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Textured and hierarchically structured calcium phosphate ceramic blocks through hydrothermal treatment



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ABSTRACT

Synthetic calcium phosphate bone graft substitutes are widely recognized for their biocompatibility and resorption characteristics in the treatment of large bone defects. However, due to their inherent brittleness, applications in load-bearing situations always require reinforcement by additional metallic implants. Improved mechanical stability would eliminate the need for non-resorbable metallic implants. In this context a new approach to obtain calcium phosphate scaffolds with improved mechanical stability by texturing the material in specific crystal orientations was evaluated. Texture and reduction of crystal size was achieved by recrystallizing α -TCP blocks into calcium deficient hydroxyapatite (CDHA) under hydrothermal conditions. SEM and XRD analysis revealed the formation of fine CDHA needles (diameter \approx 0.1–0.5 μ m), aligned over several hundreds of micrometers. The obtained microstructures were remarkably similar to the microstructures of the prismatic layer of mollusk shells or enamel, also showing organization at 5 hierarchical structure levels. Brazilian disc tests were used to determine the diametral tensile strength, σ_{dts} , and the work-of-fracture, WOF, of the textured materials. Hydrothermal incubation significantly increased σ_{dts} and WOF of the ceramic blocks as compared to sintered blocks. These improvements were attributed to the fine and entangled crystal structure obtained after incubation, which reduces the size of strength-determining critical defects and also leads to tortuous crack propagation. Rupture surfaces revealed intergranular tortuous crack paths, which dissipate much more energy than transgranular cracks as observed in the sintered samples. Hence, the refined and textured microstructure achieved through the proposed processing route is an effective way to improve the strength and particularly the toughness of calcium phosphate-based ceramics.

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1. Introduction

Calcium phosphate (CaP) ceramics are widely used as bone graft substitute materials, the majority of commercial porous scaffolds being composed of β -tricalcium phosphate (β -TCP), hydroxyapatite (HA) or a blend of both phases (biphase). Many CaP ceramics combine high biocompatibility, adequate resorption rate and porosity for nutrient supply, vascularization, cell proliferation, and tissue infiltration [1,2]. While some phases are soluble at

physiological pH and dissolve spontaneously in-vivo, others are insoluble and can only be actively resorbed by bone cells [3]. However, ceramics CaP scaffolds are very brittle with a fracture toughness well below 1 MPa·m^{1/2}. In comparison, cortical bone has a true fracture toughness over 20 MPa·m^{1/2} [4]. These properties limit the use of CaP materials to indications in which the implant is not subjected to mechanical loading. Cyclic dynamic loading would lead to cracking and displacement of the surrounding bone fragments would delay or inhibit bone formation and thus impair successful healing of the defect. All CaP scaffolds commercially available can therefore only be applied in situations where either intact bone or additional metal implants protect the ceramic bone void filler from mechanical stress. The availability of novel load-

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bearing resorbable scaffolds would eliminate the need for additional reinforcement and widen the scope of indications. Such a scaffold should be strong enough to support normal loading applied on the bone, its elastic modulus should be similar to the one of bone to avoid stress shielding, and high toughness would be necessary to prevent catastrophic failure.

Combination of high strength and toughness is rare in engineered materials because these properties are antagonistic [5]; single-phase materials are normally either strong and brittle, or ductile and weak. Obtaining a combination with biodegradable materials is even more challenging because biodegradability generally implies weak chemical bonds, which are in consequence rarely mechanically strong. Moreover, biocompatibility and biodegradability strongly limit the choice of materials. Ceramics are strong, but highly brittle. Metals can be adequate in terms of toughness, but they lead to stress shielding and are, with the exception of a few alloys [6–8], non-degradable. Generally, polymers do not reach the required strength and their degradation products can be acidic and/or provoke an inflammatory response, both adversely affecting the healing process [9].

Since no single-phase material seems to fulfill all requirements imposed by a load-bearing, resorbable bone graft substitute, the focus of researchers has shifted towards composite materials, which combine properties of materials of different nature. Reinforcement of degradable polymers by ceramic particles has already been extensively investigated [10–15]. However, in all of these studies, the organic fraction remained large which might cause the above-mentioned biological complications [9]. In addition, mechanical properties of such artificial composites are by far inferior to comparable natural materials [16], which is mainly attributed to a poor adhesion between organic and inorganic phases [17] and a lack of controlled architecture of the reinforcing particles within the matrix. To achieve the ideal mechanical and biological properties for a load-bearing, resorbable bone graft substitute, the materials should mainly consist of ceramic, should be toughened with only minor amounts of a ductile polymer and the ceramic-polymer adhesion should be good. To approach this ideal material incorporating only thin interlayers of a tough secondary phase [18], bio-inspired structures featuring a highly organized architecture of the ceramic particles are necessary. A low polymer content and a large contact area between polymer and ceramic particles can only be obtained with a very well organized architecture. In fact, mechanical properties approaching those of natural composites like bone or nacre have been achieved with very well-controlled alignment of ceramic particles [4,19,20]. However, despite the highly ordered particle shape and arrangement, the polymer fraction was still much higher than the content found in nacre or even bone, and the ceramic particles were not degradable.

