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ScienceDirect

Ceramics International 42 (2016) 2542–2549

CERAMICS INTERNATIONAL

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Hydroxyapatite synthesis and the benefits of its blend with calcium aluminate cement

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Received 13 September 2015; received in revised form 11 October 2015; accepted 12 October 2015
Available online 21 October 2015

Abstract

Hydroxyapatite (HA) is a calcium phosphate and the main mineral component of bones and teeth. However, its use as a biomaterial is limited due to the poor mechanical strength presented by this compound. Various techniques have been investigated for HA production, considering its good biocompatibility and chemical stability in the implanted area. In this paper, two methods for hydroxyapatite synthesis (precipitation and mechanosynthesis) were evaluated and compared, in order to select the most viable HA processing route before adding this component to calcium aluminate cement (CAC). The blend of HA + CAC aimed to attain a biomaterial presenting the biological activity of calcium phosphate and the optimized green mechanical strength derived from the selected cement. The obtained HA powders were characterized via XRD, SEM and particle size distribution measurements. The mechanical strength, apparent porosity and pore size distribution of the prepared HA + CAC samples were analyzed. Both studied routes induced hydroxyapatite generation, but the mechanosynthesis was the most suitable one due to the reduced reaction time required. The main advantage of adding HA powders to CAC was associated with the production of a compound with higher mechanical strength, when compared to the original materials. Besides that, the HA favored the bioactivity of the prepared compositions, as observed by the Ca^{2+} ions release and pH increase of the analyzed aqueous medium, leading to apatite precipitation on the HA + CAC samples' surface. This latter transformation also resulted in the decrease of both, apparent porosity and pores diameter, of the samples.

Keywords: Precipitation; Mechanosynthesis; Hydroxyapatite; Calcium aluminate cement

1. Introduction

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HA] is one of the most interesting bioceramics due to its chemical and crystallographic similarities with inorganic components found in hard tissues (bones and teeth) [1]. Thus, this material (dense or powdered) is applied to metallic implants, prostheses for bones and teeth replacement, and to produce biocomposites [2]. Furthermore, HA presents high biocompatibility, preventing bone rejection and inducing osseointegration and osteoconduction [3].

Due to its important properties, the production of this material has been investigated by many research groups, aiming to attain a compound without other additional phases in the Ca–P system [4–6]. Most of the developed methods for hydroxyapatite generation can be classified according to their processing conditions: (i) humid (precipitation, hydrothermal technique and hydrolysis of calcium phosphates) or (ii) solid state reactions (mechanosynthesis) [7,8].

Precipitation processes are usually based on phosphate groups' addition to suspensions containing calcium ions, considering different initial reagents. The neutralization reaction (with orthophosphoric acid and calcium hydroxide) presents the greatest potential to be applied for hydroxyapatite production, as water will be the only reaction by-product [5].

Calcium phosphate synthesis via precipitation methods is a simple and low cost route. Nevertheless, these procedures result in the formation of non-stoichiometric products and a mixture of phases (which is related to the presence of vacancies and ionic

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http://dx.doi.org/10.1016/j.ceramint.2015.10.056
0272-8842/

substitutions in the resultant networks), such as carbonates, hydrogen-phosphates, potassium, sodium, nitrate and chloride [4,5]. Moreover, different parameters should be taken into account (i.e., pH, temperature, reactants molar concentration, addition rate of the reactants, mixing time, ageing time and calcination temperature). Reaction kinetics and ageing time are critical variables for the purity and crystallographic features of the resulting HA [5].

On the other hand, the mechanosynthesis technique is widely used for producing various commercial products. In this process, solid state reactions are induced by the impact of the powder material with the ceramic grinding media contained in high energy mills. This procedure has been used for decades to prepare metastable crystalline and amorphous phases, as well as nanostructure materials, which cannot be attained using conventional techniques due to the short reaction time, low temperature required for the development of the solid state reaction and likelihood of generating materials with special properties [9].

The mechanosynthesis principle is related to the energy provided by the impact of the grinding media on the powder and mill wall. The added powder is subjected to intense mechanical deformation which leads to the local temperature increase, resulting in the generation of crystalline flaws. Therefore, besides the balance between coalescence and fracture events among the particles, structural changes are also observed [10].

