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Preparation of Porous Bioceramics by a Simple PVA-Processing Route

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Abstract. A robust procedure of preparing macro- and micro-porous calcium phosphate bioceramics is presented. The method involved the simple blending of a water soluble polymer (PVA, polyvinyl alcohol) solution and a fine calcium phosphate powder, followed by immediate *in situ* gelation and then calcination at high temperatures to burn off the polymer to form the interconnected porosity. Porous shapes (even morsels or blocks) are obtained with porosity over the variable range of 35 to 70%, with macropores ranging from 100 to 1000 μm. Sample characterization was performed via X-ray diffraction, quantitative chemical analysis, optical and electron microscopy, and compressive strength measurements.

Introduction

Eighty percent of bone (whose inorganic part is mainly a phase of alkali (Na and K) and alkaline earth (Mg) element-doped, nonstoichiometric and *carbonated-apatitic calcium phosphate*) is comprised of dense cortical bone, within which is found the highly porous and vascular cancellous bone (20%). However, the cancellous (trabecular) bone is responsible for 88% of the amount of the normal bone turnover or remodeling, mainly owing to its macroporous (100 μm< pores <1500 μm) nature. Cancellous bone has minimal weight-bearing function and is mainly susceptible to compressive forces; i.e., it is a load distributor rather than a weight-bearer [1]. Pores of bones are perfectly interconnected (to allow vascularization and the flow of inorganic and organic nutrients) and the pore sizes are so adjusted that the osteoblasts and osteoclasts, as well as the cells present in human blood, can easily attach themselves to the lacuna of these pores and easily move around. A bioceramic scaffold material must mimic the pore size distribution of natural bone in order to be named as osteoconductive and biocompatible. Several technologies exist today to manufacture strong and reliable porous ceramics. Important production advantages can be ascribed to the preparation of macroporous bioceramics through the route of gelcasting. The method we present here is a simpler and inexpensive variant of the well-documented [2-8] gelcasting procedure, which works quite satisfactorily with the specific powders of this study. Although we only report here our results in producing porous samples of tricalcium phosphate (TCP: $Ca_3(PO_4)_2$), we have seen that this method also worked equally well for producing porous calcium hydroxapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$), calcium pyrophosphate ($Ca_2P_2O_7$), and for even all the desired *bi-phasic* mixtures (e.g., HA-TCP, TCP-$Ca_2P_2O_7$) of the aforementioned calcium phosphate phases, which are able to withstand the high-temperature calcination without undergoing a change in their stoichiometry.

Experimental

Concentrated solutions (140 g/L) of PVA (MW: 15000, Fluka-Chemika) were first prepared by dissolving polymer powders in distilled water. Appropriate amounts of the PVA solution were then physically mixed with sub-micron particulated calcium phosphate powders (such as, commercial TCP, Cat. No. 1.02143, Merck), namely, with the ratio of *PVA solution-to-powder* being equal to 0.68 mL/g, in a kitchen blender for few minutes. The viscous *ceramer* (or gel) was then poured into an Al_2O_3 mold. The cast gel was immediately heated (in an electrical furnace, in air atmosphere) to 500°C in 1 h, held at 500°C for 15 minutes, then ramped up to 1295°C in 3.5 h, soaked at that

temperature for 6 h, followed by cooling back to RT in 6 h. The porous chunk obtained was cut into smaller pieces by using a diamond saw to produce the desired shapes. Compressive strength measurements on the cut samples were performed with an Instron machine, and morphology and phase constitution of those were evaluated by using scanning electron microscopy (JSM-640, Jeol) and powder XRD (D-5000, Siemens), respectively.

Results

Macro- and micro-porosity on the fracture surfaces of the β-TCP (Whitlockite) samples produced by using the above processing recipe are shown in Figure 1 below. The characteristic cellular morphology with smaller holes present in each cell facilitates the *interconnectivity* of the pores. The dense-looking walls (as seen in Figs. 1a and 1b) are also porous as depicted by the higher magnification photomicrographs of Figs. 1c and 1d.

