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Preparation and properties of dense and porous calcium phosphate

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Abstract

A dense tricalcium phosphate possesses E- and shear-modulus of 115 and 86 GPa, respectively. By polyurethane foam and C-fibres a high porous structure with integral porosity of 55–70% was created. The porous tricalcium phosphate possesses a E-modulus of 2–5 GPa, bending strength of 6–11 MPa and compressive strength of 11–22 MPa. Regarding mechanical properties this system could be ranged between cortical and cancellous bone.

Keywords: B. Microstructure; B. Porosity; C. Thermal expansion; Tricalcium phosphate; Macrostructure; E-modulus; Shear modulus

1. Introduction

Calcium phosphate ceramics are widely used as bone replacements in the field of oral and plastic surgery. In the field of dental surgery, the primary applications of ceramics include the filling of pockets and augmenting of deficient mondibular of maxillar ridges, caused by loss of dentition with advancing age or due to disease [1–4].

The subject of this paper is to define the condition of consolidation, properties of dense (sintered) tricalcium phosphate (TCP), the creation and properties of a porous TCP with pore size > 100 μm, by use of the polyurethane foam as well as carbon fibres.

2. Experimental procedure

Tricalcium phosphate (Merck) has been used for these investigations. The grain and agglomerate morpholy were observed by scanning electron microscopy (Leica S 440I). The specific surface area was determined by 5-point- BET measurement (Micromeritics Gemini 2370).

Starting from the initial powder, samples were prepared by isostatic pressing without a binder under 600 MPa (Weber Pressen KIP 300E). In order to optimise the parameters of sintering (heating rate, temperature,-time) the samples were sintered in air atmosphere under polythermal conditions up to 1200°C, using heating rates of 2, 5,10 and 15°C/min and under isothermal conditions in the interval 900–1200°C/4 h, heating rate of 5°C/min, (dilatometer Netzsch 402E).

Bulk densities of the sintered samples were determined by water displacement method. The ceramografic investigations were made with a scanning electron microscope (Leica S 440I).The structure of the sintered material was analysed by X-ray diffraction method using a Philips PV 105-1 diffractometer, operating at CuK_α-radiation.

Open-celled macrostructures were fabricated by coating the struts of polyurethane foam with a ceramic slurry and then firing the resultant structure to pyrolyse the substrate and sinter the ceramic system [5]. Commercial polyurethane foam with density of 32 kg/m^3 was used as a substrate which was coated using Dolapix CE 64 as a defloculant. The slurry contained 45% solid, 15% defloculant and the rest distilled water. It coherently coated the polyurethane substrates. The foam was squeezed and dipped into slurry, looking in that case like a sponge. During the expansion to the original shape and size, the foam was impregnated by the mentioned slurry. After drying, the coated substrates were heated up to 1200°C in a schedule which minimized disruption during pyrolysis and allowed the ceramic to achieve high density. This heating schedule consisted of a heating rate of 0.5°/min up to 800°C and rapid heating of 10°C/min from 800 to 1200°C, 0.5 h held at 1200°C and then cooling in the furnace.

Creation of a porous structure by use of C-fibres was made by the following procedure: C-fibres as bundles

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with diameter of 500 μm have been embedded in a very dense pulp of calcium phosphate. The number of fibres was ca. 60/cm^2. After drying of the system, it was sintered under the following conditions: in the temperature region from 20 to 1200°C, the heating rate was 1°C/min, the holding time at 1200°C was 0.5 h.

Linear thermal expansion of the dense material was measured with a dilatometer Netzsch 402E in air atmosphere and temperature interval RT–1000°C–RT. The measurements were performed with a heating rate of 2°C/min.

Investigations of mechanical properties (E- and shear modulus) of the dense samples were made at room temperature using ultrasonic method (Krautkramer) and 3-point bending test. E-modulus and bending strength of the porous samples were investigated also at room temperature on specimens (10 pieces, 50×5×5) polished with 9 μm diamond paste and subjected to the 3-point bending tester Netzsch 401/3 with 30 mm span and 0.5 mm/min crosshead spead.Compressive strength test (10 pieces, $\phi = 15$ mm, h = 10 mm) were performed on an Instron-model 1126 tester with a crosshead speed of 0.5 mm/min.

3. Results and discussion

The morphology of the powder is presented in Fig. 1. The average particle size of powder is 3.2 ± 1.0 μm. The particles are composed of the primary particles with size smaller than 10 nm. Specific surface area of the powder was 67 m^2/g.

