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Preparation and Evaluation of Macroporous Sol-gel Bioglass with High Mechanical Strength

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Abstract. Bioactive glasses are known to have the ability to regenerate bone, but their use has been restricted mainly to powder, granules, or small monoliths. This work reports on the development of bioactive glasses with macroporosity of controlled size and volume through sol-gel and pore forming technologies. The macroporous structure (greater than 100μm) can provide the potential for tissue ingrowth. Simultaneously the samples exhibit mesoporous (2-50nm) texture and high specific surface which can enhance bioactivity and release of ionic products. The most important advantage is that these samples show satisfactory mechanical strength. This method should be a useful approach for preparation scaffolds with applications to repair and reconstruct damaged tissue.

Introduction

Due to the shortage of organ or tissue donors and difficulties with immunoreponse, there is great demand for biomaterial-cell scaffolds to provide a template and support tissue growth [1]. A scaffold should be a macroporous material with several important characteristics: first, an interconnected network with large pores (greater than 100μm) to enable tissue ingrowth and nutrient delivery to the center of the regenerated tissue; second, pores in the mesoporous range to promote cell adhesion, adsorption of biologic metabolites, and resorbability at controlled rates to match that of tissue repair [1-4]; third, certain mechanical strength to provide the needed early strength to the implant while tissue regeneration was occurring [5-6].

Sol-gel bioglass exhibit a mesoporous texture and high specific surface area. In addition they have several advantages over melt glasses that are important for biomedical applications such as enhanced resorbability and high bioactivity [7-8]. The sol-gel derived bioglass with macropores and mesopores simultaneously would be an ideal scaffold material.

Although there are many well developed methods to obtain porous ceramics now, it is still very difficult to produce macroporous sol-gel glasses with pore diameter above 100μm because the great shrinkage of gel during drying procedure often results in severe cracks. Recently, Pilar et al. had reported a foaming method to prepare such a structure. But the pore size of the bioglasses they prepared is not so controllable and the mechanical strength is not mentioned at all [2].

In this work, pore former and sol-gel route were employed to produce macroporous bioglasses. By selecting proper pore former, the crack can be avoided. The pore size and volume can be tuned by changing the pore former diameter and content. Furthermore, the matrix of these macroporous samples exhibited mesoporous structure and high specific areas. It is worth noting that the obtained samples have the high mechanical strength. By further optimization of the procedure parameters, it is possible to obtain more ideal scaffolds.

Experiment

Sample Preparation. The ternary 58wt%SiO_2-33wt%CaO-9wt%P_2O_5 (58S) gel-glasses were prepared by the sol-gel method. The procedures were similar to those used by Zhong *et al* [9]. In this Study, the 58S sol was prepared by mixing distilled water, HNO_3 (2M), tetraethoxysilane, triethylphosphate; and calcium nitrate tetra-hydrate in order. The sols were aged in a drying oven at 60 ºC to reach the high enough viscosity. Then the prepared bread particles were added into them with strong stirring for mixing uniformly. In this work, two particle / sol ratios (weight of bread particles / volume of sol = 0.8 g / 20 mL and 1.1 g / 20 mL) were used. The bread was ground and sieved before experiment and two size ranges (S = 150-200 μm and L = 200-315 μm) were chosen for pore former. After aging for one day, the gels were moved into drying vessels. They were dried in an environment containing water; the temperature was raised to 120 ºC slowly and kept for 48 h [10]. Finally the dried gels were heated to 700 ºC over 2 days.

Characterization of the Samples. Pellets were chemically and physically characterized, by using scanning electron microscopy (SEM), N_2 absorption isotherm, Mercury Intrusion porosimetry analyses and mechanical test. The SEM study was made in an electron probe X-ray microanalyser (EPMA-8705QH_2, Shimadzu, Japan), on samples sputter coated with Au. Specific surface area was calculated from the N_2 absorption isotherm by using the BET method in a Micromeritics Tristar 3000. Macropore size distribution and porosity was determined in a Micromeritics Poresizer 9320. Large and total pore results are measured from pressure 0 to 25 psia (the macro results) and 0-30000 psia (the total results) respectively. The compressive strength measurement was conducted with a mechanical tester at 0.5 mm/min crosshead speed (INSTRON 8501) according to the JIS R1601 standard.

Results and Discussion

Flawless monolithic macroporous sol-gel bioglasses can be produced with different pore sizes and porosities. A wide range of shapes and sizes was attained with different molds, with no evidence of heterogeneities or phase separation, demonstrating the techniques' reliability.

Pore structure. Fig.1 shows the microstructure of macroporous bioglasses observed by SEM for the different samples. As-produced samples were labeled as B-X-Y, where X and Y represent pore former size and weight respectively. The pictures indicated a homogeneous macroporous material. The pores are almost above 100μm. We can see the influence of bread volume and particle size on the pore-size distribution clearly. The larger bread volume resulted in more pores. And, the larger bread particle size, the larger average pore diameter.