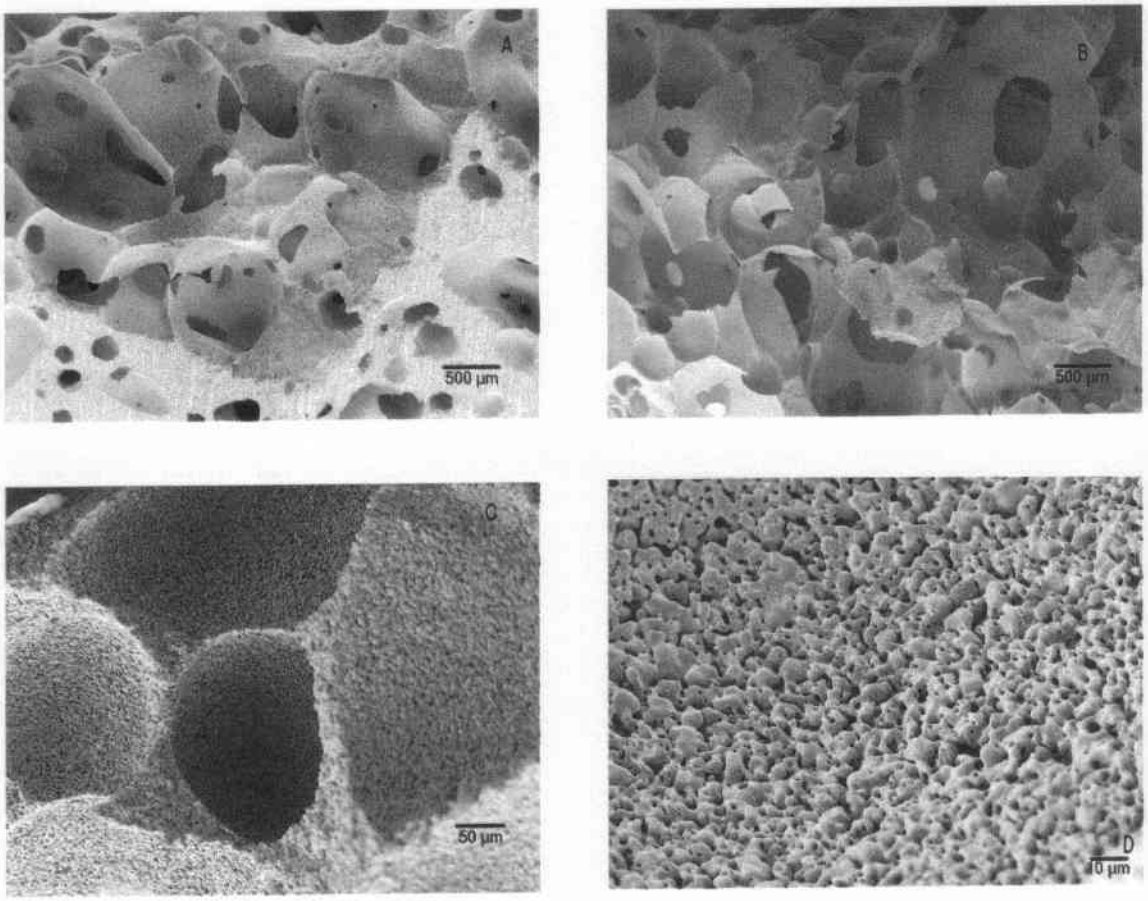

Figure 1.SEM pictures of porous TCP blocks; (a) and (b) interconnected macropores, (c) wall area enlarged, (d) microporous walls separate the macropores from one another

Compressive strength of rectangular blocks (2 x 2 x 1 cm) cut from the calcined gel-cast chunk has been found to be 24 ± 3 MPa. In comparison to the strength [9] of trabecular bones (2 to 10 MPa), this porous Whitlockite material has the unique feature of being quite strong in spite of its high porosity (around 65-70%), measured by the Archimedes' technique [10].

