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Two different techniques used in the production of foam structures: 3D printing and glass foaming

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Abstract

This paper reports on the preparation of cellular materials by different techniques. Bioactive and resorbable scaffolds based on biphasic calcium phosphate were produced by 3D-printing using extrudable pastes through fine nozzles, according to a pre-defined spatial arrangement considered suitable for bone regeneration and tissue engineering applications. Milled powders of cathode ray glass tubes and egg shell wastes were mixed and compacted to produce recycled glass foams via viscous flow sintering and thermal decomposition of the egg shell component that played the role of foaming agent.

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1. Introduction

Cellular solids (ceramics, polymers, metals) have features that depend on the specific properties of materials they are made of, and on the porous structure conferred by processing. Over the past few years there has been an increasing interest in producing and using highly porous ceramic (or glass) materials. The motivations relay on typical features of cellular structures (e.g. high surface area, high permeability, low density, low specific heat, and high thermal insulation), which are important for diverse applications (e.g. catalyst supports, filters for molten metals, hot gases, and ion exchange, refractory linings for furnaces, thermal protection systems, heat exchangers, and as porous biomaterials). On the other hand, the cell size, morphology, and degree of interconnectivity are important factors that determine their suitability for the various applications. For

instance, closed-cell materials are desirable for thermal insulation, while open-cell, interconnected materials are necessary for applications involving fluid transport such as filters or biomaterial scaffolds. The selection of starting materials (composition) and processing routes are crucial to obtain the desired structure (open or closed-cell) and properties of the porous materials [1]. Biphasic [Hydroxyapatite (HA)/ β -tricalcium phosphate (β -TCP)] calcium phosphates (BCP) have great potential for bone-tissue engineering applications [2–3]. The strategies to regenerate bone include the use of scaffolds with suitable 3D porous structures to support cell attachment, proliferation and differentiation. Robocasting is a direct-write assembly (DWA) technique that allows the production of scaffolds with customized shape and predefined, reproducible internal morphology, according to a computer design, without the need for subsequent machining [4–5]. Porosity and pore size of biomaterial

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scaffolds play a critical role in bone formation *in vitro* and *in vivo*. Porosity is necessary for bone tissue formation since it allows migration and proliferation of osteoblasts and mesenchymal stem cells, matrix deposition in the empty spaces, as well as vascularization. Several studies investigated the effects of pore size on the regeneration efficacy of mineralized bone. The results indicated that the minimum pore sizes of about 100 μm are required for cell migration and transport [6]. Taking this in mind, the first part of this work aims at developing porous scaffolds for bone replacement with a pore sizes within the range of 120–220 μm using a robocasting technique.

Glass foams are generally obtained by the action of a gas generating agent (foaming agent), which is ground together with the powdered starting glass or glassy waste material. The mixture of glass powder, foaming agent, and occasionally other mineral agents, is then heat treated at a suitable temperature to promote viscous flow sintering and the thermal decomposition of the foaming agent. The evolution of gas inside the softened pyroplastic mass of glass causes the expansion of the structure. The properties of finished foamed glass products depend strongly on the type and quantity of the added foaming agents, the initial size of the glass particles, and on the firing schedule [1]. One of the aims of this work was investigating the feasibility of using egg shells, a calcium carbonate (CaCO_3) based residue, as foaming agent to produce glass foams from CRT glasses.

In the present paper we report on the two above referred processing routes to produce two types of porous structures derived from different starting materials: (1) open-cell porous bioceramics based on high purity calcium phosphate glasses prepared by 3D-printing; and (2) closed-cell glass foams obtained from electronic residues (CRT glasses) foamed by thermal decomposition method using industrial using egg shell wastes as foaming agents. These are just a few examples of the diverse cellular materials developed in our research group during the last years.

2. Experimental procedure

2.1. Synthesis and characterization of BCP starting powders and preparation of scaffolds by 3D-printing

The synthesis of BCP with HA/ β -TCP ratio of ~ 1.5 was done by aqueous precipitation. Briefly, precipitation was accomplished by the slow addition of the precursor $(\text{NH}_4)_2\text{HPO}_4$ solution to a continuously stirred $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution (Quality Chemicals, Spain).

