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Preparation and Characterisation of Porous Hydroxyapatite Bioceramic via a Slip-Casting Route

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Abstract: Porous hydroxyapatite bioceramic was fabricated using a casting method by mixing a polymeric powder with a slip containing fine hydroxyapatite powders. The rheology of the ceramic slip was examined. After sintering, the resultant porous hydroxyapatite bioceramic was characterised in terms of the porous microstructure and mechanical properties. The experimental results demonstrated that the resultant porous ceramic with a successful control of pore size and porosity characters can be obtained. The flexural strength (σf) of the porous hydroxyapatite ceramic decreased with increased macropore size and correlated well with the porosity (p) by an exponential function: $\sigma f = 115 \exp(-4.5\,p)$ MPa. The Young's modulus (E) of the porous bioceramic can also be adequately described by $E = 140 \exp(-4.2\,p)$. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Hydroxyapatite (HAp) ceramic has chemical compositions closely resembling that of mineral phase of natural bone. Many in-vivo experiments have confirmed the HAp as a potential implant material for biomedical applications. To fabricate a bioceramic with porous configuration, the evidence of tissues ingrowth and biological responses provide obvious advantages in tissue-implant fixation and controlled biodegradation rate for both short-term and long-term implantation purposes.[1–5]

Recently, the present author[6] has demonstrated a method to produce porous HAp ceramic with controlled porosity characters and pore geometry[7] by a simple die-pressing route. The pore size (i.e. here referred to as "macropore" having several hundred micrometers in dimension) or pore size distribution is directly related to the particle size or particle size distribution of introduced polymeric powders. However, it is rather difficult to obtain a porous HAp ceramic with complex geometry via conventional die-pressing route. Several advantages can usually be obtained for casting a ceramic slip into a mould such as controlled geometry, structural uniformity, and minimum defects/defect size, etc. and which methodology has long been considered as a major processing for production of ceramics with a more uniform and dense microstructure. Recently, Arita *et al.*[8] performed a tape casting method to produce thin hydroxyapatite layer (150–200 μm in thickness) and the HAp layer obtained allows them to produce laminates with desired porosity gradient. The pore size developed by their production technique is limited due to the nature of chemical reaction and porosity maximum achievable is ~63 vol%.

In this investigation, ceramic slurry was prepared at desired rheology, followed by mixing with polymeric powders with controlled particle size and quantity. The resultant pore size and porosity of the porous HAp ceramic were examined. The flexural strength and Young's modulus of the porous bioceramic with respect to the porosity were also determined.

2 POWDER PREPARATION AND EXPERIMENTAL PROCEDURES

Hydroxyapatite powders were synthesised according to the following reaction:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (1)$$

The reaction proceeded under a solution pH = 9.5 at a vigorously stirred condition for 24 h. After heat treatment at a pre-determined temperature of 1200°C, the powder was exposed to X-ray diffraction analysis and the resulting diffraction pattern revealed a typical of apatitic structure (Fig. 1). The atomic Ca/P ratio was determined to be 1.67 using atomic emission spectrometry (ICP-AES, Spectro, Spectorflame-P) which is almost the same as the stoichiometric ratio of the hydroxyapatite. The synthetic powder exhibited a needle-like shape with ~10 nm in diameter and ~150 nm in length as shown in Fig. 2.

The HAp powder with varying solids loading, i.e. 10–15 vol%, was mixed with deionised water and synthesised dispersant to form a ceramic slurry by means of ball milling within a polyethylene jar. The rheological property of the slurry was then characterised using a viscometer (Brookfield). Prior to casting, polyvinyl butyral (PVB) powders were blended with the slurry for a further period of mixing. The PVB powders have different size fractions, i.e. 0.188 mm and 0.42 mm. The prepared slip after being degassed was then caste onto a plaster mould with a rectangular geometry. After oven drying at 80°C for 24 h, the cast specimens were heat-treated at 500°C at a reasonably slow heating rate, followed by sintering at 1200°C for 3 h.