The raw material we used in producing the *bioresorbable* (higher than 60% *in vivo* resorption in 4 months and more than 85% in around 1 year) β-TCP samples was a chemically processed, commercially available (Article 1.02143, Merck KGaA) submicron calcium phosphate powder with a Ca/P molar ratio in the vicinity of 1.50, whose XRD data is shown in Fig. 2 by the bottom trace (a). The raw material actually consists of two phases, $CaHPO_4$ and microcrystalline calcium-deficient hydroxyapatite (CDHA: $Ca_9(HPO_4)(PO_4)_5(OH)$). Porous blocks (whose SEM pictures were given in Fig.1) obtained were single-phase β–TCP, as shown by the middle trace (b) in Fig. 2.

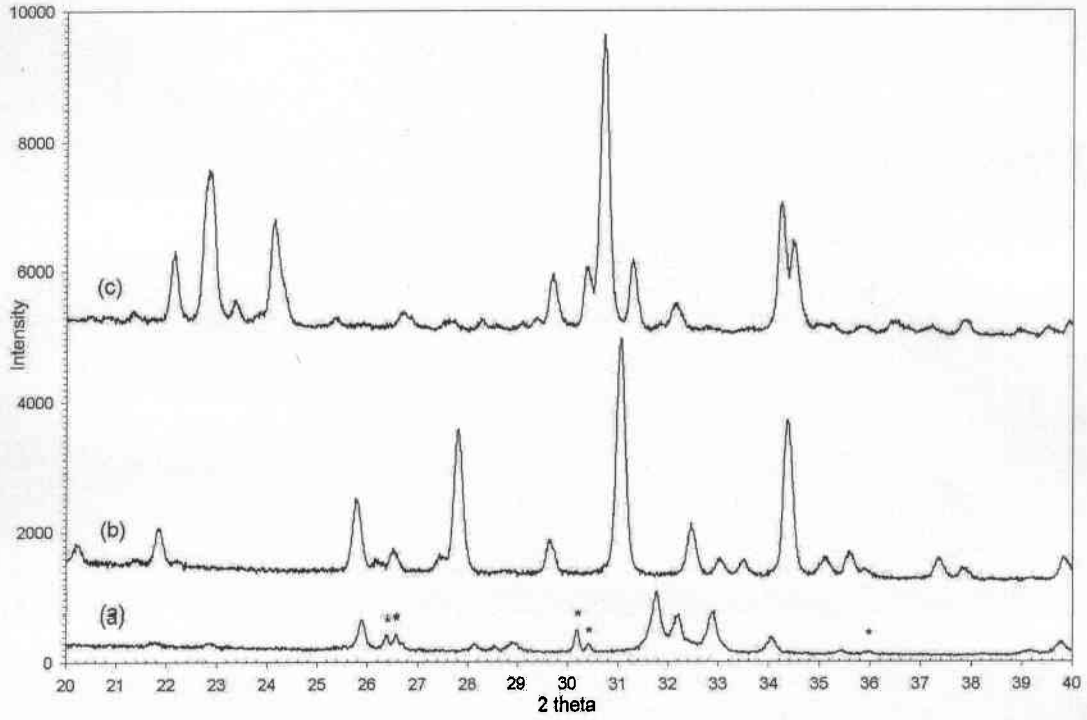

Figure 2.XRD data: (a) raw material used for the data shown in this article, * indicates the peaks of the phase $CaHPO_4$, remaining peaks are of CDHA, (b) data for porous blocks produced as described in the experimental section, single-phase β–TCP, (c) data for porous blocks quenched from the high temperature, single-phase α-TCP

β–TCP is known to resorb quite fast in the body, owing to its high solubility. However, the high-temperature polymorph of TCP, namely, α-TCP, does not resorb as fast as β–TCP [11]. Alpha-TCP has another interesting property, and it hydrolyzes itself in human plasma (and in general, in aqueous systems) into CDHA [12]. Whence this transformation (*in vitro* or *in vivo*) is significantly complete, the product will not simply dissolve away (as does β–TCP) within the first few months following the implantation. Therefore, porous α–TCP based implants will transform themselves into CDHA while retaining their macro-porous structure, and they will resorb *in vivo* by the osteoclastic action, which takes place at a pH value of 3 to 4. If an implant material is just dissolving at the bone defect-site within a short period of time, then it will obviously be quite far from providing a biomechanically sound healing phase during the bone remodeling process.

