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Barium hydrogen phosphate/gelatin composites versus gelatin-free barium hydrogen phosphate: Synthesis and characterization of properties

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ABSTRACT

Recently, attention has been spent on crystal growth of phosphate compounds in gels for studying the mechanism of in vitro crystallization processes.

Here, we present a gel-based approach for the synthesis of barium hydrogen phosphate (BHP) crystals using single and double diffusion techniques in gelatin. The composite crystals were compared with analytical grade BHP powder, single and polycrystalline BHP materials using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), scanning pyroelectric microscopy (SPEM), optical microscopy (OM), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). FTIR spectra showed surface adsorption of gelatin molecules by using BHP stacked sheets due to CH_2 stretching, CH_2 bending and amide I vibrations are found in a gelatin content of about 2% determined by dissolution. SEM shows various crystal morphologies of the BHP/gelatin composites forming bundled micro-flakes to irregular bundled needles and spheres different from gel-free crystals. The variety in morphology depends on the ion concentration, pH of gel as well as the method of crystal growth. SPEM investigation of BHP/gelatin aggregates revealed polar domains showing alteration of the polarization. Moreover, BHP/gelatin composite crystals showed a higher thermal stability in comparison with analytical grade BHP or/and BHP single crystals due to strong interactions between gelatin and BHP. The XRD diffraction analysis demonstrated that the single and double diffusion techniques in gelatin led to the formation of orthorhombic BHP. This study demonstrates that gelatin is a useful high molecular weight biomacromolecule for controlling the crystallization of a composite material by producing a variety of morphological forms.

1. Introduction

Gel systems are three dimensional networks to grow materials of low thermal solubility. Depending on the cross-linking density of gels, they can particularly provide nucleation sites for the formation of inorganic–organic composite crystals because of functional group to ion interactions. Hence, such a medium can thus control the crystallization of inorganic compounds through a network inducing new morphologies and textures which are not possible to be produced with other methods [1–3].

Barium hydrogen phosphate (BHP) consists of tetrahedral phosphate groups, linked by hydrogen bonds and Ba^{2+} ions. For this alkaline earth phosphate, ferroelectricity is anticipated to occur in the orthorhombic structure [4,5]. Former works on the synthesis of BHP were focused on a precipitation in water and crystallization in silica gel [5–8]. Nishino and Ishizawa demonstrated precipitation of BHP using a solid–liquid reaction of α-$Ca_3(PO_4)_2$ and $Ba(H_2PO_4)_2$ solutions [9]. Arora et al. also have shown that BHP features an electrical ionic conductivity that is between semiconductors and insulators [10–13].

It was found that the morphology of BHP can be influenced by changing the pH in the presence of poly(ethylene glycol) acrylate–copoly(methacrylic acid) (PEGA–PMAA) to form irregular hexagonal shapes to uniform spheres [14]. Moreover, barium borate glass particles can be converted to plate-like BHP at pH = 9 [15]. Metathetic synthesis of barium hydroxyapatite (Ba-HAp) in a reverse medium of micelles has shown a multiphasic mixture of BHP, Ba-HAp and $Ba(H_2PO_4)_2$ due to slow reactivity of barium ions [16]. An effort by Höppe et al. to study lithium doped BHP crystals grown in silica gel showed that lithium can improve the mechanical strength and shift the ferroelectric transition temperature of

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BHP [17]. More recently, Chen et al. introduced a novel method for the corrosion protection of magnesium alloys using $Ba(NO_3)_2$ and $NH_4H_2PO_4$ as precursors. A two-layer coating was generated revealed an under layer of mixed amorphous phosphates and a top layer of crystalline BHP [18]. In this work, gelatin was applied for gel growth because it displays a hydrophilic character as compared to others, due to several types of polar domains present in polypeptide chains. Therefore, the present work may thus contribute to the understanding of how different factors such as ion concentration, pH of a gel and the method of crystal growth affect the morphology and crystallization of BHP/gelatin composites.

2. Experimental

Synthesizing BHP was performed by dissolving a 10% pig skin gelatin (300 bloom, Sigma–Aldrich) in deionized water for the use of several single- and double-diffusion glass tubes. Table 1 recollects all experiments on crystallization. For single tube 1, 10 mL of the dissolved gelatin was slowly mixed with 7.5 cc of 0.5 M Na_2HPO_4 solution (Sigma–Aldrich) and stirred for 2 h at 50 °C. The pH of mixtures was set to 7.4. Tubes were filled with such a mixture and left at room temperature for 24 h until gelation had occurred. Then 7.5 cc of 0.5 M $BaCl_2$ solution was adjusted with 10 mM tris(hydroxymethyl)aminoethane (Trizma®base from Sigma–Aldrich) to maintain a pH of 7.4 and it was poured onto the gelatin. In single tubes 2–4, a lower molarity of Na_2HPO_4 solution (0.05 M) was used in comparison to tube 1. The pH of tubes was buffered to yield 5.5, 7.4 and 8.4 respectively, using 10 mM tris(hydroxymethyl)aminoethane.

