Development of porous ceramics by lycopodium using uniaxial pressing and sintering

Rita Serzane[*], Janis Locs, Liga Berzina-Cimdina, Romans Sadretdinovs

Riga Biomaterials Innovation and Development Centre, Riga Technical University, Pulka Str. 3/3, Riga, LV-1007, Latvia

Abstract

In this work microporous hydroxyapatite (HAp) ceramics were fabricated using lycopodium as a porosifier. The samples were produced by uniaxial pressing and then heating at high temperatures, 1100°C and 1200°C, to burn-out porogens and sintering. The obtained samples had porosity over the variable range of 12 to 45% with different pore size ranging from 0.2 to 25 μm. Chemical and physical characterization was determined by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and bending strength measurements. The bending strength of the prepared samples was in the range of 1.97–21.81 MPa.

I. Introduction

Synthetic calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) HAp is a well-known bioceramic material used in medical field as bone substitute material. This is mainly due to its excellent bioactivity, biocompatibility, osteoconduction and bone-bonding properties as well as its structural and compositional similarity to that of the mineral phase of hard tissue in human beings [1–4].

However, in order to induce bone ingrowth into porous bioceramic, it is necessary to control the physical characteristics of the implant porosity. Many authors have studied the relationship between bone ingrowth and pore parameters and in particular pore size and interconnection size. Results of these works are very broad showing that macropore size can vary in the range of 100–1000 μm and a minimal interconnection size has to be about 20 μm [5]. Besides the requirement that pores have to be larger than 100 μm in diameter, the pores must be interconnected to guarantee the supply and the circulation of the necessary nutrients through the ingrowth of fibrous tissue, vascular tissue and bone tissue [6,7]. The implant also has to have smaller pores, which favour protein adsorption and adhesion of osteo-

genic cells. Thus, the pore size distribution of porous bioceramics should be bimodal [8].

Several processing routes for fabricating porous bioceramic have been developed, such as foaming processes, pyrolysis of volatile organic phases, freezing technique, replication of polymer foams, solvent casting and particulate leaching, etc. Each of these techniques in spite of its merits will have inherent drawbacks, and cannot fully satisfy characteristics (e.g. highly porous, large-sized pore structure with large interconnection and reasonable mechanical strength) required for a totally accepted porous bioceramic [9].

Our work has been mostly connected with casting/foaming, pressing with burn-out additives, plastic forming and polymer foam infiltration. The aim of work is to develop a porous bioceramics material with adequate pore structure and appropriate mechanical properties (compression, bending strength) for bone ingrowth and regeneration based on HAp, which are used on a large scale for biomedical applications such as dentristy, bone replacement, for applications such as scaffolds for tissue engineering, and drug delivery systems.

In this paper, we used lycopodium powder [10,11], as a pore forming agent, for the preparation of porous HAp ceramics using uniaxial compaction. This is a simple and inexpensive variant and widely used method in produc-

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[*] Corresponding author: tel: +371 67089605
fax: +371 67089619, e-mail: *riota@inbox.lv*

ing HAp ceramic with diverse porosity. Crystalline phases, morphology, porosity, and mechanical properties of the fabricated porous HAp samples were investigated.

II. Experimental

The materials used in this work were: commercially available HAp powder (Riedel-de Haën®) with grain size approximately 0.1–30 μm, paraffin and lycopodium powder (A/S Rigas Pharmaceutical Factory) with an average grain size of 30 μm. Micrograph of porogen - lycopodium used for preparation of samples is shown in Fig. 1. According to literature data [10,11], the thermogravimetric and differential thermal analysis shows that lycopodium powder burns out in an exothermic reaction in the temperature between 200 and 530°C.

The used pore forming method consists of dry-mixing of HAp powder with porogens - paraffin (25 wt.%) and lycopodium (5, 10 and 15 wt.%), without using plasticizer. Disc samples of 10 mm diameter and about 2.5 to 3 mm thickness were uniaxially pressed at 5 MPa at room temperature. The bending strengths were determined using four-point bending tests. Samples used in these tests had typical dimensions of 50×5×4 mm. The green bodies were sintered at different temperatures (1100 and 1200°C, respectively) for 1 h in air.

