Key Engineering Materials *Online: 2004-05-15*
ISSN: 1662-9795, Vols. 264-268, pp 2047-2050
doi:10.4028/www.scientific.net/KEM.264-268.2047

Hydroxyapatite Ceramics with Tailored Pore Structure

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Keywords: hydroxyapatite ceramic, interconnecting porosity, slip casting, bone substitute material, rapid prototyping

Abstract. The porosity of a hydroxyapatite ceramic was tailored by transferring polymeric pore models into ceramic forms via the slip casting technique. The rheological properties of the hydroxyapatite slurries play an important role in facilitating the casting operation. Aqueous hydroxyapatite slurries with a high solids content were fabricated. The optimised slurry with 60 wt% hydroxyapatite had a slight shear thickening flow behaviour and a low viscosity. The resulting porous ceramic could be reasonably handled and had a very high interconnecting porosity of 91 – 96 vol%. The pore size varied between 300 and 800 µm. The density value of the bulk hydroxyapatite ceramic covered the range between 94 and 96 % th.d.. The characteristics of the porous ceramics could be varied between high and undirected porosity and low porosity with defined pore channels in the three dimensional directions.

Introduction

There is an increasing clinical requirement for bone graft material, because there are many possible applications such as revision hip surgery, defect filling after e.g. a tumor surgery, or reconstructive orthopaedic surgery. As hydroxyapatite closely resembles the mineral phase of natural bone and is highly biocompatible, it is among other calcium phosphates widely used as bone substitute material [1]. Synthetic hydroxyapatite can be reproducibly processed, and additionally, provides no danger of infections. A large number of research activities has been dealing with the fabrication of synthetic hydroxyapatite ceramics [2, 3, 4, 5].

In this work the porosity of a hydroxyapatite ceramic was tailored, so that the resulting bone substitute material is adapted to the requirements of the implantation site. The tailoring of the pore structure was carried out by using commercially available polymeric foams and polymeric pore models, which were produced via rapid prototyping. These polymeric models were coated or impregnated with hydroxyapatite using the slip casting technique.

This work is part of the research network ForTePro (Bayerische Forschungsstiftung, Germany), in which scientists of different research areas, particularly medical doctors, develop individually adapted implants for bone and cartilage defects, which will be cultivated with the patient's own cells.

Materials and Methods

For producing the slurry the commercially available hydroxyapatite powder from Merck, Germany, was used. The specific surface area was characterised by the BET method (model Gemini 2370, micromeritics, Germany). The mean particle size d_{50} was determined with a laser particle size analyser (model Granulomètre 850, Cilas Alcatel, France). The powder was slowly added to distilled water under constant stirring. The dispersant agent was a solution of a natrium salt of an acrylic acid copolymer. Additionally, a surfactant for better wettability and a binder were used. The

viscosity of the slurries was measured in a rotational rheometer (model Rheolab MC 100, Physica, Germany) with shear rates from 0 to 800 1/s.
Porous hydroxyapatite ceramic was fabricated by coating or impregnating polymeric pore models, e.g. a polyurethane (PU) foam (KURETA, Germany) of three different pore sizes 30, 35 and 45 ppi (pores per inch), with the hydroxyapatite slurry. The resulting structure was dried and then heat-treated at 1250 °C. The pyrolysing behaviour of the PU foams and rapid prototyping models was characterised by thermo-gravimetric measurements (model STA 409, Netzsch, Germany).
The porosity of porous hydroxyapatite ceramics was determined with a helium picnometer (model Accu-Pyk 1330, micromeritics, Germany) and a scanning electron microscope (model Jeol 6400, Jeol, Japan). To analyse the phase composition of the ceramic, an X-ray diffractometer (model XRD 3000P, Seifert, Germany) was used.
For comparison, dense hydroxyapatite cylinders were prepared by casting the slurry into plaster moulds. After drying the resulting green bodies were sintered at 1250 °C. Green density was determined by geometrical weight-volume evaluation. Sintering density was measured by the Archimedes' method. The shrinkage and sintering start temperature were determined with a dilatometer (model 402 E/7, Netzsch, Germany).

