Effect of aging time on calcium phosphates powders obtained by sol-gel method

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ABSTRACT

Calcium phosphates (CaP) based bioceramics play role in several biomedical applications. In this study, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was synthesized by sol-gel method. Calcium nitrate ($Ca(NO_3)_2.4H_2O$) and phosphoric acid (H_3PO_4) were used as calcium and phosphate precursors in methyl alcohol solvent. The influence of the aging time (12 h, 24 h, 10 days, 20 days and 30 days) of the sol on the structure of the CaP powders was investigated. The results of stability showed that it remained stable not altering the final powder during one month. After remove the solvent by heating at 100°C a white powder was obtained. The effect of calcination temperatures on composition of the HA phase were characterized by FTIR, XRD and SEM. These techniques confirmed the presence of the typical hydroxyapatite phase and CaO. The results of hydroxyapatite synthesized by sol-gel method showed a required stability to be applied on coating of dentistry and orthopedic implant using the sol prepared at the period of one month.   © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), is a naturally mineral form of calcium apatite constituting of bone structures. Micro and nanosized synthetic calcium phosphate compunds have been used in orthopaedic, dental, and maxillofacial applications to treatment of bone-related losses diseases. The hydroxyapatite crystallites in human bone, dentin, enamel and cementum are small in size and can be considered as nanostructured materials[1,2,3]. Nanosized-HA has been alsoapplied toanti-tumoraldrug delivery systems, osteomyelitis treatment and suppressor agent of tumor cell proliferation[4,5,6,7,8]. Typical applications of medical grade hydroxyapatite are powders, dense blocks, macroporous blocks and granules (~55-60% porosity), for implant coating, bone grafting, augmentation, infilling and preforms that the surgeon will shape during surgery[3].

In literature, several synthesis methods for hydroxyapatite have been described, including mechano-chemical synthesis, combustion preparation and wet chemistry technique. The sol–gel method is a wet chemical method that involves five main stages: (1) sol preparation, (2) gelation, (3) aging, (4) drying, and (5) densification and crystallization. This final stage providesa controlled porous structure, a residual reactants removed, and crystallization of inorganic phases after low temperatures[4,5]

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Therefore, sol-gel method has received increasing attention in recent years due to its versatility and excellent control over physicochemical properties of obtained materials. Some potential advantages should be reported, such as low pH value, simplicity, low cost of the equipment, homogeneous composition and high purity phase obtained. This method also offers a molecular mixing of the calcium and phosphorus which is capable of improving the chemical homogeneity. Moreover, the high reactivity of the sol–gel powders allows a reduction of the processing temperature and of any degradation phenomena during sintering[8,9]

Nowaday, there are few recent reports that describe the sol-gel method using as precursors $Ca(NO_3).4H_2O$ and H_3PO_4[6,10-15]. It should be emphasized the latest publications using these precursors are reported by Sanosh *et. al.* (2009). Therefore, there is a gap to be investigated using the sol-gel method to obtain powder of calcium phosphates of biological interest.

It has been established that, to produce HA coatings, sol–gel solutions must be aged for a period of time before deposition onto substrate materials and subsequent hydrolysis and heat treatment[4,8,9,16,17]. The aim of this work was to evaluate the influence of aging time of the sol (formed by calcium and phosphate precursors) on the synthesis of hydroxyapatite powders, in order to be applied for coatings on titanium surface and its alloys for dentistry and orthopedic implants.

