Ceramics International 23 (1997) 135–139

0272-8842/97 $17.00+.00
PII: S0272-8842(96)00009-0

Influence of Porosity and Pore Size on the Compressive Strength of Porous Hydroxyapatite Ceramic

Dean-Mo Liu

Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan

(Received 29 September 1995; accepted 17 November 1995)

Abstract: Porous hydroxyapatite (HAp) ceramics with porosity volume fractions varying from 33% to 78% were fabricated using poly vinyl butyral (PVB) as a pore-forming agent. Three types of PVB particle, of size 0.093 mm, 0.188 mm, and 0.42 mm, were employed corresponding to the porous HAp of different macropore sizes. The compressive strength of the porous HAp was investigated in terms of porosity and pore size. The compressive strength behaviour of the porous HAp can be correlated exponentially with porosity volume with a correlation factor greater than 0.96. The porous HAp consisting of smaller macropore exhibits higher strength in comparison with those of larger macropore; however, a greater porosity-dependent strength is observed for the porous HAp ceramic consisting primarily of smaller macropores. Experimental analysis also revealed that for a given porosity volume, the compressive strength behaves roughly linearly with macropore size; a smaller macropore corresponds to a higher compressive strength. These findings suggest that an optimum design of porous HAp with a variety of porosities and with sufficient strength is feasible. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Recently, the development of porous hydroxyapatite (HAp) and other related calcium phosphate (CP) ceramics associated with their application to bone replacements have become an increasingly important research subject of many medical as well as materials scientists. It has been reported *in vivo* that the use of porous HAp/CP promotes the bone ingrowth (osteoconduction).[1–4] Hulbert *et al.*[5] particularly emphasized the importance of pore size and claimed that a minimum pore size of 100 μm is necessary for the porous implant materials to function well and pore size greater than 200 μm is an essential requirement for osteoconduction. Therefore, the design of porous implant materials with pore size larger than, for example, 150 μm, appears to be an important criterion suitable for clinical applications. Fabbi *et al.*[6] have recently reported that porous HAp ceramics with a replica of the network structure of cellular polymer foam were obtained by simply coating the polymer foam with an HAp slurry, followed by appropriate heat treatments. The obtained porous HAp has a high level of porosity, e.g. >70%, with a major portion of pore size larger than 150 μm. However, the strengths were reduced substantially but they claimed to be sufficient for clinical use. More recently, Le Huec *et al.*[7] have demonstrated the influence of porosity on the compressive strength of the porous HAp. They correlated the resulting compressive strength with both microporosity and macroporosity by a polynomial equation and indicated the possibility of design of porous HAp ceramic with sufficient strength. However, the size of macropore included is limited to only ~400 μm.

In a previous study,[8] the present author has demonstrated a successful means to fabricate porous HAp ceramics with a wide variety of porosity volumes and of pore sizes. This study aims to evaluate the compressive strength of the porous

HAp ceramic fabricated by incorporating a poly (vinyl butyral), PVB, as a pore-forming material. To assess the influence of pore size, particularly the macropores, three types of PVB particles of sizes 0.093 mm, 0.188 mm and 0.42 mm, corresponding to different resulting macropore sizes, were employed. The correlation between the strength behaviour and porosity was studied and the influence of macropore size on the strength was also discussed.

2 MATERIALS PREPARATION

PVB particles with size fractions of 0.093 mm, 0.188 mm and 0.42 mm in average were used as a porosifier. Powder mixtures containing the HAp granules, ~100 μm in diameter and 24–61% in volume of PVB particles were prepared. The mixed powders were die-pressed uniaxially at a pressure of 27 MPa, to form rectangular blocks. The blocks were then heat-treated to 500 °C at a heating rate of 0.5 °C/min to drive off the PVB particles, leaving voids of identical geometry with the initial PVB particles, and other volatiles, followed by increasing to 1200 °C in ambient air from 1 h to 48 h for further densification.

The porosity of the as-sintered HAp ceramics was determined by the weight and dimensions of the specimens and/or by mercury porosimetry (Autopore II 9220). Three to four specimens were selected to determine the porosity value. The pore size as well as the pore structure of the ceramics were examined using scanning electron microscopy (Cambridge Instrument, S360).

The compressive strength of the porous HAp ceramics was measured using an Instron tester (Model 1361) with specimen dimensions 18×18×5 mm. Eight specimens were used to determine the average compressive strength.