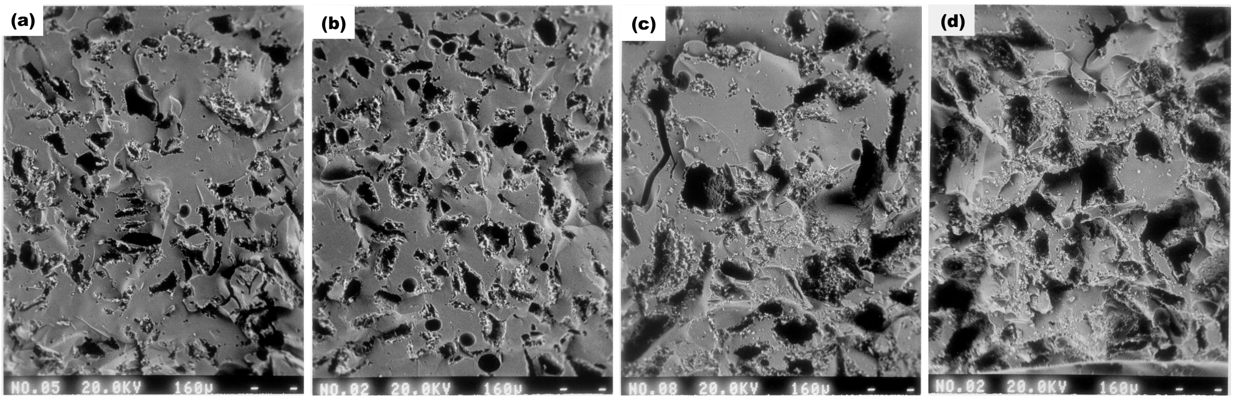

Fig. 1 Pore structure of macroporous samples: (a) B-S-0.8 (b) B-S-1.1 (c) B-L-0.8 (d) B-L-1.1.

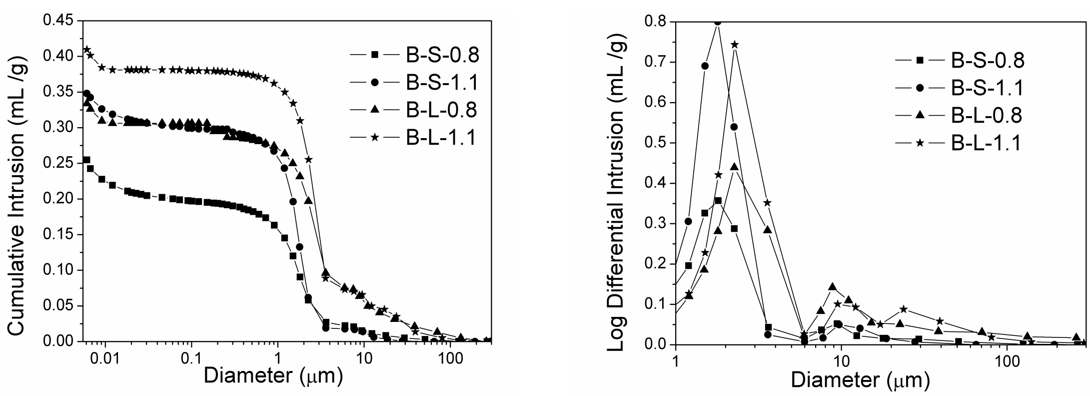

Fig. 2 Mercury porosimetry curves for macroporous bioglass.

Table 1 Data of macroporous structure measured by mercury intrusion porosimetry and mesoporous structure measured by nitrogen sorption analysis

Designation	Macropore diameter [μm]	Total Pore Volume [cm^3/g]	Total Porosity [%]	Sp [m^2/g]	V_p [cm^3/g]	R_p [nm]
BG00	-	-	-	276	0.29	3.4
B-S-0.8	14.3	0.25	23.7	351	0.37	3.3
B-S-1.1	12.6	0.35	29.8	311	0.44	4.2
B-M-0.8	16.6	0.33	32.1	327	0.38	3.3
B-M-1.1	18.9	0.41	42.8	314	0.38	3.4

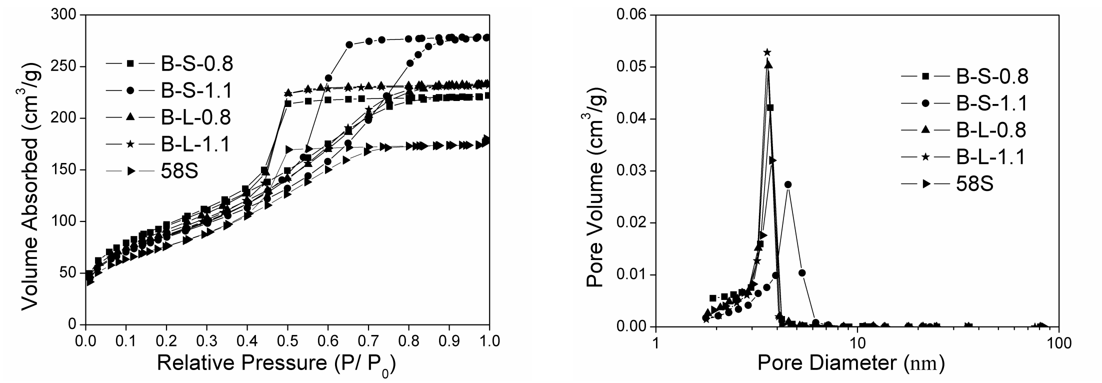

Fig. 3 Nitrogen adsoption-desorption isotherms and the corresponding pore-size distribution

