



Smart designing of new hybrid materials based on brushite-alginate and monetite-alginate microspheres: Bio-inspired for sequential nucleation and growth



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ABSTRACT

In this report new hybrid materials based on brushite-alginate and monetite-alginate were prepared by self-assembling alginate chains and phosphate source ions via a gelation process with calcium ions. The alginate served as nanoreactor for nucleation and growth of brushite or/and monetite due to its gelling and swelling properties. The alginate gel framework, the crystalline phase and morphology of formed hybrid biomaterials were shown to be strongly dependent upon the concentration of the phosphate precursors. These materials were characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX).

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1. Introduction

Hybrid materials offer the opportunity to combine the desirable properties of an organic matrix with those of inorganic solids [1–3]. This material category has a diverse spectrum of applications ranging from pharmaceutical to wastewater treatment [4–6]. On the other hand, the calcium phosphate materials contain a multitude of crystalline phases and have attracted considerable interest both in the scientific community and industry due to their physico-chemical properties and their value in many fields of technology [7–17]. However, the combination of calcium phosphates and biopolymer can confer favorable mechanical properties, including strength due to the inorganic phase, toughness and plasticity due to the biopolymer phase. Biopolymers differ from each other in chemical composition, molecular weight, polydispersity, crystallinity, hydrophobicity, solubility, chain length, and thermal transitions [18]. Different biopolymer-calcium orthophosphate composites have been successfully obtained with alginate [19], chitosan [20,21], cellulose [22] and starch [23,24]. Alginate is a natural polysaccharide extracted from the marine brown algae and it is composed of

two uronic acid monomers derived from mannose: the acid β -L-guluronic (G) and the acid α -D-mannuronic (M) are linked by glycoside bonds β -(1–4) and α -(1–4) (see Fig. S1 in Supporting information) [25,26]. Alginate gelation occurs when multivalent ions take their place between the G blocks of guluronic monomers, forming junctions of electrostatic nature, and the bond strength varies depending on the type of cation [27,28]. Most of the published works on hybrid composite alginate–calcium phosphate are based on preparation, nucleation and growth of apatite particles in a matrix of alginate biopolymer. In this context, Rajkumar et al. synthesized a nano-hydroxyapatite alginate nanocomposite with different weight percentages of sodium alginate; its biological and mechanical properties were studied [29]. Zhang et al. prepared a series of new nanocomposite beads of sodium alginate/hydroxyapatite, in order to find a new way to slow drug release, but unfortunately they did not show the XRD spectra which can confirm if that it was really the hydroxyapatite or another phase [30].

Brushite (dicalcium phosphate dihydrate (DCPD)) and monetite (dicalcium phosphate (DCP)) cements have raised considerable interest in the last decade, because they are metastable under physiological conditions and can be resorbed more quickly than hydroxyapatite cements [31]. Several authors have suggested that it's a precursor of bone mineralization, including biological apatites [32,33]. The brushite has been

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widely used in the reconstruction materials, dental cements, as well as in formulation chemistry [34,35]. These phosphates are usually synthesized in an aqueous medium by double decomposition of a calcium salt and a phosphate salt or by neutralization of phosphoric acid in lime [36,37]. Other routes have been also explored to synthesis these calcium phosphates such as sol-gel [38], solid state [39], chemical precipitation [40], hydrothermal [41], hard templating [42], flame-spray route [43], dual irradiation of the microwave and ultrasound [44], and physiological conditions [45]. More recently, Gomez-Morales et al. have controlled the precipitation of calcium phosphate such as brushite by using vapor diffusion method in microdroplets and amino acids like organic additives [46].

This current study demonstrates for the first time that the synthesis of hybrid material phosphate–biopolymer can be achieved using gelation of alginate mixed with a phosphate source *via* complexation of calcium ions. The synthetic protocol reported here takes advantage of the controlled gelation of the mixture of brushite or monetite structure at room temperature.

2. Experimental section

2.1. Chemical reagents

$(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were purchased from Aldrich and used as a precursor of the HPO_4^{2-} ligand and for gelation, respectively. Other phosphate sources are also tested namely: sodium phosphate dibasic (Na_2HPO_4) and ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$). Sodium alginate was purchased from Aldrich and used as supplied. Deionized water was used in all experiments.

2.2. Synthesis of hybrid materials

Hydrogel material was achieved *via* complexation of alginate/phosphate by calcium ion (Fig. S2). Aqueous solutions of phosphorus precursor were prepared by dissolving different amounts of $(\text{NH}_4)_2\text{HPO}_4$: 0.1, 0.3, 0.5, and 1 M into 100 mL of distilled water, and then sodium alginate was added to diammonium phosphate solution with a concentration of 1%. The mixture was stirred for 1 h at room temperature. This gel was added dropwise using a syringe with a 0.8 mm diameter needle at room temperature to the stirred $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution (0.25 M). The formed beads immediately are abandoned overnight to ensure effective diffusion of calcium ions, and thereafter the homogeneity of the system and the growth of hybrid materials.

