The morphology and thermal behavior of Calcium dihydrogen phosphate monohydrate (Ca(H₂PO₄)₂•H₂O) obtained by a rapid precipitation route at ambient temperature in different media

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Calcium dihydrogenphosphate monohydrate (Ca(H₂PO₄)₂•H₂O) was prepared by a rapid and simple precipitation method using CaCO₃ and H₃PO₄ at ambient temperature in aqueous, acetone-water and ethanol-water media systems. The obtained precipitates were characterized by thermoanalytical techniques (TG/DTG/DTA), scanning electron microscope (SEM), X-ray powder diffraction (XRD), and FTIR spectroscopy. The XRD results of the prepared Ca(H₂PO₄)₂•H₂O in aqueous and acetone-water systems show similar characteristics , which differ from those of ethanol-water system. The FTIR spectra the prepared Ca(H₂PO₄)₂•H₂O in three media systems show similar characteristics. Thermal behaviors and the morphologies of the obtained Ca(H₂PO₄)₂•H₂O in three different media systems exhibit the significant difference. The studied media agents are proposed to play an important role in the synthetic process of calcium phosphates in exhibiting different physical properties, which are important for specific applications.

Keywords: Calcium dihydrogenphosphate monohydrate, Different media agents, Rapid precipitation, Plate-like particles

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1. Introduction

Calcium phosphate compounds have been investigated extensively during the part 50 years. They are primarily used as bone substitutes in the biomedical industry due to their biocompatibility, low density, chemical stability, high wear resistance, and for calcium phosphates, mainly for their compositional similarity with the mineral phase of bone [1-3]. Today, calcium phosphates are the materials of choice in both dentistry and medicine. They have been used in the field of biomedical engineering owing to the range of properties that they offer, from tricalcium phosphates being resorbable to hydroxyapatite being bioactive; they are undeniably the current range for clinical usage [4–6]. Calcium phosphates being light in weight, chemically stable and compositionally similar to the mineral phase of the bone are preferred as bone graft materials in hard tissue engineering. They are composed of ions commonly found in physiological environment, which make them highly biocompatible. In addition, these bioceramics are also resistant to microbial attack, pH changes and solvent conditions. They exist in different forms and phases depending on temperature, partial pressure of water and the presence of impurities [7, 8]. HAp, β -TCP, α -TCP, biphasic calcium phosphate (BCP) [9], monocalcium phosphate monohydrate (MCPM) and unsintered apatite (AP) are different forms of commercially available calcium phosphates currently used in the biomedical industry. Different phases are used in different applications depending upon whether a resorbable or bioactive material is desired [10]. In additional application, calcium phosphates are used as

microadditivels to fertilizers [11]. An important step in the production of phosphate fertilizers, such as calcium polyphosphates, is the acid thermal treatment of the phosphate raw materials, which is accompanied by condensation of the intermediate acidic salts, mainly $Ca(H_2PO_4)_2 \cdot H_2O$.

The previous preparation methods of these calcium phosphate ceramics include precipitation method [12], hydrothermal reaction [13], template method [14], sol-gel method [15], microemulsion synthesis [16], micelle synthesis [17], mechanochemical synthesis [18], combustion method [19] and microwave irradiation [20]. Conventional precipitation method has some drawbacks in precisely controlling the stoichiometry, crystallinity, morphology of products, which was improved via introducing surfactants as templates [14], ultrasound irradiation [20] and microwave irradiation [21], microemulsion [14] and micelle [16] as the reaction vessels. However, the successful application of the required material depends on the morphology and purity. The preparation methods need to obtain well-defined chemical microstructure depend mainly on the conditions of synthesis [22]. The preparation of some transition metal phosphates by different synthesis conditions and medium agents had been reported, which give rise to final metal phosphates with cost-effective method [23, 24]. However, the disadvantages of most general preparation methods are inhomogeneity, lack of stoichiometry control and larger particle size. These are avoided when the material is synthesized using a solution-based method. The main advantage is the molecular level mixing which facilitates the formation of polycrystalline homogeneous particles with improved properties.

Herein, the present paper reports the synthesis of $Ca(H_2PO_4)_2 \cdot H_2O$ by a simple precipitation from calcium carbonate and phosphoric acid at ambient temperature in three different media agents (aqueous, acetone-water and ethanol-water) with the short time consuming(20 min). The present of acetone and ethanol reduced hot reaction and prevented the evolved CO_2 gas in the precipitation process. These methods reported a simple, rapid and cost-effective routes to the synthesize $Ca(H_2PO_4)_2 \cdot H_2O$, which exhibit the significant difference of physical properties in the different media agents. The prepared sample and its dehydration product were characterized by TG/DTA, XRD, SEM, and FTIR techniques.