Fig. 2. Transmission electron micrograph of the HAp powders.

The dimensional shrinkage of the green compacts containing different sizes and quantities of the PVB powders was monitored before and after sintering. The pore size, porosity, and pore structure of the resulting porous HAp ceramic were examined. To investigate the mechanical strength of the porous ceramics, the specimens with dimensions $5 \times 8 \times 50\,mm^3$ were prepared and subjected to a three-point fixture by an Instron tester (Model 3162). Each strength value was obtained by averaging 5–8 measurements. The crosshead speed was fixed at a rate of $0.5\,mm\,min^{-1}$. The Young's modulus of the ceramic was determined ultrasonically.

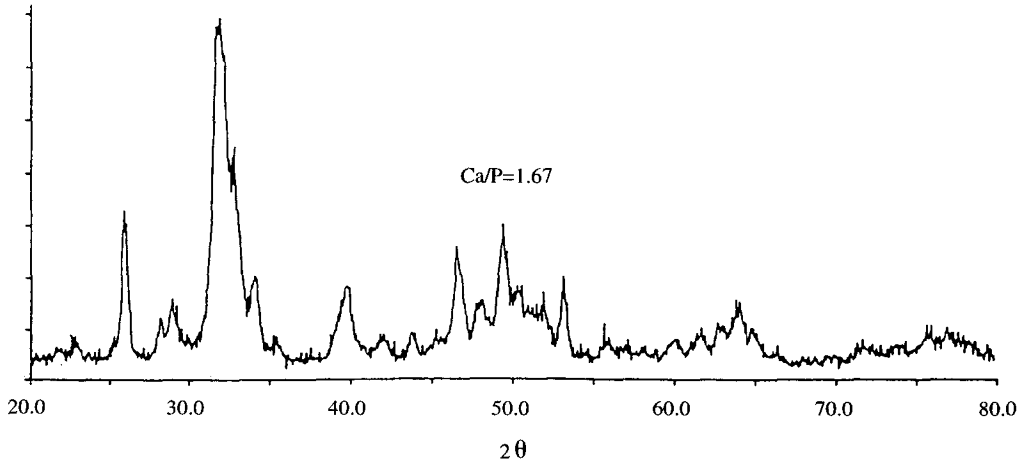

Fig. 1. XRD patterns of the synthetic hydroxyapatite ceramic powder.

3 RESULTS AND DISCUSSION

3.1 Rheological behaviour

To obtain an HAp slurry with resonably low viscosity at solids loading over the range of 10–15 vol%, dispersant contents ranging from 0.25 wt% to 0.9 wt% were employed. Figure 3 representatively illustrated that the optimal content of the dispersant is approximately 0.5 wt%, further increase of the dispersant enhanced the slurry viscosity and this finding was frequently seen in other ceramic slurry systems. The optimal value for viscosity minimum in the present HAp slurry with respect to its solid loading is relatively high in comparison to several ceramic slurry systems such as SiC (30–35 vol%),[9] Al_2O_3 (30–40 vol%).[10,11] The major reason is due to the extremely fine HAp particles which provides relatively large surface area in which the need of sufficient amount of dispersant is essential to develop barriers to prevent particle–particle attraction. Irregular particle shape may also cause the difficulty for particles to slide over one another and this effect may reduce to a certain extent upon increase of the dispersant content, corresponding to a greater particle-to-particle distance.

The HAp slurry with varying solids loading exhibited a pseudoplastic behaviour (Fig. 4). However, the apparent viscosity of the slurry with loading above 12.5% is relatively high at lower shear rates. This may render the subsequent casting operation difficult. Therefore, in the following experiment solid loading of 10 vol% was employed and as expected, an attempt to find a HAp-PVB-contained slurry with reasonable rheological behaviour to facilitate casting is achieved.