In the course of the polythermal sintering with different heating rate of 2,5,10 and 15°C/min, it was shown that the heating rate does not have a significant influence on the process of densification. The shrinkage at 1200°C was 13–14% and the density of the sintered samples was 2.96 ± 0.05 g/cm^3, that is 94 ± 1% TD.

By the isothermal sintering in the temperature interval 900–1200°C, it was shown, that at 1200°C during 0.5 h, the saturation was achieved by shrinkage of 14.1% (94% TD). Practically, the densification was finished in the nonisothermal part of the sintering process.

A SEM micrograph of the fractured surface of dense TCP, sintered at 1200°/0.5 h (density 94% TD) is shown in Fig. 2

The grain size of the sintered sample is 0.5–3 μm. The pore size is 0.2–0.5 μm. This system is characterized with the following mechanical properties: E-modulus of 115 GPa, shear modulus of 86 GPa and Poisson's ratio of 0.23. XRD analysis shows only the phase of β-calcium phosphate.

By variation of the temperature and time of sintering, compacts with different porosity (6–32%) were obtained. The variation of E- and shear-modulus with porosity is shown in Figs. 3 and 4.

Thermal expansion characteristics of the investigated system in the interval RT–1000°C–RT showed absence of hysteresis effect, that proves that the system is in thermal equilibrium (Fig. 5).

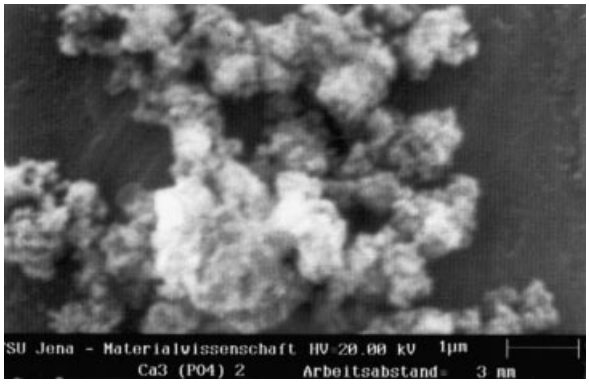

Fig. 1. SEM micrograph of TCP powder (bar 1 μm).

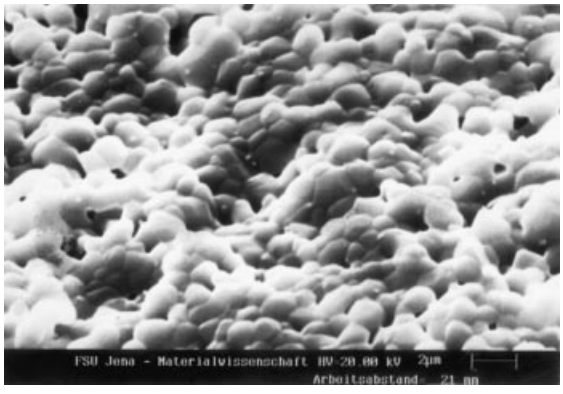

Fig. 2. SEM micrograph of the fractured surface of dense TCP (bar 2 μm).

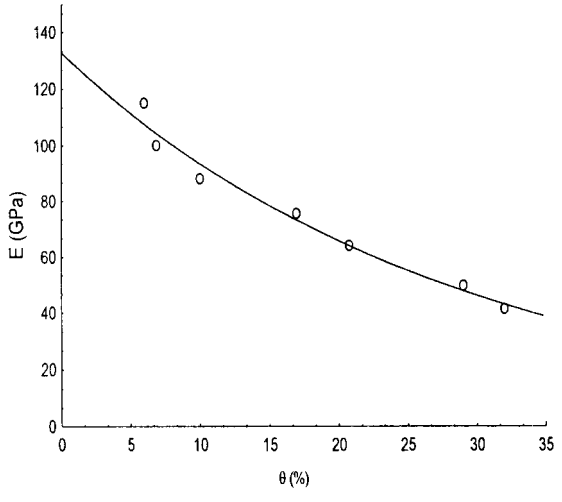

Fig. 3. Variation of E-modulus with porosity.