In the case of the double diffusion technique, U-tubes (vertical section: 20 cm, horizontal section: 12 cm, diameter: 2 cm) were filled with buffered gelatin at pH 7.4. Buffered $BaCl_2$ and Na_2HPO_4 solutions were filled into both sides of the tubes separately. The diffusion took place at 25 °C for 14 days. Finally, BHP/gelatin composite crystals were washed several times with hot water to remove excess of gel. In order to produce BHP crystals to be compared with BHP/gelatin composites, two methods were utilized: (i) $BaCO_3$ was slowly added to 1 M H_3PO_4 solution until saturation was reached at room temperature. (ii) Polycrystalline BHP was obtained by slow addition of 7.5 cc of 0.5 M $BaCl_2$ solution buffered at pH 7.4–7.5 cc of 0.5 M Na_2HPO_4 solution at room temperature and stirred until precipitation appeared. All types of obtained BHP crystals were dried at 50 °C.

Chemical characterization of gelatin and BHP crystals was carried out using a Perkin Elmer Spectrum One FTIR spectrometer.

A surface morphology analysis of the BHP crystals was carried out by means of a Hitachi scanning electron microscope S-3000N. Samples were covered with an Au layer under vacuum conditions prior to the measurements.

The polar states of BHP and BHP/gelatin composite crystals were investigated by SPEM [19]. For this purpose, a sample was placed into a capacitor. A focused and modulated laser beam (λ = 650 nm, 25 mW of maximum) is locally heating up a sample. The added thermal energy causes a change in polarization inducing a discharge current measured by a lock-in technique. A scan across the sample yields a 2D map of the polarization distribution near the surface (penetration depth of the laser is in the range of a few microns).

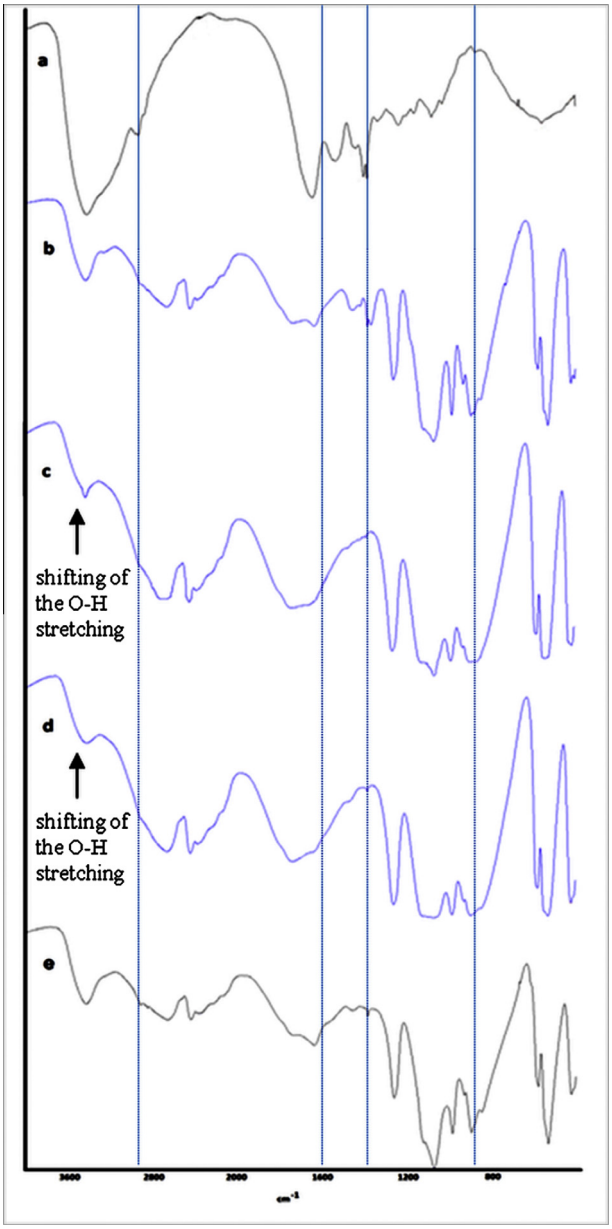

Fig. 1. The FTIR spectra of (a) gelatin, (b) analytical grade BHP (Sigma–Aldrich), (c) BHP single crystals, (d) BHP polycrystalline materials, and (e) BHP/gelatin composite crystals collected from tube 1.

The composite crystals were dissolved with 1% HCl at room temperature for measuring the amount of adsorbed gel. The uptake of gelatin into a composite was investigated using an optical microscope (Leica MZ7.5) from Leica Microsystems (Switzerland) Ltd. and a CCD camera.

Table 1
Set of experiments used in this study.

Sample tube	Method	Molar concentration of $BaCl_2$	Molar concentration of Na_2HPO_4	pH of gel
1	Single diffusion	0.5	0.5	7.4
2	Single diffusion	0.5	0.05	5.5
3	Single diffusion	0.5	0.05	7.4
4	Single diffusion	0.5	0.05	8.4
5	Double diffusion	0.5	0.5	7.4
6	Double diffusion	0.5	0.05	7.4