2. Experimental

The $Ca(H_2PO_4)_2 \cdot H_2O$ compounds were prepared by solution precipitation methods using CaCO₃ (99.99 %, Merck) and phosphoric acid (86.4 %w/w H₃PO₄, Merck) as starting materials. In a typical procedure, 81.02 mL of 86.4 %w/w H₃PO₄ was diluted in 18.98 mL of de-ionised water and then 2 mL of this solution was added to 1.0080 g of calcium carbonate, previously added in no media agent, 10 mL of acetone (99.9% Carlo Erba) and 10 mL of ethanol (99.9% Carlo Erba). These methods were referred to aqueous, acetone-water and ethanol-water systems, respectively. The resulting solution was mechanical stirred at ambient temperature and the precipitates were obtained within about 10 min. The white solids of Ca(H₂PO₄)₂•H₂O products were filtered by suction pump, washed with media agent until free from phosphate ion and dried in air. The prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in acetone-water and ethanol-water solutions had no CO_2 gas evolved, which differ from this prepared compound in aqueous solution. Thermal properties of Ca(H₂PO₄)₂•H₂O were investigated on a TG-DTA Pyris Diamond Perkin-Elmer Instruments. About 8 -10 mg of samples were heated over the temperature range from 30 to 800 °C with the heating rate of 10 °C min⁻¹ and the O₂ flow rate of 100 mL/min. The thermograms of samples were recorded in open alumimun pans using α -Al₂O₃ as the reference material. The structure and crystalline size of the prepared product in different media agents were studied by X-ray powder diffraction using a D8 Advanced powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K α radiation ($\lambda = 0.1546$ nm). The Scherrer method was used to evaluate the crystalline size (i.e. $D = K\lambda/\beta \cos\theta$, where λ is the wavelength of X-ray radiation, K is a constant taken as 0.89, θ is the diffraction angle and β is the full width at half maximum (FWHM)) [25-27]. The morphology of the selected resulting samples was examined with Scanning Electron Microscope (SEM) using LEO SEM VP1450 after gold coating.

The room temperature FTIR spectra were recorded in the range of 4000-370 cm⁻¹ with 8 scans on a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4 cm⁻¹ using KBr pellets (KBr, spectroscopy grade, Merck).

3. Results and discussion

The TG/DTG/DTA curves of the As-prepared precipitate obtained from aqueous system are shown in Fig.1a. The TG curves show the weight loss between 30 and 800 °C, which are related to the elimination of water molecules in crystallization water and an intermolecular condensation. The eliminations of water were observed in five areas: 104-140, 155-208, 208-260, 295-395 and 290-500 °C. The corresponding observed weight losses are 6.56, 3.58, 3.36, 3.95 and 2.85 % by mass, which correspond to 0.92, 0.50, 0.47, 0.55 and 0.40 mol of water for $Ca(H_2PO_4)_2 \cdot H_2O$, respectively. The DTA curves show five endothermic effects over the temperature region at 124, 188, 237, 332 and 441 °C, which correspond to the peaks at 124, 185, 235, 331 and 446 °C in the DTG curve.

The TG/DTG/DTA curves of the As-prepared precipitate obtained from acetone-water system are shown in Fig.1b. The TG curves show the weight loss between 30 and 800 °C, which are related to the elimination of water molecules in crystallization water and an intermolecular condensation. The eliminations of water were observed in six areas: 50-95, 95-151, 151-238, 238-277, 277-417 and 417-500 °C. The corresponding observed weight losses are 8.35, 5.55, 2.90, 3.28, 3.90 and 4.02 % by mass, which correspond to 1.17, 0.78, 0.40, 0.46, 0.54 and 0.56 mol of water for Ca(H₂PO₄)₂•H₂O, respectively. The DTA curves show five endothermic effects over the temperature region at 48, 132, 171, 264, 292 and 437 °C, which correspond to the peaks at 48, 130, 170, 262, 292 and 436 °C in the DTG curve, respectively. The major weight loss of 8.35 % (1.17 H₂O) and corresponding DTA and DTG peaks at 48 °C was related to the loss of moisture for the As-prepared precipitates obtained from acetone media agent.

The TG/DTG/DTA curves of the As-prepared precipitate obtained from ethanol-water system are shown in Fig.1c. The TG curves show the weight loss between 30 and 800 °C, which are related to the elimination of water molecules in crystallization water and an intermolecular condensation. The eliminations of water were observed in four areas: 97-151, 151-278, 278-380 and 380-500 °C. The corresponding observed weight losses are 3.00, 2.10, 12.42 and 2.00 % by mass, which correspond to 0.42, 0.29, 1.73 and 0.28 mol of water for $Ca(H_2PO_4)_2 \cdot H_2O$, respectively. The DTA curves show four endothermic and one exothermic effects over the temperature region at 117, 184, 383, 397 and 597 °C, which correspond to the peaks at 117, 184, 383 and 397 °C in the DTG curve, respectively. Further, a small exothermic effect at 597 °C without appreciable weight loss was seen in the DTA curve. This event was assigned to a transition phase from amorphous to crystalline [23].