Crystalline phases of the porous materials were identified by X-ray powder diffractometry (XRD, PANalytical X'Pert PRO) at 40 kV and 30 mA with Cu-K$_\alpha$ radia-tion. Samples were scanned in the range $2\theta = 20–60°$ at a step size of 0.017°, and with a hold time of 20 s.

A Fourier transform infrared spectrometer (FT-IR, Varian Scimitar 800) in the wave number range 4000–400 cm^{-1} was used for sample investigations in the transmission mode in a dry air atmosphere using the KBr pellet technology. In the apatite structure, the phosphate group has a T_d symmetry resulting in four internal modes (v1: 956 cm^{-1}, v2: 430–460 cm^{-1}, v3: 1040–1090 cm^{-1}, v4: 575–610 cm^{-1}), while the two hydroxyl absorption bands are located at 630 cm^{-1} (vibrational mode) and 3570 cm^{-1} (stretching mode) [12].

The morphological properties of the samples were investigated using a scanning electron microscope (SEM, Tescan Mira/LMU) at 15 kV acceleration voltage and 6–10 mm working distance. The samples were mounted and sputter-coated with gold to reduce charging and to improve image quality.

Four-point bending tests of the samples were carried out with a Universal Test Machine (Instro 4301 which is based on 1011 Instron model and MS–DOS that is in accordance PS with IX series software), at a crosshead speed of 0.5 mm/min.

The apparent density was measured by the Archimedes method, which also allowed estimating the sample porosity.

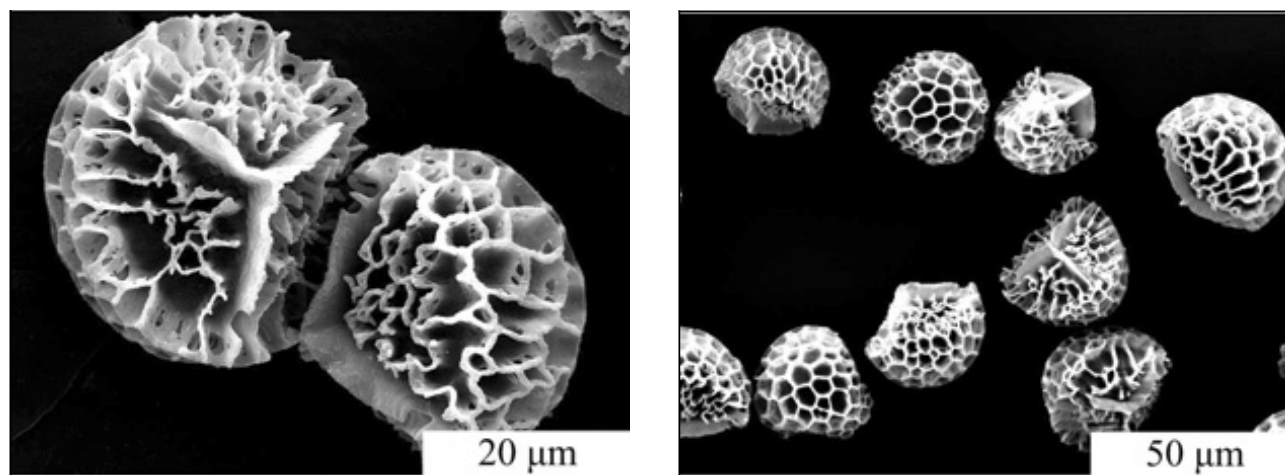For mechanical strength and porosity five samples of each group were tested.

Figure 1. SEM micrograph of lycopodium

Table 1. Porosity, density and bending strength of samples sintered at different temperatures

	5 wt.% lycopodium		10 wt.% lycopodium		15 wt.% lycopodium	
Sintering temperature	1100°C	1200°C	1100°C	1200°C	1100°C	1200°C
Open porosity [%]	35	12	37	16	45	20
Apparent density [g/cm³]	1.90	2.49	1.79	2.23	1.49	2.16
Bending strength [MPa]	3.96 ± 0.80	21.81 ± 5.13	3.74 ± 0.71	19.93 ± 4.12	1.97 ± 0.52	7.56 ± 1.99

III. Results and discussion

Processing variables (e.g. sintering temperature, and sintering additives) can play an important role in determining the characteristics (e.g. microstructure, porosity, and mechanical strength) of the sintered samples. The main properties of the samples were determined after sintering at 1100 and 1200°C and the measurment results are shown in Table 1. The apparent density of the samples with 5, 10, 15 wt.% addition of lycopodium is 1.79–2.49 g/cm³, the estimated porosity 12–45% and the bending strength is 1.97–21.81 MPa. Note that the flexural strength of the trabecular bones of the human body were 2–10 MPa [1]. The bending strengths quoted in the literature by other autors, carried out by either four-point bend or three-point bend tests, are below 11 MPa and the highest bending strength of porous calcium phosphate ceramics in the literature is ~ 40 MPa [13]. As the lycopodium content increases from 5 to 15 wt.%, the apparent density and bending strengths increases and the estimated porosity decreases.