The SEM micrographs provided qualitative information on the material structure, while mercury porosimetry allowed a quantitative investigation of the porosity [11]. Figure 2 compared the pore volumes and pore size distribution of the specimens measured by mercury intrusion porosimetry. Mercury intrusion porosimetry is usually used to measure the smaller pores, corresponding to the connecting areas or necks between much larger pores created by bread particles [12]. So the true porosity and pore diameter values should be higher. The macropore diameter, total pore volume and total porosity of various samples are given in table 1. The results are in accord with the trend of macropore structure observed by SEM.

N_2 adsorption-desorption isotherms of the samples are shown in Fig. 3. These were type IV isotherms, according to the BDDT classification originally proposed by Brunaer and coworkers, which are characteristic of mesoporous (2-50nm pore diameter) materials. The isotherms exhibit type H2 hysteresis loops in the mesoporous range, which is characteristic of the so-called ink bottle pores that have pore cavities larger in diameter than the openings (throats) leading into them [11]. Specific surface area (S_p), specific pore volume (V_p) and average pore radius (R_p) for the dense 58S and macroporous materials are presented in Table 1. The surface area decreased with the increase of bread volume and size, while the pore diameter and volume increased with the increase of bread volume, decreased with the increase of particle size.

The main large pore size created in this work is above 100μm. That is not only large enough for cell's attachment, but also suitable for tissues and blood vessels to grow in. Tissue ingrowth rates depended greatly upon pore morphology, the degree of pore connectivity, and pore volume. By altering the volume and size of pore former, in this work, the porosity and macropore size could be controlled, so the tissue ingrowth rates is considered to be controlled.

Mesopores about 4nm also characterize these sol-gel materials. Sol-gel materials exhibit high surface areas which intensify the rate of surface reactions, leading to faster release of ionic species during glass dissolution and a large number of nucleation sites for apatite layer deposition compared to dense melt derived bioglasses [12]. In addition, mesoporosity promote cell adhesion and adsorption of biologic metabolites. Different texture of sol-gel materials could be obtained by changing the processing or treatment parameters [2]. Thus dissolution rates and surface chemical binding sites can be controlled to match that of tissue repair.

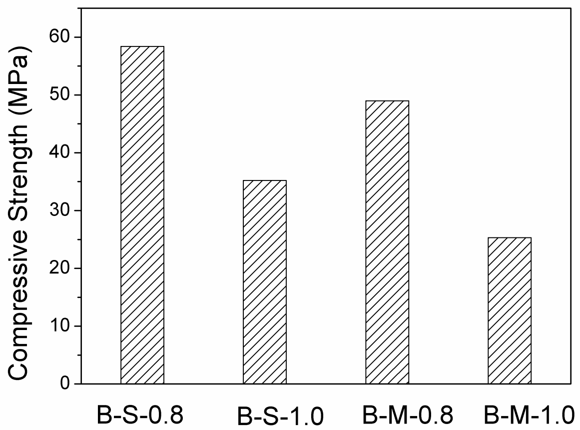

Fig. 4 Compressive strength of the macroporous samples.

Mechanical strength. Fig. 4 shows compressive strength of the obtained samples. All the macroporous samples show higher strength than that of human cancellous bone (2-10MPa). The high strength of these materials is beneficial to withstand physiological stresses and minimize stress shielding in the surrounding host bone [6]. The strength decreased with the increase of the pore former diameter and volume, especially the pore former volume. The results verified the microstructure and the Mercury Intrusion tests for the porosity and the pore size distribution are in direct relationship with the strength. Any solid pore former added into gel will prevent the shrinkage of gel. That could result in severe crack of gel during drying procedure. Using the improper pore former, the gel structure was loosened even if the severe crack didn't occur. The bread particle is an appropriate pore former according to the fact that the samples are in good condition and showed very high compressive strength.

Conclusions

In this work, sol-gel and pore former technologies were combined to create novel materials with a hierarchical structure composed of macropores (10-200 μm) and mesopores (2-50 nm). Using this method, it is easy to control pore diameter and volume by using bread particles with different size range and volume. Moreover, the samples showed high strength and specific surface area. These macroporous materials potentially can support 3D organization of cells, and resorb by controlled rates, is promising to serve as 3D cell scaffold for bone tissue engineering.

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