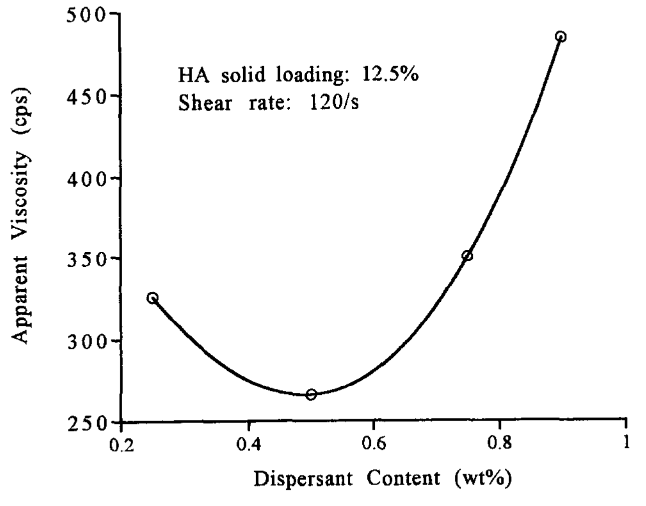

Fig. 3. The apparent viscosity of the HAp slurry varies with dispersant content at a given shear rate of $120\,s^{-1}$.

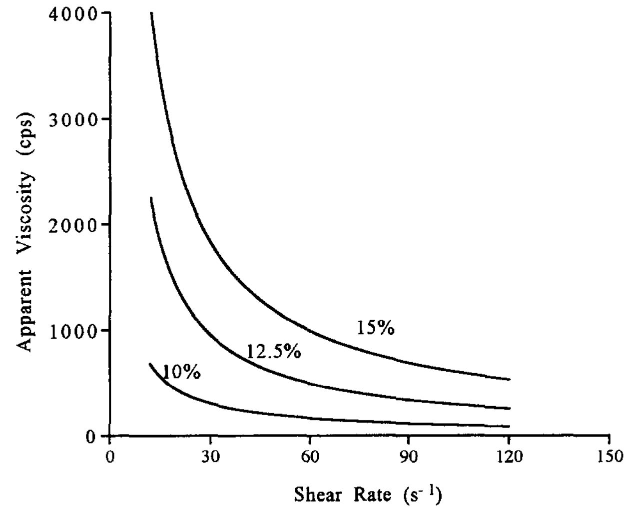

Fig. 4. The HAp slurry with different solids loading exhibits a pseudoplastic behaviour.

3.2 Shrinkage

Upon casting the slurry containing varying quantities and sizes of the PVB powders into rectangular-shaped moulds, the specimens with defined dimensions were obtained and subjected to heat treatments to drive off the volatiles and the PVB powders to form a porous network. The shrinkage of the porous specimens was monitored before and after sintering. It is interesting to note that at a given sintering condition, the shrinkage of the specimens is irrelevant with the size of the PVB particles in the study range, i.e. the shrinkage is relatively constant for varying PVB particle sizes, but is a strong function with respect to the PVB content (Fig. 5). The specimen shrinkage becomes less pronounced while increasing the PVB content from 24 vol% up to 62 vol%. The increase in PVB content, corresponding to an increase in macroporosity, substantially inhibited the shrinkage of

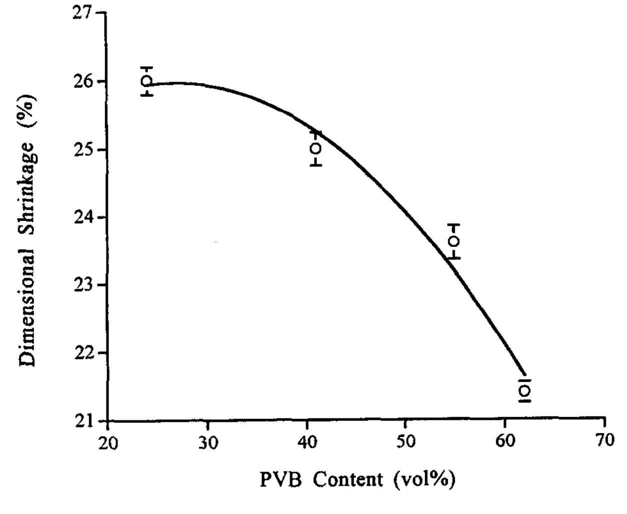

Fig. 5. Dimensional shrinkage of the porous HAp ceramic as a function of initial content of the PVB phase.