Various reagents can be combined for the hydroxyapatite production via mechanosynthesis [4,6]. Due to the redox interactions among the raw materials, this process should lead to water formation, which will act improving the contact of the attained components and favoring the generation of the final product under lower mechanical loads [11]. It has been reported that this technique induces: (i) a good Ca/P molar ratio control of HA powders, allowing the synthesis of hydroxyapatite with calcium deficiency in an effective and reliable manner; (ii) conventional and carbonated HA synthesis; and (iii) the production of apatites with different ionic substitutions, which are alternative compounds to enhance the biological performance of these materials [10,12].

However, the investigation of different routes for HA production is an important issue to select a less costly process for the effective application of this material in odontology and orthopedic areas. Nowadays, the use of HA in both of these fields is limited due to its poor mechanical resistance, mainly under tensile and compression loads [13]. Thus, the blend of HA with other materials (such as calcium aluminate cement, CAC) is an attractive method, resulting in a mixture presenting the biological activity of hydroxyapatite and the green mechanical strength of cement.

Ca-aluminate as a biomaterial has been evaluated for over two decades with regard to general physical, mechanical and biocompatible properties. The Ca-aluminate based materials exhibit, due to their unique curing/hardening characteristics and related microstructure, a great potential in the biomaterial field [14]. An overview of the use of Ca-aluminate as a biomaterial in odontology and orthopedics was already published [14]. Aluminate cements are used as dental restorative materials [15] and in orthopedics for repairing bone flaws based on their composition and thermal expansion coeficient, which are very similar to the ones of bones and teeth [16,17].

CAC has been applied as a root-end filling material, as it overcomes some drawbacks of the commercial product (mineral trioxide aggregate, MTA) used for such a purpose, for instance, long setting time, high porosity level and low mechanical strength. Calcium aluminate cement also presents some desirable features as a biomaterial: (i) improved flowability and setting time [18,19], (ii) biocompatibility when tested in subcutaneous tissues of rats without inflamatory reactions [20,21], (iii) ability to induce hydroxyapatite deposition in simulated body fluid solutions [22], (iv) a barrier preventing bacterial microleakage [23], and (v) suitable compatibility when considering its mechanical properties and radiopacity in the presence of 15 wt% ZnO:10 wt% Bi_2O_3 [24].

In this paper, compositions comprising HA+CAC were evaluated in order to develop materials with enhanced mechanical strength and bioactivity. HA powders were synthesized via precipitation and mechanosynthesis techniques.

2. Materials and techniques

The following materials were used in this work: (1) CAC, derived from a dry mixture of calcium aluminate cement (Kerneos Aluminates, France) with a polyglycol-based dispersant (Basf, Germany, 0.6 wt%) and a plasticizer $CaCl_2 \cdot 2H_2O$ (Labsynth, Brazil, 2.8 wt%) in a ball mill for 1 h, (2) HAC (commercial hydroxyapatite, Sigma-Aldrich 21223), (3) HAP (hydroxyapatite obtained via precipitation), and (4) HAM (hydroxyapatite produced via mechanosynthesis). The chemical analysis of the cement used showed that the nature and content of heavy metals present were acceptable for endodontic purposes [19]. Standard ISO 9917-1 states that the arsenic and lead contents in dental water-based cements should be less than 2 and 100 ppm, respectively [25].

The precipitation process [5] of hydroxyapatite was carried out using phosphoric acid (H_3PO_4, Synth, Brazil) and calcium hydroxide [$Ca(OH)_2$, Synth, Brazil] as reactants, in order to induce the acid–base reaction as follows:

$$6H_3PO_{4(aq)} + 10Ca(OH)_{2(aq)} \rightarrow Ca_{10}(PO_4)_6(OH)_{2(s)} + 18H_2O_{(l)} \quad (1)$$

Aqueous solutions of phosphoric acid (2 mol/L) and calcium hydroxide (2 mol/L) were prepared and 5 drops of ammonium polyacrylate (Miracema-Nuodex, Brazil) were added to the $Ca(OH)_2$ for its dispersion. The calcium hydroxide suspension (500 ml) was then placed in a three-neck round bottom flask and kept at 90 °C under constant stirring (±200 rpm), with the help of a glycerin bath, mechanical mixer and a condenser. After that, 300 ml of H_3PO_4 solution was incorporated into the mixture with a 2 ml/min rate. During the acid addition process and the 24 h ageing step, the temperature and stirring conditions of the system were kept constant. The pH of the