EXPERIMENTAL

The starting materials used in the synthesis and experimental procedure were analytical grade reagents. The detail process to obtain HA via sol-gel method was shown in the flow chart (Figure 1). $Ca(NO_3)_2.4H_2O$ dissolved in methyl alcohol remaining under stirring and H_3PO_4 dissolved in methyl alcohol remaining under stirring but the second in ice bath. The second solution was added at first solution in ice bath remaining under stirring. The concentrations of the reactants were chosen in order to obtain a Ca/P molar ratio in solution of 1.67, corresponding to stoichiometric HA. The pH value of the final solution was close to 2. The reaction was submitted bellow:
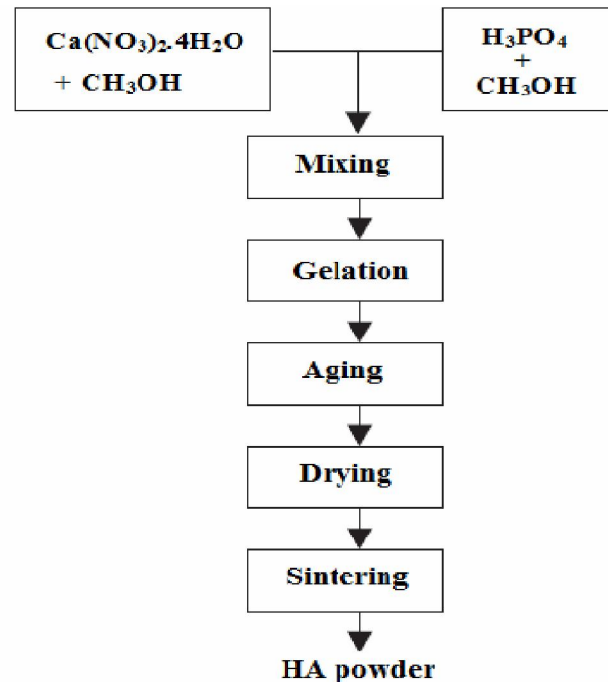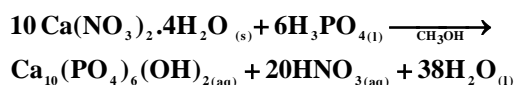
$$10\,Ca(NO_3)_2.4H_2O_{(s)} + 6H_3PO_{4(l)} \xrightarrow{CH_3OH}$$
$$Ca_{10}(PO_4)_6(OH)_{2(aq)} + 20HNO_{3(aq)} + 38H_2O_{(l)}$$

Figure 1 : Schematic flow diagram for obtained HA powder by sol-gel method.

The final solution was maintained under refrigeration for 12 and 24 h, 10, 20 and 30 days in order to investigate the effect of aging time in the formation of HA phase powder. After that, aged samples were dried in a heating plate at 100°C for 12 hour or until all the solvent was removed. Sequentially, the samples were submitted to heat treatment at 700°C for 1h, using a heating/cooling rate of 5°C/min.

The powders were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Diffuse-Reflectance *Fourier-Transform Mid-Infrared Spectroscopy* (DRIFT). The scanning electron microscopy (SEM) was performed using a LEO microscope, model 440, coupled to a Si (Li) energy dispersive analyzer with Be window, model 760 and 133 eV spectroscopic resolution by dispersive energy – EDS. X-ray diffraction (Siemens D5000 X-ray diffractometer) was carried out using Cu Kα radiation (λ=0.154 nm) at 50 kV and 100 mA between 2θ values of 4° - 60° with a step size of 0.02°. Fourier transform infrared spectroscopy (Nicolet Magna 550 spectrophotometer with diffuse reûectance DRIFT Collector TM) was used to analyze the phase and structure of the apatites coatings, and the spectra were collected over the range 4000–500 cm^{-1}.

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RESULTS AND DISCUSSION

The Figure 2 corresponds to the results of thermal analysis (TGA-DSC) of the dried powder before the heating treatment. The thermogravimetry (TG) showed a total weight loss of 45%. At temperatures below 200°C a weight loss of 15% was observed that associated to an endothermic event between an exothermic region, can be attributed to the physically adsorved water[16]. TG curve has remarked a weight loss of 10% in the temperature range from 410 to 425°C. The event can be attributed to condensation of HPO_4^{-2} allowing the formation of pyrophosphate phase. The DSC curve shows a peak maximum temperature at 550°C that can be attributed to endothermic event of crystallization of hydroxyapatite phase, associating a mainly weight loss of 20%. At higher temperatures no more weight losses[7,16].

Figure 3 shows the XRD patterns of obtained powders from aged solutions of12 and 24h, 10, 20 and 30 days, and calcined at 700°C. XRD patterns revealed $Ca_{10}(PO_4)_6(OH)_2$(#:89-4405). A small amount of calcium oxide (#: 37-1497) were observed as a secondary phase (2θ, 37.4 and 53.9). Therefore, further completion of these reactions was found to reduce CaO content and Ca/P molar ratio of calcined samples approaches stoichiometric value 1.67 since the $Ca(NO_3)_2$

generation of alkoxy-nitrate salts that participate in a polymerization reaction with the partially hydrolyzed phosphate precursors. The polymerization reaction, thereby, results in the gel. Since all the calcium nitrate is not transformed into alkoxy-nitrates, for those gels subject to long and short-term aging, the presence of CaO phase results primarily from incomplete reaction, leaving a residual nitrate. Since the hydrolysis of phosphoric acid is much slowerthan alkyl phosphate[5], time aging, may not be helpful in hydrolysis and the P–O–Ca linkage formation. Researchers have also reported similar formation of CaO in sol–gel processing of HA phase[18-19]. According toChai and Ben-Nissan (1999)[20] phosphorus containing precursors have high potential for volatilization above 650°C[21], hence $Ca(NO_3)_2$ molecules may not get completely incorporated into the complex which is evident by higher Ca/P molar ratio at 700°C and above Sanosh et al.[22] investigated thatheating HA powder at 700°C and above induced a high crystalline HA diffraction peaks together with minor CaO peaks, the formation of CaO phase, which was attributed to phosphorous volatilization.