The thermal decomposition of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ from three different media systems is a complex process, which involves the dehydration of the coordinated water molecules (1 mol H₂O) and an intramolecular dehydration of the protonated phosphate groups (2 mol H₂O). A large number of intermediate compounds, such as acid polyphosphate $Ca(H_2PO_4)_2$, acid condensed phosphate $CaH_2P_2O_7$ and mixtures of intermediate have been registered. Total mass loss of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ precipitates obtained from aqueous, acetone-water and ethanol-water systems are 20.30 % (2.84 H₂O), 19.65 % (2.74 H₂O) and 19.52 % (2.73 H₂O), respectively. The results are also in agreement with the theoretical value (21.48 %, 3.00 H₂O). Calcium polyphosphate, $Ca(PO_3)_2$ is found to be the final products of the thermal decomposition at T > 500 °C (Fig. 1), which was investigated by FTIR and XRD results and these results are also in agreement with the reported by Ioitescu et. al.[28]. The thermal analysis of the prepared $Ca(H_2PO_4)_2 \cdot H_2O$ from three different media systems show the significantly difference behavior, which should be the effect of the media agents.



Figure 1 TG/DTG/DTA curves of As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ from aqueous (a); acetone-water (b); and ethanol-water (c) solutions.

The XRD patterns of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in three different media systems are shown in Fig. 2. All detectable peaks are indexed as $Ca(H_2PO_4)_2 \cdot H_2O$ with structure comparable to the standard data as PDF # 0903047. The XRD patterns of the AS-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in aqueous and acetone-water systems are very similar to that of the standard data. While the XRD pattern of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in ethanol-water solution show the impurities phase of calcium polyphosphate. The XRD results indicated that crystal structures are in monoclinic system with space group $P2_1/n$ (Z = 2) for $Ca(H_2PO_4)_2 \cdot H_2O$. The average crystallite sizes for 64 ± 11 , 36 ± 10 and 40 ± 4 nm were calculated from X-ray spectra of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ precipitates from aqueous, acetone-water and ethanol-water solutions, respectively. The particle sizes of the $Ca(H_2PO_4)_2 \cdot H_2O$ precipitates obtained from acetone-water and ethanol-water solutions are smaller than that the As-precipitate obtained from aqueous solution.



Figure 2 XRD patterns of As-prepared Ca(H₂PO₄)₂•H₂O from different media systems.

The FT-IR spectra of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in three different media systems are shown in Fig. 3 and found to be very similar to those observed by Chapman et al. [29], which are assigned relating to the fundamental vibrating units, $H_2PO_4^-$ and H_2O . The highest site symmetry of H₂PO₄ ion is C_{2v}, in the crystallographic unit cell (P2₁/n, Z = 2) [29], however, the four $H_2PO_4^-$ ions are located on the set of non-equivalent site symmetry of C₁. A pair of $H_2PO_4^$ ions is related to each other by a center of symmetry. The four fundamental modes of the free phosphate ion undergo factor group splitting [29]. The O-H stretching of the $H_2PO_4^-$ ion gives rise to a complex feature (the A, B, C trio) of which only the two former components are clearly visible, the third component (C) possibly contributing to the breath of the bands in the water bending region (1850-1495 cm⁻¹) and/or the multiple bands in this region [29]. Two bands centered at 2926 and 2336 cm⁻¹ in FTIR spectra are referred to as bands A and B, respectively. The third component (band C) is observed around 1740-1600 cm⁻¹. The intense band at about 1240 cm⁻¹ is due to the in plane P-O-H bending (A_2) , while the out of plane bending (A_1) vibration is observed at about 887 cm⁻¹. Vibrational spectra of present hydrate were assigned by factor group analysis and derived from the same mode in the free $H_2PO_4^-$ ion [29]. A strong band at about 1111 cm⁻¹ in FTIR spectra is assigned to PO₂ asymmetric stretching (B_1) , while the other one at about 1052 cm⁻¹ correspond to PO₂ symmetric stretching modes (A_1). The FTIR frequency of the P(OH)₂ asymmetric stretching (B_2) shows the strong band at about 960 cm⁻¹. The weak band at about 863 cm⁻¹ is assigned to P(OH)₂ symmetric stretching modes (A_1). The medium band at about 540 cm⁻¹ is corresponding to PO₂ bending modes (B_1). Two strong bands appeared at about 500 and 430 cm⁻¹ are attributed to PO₂ rocking modes as B_1 and A_2 vibrations, respectively. In addition, weak bands in FTIR spectra are observed at around 390 cm⁻¹ according to $P(OH)_2$ bending mode(A_1).