Toughening ceramic based materials by incorporating low fraction of polymer phases (“intrinsic toughening” [18,21]) remains a very challenging approach with current engineering methods and the reported improvements are limited. Considering the difficulty to achieve intrinsic toughening where a ceramic is arranged in a very well ordered manner and glued together by the polymer, a first approach might be to try to produce highly ordered polymer-free architectures, where the toughness is mainly improved due to structural changes (defined as “extrinsic toughening” mechanisms in Refs. [21,18]).

Indeed, strength and toughness of structural ceramics are usually improved by microstructural developments like (a) grain size refinement [22] – which already proved being efficient in bioceramics, in particular in HA [23], (b) transformation-toughening [24–27], (c) incorporation of second phase particles [28,29] or (d) creation of tortuous structures [18,30]. Tortuous structures are constituted of anisotropic particles, assembled in a staggered

fashion to promote crack deflection. Its good potential was demonstrated by the recently obtained “Nacre-like Alumina” [30]. However, to the best of our knowledge, this has not been investigated yet with bioceramics. A combination of grain size refinement and design of tortuous microstructures is a promising strategy to increase the work-of-fracture (WOF) of resorbable CaP ceramics by simultaneously decreasing the size of critical defects and inducing crack deflection.

CaP ceramic scaffolds are commonly shaped by pressing of a dry powder or drying/setting of a slurry, followed by a heat treatment (sintering) to consolidate the structure. With such methods, the final grain size strongly depends on the particle size of the initial powder, hence requiring nano-powders followed by quick sintering or two-step sintering processes in order to obtain a small final grain size [31]. Hydrothermal synthesis has already shown the potential of forming fine CaP (particularly HA) particles [32–34]. However, assembly and consolidation of these particles to form fine structured blocks, either by cement reaction or sintering, leads to grain growth and finally poor improvements of mechanical properties compared to larger microstructures [23,35,36]. Another approach, explored in particular by Ioku's group, consist in first compacting an α -TCP powder, with or without other additives, followed by submitting the pressed forms to hydrothermal treatment [37,38]. The obtained CDHA blocks were made of entangled rod-shape particles and were even more biodegradable and induced more bone formation than stoichiometric HA samples obtained by conventional sintering process [39]. However, the rod-shape crystal assembly was quite loose and disordered.

To densify and align the structures obtained in previous hydrothermal studies, our approach in this work was to first solidify and densify CaP blocks by sintering, and then globally refine the microstructure of these monoliths by *in situ* recrystallization under hydrothermal conditions. By obtaining a dense assembly of sub-micrometric elongated particles in complex architectures, we aimed at improving the strength and toughness of CaP scaffolds using a straightforward processing route.

2. Materials and methods

2.1. Sample preparation

CaP blocks were prepared in a process of 5 steps:

- (i) **Powder synthesis:** α -TCP powder was prepared in-house by ball-milling for 6 h at 60 rpm a sintered (4 h at 1350 °C, followed by air quenching) mixture of calcium carbonate (CaCO₃, art. no 102066, Merck, Darmstadt, Germany) and calcium hydrogen phosphate (CaHPO₄, 99.95%, art. no 1548, GFS Chemicals, Columbus OH, USA) such as to obtain an initial calcium to phosphate molar ratio of 1.47.
- (ii) **Cement paste preparation:** The liquid phase was a 0.1 M citric acid solution (C₆H₈O₇·H₂O, art. no 100243, Merck, Darmstadt, Germany). The powder was added to the liquid in a 0.6:1 liquid: powder weight ratio and immediately mixed (stirrer VOS 14, art. no. 441-0026P, VWR, Dublin, Ireland) at 2000 RPM for 20 s and then poured into cylindrical Teflon molds (8 mm diameter, 8 mm height).
- (iii) **Setting:** Setting took place in 100% RH at 60 °C for 72 h.
- (iv) **Sintering:** After unmolding, the samples were sintered at 1500 °C for 8 h with a heating rate of 5 °C/min and cooling at –10 °C/min in a muffle furnace (LHT 02/16, Nabertherm, Germany).
- (v) **Hydrothermal incubation:** Hydrothermal incubation was conducted in steel autoclaves (Acid Digestion Vessel, model 4744, Parr Instruments, Moline IL, USA) with homemade

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