According to XRD analysis, HA crystalline was synthetized at 700°Cfor all aging times[16,17]. Thereby, it was observed a high stability of aged sample for 30 days.
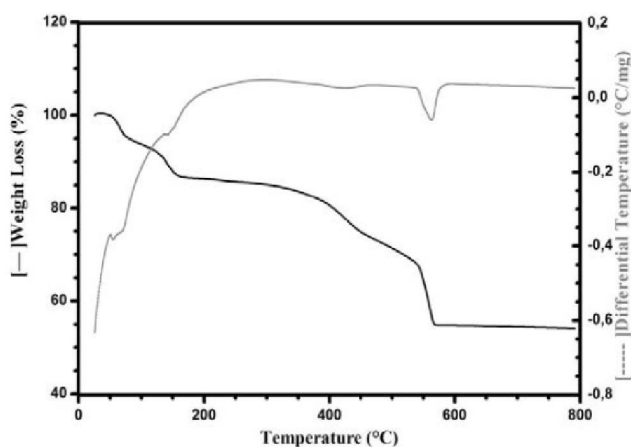

Figure 2 : Thermal analysis of the powder after dried at temperature of 100°C.

Figure 3 : XRD analysis of the powders after heat treatment for different aging times.

molecule has almost been incorporated into the complex. The reaction of H_3PO_4 with $Ca(NO_3)_2 \cdot 4H_2O$ results in the formationof a gel, and with the progress of the reaction a viscous liquid was obtained. It can be speculated that $Ca(NO_3)_2 \cdot 4H_2O$ probably results in the
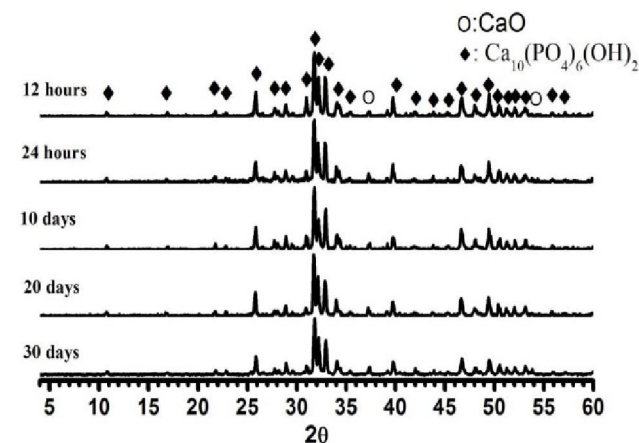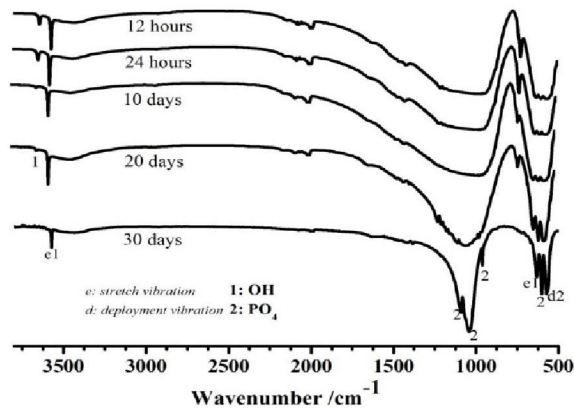
Figure 4 shows the analysis of FTIR, conducting to identify the functional groups of HA phase in agreement with the XRD results. Thesharp band at 3644cm^-1appeared due to the stretching vibration mode of the lattice OH^- ions. The band at 635 cm^-1is attributedto O-H deformation mode. The principal vibrational modes

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Figure 4 : FTIR of the powders after heat treatment for different aging times.

