Preparation of Porous Calcium Phosphate Cement from α-TCP Balls

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Introduction: Calcium phosphate cements (CPC) have been used in clinics since they set to form calcium phosphates, i.e., hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$) or dicalcium phosphate dihydrate (DCPD: $CaHPO_4{\cdot}2H_2O$) at the bone defect. However, current set CPCs do not have interconnected porous structure suitable for tissue ingrowth and cell penetration. Therefore, many attempts have been made to introduce porous structure for CPC such as addition of bioresorbable materials or porogen. Unfortunately, methods to fabricate ideal interconnected porous structure have not been reported up to date. On the other hand, Karashima et. al. fabricated interconnected hydroxyapatite block with molding ability by setting reaction of α-tricalcium phosphate (α-TCP: $Ca_3(PO_4)_2$) granules with distilled water at 200°C for 24 hours. However, he failed to form interconnected HAP structure at 37°C. Mirtchi et al. reported that β-TCP could be converted to DCPD rapidly. Based on the ideas of Karashima and Mitchi, reaction of α-TCP with monocalcium phosphate monohydrate (MCPM: $Ca(H_2PO_4)_2{\cdot}H_2O$) was investigated to evaluate the feasibility of porous CPC.

Methods: The α-TCP spherical balls with 1.3mm in diameter were exposed to MCPM-H_3PO_4 (0.1 mol·L^{-1} H_3PO_4 solution containing 0.2 mol·L^{-1} MCPM) solution for 1 to 10 min at 37°C. Surface morphology at the interface between two α-TCP balls before and after reaction with MCPM-H_3PO_4 solution were observed using SEM and μ-CT. Composition of α-TCP balls before and after the reaction with MCPM-H_3PO_4 solution were evaluated by XRD. Adhesive strength of the set interconnected porous CPC was evaluated by measuring tensile strength of set 2-ball connection specimens using universal testing machine with the cross-head speed of 0.5 mm/minute. The average pore size of the set interconnected porous CPC was observed using μ-CT.

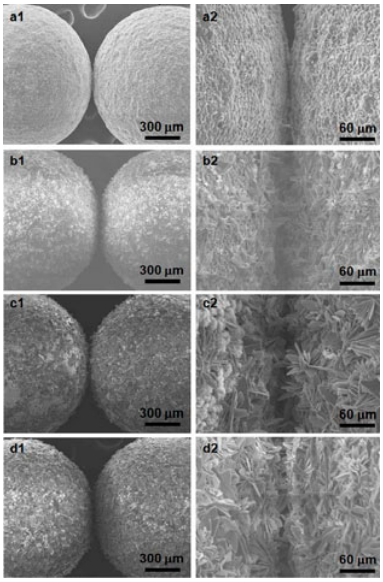

Fig. 1 SEM photographs at the α-TCP spherical balls interface when exposed to MCPM-H_3PO_4 solution at 37°C before (a1, a2) and after the reaction; (b1, b2) 1 min; (c1, c2) 5 min and (d1, d2) 10 min.

Results and discussion: When α-TCP balls were exposed to MCPM-H_3PO_4, α-TCP balls were found to set with time. Fig 1 summarizes the SEM images of α-TCP ball before and after treated with MCPM-H_3PO_4 solution at 37°C for 1, 5 and 10 min. Before exposure to the solution, α-TCP balls show typical smooth surface (Figs a1, a2). The new crystals were observed partially on the α-TCP balls when treated for 1 min (Figs b1, b2) whereas whole surface was covered with the new crystals when α-TCP balls were treated for 5 min (Figs c1, c2) or 10 min (Figs d1, d2). Newly formed plate-like crystals were interlocked to each other, which made the balls connected.

Thin-film XRD patterns of α-TCP balls indicated that the peaks attributed to α-TCP decreased and the peaks attributed to DCPD increased with increasing reaction time. The XRD analysis and SEM observation revealed that DCPD crystals were formed on the surface of α-TCP balls and α-TCP balls set to form fully interconnected porous calcium phosphate block when exposed to MCPM-H_3PO_4 solution.

The tensile strength between two α-TCP balls after 5 and 10 min were 3.2±0.9 and 4.8±0.3mN, respectively.

Fig 2 summaries the μ-CT images of set α-TCP balls when they were exposed to MCPM-H_3PO4 solution at 37°C in a mold (6 mm in diameter and 6 mm in height) for 10 minutes. The average pore size was calculated as approximately 317 ± 170 μm. And the porosity of the set CPC was approximately 50%.

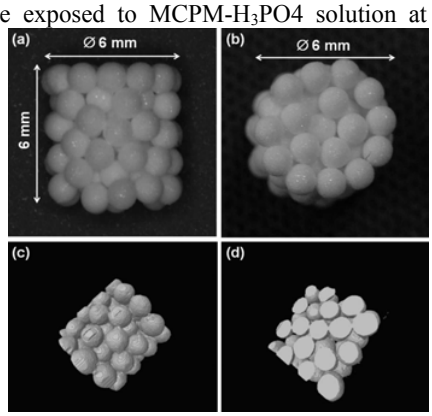

Fig. 2 Photographs (a, b) and μ-CT scan (c, d) of set interconnected porous CPC fabricated from α-TCP balls at 37°C.

Conclusions:
The α-TCP balls were found to set and formed interconnected porous structure when exposed to MCPM-H_3PO_4 (0.1 mol·L^{-1} H_3PO_4 solution for 10min at 37°C. This method may be useful for the reconstruction of bone defect as well as the scaffold for tissue engineering.