The concentrations of the precursor solutions were designed to achieve a Ca/P molar ratio of 1.62. The synthesized powders were calcined at 1100 $^\circ\text{C}$ and then dry milled for 30 min in a high energetic ball milling up to achieving mean particle size $\sim 1 \mu\text{m}$. The phase assemblage of calcined powders was studied by X-ray diffraction using a high-resolution Rigaku Geigerflex D/Mac, C Series diffractometer with Cu K α radiation ($k = 1.5406 \text{ \AA}$) produced at 30 kV and 25 mA, which scanned the diffraction angles (2θ) between 20 and 80 $^\circ$ with a step of 0.02 $^\circ/\text{s}$. The particle size distribution of the starting powder was evaluated using a particle size analyser. The robocasting inks were prepared by dispersing the starting powder in aqueous media with some processing additives. Initially, a highly concentrated aqueous suspension (55 vol. %) was prepared by adding 0.4 wt.% Targon 1128 as dispersing agent, relative to powder content. To increase the intrinsic viscosity of the liquid, an appropriate amount of previously dissolved hydroxypropyl methylcellulose (average $M_n \sim 10,000$, Sigma-Aldrich) was added. Subsequently, the ink was gellified by adding a cationic agent, polyethylenimine (PEI, Sigma) as flocculant. The final ink had a 48 vol. % solid loading. After each addition, the mixture was placed in a planetary centrifugal mixer (ARE-250, Thinky Corp., Tokyo, Japan) for a few minutes to improve its homogeneity and stability. The addition of flocculating agent then drastically changed the rheological properties of the system to obtain inks with suitable viscoelastic behaviour for robocasting.

3-D BCP scaffolds consisting of a mesh of ceramic rods were constructed layer by layer via direct write assembly of the ink using a robotic deposition device (3-D Inks, Stillwater, OK). The ink was deposited through cylindrical metallic deposition nozzles (EFD Inc., East Providence, RI) with a diameter $d = 410 \mu\text{m}$, at a printing speed of 10 mm/s. The external dimensions of the scaffolds were set at about $3 \times 3 \times 3 \text{ mm}$ so that a total of 12 layers were deposited with a two different pore sizes 120 and 220 μm . The deposition was in a paraffin oil bath to ensure uniform drying during assembly. The samples were removed from the bath and dried in air at room temperature for 24 h and then at 400 $^\circ\text{C}$ (1 $^\circ\text{C}/\text{min}$ heating rate) for 1 h to burn out the organics. Finally, the dried samples were sintered at 1100 $^\circ\text{C}$ for 2 h with a heating rate of 5 $^\circ\text{C}/\text{min}$. The morphological features of the scaffolds were analysed by scanning electronic microscopy (SEM, Hitachi SU-70, Hitachi High-Technologies Europe, GmbH, Germany), under an acceleration voltage of 25 kV and a beam current of 10 μA . The

compressive strength of the scaffolds was determined by performing uniaxial tests on approximately cubic blocks of 3 mm side cut from the sintered specimens. The tests were carried out in air on a universal testing machine (AG-IS10kN, Shimadzu, Kyoto, Japan) at a constant crosshead speed of 0.6 mm/min.

2.2. Synthesis and characterization of glass foams from CRT and eggshell wastes

Panel (P) and funnel (F) glass wastes were used as starting materials after milling to obtain powders with mean particle size about 10 μm . The egg shell waste (E) was also milled ($\sim 8 \mu\text{m}$) and used as foaming agent. The batch compositions of the investigated glass foams were prepared according to the general formula $97(\text{P}_{100-x}\text{F}_x)-3\text{E}$ (wt. %), with $x = 0, 25, 50, 75$ and 100. Cylindrical pellets ($\varnothing=20 \text{ mm}$) were prepared by uniaxial pressing (40 MPa) and the green samples were heat treated in air in the temperature range of 650–750 $^{\circ}\text{C}$ in air for 15min (heating rate $\beta = 5 \text{ K/min}$). Glass foams were characterized as follows: (1) apparent density was determined by measuring the weight and the dimensions of the produced materials; (2) compression strength of cubic samples was measured in a Shimadzu machine (Trapezium 2, Japan, displacement 0.5 mm/min); (3) the crystalline phase assemblage was detected by X-ray diffraction analysis and (4) microstructure observations were done by scanning electron microscopy.