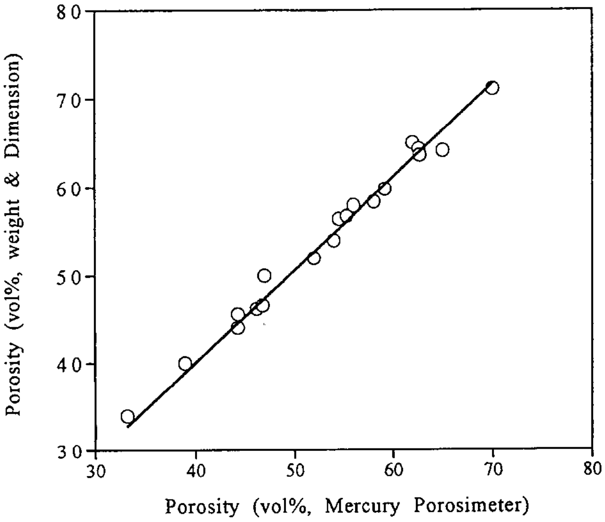

Fig. 1. Linear relation with a slope of ~1 of the total porosity measured by density and mercury porosimeter.

3 RESULTS AND DISCUSSION

3.1 Microstructure

A comparison of porosity volume over the ranges of 33–71%, measured by either the dimension of the sintered body or mercury porosimeter is given in Fig. 1. A straight line with slope ≃1 (determined by least-squares method) suggests that the total pore volume can be fully characterized by the porosimeter indicating an open-pore network. The network structure of the porous solid (with 55 vol%, 0.42 mm PVB) is shown in Fig. 2(a) and 2(b), at larger magnification. The macropores with near sphere in shape are uniformly and separately distributed, i.e. a closed-pore structure. A detailed examination of the solid walls (Fig. 2(b)), having an average thickness of ~50 μm, reveals that two types of micropore with a size of ~15 μm and ~2 μm, respectively, exist. Therefore, the pore structure of the porous HAp ceramic can essentially be considered as an assembly of macroporosity (with pore size similar to the starting PVB

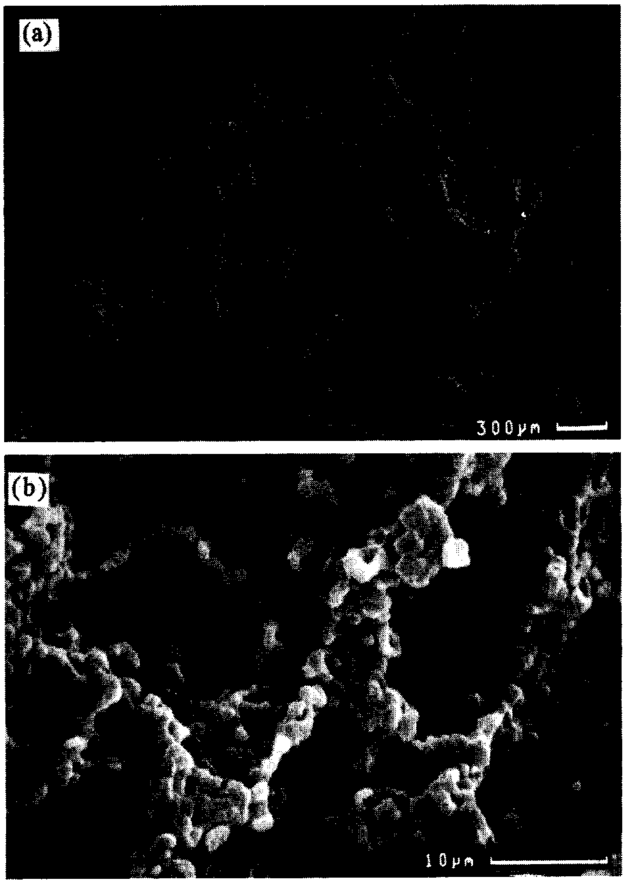

Fig. 2. Scanning electron micrographs show the porous HAp ceramic, prepared at 1200 °C for 2 h, consisting of (a) macropores and (b) micropores.

particle size) and microporosity. These micropores are interconnected as confirmed earlier by the mercury penetration measurement. According to literature reports,[9,10] such porous walls with interconnective pores are beneficial for osteoinduction because these pores enable the circulation of the body fluid with the supply of nutrients and the ions exchange, e.g. Ca and P.