The XRD patterns of the samples sintered at 1100°C (Fig. 2) exibited peaks corresponding only to HAp phase. All the peaks matched the standard HAp diffraction pattern (ICDD PDF-2, ref. code 01-076-0694). The XRD pattern of the sample sintered at 1200°C with 10 wt.% lycopodium (Fig. 3b) reveals only HAp as crystalline phase. The sample with 15 wt.% lycopodium (Fig.
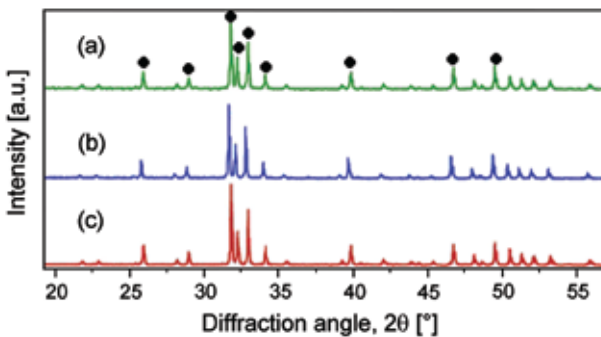

Figure 4. FTIR spectra of lycopodium powder and samples with different amount of lycopodium, before sintering

Figure 5. FTIR spectra of samples with different amount of lycopodium, sintered at 1100°C

Figure 2. X-ray diffraction patterns of samples with different amount of lycopodium: a) 5 wt.%, b) 10 wt.% and c) 15 wt.% sintered at 1100°C (• HAp)
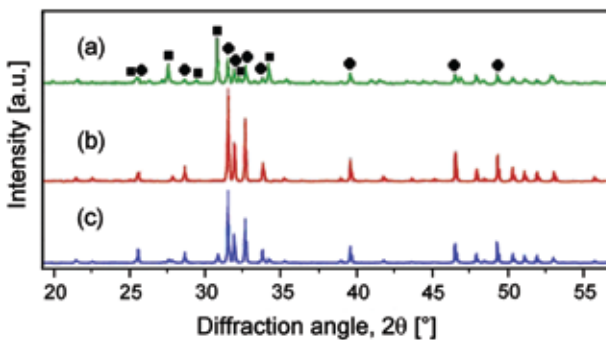

Figure 3. X-ray diffraction patterns of samples with different amount of lycopodium: a) 5 wt.%, b) 10 wt.% and c) 15 wt.% sintered at 1200°C (• HAp, ▪ β-TCP)
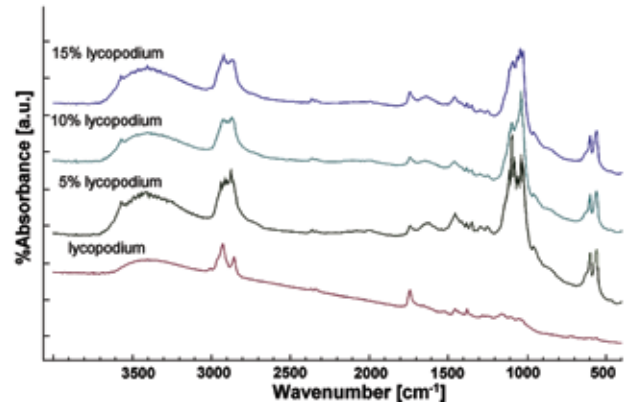

Figure 6. FTIR spectra of samples with different amount of lycopodium, sintered at 1200°C