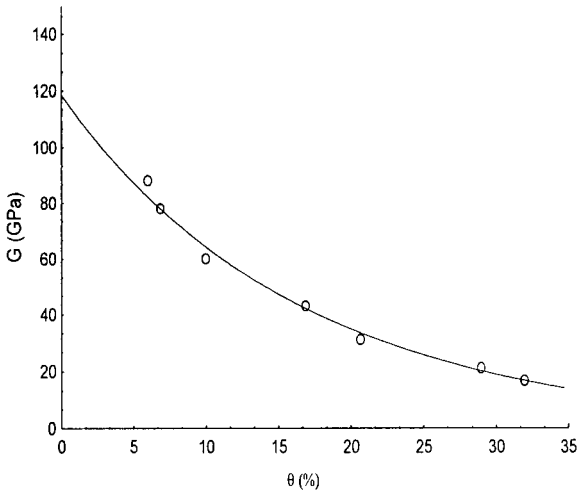

Fig. 4. Variation of shear modulus with porosity.

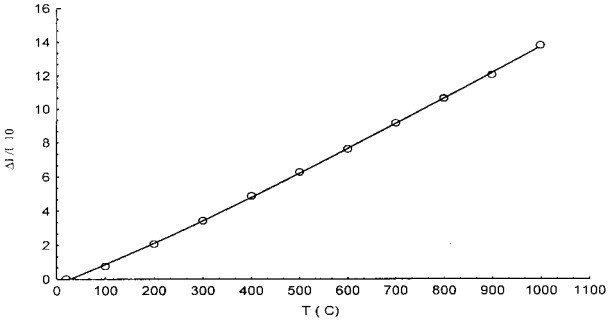

Fig. 5. Thermal expansion of TCP.

The temperature dependence of the thermal expansion in the interval of RT–1000°C can be represented by a III order polynomial form:

$$\Delta L/L = -3.3 \times 10^{-1} + 1.2 \times 10^{-2} T + 3.3 \times 10^{-6} T^2 - 9.3 \times 10^{-10} T^3 \quad (1)$$

Differentiation of the above expression, the temperature dependence of the physical coefficient of thermal expansion could be derived:

$$\alpha = 1.2 \times 10^2 + 6.6 \times 10^{-6} T - 2.8 \times 10^{-9} T^2 \quad (2)$$

The technical coefficient of thermal expansion in the interval RT–1000°C is $14.2 \times 10^{-6}/°C$.

Figs. 6 and 7 show typical macrostructure of the porous samples, observed on the side surface of mechanical test pieces.

By use of a polyurethane foam as a creator of porous structure, samples with porosity of $70 \pm 4\%$ were fabricated. The pores with diameter from 300 to 800 μm are mainly interconnected. E-modulus of this system was 2.1 ± 0.3 GPa, bending strength of 6 ± 3 MPa and compressive strength of 11 ± 3 MPa. After pyrolysis of the foam, no residue was considered.

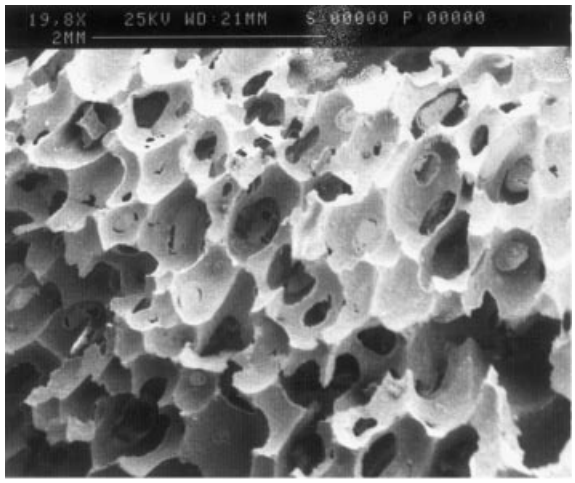

Fig. 6. Macrostructure of cell foam, using polyurethane foam as pores creator.

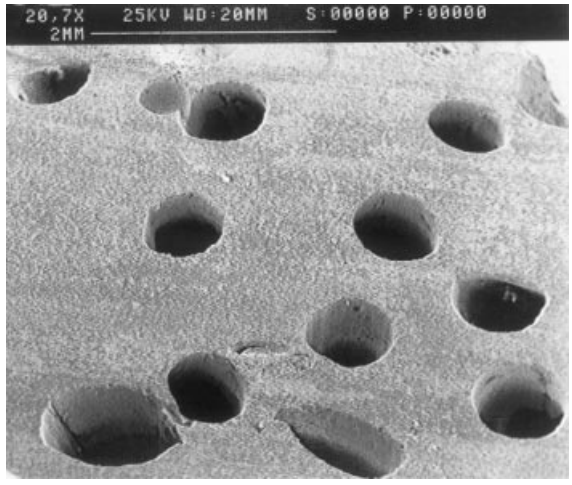

Fig. 7. Macrostructure of cell foam, using C-fibres as pores creator.

