 7 days of immersion,

the surface of all three groups of samples had accumulated into a stacked structure with the glass substrate completely obscured, which strongly suggests that the white precipitate layer has a highly porous structure, and that its formation on the surface of the glass does not prevent further mineralization of the inner glass.
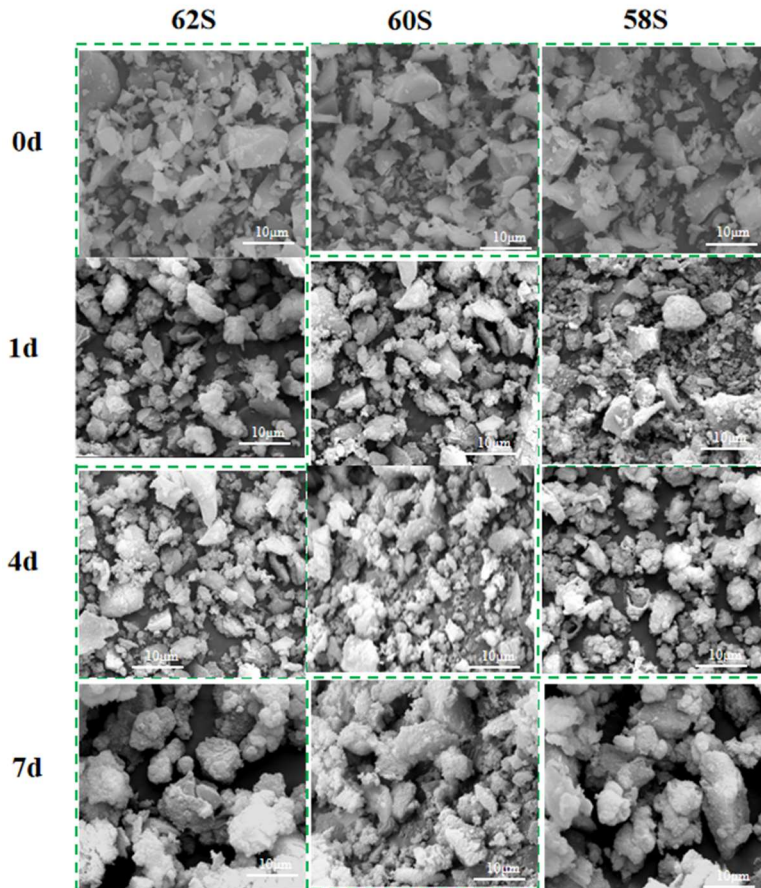

Figure 5. Conformational changes of bioactive glasses with different fractions

4. Conclusion

In this paper, three groups of bioactive glasses with different components were successfully prepared by the sol-gel solution method, and in vitro degradation tests revealed that all three groups of glasses had good degradation properties, among which those with more P content had better degradation properties. Demonstration of the role of P in controlling the rate of degradation of biologically active glass.

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