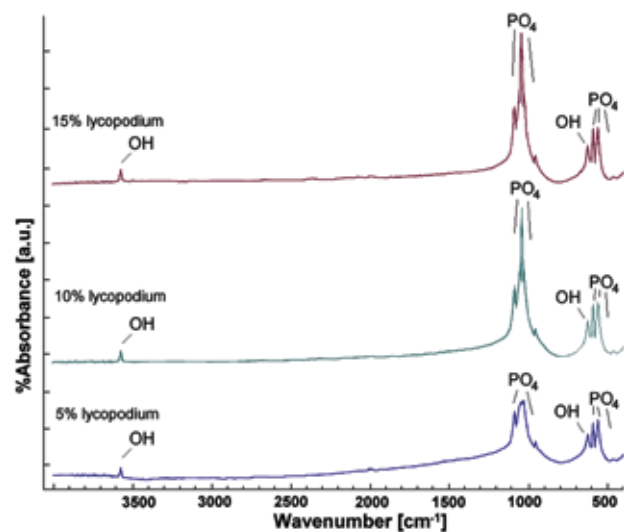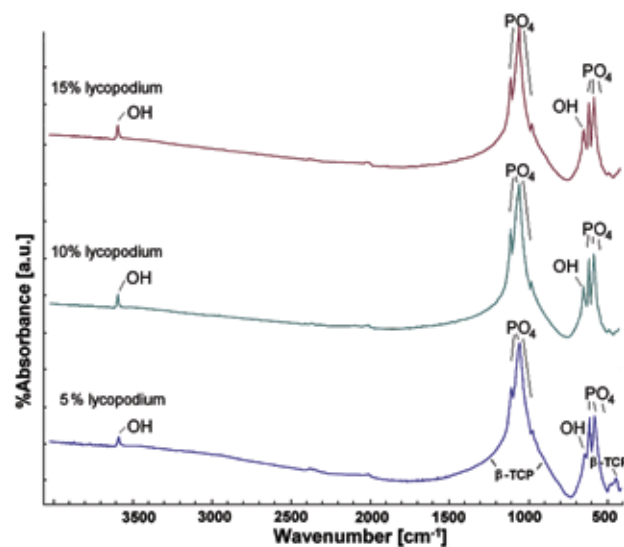3c) consisted of HAp as the dominant crystalline phase with small amount of β-TCP (HAp/ β-TCP ratio, determined by half quantitative method, is 95/5). All the peaks matched the standard β-TCP diffraction pattern (ICDD PDF-2, ref. code 00-055-0898). On the other side, the sample with 5 wt.% lycopodium (Fig. 3a) has two phases: HAp and β-TCP (HAp/ β-TCP ratio, determined by half quantitative method, is 63/37).

From the literature data [15] HAp has also been shown to convert to β-TCP at temperature below 1200°C and to α-TCP at temperature above 1200°C. The formation of β-TCP is possible in the material as a result of the thermal decomposition of HAp.

In the FT-IR absorption spectra (Fig. 4), peaks characteristic for both lycopodium powder and as-synthesized sample are visible. Figs. 5 and 6 shows FT-IR patterns of the porous HAp ceramic samples sintered at 1100 and 1200°C, respectively. The characteristic absorption bands of the PO_4^{-3} groups (473 cm^{-1}, 571 cm^{-1}, 601 cm^{-1}, 961 cm^{-1}, 1047 cm^{-1}, 1091 cm^{-1}) and structural OH$^-$ (632 cm^{-1}, 3572 cm^{-1}) of HAp can be observed. The sharp peaks of O-H indicate that the material had a high degree of crystallinity [14]. The thermal decomposition of HAp into β-TCP and appearance of the secondary phase, in the sample with 5 wt.% lycopodium sintered at 1200°C, can be seen in Fig. 6. Thus, PO_4^{-3} absorption band becomes wider, featuring shoulder peaks β-TCP phase at intervals 1100–1200 cm^{-1}, 800–900 cm^{-1} and 400–500 cm^{-1}, as well as the OH$^-$ group intensity decreases. They were found to correspond with the XRD pattern of Fig. 3a.