the green powder compact during sintering. This finding is important in controlling the dimensions of the ceramic materials while acting as a bone graft substitute into a surgically created bone cavity with defined geometry.

3.3 Porous microstructure

One important aspect in preparing the ceramics by means of the slip casting route is microstructural uniformity. For the fabrication of the porous HAp ceramic, the uniformity of macropore distribution is the major consideration. Therefore, it is critically important to retain a reasonable slurry rheology to facilitate the casting operation and/or to stabilise the PVB particles uniformly dispersed in the slurry. In this investigation, the HAp-PVB-contained slurry with a viscosity over the ranges of 150–300 Pa s appeared to be suitable for casting and the resultant porous ceramic exhibited a uniform macropore distribution as illustrated by a cross-section view of the specimen in Fig. 6. The macropore size is approximately 160–200 μm, closely resembling that of the starting PVB particle size, ~188 μm in average. Except that of the macropore, a vast number of micropores, generally in the sizes of 2–20 μm, can be easily observed (Fig. 7) distributed at the macropore walls. These micropores appear to be highly interconnected and is confirmed by mercury porosimeter (MP, Autopore II 9220) at which the MP-derived porosity (accessible to open pore only) is almost identical to the porosity (for both open and close pores) determined by the weight-and-dimension of the specimens. Such interconnected small pores are critically important in facilitating the circulation of body fluid which further supplies the necessary nutrients and mineral ions for biological functions.

Fig. 6. Scanning electron micrograph showing a uniform macropore distribution within the porous HAp ceramic via the casting route.

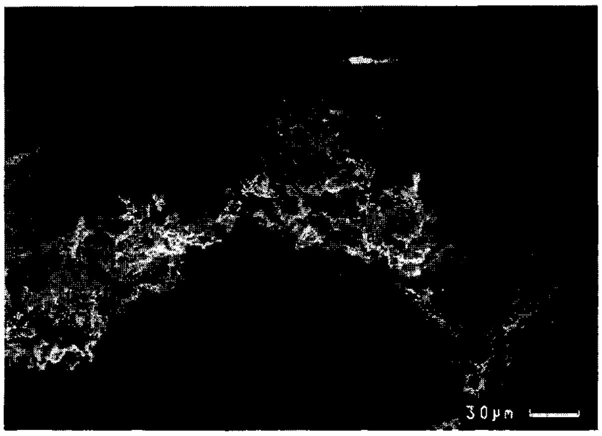

Fig. 7. Numerous micropores distributed throughout the macropore walls.

The total porosity of the specimens obtained in this study is generally over the range of 32~78 vol% which is greater by approximately 10–16 vol% than original fractions of the introduced PVB phase. This extra porosity fraction is attributed solely to the microporosity as above mentioned and is a result of incomplete sintering as also observed in a previous study.[6] For a fixed volume fraction of the PVB phase, the micropore or alternatively microporosity appeared to increase as the PVB particle size is reduced (Fig. 8(a) and (b)). The thickness of the pore walls depends on the volume fraction and particle size of the PVB phase and for example, 20–100 μm in thickness for 55 vol% PVB.