The crystallographic transition from α–TCP to β–TCP occurs at around 1180°C, upon cooling [13]. We have been able to totally convert the porous materials of this study into single-phase α–TCP (as shown by the XRD trace labeled as (c) in Fig. 2), just by quenching the material from 1295°C to 900°C in 10 minutes. The compressive strength of porous α–TCP blocks (9 ± 2 MPa) were observed to be much lower than those of β-TCP, as expected, and this is due to the microcracks [11] forming in the quenched porous body, originating from the significant unit cell volume difference between the orthorhombic (α) and hexagonal (β) polymorphs of TCP.

The cooling/quenching rate to be carefully adjusted and to be employed through the polymorphic transformation temperature of TCP can in turn be used as a fine-tuning parameter in producing novel bi-phasic "α–TCP + β-TCP" bioceramics, with variable degrees of *in vivo* resorbability. We have found, for instance, that if we cooled our porous TCP samples from 1295°C to 900°C in 45 minutes, instead of 10 minutes, the end product consisted of a phase mixture of about 70% α- and 30% β-phases. This material does have a higher *in vivo* resorbability as compared to pure α-TCP.

The procedure reported here for preparing macroporous calcium phosphates has also been successfully applied to fine calcium hydroxyapatite (HA) powders, as well as submicron, chemically precipitated $Ca_2P_2O_7$ powders; the latter of these powders has a quite high *in vitro* solubility. The use of HA and $Ca_2P_2O_7$ powders as the starting materials were so selected that the easy adjustment of the Ca/P molar ratio in the final product over the broad range of 1.0 through 1.6 would be feasible.

Summary

Simple blending of concentrated polyvinylalcohol solutions with submicron-particulated calcium phosphate powders, followed by a suitable polymer burn-out calcination step was found to provide a robust and inexpensive route for producing macro- and micro-porous bioceramic implants. This simple process was found to be suitable for the manufacture of porous TCP, HA or $Ca_2P_2O_7$ (or their bi-phasic mixtures) morsels or prismatic blocks for clinical applications.

References

[1] R. Gunzburg, M. Szpalski, N. Passuti and M. Aebi: *The Use of Bone Substitutes in Spine Surgery* (Springer-Verlag, Germany, 2002).
[2] P. Sepulveda, F.S. Ortega, M.D.M. Innocentini and V.C. Pandolfelli: J. Am. Ceram. Soc., Vol. 83 (2000), p. 3021.
[3] M. Trunec and J. Cihlar: J. Eur. Ceram. Soc., Vol. 22 (2002), p. 2231.
[4] S.L. Morissette and J.A. Lewis: J. Am. Ceram. Soc., Vol. 82 (1999), p. 521.
[5] M.A. Huha and J.A. Lewis: J. Am. Ceram. Soc., Vol. 83 (2000), p. 1957.
[6] S. Ghosal, A. Emami-Naeini, Y.P. Harn, B.S. Draskovich and J.P. Pollinger: J. Am. Ceram. Soc., Vol. 82 (1999), p. 513.
[7] F.S. Ortega, P. Sepulveda and V.C. Pandolfelli: J. Eur. Ceram. Soc., Vol. 22 (2002), p. 1395
[8] M. Zhai, F. Yoshii, T. Kume and K. Hashim: Carbohyd. Polym., Vol. 50 (2002), p. 295.
[9] N.O. Engin and A.C. Tas: J. Am. Ceram. Soc., Vol. 83 (2000), p. 1581.
[10] ASTM Designation C20-00, *Annual Book of ASTM Standards* (American Society for Testing and Materials, USA 2001).
[11] J. Wiltfang, H.A. Merten, K.A. Schlegel, S. Schultze-Mosgau, F.R. Kloss, S. Rupprecht and P. Kessler: J. Biomed. Mater. Res. Appl. Biomater., Vol. 63 (2002), p. 115.
[12] K.S. TenHuisen and P.W. Brown: Biomaterials, Vol. 19 (1998), p. 2209.
[13] N. Kivrak and A.C. Tas: J. Am. Ceram. Soc., Vol. 81 (1998), p. 2245.