Preparation of Nanocrystalline Hydroxyapatite Scaffolds at Room Temperature by 3D Powder Printing

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Statement of Purpose

Currently available materials for bone replacement are usually based on calcium phosphate chemistry and are usually provided as sintered blocks of hydroxyapatite, granules of tricalcium phosphate or self setting cement formulations [1]. In this work we describe the manufacturing of custom made hydroxyapatite implant structures via a calcium phosphate cement setting reaction during 3D powder printing such that calcium phosphate samples with a well defined architecture and porosity were available.

Materials and Methods

Tetracalcium phosphate (TTCP) was synthesized by heating an equimolar mixture of dicalcium phosphate anhydrous and calcium carbonate to 1500 °C for 18 h followed by quenching to room temperature. The sintered cake was crushed with a pestle and mortar and passed through a 160 µm sieve, followed by grinding to a medium particle size of 15µm. Fabrication of nanocrystalline HA implants was performed using the 3D printing technique in a three step process. (1) Printing of cement samples was performed with a 3D-powder printing system (Z-Corporation, USA) using the TTCP powder and a mixture of 10% phosphoric acid and 1 mol/l NaH_2PO_4 as liquid printing phase. (2) Samples were then stored in 10% H_3PO_4 for 30 s for post hardening followed by (3) 7d immersion in 2.5% Na_2HPO_4 solution at 37°C for hydrothermal conversion to HA. The materials were characterised due to their mechanical performance and porosity. The phase composition was analysed by X-ray diffraction analysis (Siemens D5005) with CuKa radiation and the spectra were quantified using Rietveld refinement analysis (TOPAS 2.0).

Results and Discussion

The printing process enabled the production of complex HA components with an x-y-z resolution of ± 100 µm. The quantitative phase compositions of the samples are given in Table 1. Printing of TTCP powder with phosphoric acid binder (1) and post hardening (2) resulted in the formation of a brushite (DCPD) and monetite (DCPA) binder phase:

$$Ca_4(PO_4)_2O + 2H_3PO_4 \longrightarrow 4CaHPO_4 (x\ 2H_2O)$$

This phase was then converted with unreacted TTCP to nanocrystalline HA due to dissolution / precipitation process:

$$Ca_4(PO_4)_2O + CaHPO_4 \longrightarrow Ca_5(PO_4)_3OH$$

After this treatment, the structures are composed of nanosized HA crystals as shown by SEM analysis (Figure 1). Compressive strength of the printed structures were found to be approx. 2MPa directly after printing, which increased to 5-6MPa after additional post-hardening and hydrothermal conversion to hydroxyapatite.

Table 1: Phase compositions of printed samples

Sample	Comp. strength [MPa]	Phase Composition
(1) printed	1.9 ± 0.2 Porosity 47.8%	81% TTCP, 9% DCPA, 5% DCPD, 5% HA
(2) 30s in 10% H_3PO_4	5.1 ± 0.5 Porosity 44.8%	49% TTCP, 15% DCPA, 26% DCPD, 10% HA
(3) 7d in 2.5% Na_2HPO_4	5.8 ± 0.3 Porosity 51.9%	27% TTCP, 8% DCPA, 8% DCPD, 57% HA

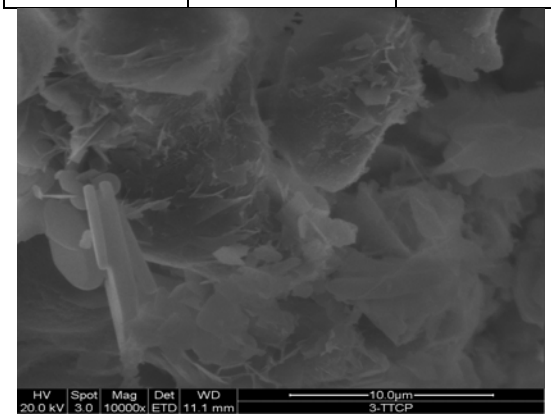

Figure 1: SEM micrograph of porous hydroxyapatite structure made by 3D powder printing

Conclusions

Nanocrystalline HA components could be produced with defined architecture at room tempreature using a rapid 3D direct printing technique which utilised calcium phosphate setting systems. This method allowed spatial control of component architecture and the preparation of nanocrystalline hydroxyapatite structures. This finding has tremendous potential in the field of bone grafting since hitherto impossible geometries can be fabricated allowing construction of precisely defined channels for vascular in-growth, a process essential for the initiation of wound healing of practically all tissues. The lack of heat treatment during processing offers the potential to add organic molecules within the material and hence opens a wide variety of opportunities to develop new strategies for repair and reconstruction of bone tissue.

References

[1] Gross KA, Berndt CC. Reviews In Mineralogy & Geochemistry 2002; 48: 631-672.