of PO_4^{3-} tetrahedron were assigned at 1040, 960, 601 and 565 cm^{-1}[17,23]. The band at 960 cm^{-1} referred to symmetric stretching mode of P-O bonds v_1, the doubly degenerate O-P-O bending modes v_2 at 565 cm^{-1}, the triply degenerate asymmetric P-O $_3$ at 1040 cm^{-1}as well as the triply degenerate O-P-O bending mode v_4 at 601 cm^{-1}[17,23]. Therefore, FTIR analysis showed all typical absorption bands of HA phase calcined at 700

°C for all aging times. The broad band at 3430 cm^{-1} and 1646 cm^{-1} are associated to vibration of hydrogen bonded OH of adsorbed water[1,17,23]. Additionally, a weak band at ~3640 cm^{-1}in the spectra of the powders calcinated at 700 °C can be assigned to the stretching vibrations of OH groups contained $Ca(OH)_2$, resulting to HA decomposition giving free CaO followed by its reaction with water.

Figure 5shows the micrographies of HA phase powders calcined at 700°C for different aging times. The aged samples for longer aging time tend to be highly agglomerated due to primary drying of gel formation. It was also observed an increasing of the cross-linked structure. The nucleation and growth of HA phase with temperature can be described by nucleation–aggregation–agglomeration growth mechanism theory explained by Randolph and Larson (1986)[24] and Rodriguez et al. (1998)[25], Figure 6. According to mechanism, HA particle synthesisinvolves following steps: (a) nucleation and growth to form HA crystallites, (b) aggregation of elemental crystals by molecular attractions[26] of differ-
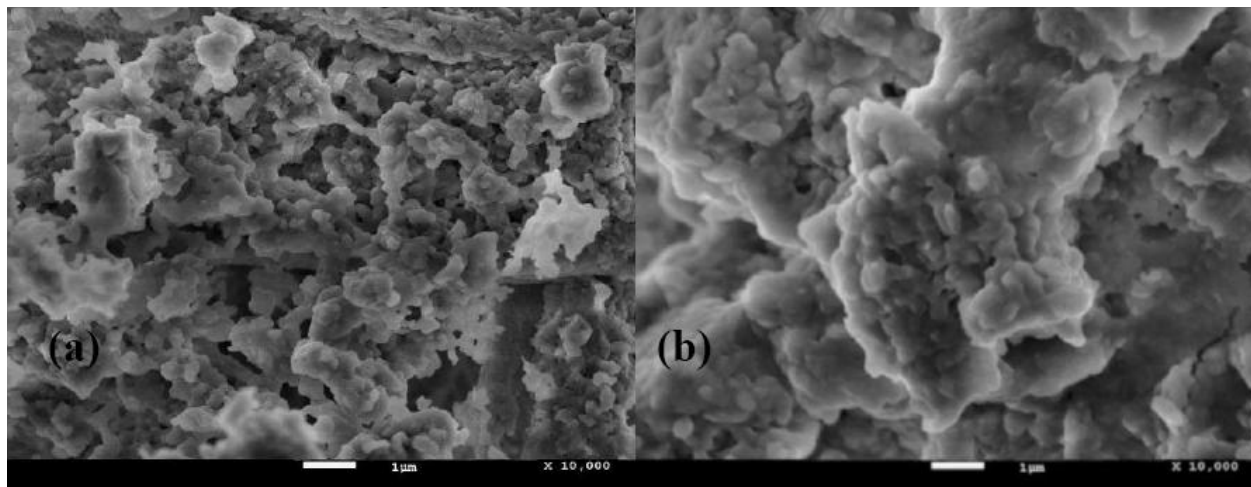
Figure 5 : Sem micrographies of the ha powders calcined at 700°c for different aging times: (a) 12 h and (b) 30 days.

ent micrometric/colloidal scale forces which cause surface free energy minimization, (c) further crystal growth, at a constant residual supersaturation, acting as cementing agent inside the aggregates to form agglomerate. The increase in particle size with temperature takes place by aggregation of these agglomerated particles to form secondary particle. Feng et al. (2005) explain that resulting cross-linked structure of the molecules should increase during aging. However the synthesis mechanism of the HA powders obtained by sol-gel methods is not well known[4].

CONCLUSIONS

The results of HA phase powders synthesized by the sol-gel method, using the alternative precursors ($Ca(NO_3)_2$and H_3PO_4), showed a good stability for aging time of 30 days. The crystallinity and Ca/P ratio of the resulting particles were found to be dependent on the calcination temperature. When Ca/P ratio exceeded 1.75, formation of CaO phase was observed, which was attributed to phosphorous volatilization. The

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method of synthesis showed that the HA, with varying in the period of one month, can be effective using this simple technique. It should be advantageous for application of sol-gel method in calcium phosphates coatings on titanium surfaceand its alloys for dentistry and orthopedic implants.