Results and Discussion

The commercially available hydroxyapatite powder has a specific surface area of 64 m²/g. Using this powder only slurries with a relatively low solid content of 35 wt% and a high viscosity could be prepared. After calcination of the powder at 900 °C the specific surface area was reduced to 12.5 m²/g. Using the calcined powder slurries with high solid content from 55 to 65 wt% were produced. The flow behaviour of these slurries is affected by the character and the amount of the dispersant (Fig. 1). Other additives like the binder can change the viscosity as well, but to a minor degree. The binder used in this work reduced the viscosity. The slurries showed a shear thickening flow behaviour, whereas the viscosity increased with rising solids content. As an optimum between the two desired properties low viscosity and high solids content, slurries with solid content of 60 wt% were chosen for further experiments. The mean particle diameter in the stabilized slurries is approximately 2.8 – 3.2 µm. No sedimentation occurred for several hours.

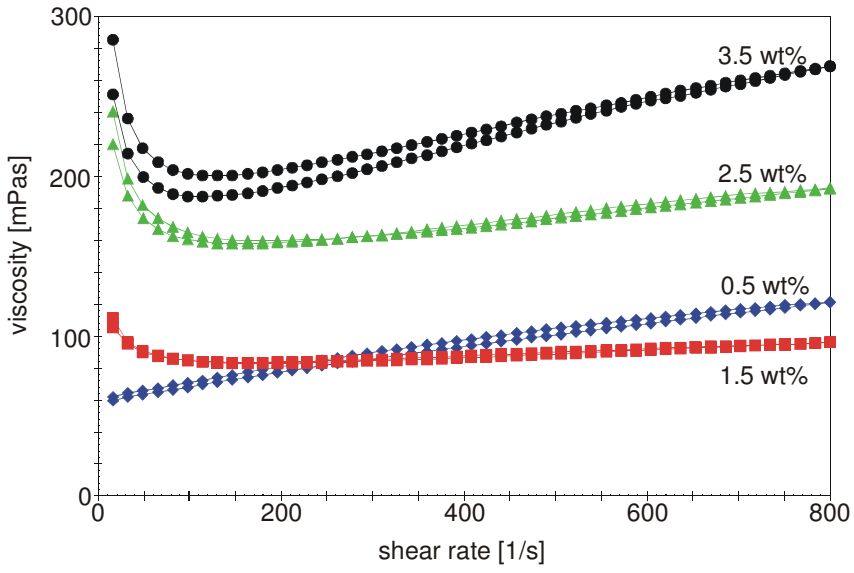

Fig. 1. Flow behaviour and viscosity of the hydroxyapatite slurry with respect to the amount of dispersant agent.

Green and sintered density values were determined with cast dense cylinders. As can be seen from Table 1, these values decrease slightly with increasing dispersant amount. Dilatometer measurements exhibit a mean shrinkage of the cylinders of 20.6 %.
The sintering started at approx. 950 °C. From X-ray diffraction patterns of the dense samples sintered at 1250 °C, it is evident that the final product consists of pure hydroxyapatite. No other phase was detectable.

Table 1. Green and sintering density dependent on the amount of the dispersant agent.

dispersant content [wt%]	green density [% th.d.]	sintering density [% th.d.]
0.5	47.0	96.5
1.5	47.5	94.6
2.5	46.6	94.3
3.5	45.9	94.3

Error: for green density: +/- 1.5 %, for sintering density: +/- 0.9 %

With the optimised slurry, PU foams were coated and the rapid prototyping polymeric models were impregnated. Subsequently, the polymer was pyrolysed and the ceramic sintered with a defined temperature profile. The thermo-gravimetric measurement revealed that the PU foam decomposes in two steps. The weight loss started at 210 °C, and at 650 °C the foam was almost completely removed. In the case of the rapid prototyping models, the polymer burn out was finished at 700 °C.
The porosity of the resulting ceramic is very high (91 to 96 vol% - Table 2). The ceramic has density values between 94 and 96 % th.d. which are comparable with the density of the bulk ceramic cylinders (see Table 1).

