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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.


*Keywords:* 3D-printing; Calcium phosphate; Scaffolds; Glass foams; CRT glasses.

## 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 $(NH_4)_2HPO_4$ solution to a continuously stirred $Ca(NO_3)_2{\cdot}4H_2O$ 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 ºC and then dry milled for 30 min in a high energetic ball milling up to achieving mean particle size ~1 μm. 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 Ka radiation (k = 1.5406 Å) produced at 30 kV and 25 mA, which scanned the diffraction angles (2θ) between 20 and 80º with a step of 0.02º/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 Mn~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 μm, at a printing speed of 10 mm/s. The external dimensions of the scaffolds were set at about 3×3×3 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 ºC (1 ºC/min heating rate) for 1 h to burn out the organics. Finally, the dried samples were sintered at 1100 ºC for 2 h with a heating rate of 5 ºC/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