XRD and FT-IR studies of porogen additions confirmed that in the final ceramic those chemicals were not present anymore and the chemical composition of the samples were not altered.
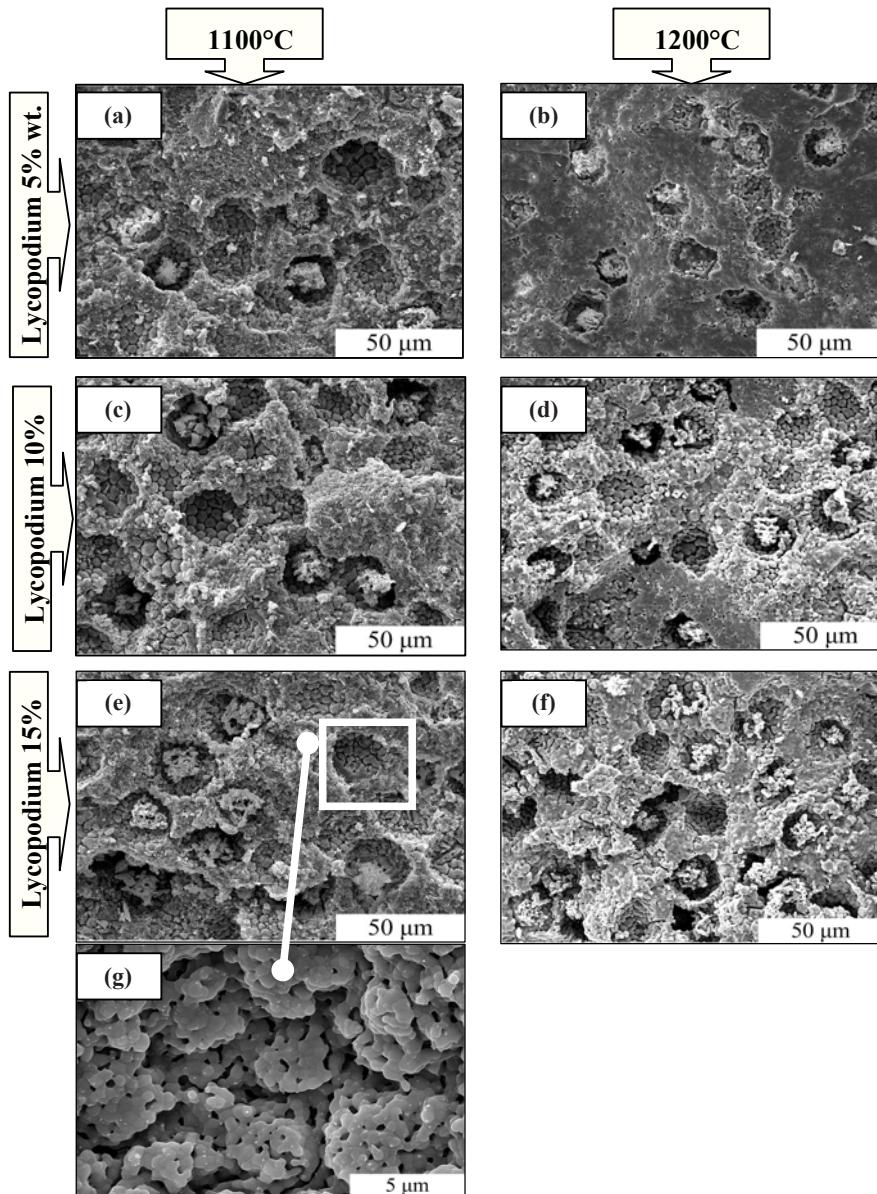

Figure 7. SEM micrographs of samples with different amount of lycopodium showing the microporous structure (a-f) and micropore wall (g)

Fig. 7 shows the morphology of the samples obtained using SEM. The pores of porous HAp ceramics were rounded with the same shape as within added lycopodium particles (Fig. 1) and the shape of pores did not change during sintering process. Moreover the mean pore size is about 25 μm, which is almost coincident with the mean particle size of the lycopodium (30 μm). A detailed examination of the micropore wall (Fig. 7g) revealed the presence of micropores in the scale of ~ 1 μm, and small rounded grains with size of 0.2–0.8 μm and open structure was formed.

IV. Conclusions

Microporous, HAp bioceramics were produced by dry pressing method using lycopodium powder as a pore-forming agent and then sintering. The pore-forming agent was completely removed due to the burn-out and sintering processes and the chemical composition of the samples was not altered. The ceramics were obtained with final porosity up to 12–45% with different pore size distribution in the range 0.2–25 μm. The porosity of HAp can be varied easily with different content of the porogens and sintering temperature. The bending strength of the prepared samples was in the range of 1.97–21.81 MPa, which is comparable to that of the cancellous bones.

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