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REFERENCES

[1] J.Chen, Y.Wang, X.Chen, L.Ren, C.Lai, W.He, Q.Zhang; Mat.Let., **65**,1923 **(2011)**.

[2] U.Vijayalakshmi, S.Rajeswari; J.Sol-Gel Sci.Technol., **63**, 45 **(2012)**.

[3] S.Jinawath, P.Sujaridworakun; Mat.Sci.and Eng.C, **22**, 41 **(2002)**.

[4] W.Feng, L.M.Sena, L.Y.Peng, Q.Y.Xin; Mat.Let., **59**, 916 **(2005)**.

[5] H.Eshtiagh-Hosseini, M.R.Housaindokht, M.Chahkandi; Mat.Chem.and Phys., **106**, 310 **(2007)**.

[6] K.P.Sanosh, M.Chu, A.Balakrishnan, Y.Lee, T.N.Kim, S.Cho; Curr.Appl.Phys., **9**, 1459 **(2009)**.

[7] S.K.Padmanabhana, A.Balakrishnana, M.Chub, Y.J.Lee, T.N.Kima, S.Chob; Particuology, 7466 **(2009)**.

[8] M.H.Fathi, A.Hanifi; Mat.Let., **61**, 3978 **(2007)**.

[9] M.Hsieh, L.Perng, T.Chin, H.Perng; Biomaterials, **22**, 2601 **(2001)**.

[10] K.P.Sanosh, M.C.Chu, A.Balakrishnan, T.N.Kim, S.Cho; Bull.of Mater Sci., **32**, 465 **(2009)**.

[11] A.L.Wang, L.Dong, Y.Hengbo, W.Huixiong, W.Yuji, M.Ren, J.Tingshun, X.Cheng, Y.Xu; Mat.Sci.Engin.C-Biomim.andSupram., **27**, 865 **(2007)**.

[12] B.H.Kim, J.H.Jeong, Y.S.Jeon, KO.Jeon, K.S.Hwang; Ceram.Inter., **33**, 119 **(2007)**.

[13] M.Manso, M.Langlet, C.Jimenez, J.M.Martinez-Duart; Biom.Engin., **19**, 63 **(2002)**.

[14] Y.M.Lim, K.S.Hwang, Y.J.Park; J.Sol-Gel Sci.Tech., **21**, 123 **(2001)**.

[15] K.Hwang, Y.Lim; Surf.Coat.Tech., **115**, 172 **(1999)**.

[16] B.Sunendar, W.Abhinimpuno; Journal Ilmu-Ilmu Hay.danFis., **11**, 1411 **(2009)**.

[17] A.Stoch, W.Jastrzebski, A.Brozek, J.Stoch, J.Szaraniec, B.Trybalska, G.Kmita; J.of Molec.Struct., **555**, 375 **(2000)**.

[18] C.M.Lopatin, V.Pizziconi, T.L.Alford, T.Laursen; Thin Solid Films, **326**, 227 **(1998)**.

[19] H.K.Varma, S.N.Kalkura, R.Sivakumar; Ceram.Int.,**24**, 467 **(1998)**.

[20] C.S.Chai, B.Ben-Nissan; J.Mater.Sci.Mater.Med., **10**, 465 **(1999)**.

[21] S.P.Szu, L.C.Klein, M.Greenblatt; J.Non-Cryst.Solids, **14**, 321 **(1992)**.

[22] K.P.Sanosh, M.C.Chu, A.Balakrishnan, T.N.Kim, S.J.Cho; Bull.Mater.Sci., **324**, 65 **(2009)**.

[23] I.S.Kim, P.N.Kumta; Mat.Sci.Eng.B, **11**, 1232 **(2004)**.

[24] A.D.Randolph, M.A.Larson; Theory of particulate processes.NY: Academic Press, 2nd, **(1986)**.

[25] R.Rodríguez-Clemente, A.López-Macipe, J.Gómez-Morales, J.Torrent-Burgués, V.M.Castãno; J.Eur.Ceram.Soc., **18** 1351 **(1998)**.

[26] J.Gomez-Morales, J.Torrent-Burgues, R.Rodriguez-Clemente; Cryst.Res.Technol., **36**, 1065 **(2001)**.