3. Results and discussion

3.1. Scaffolds based on biphasic calcium phosphates produced by 3D-printing

Biphasic calcium phosphates (HA/ β -TCP) have great potential for bone-tissue engineering applications. The crystalline phase assemblages of calcined powders at 1100 $^{\circ}\text{C}$ are presented in Fig. 1. The X-ray diffraction patterns confirm the formation of the HA phase (ICDD 01-079-5683) and of the β -TCP phase (ICDD 04-014-2292). Particle/agglomerate size, solids loading and the concentrations of the processing additives played the major roles in determining the ink performance. Good extrusion of highly concentrated suspensions was only possible when using well deagglomerated particles and relatively wide particle size distributions [7], as the packing ability is enhanced with smaller colloids filling voids among the coarser ones [8].

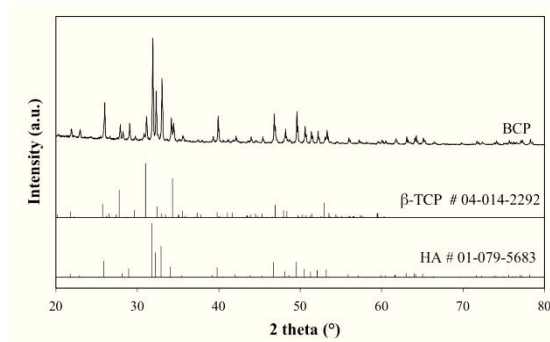


Fig. 1. XRD patterns of the BCP powders calcined at 1100 $^{\circ}\text{C}$. The patterns of the standard ICDD PDF 01-079-5683 and 04-014-2292 of pure HA and β -TCP, respectively, are also presented for comparison.

The colloidal ink must exhibit tailored rheological properties to exit the nozzle in a liquid-like state while retaining its shape immediately. This requires an optimal balance between shear thinning behavior and structural recover after extrusion. Fig. 2 shows some SEM micrographs of sintering BCP scaffolds. The regularity of the structure and the straight geometry on the rods attest the suitable rheological property of the ink used for its fabrication. These results demonstrate the successful production of 3-D structures suitable for bone tissue engineering by robocasting. This manufacturing technique provides great design flexibility and offers the possibility of manipulating the macroporosity of the scaffolds. Besides drawing out the shape of each layer in a CAD model, the key requirement is to prepare an extrudable ink. The compressive strength of robocast scaffolds for both pore sizes (120 and 220 μm) was in the range 15–35 MPa, higher than that of cancellous bone (2–12 MPa) [9].

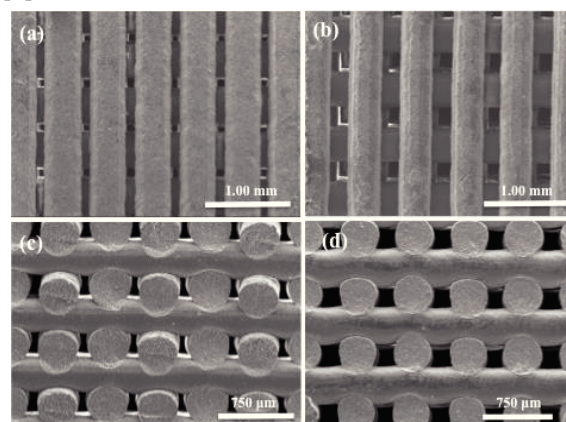


Fig. 2. SEM micrographs show the morphology of BCP scaffolds with 120 (left) and 220 μm (right) pore size after sintering: printing plane view (a, b); side view (c, d).

These results make the scaffolds interesting candidate materials for further *in vitro* or *in vivo* experiments aiming at qualifying them for applications in tissue engineering and bone regeneration.

3.2. CRT glass foams

A good foaming behaviour was observed for all CRT glass mixtures upon heat treating at 700 °C for 15 min. The mineral phase analysis (not shown here) revealed the presence of small content of quartz for all experimental samples heat treated at 700 °C. The composition containing equal parts of F and P featured the minimum apparent density (0.29 g/cm³) and good compressive strength result (2.3 MPa), as shown in Fig. 3.

