Preparation and fabrication studies of **Three Dimensionally Ordered** nano-, micro- and meso-scale calcium phosphate crystallites scaffold for artificial bone materials (3-DOMm)

Myung Chul Chang

Kunsan National University

Introduction

In order to obtain β-tricalcium phosphate (β-TCP) nano-crystalline calcium phosph ate (CaP) was precipitated at 37 °C and at pH5.0±0.1 under stirring using highly act ive $Ca(OH)_2$ in DI water and an aqueous solution of H_3PO_4. The various sizes of the rectangular CaP crystallites were prepared at 90°C through the growing process of precipitated nano-crystalline CaP solution according to the crystal growing hours. T he dry nano-crystalline CaP powders at 37 °C were mixed with the dry macro-crysta lline CaP crystallites and the shaped mixture sample was fired at 1150°C to make a β-TCP block. The several ten nm powders were uniformly coated on the surface of s everal ten μm powders by using a vibrator. The mixing ratio between nanometer po wders and micrometer powders greatly affected the mechanical strength of the mixt ure block. The sintered block showed improved mechanical strength, which was cau sed by the solid state interaction between nano-crystalline β-TCP and macro-crystal line β-TCP. Introduction

Aim

The primary study was how to mimic porous bone scaffold in calcium phosphate/collagen matrix. The second issue was how to attain the mechanical property of real humane bone.

Materials & Methods

TCP powders were prepared through precipitation at 37 °C by using $Ca(OH)_2$ and H_3PO_4. In order to make CaO powders $CaCO_3$ powders were calcined at 1100°C for 3 h and cooled down to 200°C. The CaO powders at 200°C were reacted with 3mol% of H_2O in an autoclaved stainless steel reactor in order to make $Ca(OH)_2$. The obtained TCP slurries in a beaker were kept at 37°Cin water bath for 12 h. After then the TCP slurry sample in a beaker were kept at 90°C in the drier according to the schedule from 24 h to 360 h. The beaker was tightly covered with PE pack.

After the crystal growth the sample powders were filtered and dried. The powders were shaped and fired at 1100°C for 3h. The sintered blocks were tested using UTM to measure the compressive strength and tensile strength. For all samples FE-SEM microstructure observation and XRD , measurement were done for grain size evaluation.

Fabrication of DCPD bone cement blocks

For the bone cement preparation, the formulation recipe was as follows:

mDCPD 68 wt%, CSH [CaSO4·1/2H2O] 24 wt%, MCPM

[Ca(H2PO4)2·H2O] 8 wt%

The total amount of the above mixture was controlled as 2.6676 g. Aqueous poly-phosphoric acid solution was prepared by stirring 1.6667 g of DI H2O with 0.000394 g of poly-phosphoric acid.

Results & Discussion

Crystal growth

1) Macro-crystallites 20 - 70 μm

2) Nano-crystallites 20- 450 nm

0 – 75 h Macro-crystallites with time, 120 – 216 h Coated with nano-crystallites, growth of nano-crystallites, decomposition of TCP composition 250 – 360 h , recrystallization of TCP with time

Crystal growth and XRD, FESEM analysis

For the CaP precipitates prepared at 37°C and grown at 90°C XRD phase analysis shows the crystal growth during the scheduled time from 24h to 360h. Nano-crystalline slurries formed at 37°C were well grown to rectangular morphology (25 -60 μm) in the water bath at 37°C after the precipitation. During the crystal growth in the drier at 90°C the thickness was increased. Nano-crystalline powders were attached on the macro-crystallites and also the nano-powders also were grown. After 172 h there be decomposition of crystallites and recrystallizing process would be shown.

Mechanical strength

The compressive strength for the calcined samples was evaluated by using UTM.

Mechanical property of bone cement block

One research aim was to understand the cement interaction in DCPD bone cement. The cement hardening effect was investigated with PAA amounts between 0.8 and 2.0.

Conclusion

1. When the nano- B-TCP37 powders were mixed with macro- B-TCP90 powders, the fired TCP blocks showed higher mechanical strength. In the mixture blocks of nano-B-TCP37 and macro- B-TCP90-72, the wt% mixing ratio of 50 to 50 showed the highest compressive strength of 196 MPa. The crystal growing temperature and the time greatly affected the compressive strength of nano- and macro- β-TCP mixture block.

2. The crystal growth at 90°C of Bio-TCP powders prepared at 37°C was investigated with time. The compressive strength increased with hours until 72 h, but after then the increase of growth time didn't affect the increase of mechanical strength. It requires the understanding of crystal growth mechanism of Bio-TCP with time schedule.

Acknowledgements

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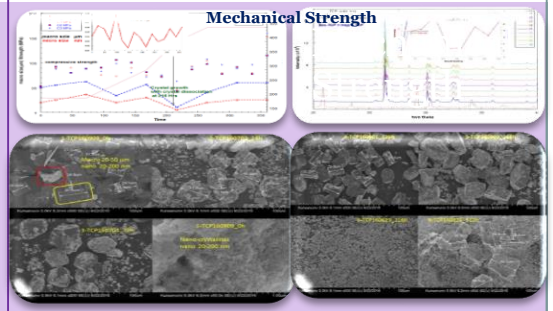
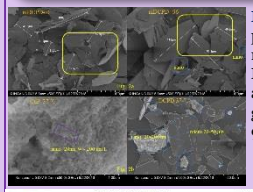
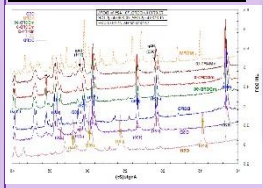
Mechanical Strength

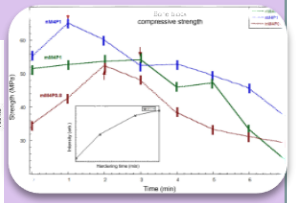




Microstructures of the precursor powders for the cement blocks: (a) mDCPD-0, (b) mDCPD-96. Microstructures of CaP, precipitated at pH5.0 at 37°C, and the crystal-grown macro-crystalline samples at 90°C show enhanced grain growth.



XRD patterns for mDCPD powders, cement blocks, and precursor powders: (a) For CSH, MCPM, m-DCPD-96, m-DCPD-0, nM4P1-to cement block, CSH, and DCPD.



Compressive strength of the bone cement blocks with hardening time and the amount of PAA solution. The data bar shows the measured values for five samples. The inner graph shows the (211) XRD intensity, indicating HAp.