Using C-fibres as creators of a porous structure, according to the diameter and number of fibres in the bundle, a correspondent macroporous structure was created. In this case an integral porosity of $55 \pm 6\%$ was achieved. The pores had cylindrical form with diameter 300/700 μm. Fractures among the pores walls were not evident. This system was characterized with the following mechanical properties: E-modulus of 5 ± 0.3 GPa, bending strength of 11 ± 3 MPa and compressive strength of 22.5 ± 4 MPa. Ioku et al. [6] referred to the value of compressive strength of 21.4 ± 2.6 MPa for TCP with porosity of $57 \pm 5\%$, which is in accordance with our investigations.

Microstructure of the dense part of each porous specimen (the wall among the pores) is shown in Fig. 8.

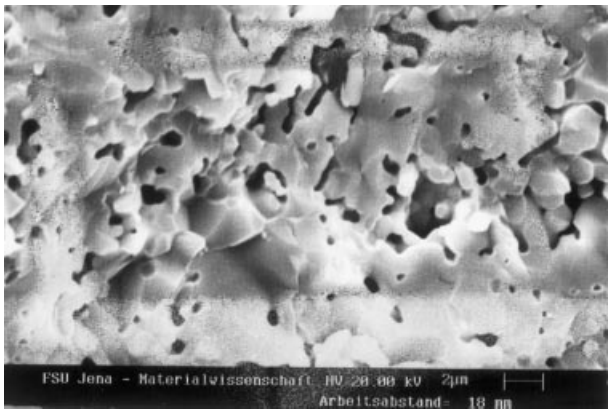

Fig. 8. Microstructure of the dense part of the specimen (bar 2 μm).

Table 1
IE-modulus, bending and compressive strength of cortical and cancellous bone [1]

properties	Cortical bone	Cancellous bone
E-modulus (Gpa)	7–25	0.05-0.5
Bending strength (Mpa)	50–150	
Compressive strength (MPa)	130–180	2–12

Interactive image analysis showed that the porosity of the dense part of the all specimens was $22 \pm 2\%$.

In Table 1, the values of E-modulus, bending and compressive strength of cortical and cancellous bone [1] are shown.

On the basis of the data presented in Table 1, it could be concluded that calcium phosphate ceramics, considering mechanical properties and porosity, could be ranged between cortical and cancellous bone. Having in mind its bioactivity it could be successfully applied in medicine.

4. Conclusion

- Sintered compacts with density of $94 \pm 1\%$ TD , E-modulus of 115 GPa, shear modulus of 86 GPa and Poisson's ratio of 0.23 can be obtained at 1200°C/0.5 h.
- Low density open cell ceramic foam (porosity 55–70 %) can be obtained using polyurethane foam and C-fibres.
- By use of polyurethane foam as a pores-creator an integral porosity of $70 \pm 4\%$ can be achieved. The pores are with size of 300–800 μm, E-modulus of this system was 2.1 ± 0.3 GPa, bending strength 6 ± 3 MPa and compressive strength of 11 ± 3 MPa.
- Using C-fibres as a pores-creator, the porosity of $55 \pm 6\%$ can be achieved. The integral porosity depends on the number of used the C-bundles. The pores have cylindrical form with diameter of 300/700 μm. E-modulus of this system was 5 ± 0.3 GPa, bending strength of 11 ± 3 MPa and compressive strength 22.5 ± 4 MPa.
- Regarding mechanical properties all specimens could be ranged between cortical and cancellous bone.

References

[1] L. Hench, J. Am. Ceram. Soc. 74 (7) (1991) 1487.
[2] H. de Groot, Ceramics International 19 (1993) 363.
[3] S. Qu, W. Chen, J. Weng, X. Zhang, in: Y. Urpo, H. Anderson, (Eds.), Bioceramics, vol. 7, Butterworth–Heinemann, London, 1994, p. 91.
[4] C. Lavernia, J. Schoenung, Ceramics Bulletin 70 (1) (1991) 95.
[5] M. Milosevski, J. Bossert, R. Milosevska, M. Bucker, IX Meeting of EUREKA 294, 28 June 1997, Riga, Latvia.
[6] K. Ioku, H. Kurosawa, K. Shibuya, H. Yokozeki, T. Hayashi, in: H. Anderson, Y. Urpo (Eds.), Bioceramics, vol. 7, Butterworth–Heinemann, London, 1994, p.97.