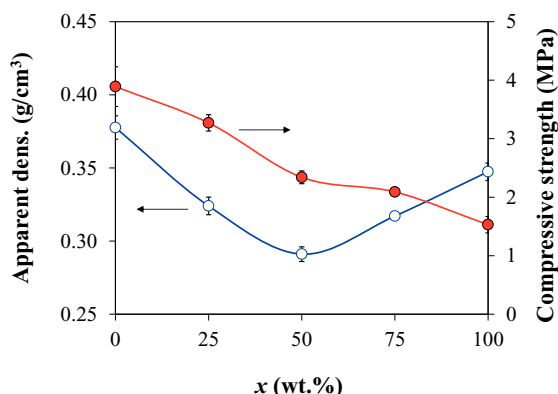


Fig. 3. Influence of the composition on the apparent density and the compressive strength of the samples heat treated at 700 °C for 15 min. Sample composition (in wt. %): 97(P_{100-x}F_x)–3E (P: panel, F: funnel, E: egg shell).

These values are similar to the typical ones presented by commercial foam products, which are within 0.1–0.3 g/cm³ and 0.4–6 MPa for apparent density and porosity, respectively [1]. The compressive strength of the glass foams decreased monotonically with the increasing F contents. This tendency is in good agreement with the variation of apparent density up to $x = 50$. However, the decreasing trend of compressive strength observed for $x > 50$ appears as counter intuitive, as mechanical properties would be enhanced with the apparent density increasing. This behaviour might be explained by a weakening of the struts which become more porous, while the overall apparent density increases.

For $x = 50$, Fig. 4 shows that both composition and temperature affect the foaming behaviour. The chemical/thermal characteristics of the starting glasses and their mixtures govern the foaming behaviour of the

powder and the physical properties of the foams. Fig. 5 shows the typical macroscopic aspect of the glass foams after rectify, while Fig. 6 presents the internal microstructural features that include the main coarse pores separated by struts, which contain small fine pores.

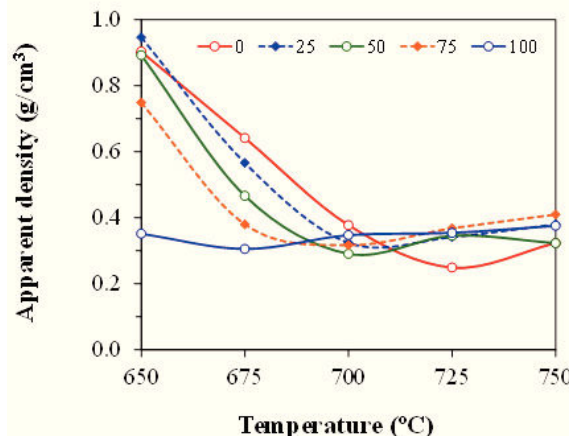


Fig. 4. Influence of the temperature of the heat treatment (between 650–750 °C, for 15 min) on the apparent density of samples with different compositions. Sample composition (in wt. %): 97(P_{100-x}F_x)–3E (P: panel, F: funnel, E: egg shell).



Fig. 5. Typical glass foam block after rectify. (The edge of the sample is about 1.8 cm and the height is 1.0 cm).

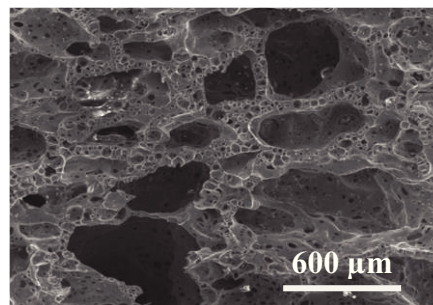


Fig. 6. Microstructure of glass foam 97(P50F50)–3E ($x = 50$) heat treated at 700 °C for 15 min.

4. Conclusions

Two distinct techniques were used to produce cellular materials, starting from different materials, and aiming different final applications.

Robocasting allowed the creation of 3-D structures from an extrudable colloidal ink with porous features that are promising for bone tissue engineering. Further work is required to better explore the possibility of manipulating the macroporosity and to investigate the *in vitro* and *in vivo* performance of the resulting scaffolds to demonstrate their suitability as candidate materials for tissue engineering and bone regeneration applications.

The use of 3 wt.% of calcium carbonate (CaCO_3) based egg shells as foaming agent and a mixture of glasses P and F ($x = 50$) enabled obtaining glass foams from 100% industrial wastes at relatively low temperatures (700 °C), featuring apparent density and compressive strength values of 0.29 g/cm³ and 2.3 MPa, respectively, which are similar to those reported for commercial glass foams. This is a feasible and efficient way to produce novel cellular materials exclusively from industrial wastes which can have high added value and potential applications as lightweight fire resistant insulator materials.

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