Table 2. Porosity of the PU foams and the hydroxyapatite (HAp) ceramic.

PU foam	Total porosity of PU foam [vol%]	Total porosity of HAp ceramic [vol%]	Density of bulk HAp [% th.d.]
30 ppi	98.4	91.3	94.8
35 ppi	97.9	96.4	95.5
45 ppi	97.9	96.2	96.2

Scanning electron microscopy images (Fig. 2) show the pore structure of the ceramic. In all cases the pores were interconnected, only the pore size varied from 300 to 800 µm in diameter. The struts had very few cracks.
Thus, the fabricated hydroxyapatite ceramic foam could be reasonably handled, although the struts of the ceramic were hollow.
While the ceramics based on the PU foam had a high and undirected porosity, the rapid prototying polymeric models resulted in bodies with a lower porosity, but defined pore channels in the three dimensional directions. In this way the porosity of the hydroxyapatite ceramic could be varied over a broad range.

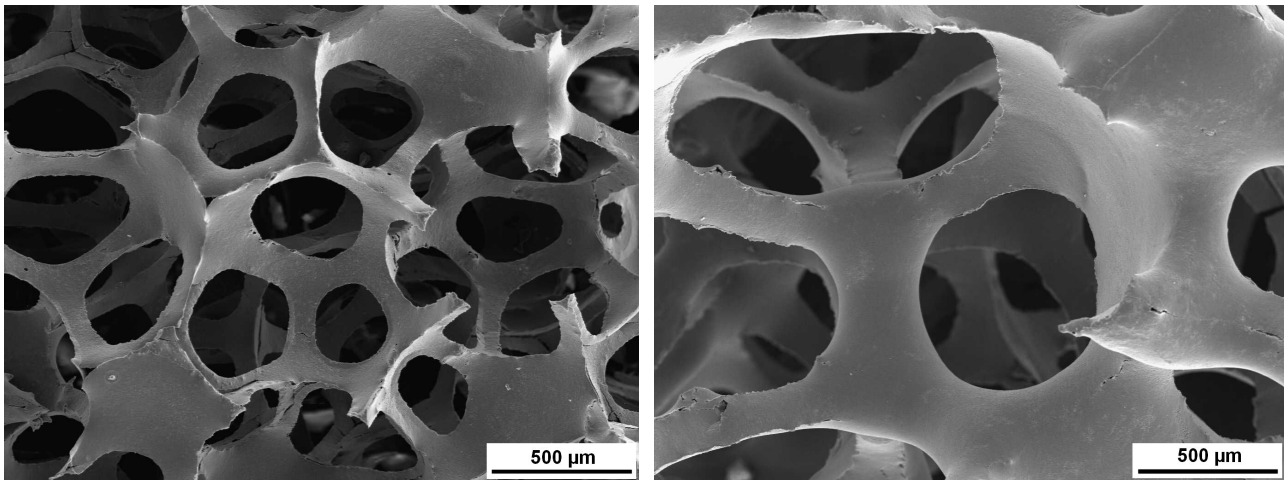

Fig. 2. SEM images of the sintered hydroxyapatite ceramics with different pore sizes (from left to right formed from PU foam with 45 and 30 ppi).

Conclusions

Hydroxyapatite ceramics could be fabricated by transferring polymeric pore models into ceramic forms using hydroxyapatite slurries with optimised characteristics. The porous ceramics revealed a uniformly distributed open and interconnected macroporosity. By using different types of polymeric pore models with diverse grades of porosity (50 to 96 vol%) and pore sizes (400 to 900 µm) as basic materials the pore structure of the bioceramic (undirected pores as well as defined pore channels) could be tailored according to the requirements of the specific implantation site. As a next step the porous ceramic scaffolds will be used for cell cultivation.

Acknowledgements

This work has been supported by the Forschungsverbund ForTePro initiated by the Bayerische Forschungsstiftung (Bavaria, Germany). The authors are grateful to several colleagues of the Institute for Materials Research (University of Bayreuth) and the Friedrich-Baur-Research-Institute for Biomaterials, who were involved in this research project.

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