3.2 Porosity–strength behaviour

The porosity–strength behaviours of the porous HAp ceramics with pore volume fraction in the range 45–78% are illustrated in Fig. 3, where different symbols refer to different macropore sizes. Interestingly, at relative high level of porosity, e.g. >70%, the compressive strength of the porous HAp appears to be insensitive to the total pore volume; however, the difference in the porosity–strength behaviour became pronounced as the porosity volume decreased. Therefore, it seems important to characterize the effect of porosity together with the macropore size on the compressive strength not only for a better understanding of the porosity–strength behaviour but also to help in design of the porous HAp with desirable mechanical property.

Generally, a number of expressions can be used to describe the porosity–strength behaviour of porous ceramics. One of the simplest methods was proposed by Rice[11] based on the minimum solid area approach and the resulting porosity–strength dependence can be approximated closely by an exponential function,

$$\sigma = \sigma_0 \exp(-bp) \qquad (1)$$

where σ_0 is zero-porosity strength, σ is the strength at pore volume fraction p, and the constant b is related directly to the pore characteristics. The porosity–strength behaviours of the porous HAp ceramics with pore volume in the range 45–78% can then be described based on eqn (1) by the solid curves shown in Fig. 3 and which give the following, associated with corresponding correlation factor (r^2);

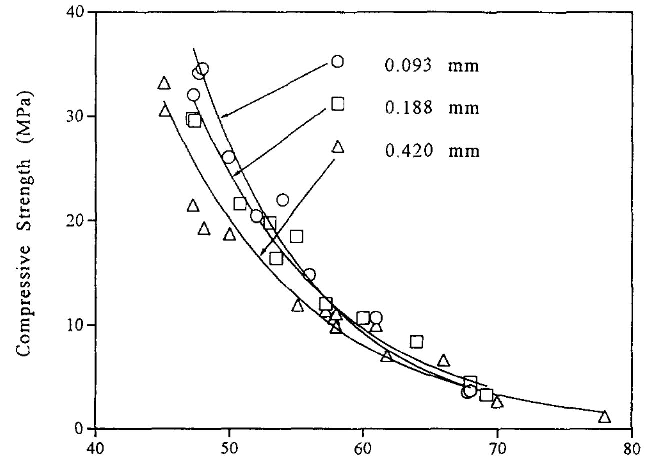

Fig. 3. The porosity–compressive strength behaviour of the porous HAp ceramics in terms of different sizes of starting PVB particles (corresponding to different macropore sizes).

for 0.093 mm (S) particles,

$$\sigma_S = 5920\ \exp(-10.8p)\mathrm{MPa},\ r^2 = 0.98 \qquad (2)$$

for 0.188 mm (M) particles,

$$\sigma_M = 2580\ \exp(-9.3p)\mathrm{MPa},\ r^2 = 0.97 \qquad (3)$$

and for 0.42 mm (L) particles,

$$s_L = 1900\ \exp(-9.2p)\mathrm{MPa},\ r^2 = 0.96 \qquad (4)$$

The high values of the correlation coefficient (r^2) in these expressions indicate that the porosity–strength behaviour of the porous HAp can be well-described by the exponent function but is strictly limited to the porosity level of 45–78%. The difference in zero-porosity strengths derived directly by the extrapolation of eqns (2), (3) and (4) seems to be in contradiction to theoretical expectation (i.e. they are supposed to be identical or similar). However, such an extensive extrapolation to zero porosity may essentially be a risk in correlating the overall porosity–strength behaviour.

Attention has to be placed on the exponent constant (b) because it relates directly to the pore characteristics. The b values obtained indicate a strongly porosity-dependent compressive strength of the porous HAp ceramics and this appears to be consistent with those theoretical predictions on the compressive property,[12] considering the possible effects of plastic deformation and/or crack accumulation. In comparison, the HAp ceramics with smaller macropores size predicts a higher zero/low-porosity compressive strength, but it is found that the smaller the macropore size, the greater dependence, i.e. the b value, of strength on porosity. However, this contradicts that of theoretical expectation[13] and experimental finding[6] as well. Since the b value, according to Rossi's model, varies strongly with the stress-pore shape orientation, particularly when the pore with a cylindrical geometry whose axis is normal to the stress.[14] The PVB particles of the smallest size may easily connect with each other to form agglomerates in a geometry substantially deviated from the original near-spherical geometry and this is particularly pronounced at higher content of the PVB phase. Therefore, some of the resulting macropores may