3.4 Mechanical properties

The flexural strength of the porous HAp ceramic was determined using a three-point fixture. Figure 9 shows the resulting porosity–strength curves for different PVB particle sizes. Obviously, at a given total porosity, the flexural strength decreased with increased PVB particle size. Since the fracture of brittle materials is primarily a weak-link process, the micropores within the porous HAP ceramic are reasonably assumed to have little or no significant influence on strength deterioration compared to that of macropores. The experimental finding (Fig. 8) in relation to the macropore size (or correspondingly the PVB size) is in agreement with the fracture theory[12] indicating that the fracture strength (σf) is inversely proportional defect size (c), i.e. $\sigma_f = K/_c 1/2$, where K is the fracture toughness of the materials and c the half-length of the defect. The macropore is inherently a macro-defect in the brittle ceramic materials.[13] Therefore, the larger the macropore, the greater the deterioration of the strength of the brittle materials. Although the strength was reduced, some experimental

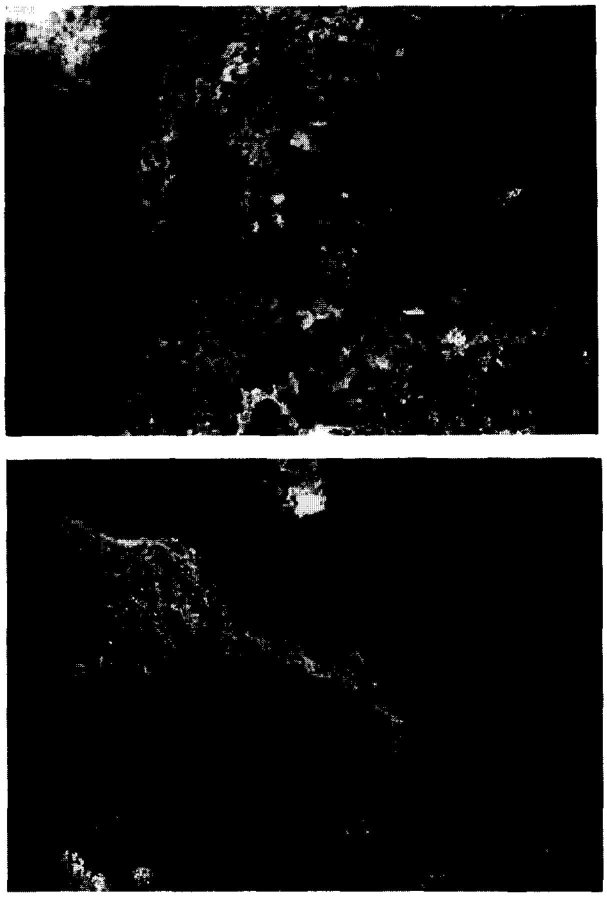

Fig. 8. The micropore/microporosity of the ceramic appears to increase while using (a) 0.188 mm PVB particles compared with (b) 0.42 mm PVB particles.

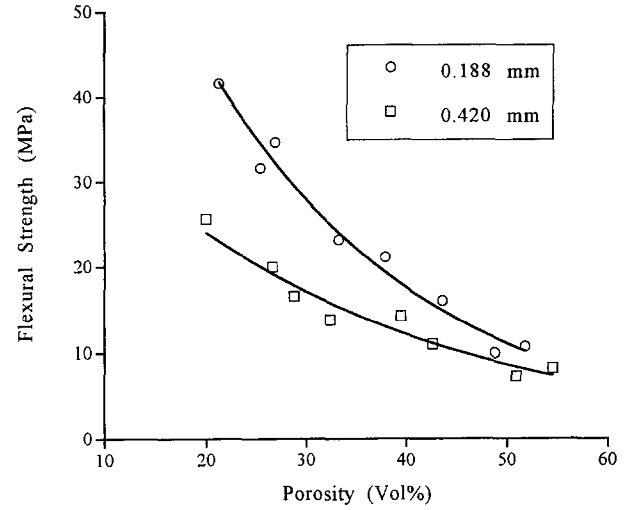

Fig. 9. The flexural strength of the porous HAp ceramic as a function of macropore size and total porosity.