Figure 3 FTIR spectra of As-prepared Ca(H₂PO₄)₂•H₂O from different media systems.

Unlike the $H_2PO_4^-$ ion, two water molecules occupy general position in the crystal [28, 29]. The band of water vibrations are illustrated in Fig. 3 as a broad band (1649 cm⁻¹) contributes both to the band C and to the water bending region [30]. A weak band occurs in the FTIR spectra at approximately 672 cm⁻¹ is assigned to rocking mode involving water molecules. The v_{OH} stretching modes of HOH in Mn(H₂PO₄)₂ • 2H₂O appear at 3242 cm⁻¹ (v₁) and 3464 cm⁻¹ (v₃). The bands associated with the v_{OH} stretching frequencies in H₂PO₄⁻ ion are observed at about 2926 (band A) and 2336 (band B) cm⁻¹ [31].

The morphology of the As-prepared Ca(H₂PO₄)₂ • H₂O in three different media systems are shown in Fig. 4. The particle shape of the As-prepared $Ca(H_2PO_4)_2 \bullet H_2O$ in aqueous and acetone-water solutions show similar plate-like crystals. However, the morphology of the Asprepared Ca(H₂PO₄)₂ • H₂O in acetone-water solution illustrated highly aggregates than that of the As-prepared Ca(H₂PO₄)₂ • H₂O obtained from aqueous solution. The As-prepared Ca(H₂PO₄)₂•H₂O obtained from aqueous solution illustrated some small and many large platelike crystals, which were about 0 $.30-0.70 \mu m$ in length and $0.20-0.60 \mu m$ in width and about 0 .70- 2.50 µm in length and 0.50-1.00 µm in width, respectively. While the As-prepared $Ca(H_2PO_4)_2 \bullet H_2O$ obtained from acetone-water solution illustrated some small and many large plate-like crystals, which were about $0.10-0.40 \ \mu m$ in length and $0.20-0.50 \ \mu m$ in width and about 0 .50- 1.50 µm in length and 0.30-8.00 µm in width, respectively. The AS-prepared $Ca(H_2PO_4)_2 \bullet H_2O$ obtained from ethanol-solution shows nonuniform shape in aggregates of irregularly-shaped crystals of different sizes, which are the range of $0.50-2.0 \ \mu m$. The morphology of the As-prepared Ca(H₂PO₄)₂•H₂O obtained from three different media agents may indicate further nucleation/growth of the nanocrystals inside the powder. These reasons indicate the effects on the grain sizes obtained from the SEM pictures are not consistent with the results obtained from XRD analysis. The exact particle nucleation and growth mechanisms are not clear. The results of SEM experiments indicate that the grain sizes of the As-prepared $Ca(H_2PO_4)_2 \bullet H_2O$ obtained from three different media systems are in consistent with the particle size form XRD analysis. The SEM results of the As-prepared $Ca(H_2PO_4)_2 \cdot H_2O$ in three systems shows the significant difference morphology, which should be the effect on various media agent. The results are also in agreement with that reported the media effect on preparation methods in the literatures [23, 24].



 $\label{eq:Figure 4 SEM micrographs of the As-prepared Ca(H_2PO_4)_2 \bullet H_2O \mbox{ from aqueous (a);} \\ acetone-water (b); \mbox{ and ethanol-water (c) solutions.}$

4. Conclusions

The Ca(H₂PO₄)₂ • H₂O samples were obtained by a rapid precipitation from CaCO₃ and H₃PO₄ in three different media systems (aqueous, acetone-water and ethanol-water solutions) at ambient temperature with short time consuming (20 min.). Additional, the preparation in acetone-water and ethanol-water systems are the soft solution synthesis method, which do not evolved CO₂ gas. The XRD and FTIR results of Ca(H₂PO₄)₂ •H₂O are quite similar for the products obtained from using aqueous and acetone-water solutions. Thermal analysis and SEM results indicate that the different media agents for precipitation effect on thermal behavior and morphology of Ca(H₂PO₄)₂ •H₂O. The particle sizes of Ca(H₂PO₄)₂•2H₂O prepared from acetone-water and ethanol-water solutions are smaller than those prepared from aqueous solution, as revealed by SEM and XRD data. This work presents the simple, cost effective and rapid time consuming method for the precipitation of Ca(H₂PO₄)₂ •H₂O. The different media agents for precipitation affect some physical and chemical properties of interesting materials, which may be the alternative methods for its potential applications such as catalytic, ceramic and the biomedical materials etc.,.

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