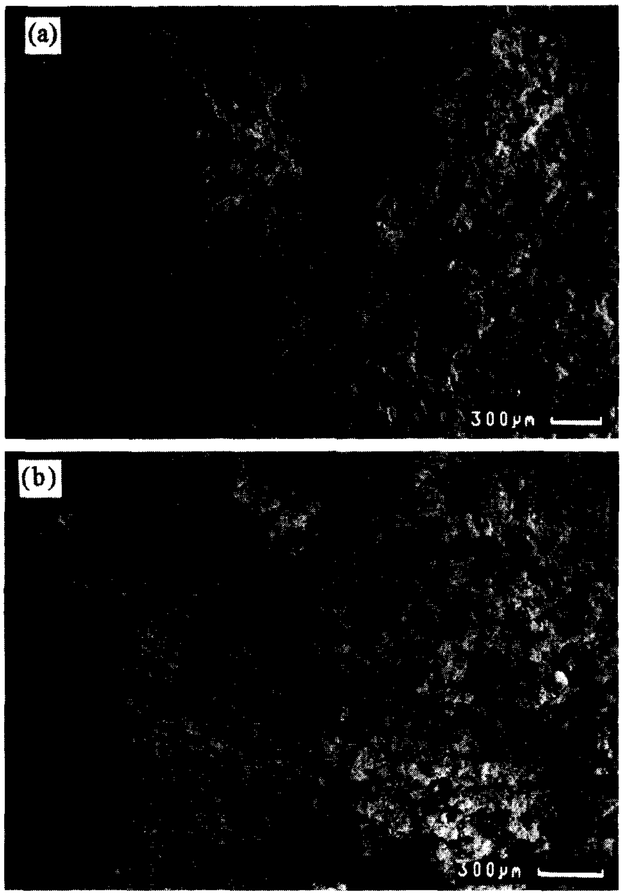

Fig. 4. A typical pore structure of the porous HAp ceramic, prepared at 1200°C for 5 h, consisting of (a) 42% and (b) 55% of PVB particulate phase.

exhibit different types of geometry, causing an increase in b value. Figures 4(a) and 4(b) show the pore structure of the HAp ceramics with 42% and 55% of 0.093 mm PVB particles, respectively. The latter shows a pore size somewhat larger and pore shape more complex than those in the former. However, this factor can be significantly or completely diminished while increasing particle size. For instance, the specimen shown in Fig. 2, containing 61% of 0.42 mm PVB particles has a clearly distinguishable pore size and pore geometry. The constant b approaches an equilibrium value, i.e. $b = 9.2$ expressed in eqns (3) and (4), relative to the nature of pore structure.

To compare the influence of macropore size (corresponding to PVB particle size) on the compressive strength of the HAp ceramics, specimens with nearly the same porosity but with different macropore sizes were prepared. Figure 5 shows the resulting PVB size (corresponding to the macropore size)–strength dependence, the values in parentheses denote the calculated porosity volume derived directly from PVB content. The compressive strength of the porous HAp ceramics decreases linearly with increasing macropore size and the degree of strength degradation tends to decrease with increased porosity volume. This is consistent with the preceeding discussion on Fig. 4 and the corresponding expressions. In fact, the porosity volume with the specimens depicted in Fig. 5 involves both macro- and microporosity. The microporosity volume in these specimens having the same total porosity volume is believed to be similar to that revealed in a previous study.[8] The decrease in compressive strength can thus be reasonably considered as the macropore effect and it is clearly differentiated (from Fig. 5) the significance of macropore size on the compressive strength of the porous HAp ceramics. This finding is not only consistent with that reported by Le Huec *et al.*[7] who indicated that microporosity is responsible for a higher compressive strength than that of macroporosity, but also implies the feasibility of employing the simple concept to optimize the porous HAp ceramics with desired strength and pore characteristics through the control of PVB particle size and size distribution.

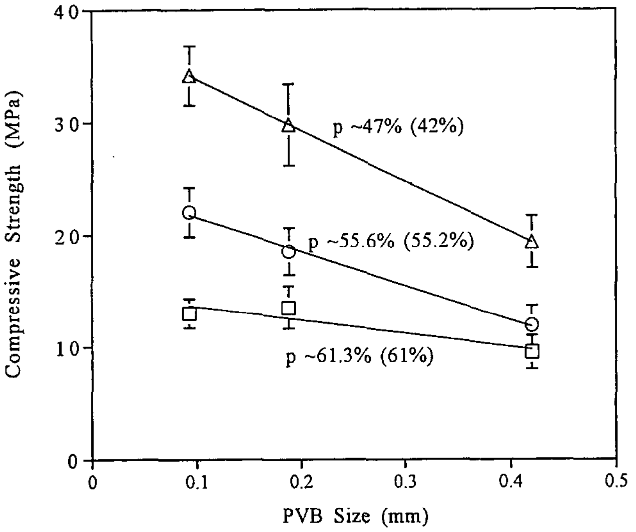

Fig. 5. The compressive strength of the porous HAp ceramics decreases linearly with increasing macropore size for a given total porosity.