After that, the beads were filtered with a 100 mesh screen, and washed three times with distilled water to remove the Ca^{2+} excess and impurities on the beads surface. In the end, the beads were dried at room temperature for 24 h before various characterizations. For different $(\text{NH}_4)_2\text{HPO}_4$ concentration (0.1, 0.3, 0.5 and 1 M), the dried hybrid materials will be henceforth identified as Phos-Alg_1 (phosphate–alginate), Phos-Alg_2, Phos-Alg_3, and Phos-Alg_4 respectively.

2.3. Thermal and structural characterization techniques

TGA were conducted under air in a TA Instrument Q500 apparatus with a 10 °C/min ramp between 25 and 1000 °C. X-ray diffraction patterns of the samples were obtained at room temperature on a Bruker AXS D-8 diffractometer using $\text{Cu-K}\alpha$ radiation in Bragg–Brentano geometry (θ – 2θ). Fourier transform infrared spectra of samples in KBr pellets were measured on a Bruker Vector 22 spectrometer. Scanning electron microscopy pictures were recorded on a FEI Quanta 200 microscope after carbon metallization.

3. Results and discussion

In order to conduct this study, we investigated several parameters, especially the concentration of phosphate precursor and the drying temperature, that influence the nucleation and growth of the inorganic matrix and obviously the hybrid material by afterwards. Thus, the concentration of the precursor of the phosphate plays an important role in the appearance of the prepared hybrid xerogels. Fig. 1 shows pictures taken by a digital camera and SEM at low magnification of the as synthesized hybrid xerogel microspheres (Phos-Alg_1 and Phos-Alg_2), micro-lentils (Phos-Alg_3) and granulated powder (Phos-Alg_4). This change in the external shape can be explained by the increase of the concentration of HPO_4^{2-} ligand which occupies the space in the alginate chains and subsequently distorts the spherical shape of the droplet.

The XRD patterns have been used to investigate the phases in our hybrid xerogels at different phosphate concentrations. Fig. 2 shows diagrams of the samples such as Phos-Alg_1, Phos-Alg_2, Phos-Alg_3 and Phos-Alg_4 corresponding to $(\text{NH}_4)_2\text{HPO}_4$ concentrations: 0.1 M, 0.3 M, 0.5 M and 1 M respectively. The Phos-Alg_1 is poorly crystalline maybe because the amount of phosphates is poor, but has a pure brushite phase or dicalcium phosphate dihydrate with monoclinic crystal structure (JCPDS 4-013-3344). Brushite crystallized in the monoclinic system (space group *1a*) with the crystallographic parameters $a = 6.239 \text{ \AA}$, $b = 15.180 \text{ \AA}$, $c = 5.812 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and

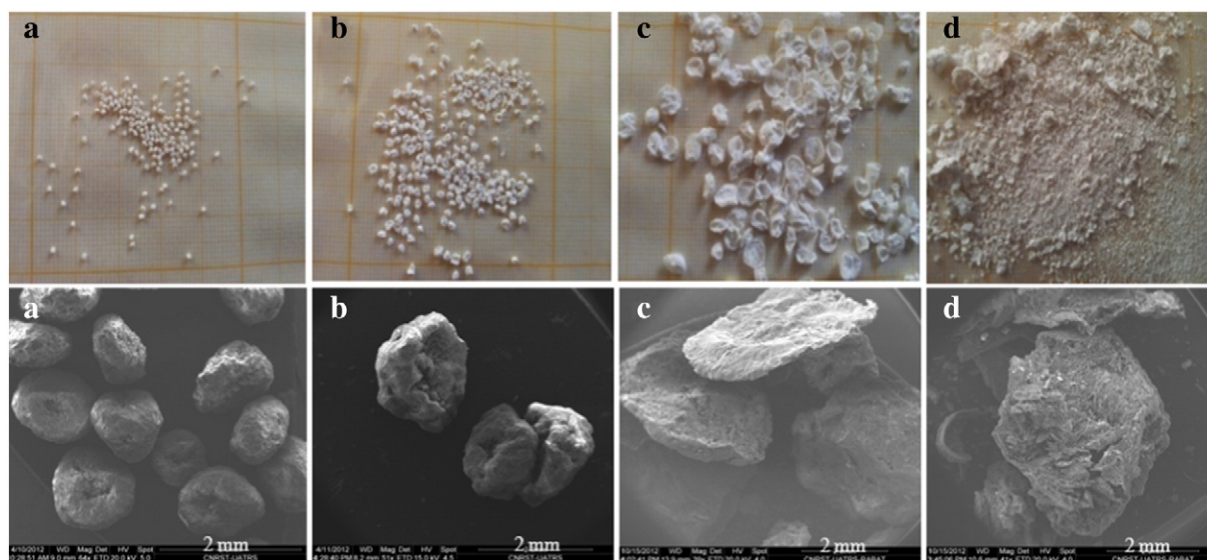


Fig. 1. Digital photographs and low-magnification SEM images of hybrid beads Phos-Alg_1 (a), Phos-Alg_2 (b), Phos-Alg_3 (c) and Phos-Alg_4 (d).

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