observations showed the arrest of the cracks under stressing with which the specimens with larger macropores fractured in a less brittle manner, suggesting an improvement in material's fracture toughness.[14] To correlate the porosity-dependent mechanical strength, an exponential function, which is the most widely used semi-empirical expression, was employed to describe the porosity–mechanical property behaviour. The solid curves (in Fig. 9) calculated from the exponential expression correlate well the experimental observations and can be described as (r^2 refers to as correlation coefficient):

$$\sigma_f = 115 \exp(-4.5\,p)\ \text{MPa}\ r^2 = 0.97 \qquad (2)$$

for 0.188 mm PVB particles, and

$$\sigma_f = 48 \exp(-3.5\,p)\ \text{MPa}\ r^2 = 0.97 \qquad (3)$$

for 0.42 mm PVB particles

The zero-porosity strength, 115 MPa, derived from eqn (2) for smaller macropore (0.188 mm) is almost identical to that of full-dense hydroxyapatite ceramic obtained by Li *et al.*[15] However, significant deviation occurs by extrapolation of the porosity–strength behaviour (eqn (3)) for larger macropore (0.42 mm) to zero-porosity. Although the actual reason is not clear at present, the presence of larger cracks (resulting from the burnout of the larger-sized PVB particles) associated with larger macropore may be a major cause. The exponent coefficients in eqns (2) and (3) are roughly close to theoretically predicted value for spherical pores as recently addressed by Rice.[16]

Similarly, the exponential function also provides an adequate description on porosity–Young's modulus (E) behaviour of the porous HAp ceramic (solid curve in Fig. 10) by

$$E = 140 \exp(-4.2\,p)\ \text{GPa}\ r^2 = 0.98 \qquad (4)$$

The zero-porosity Young's modulus of the hydroxyapatite derived from eqn (4), 140 GPa, is close to the calculated value of 120 GPa. The exponent constant in eqn (4) is very similar to that appeared

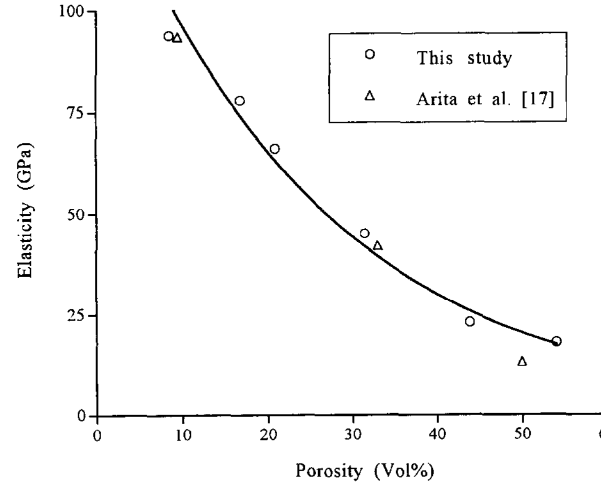

Fig. 10. The Young's modulus of the porous HAp ceramic follows an exponential correlation with total porosity.

in eqn (2) for the macropores of identical pore geometry. This finding is theoretically in good agreement with the porosity-mechanical property behaviour[16] derived directly from the elasticity–strength relationship.[12] On the basis of eqn (4), it is possible to minimise the elasticity mismatch between the porous HAp ceramic while using as an implant material and adjacent hard tissue by adjusting the pore volume fractions.

4 CONCLUSIONS

The porous HAp bioceramic with uniformly distributed macropores and controlled pore size and porosity can be easily fabricated by a conventional slip-casting method. The rheological property of the HAp slurry (or more specifically the HAp-PVB slurry) plays an important role in facilitating the casting operation and dispersing the PVB particles. The flexural strength and Young's modulus of the porous HAp ceramic correlated well with the total porosity of the ceramic through an exponential function, which further suggested the feasibility of obtaining the porous HAp ceramic with optimal strength and elasticity by controlling the quantity and particle size distribution of the introduced PVB particulate phase.

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