4 CONCLUSIONS

The compressive strength of the porous HAp ceramics with porosity varying from 33% to 78% was investigated by control of porosity volume and macropore size. The macropore size ranging from ~0.093 to ~0.42 mm can be easily fabricated by the control of the size of starting PVB particle, a pore-forming agent. The resulting porosity–strength behaviours of the HAp ceramics are generally well-described by an exponential function based on the minimum solid area approach. The specimens with smaller macropores exhibit a higher strength than those with larger macropores. However, the strength tends to become insensitive to macropore size at higher level of porosity. At a given porosity, the compressive strength decreases linearly with the size of macropore. This study implies a possibility to fabricate the porous HAp ceramics with optimization of pore characteristics to meet the diversified requirements of living bone structures by simple control of the size, as well as the size distribution, of starting PVB particles.

ACKNOWLEDGEMENT

The author thanks the Ministry of Economic Affairs, R.O.C. for funding toward this research under contract No. 843CF4130.

REFERENCES

1. RAHN, B. A., NEFF, J., LEUTENEGGER, A., MATHYS, R. & PERREN, S. M., Integration of synthetic apatite of various pore size and porosity in bone. In *Biological and Biomechanical Performance of Biomaterials*, ed P. Christel, A. Meunier & A. J. C. Lee. Elsevier Science Publisher B.V., Amsterdam, 1989, p. 21.
2. SAYLER, K., HOLMES, R. & JOHNS, D., Replamineform porous hydroxyapatite as bone substitutes in cranofacial osseous reconstruction. *J. Den. Res.*, **56B** (1977) 173.
3. PASSUTI, N., DACULSI, G., ROGEZ, J. M., MARTIN, S. & BAINVEL, J. V., Macroporous calcium phosphate ceramics performance in human spine fusion. *Clin. Orthop.*, **248** (1989) 169.
4. IOKU, K., SAMIYA, S. & YOSHIMURA, M., Dense/porous layered apatite ceramics prepared by HIP post-sintering. *J. Mater. Sci. Lett.*, **8** (1989) 1203.
5. HULBERT, S. F., KLAWITTER, J. J. & LEONARD, R. B., In *Ceramics in Severe Environments*, ed. W. W. Kriegel & H. Palmour. Plenum Press, New York, 1971, p. 417.
6. FABBI, M., CELOTTI, G. C. & RARAGLIOLI, A., Hydroxyapatite-based porous aggregates: Physicochemical nature, structure, texture and architecture. *Biomaterials*, **16** (1995) 225.
7. Le HUEC, J. C., SCHAEVERBEKE, T., CLEMENT, D., FABER, J. & Le REBELLER, A., Influence of porosity on the mechanical resistance of hydroxyapatite ceramics under compressive stress. *Biomaterials*, **16** (1995) 113.
8. LIU, D. M., Fabrication of hydroxyapatite ceramics with controlled porosity. *J. Mater. Sci. Mater. Med.*, to be published.
9. CHEN, W., ZHANG, X., WENG, J. & ZHAO, X., Effect of small pores on the osteoinductivity of macroporous calcium phosphate ceramics. In *1st Far-Eastern Symp. on Biomedical Mater.*, ed. X. Zhang & Y. Ikada. Kobunshi Kankokai Inc., Kyoto, 1993, p. 157.
10. YAMASAKI, H., Osteogenic response to porous hydroxyapatite ceramic under the skin of dogs. *Biomaterials*, **13** (1992) 308.
11. RICE, R. W., Comparison of stress concentration versus minimum solid area based mechanical property–porosity relations. *J. Mater. Sci.*, **28** (1993) 2187.
12. RICE, R. W., Microstructural dependence of mechanical behaviour of ceramics. In *Treatise on Materials Science and Technology*, Vol. 11, ed. R. McCrone. Academic Press, New York, 1977, p. 199.
13. KINGERY, W. D., BOWEN, H. K. & UHLMANN, D. R., *Introduction of Ceramics*. Wiley, New York, 1976.
14. ROSSI, R., Prediction of the elastic moduli of composites. *J. Am. Ceram. Soc.*, **51**(8) (1968) 433.