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EFFECT OF ZINC DOPED CALCIUM PHOSPHATE THROUGH MECHANOCHEMICAL SYNTHESIS

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ABSTRACT

In this research, zinc was doped into calcium phosphate through mechanochemical synthesis. Zinc mol concentration was varied from 0.1%, 0.3% and 0.5%. The main precursors employed in this work are calcium hydroxide, phosphoric acid and zinc hydroxide. The synthesized powders were examined through FTIR and XRD analyses to validate the presence of all the chemical elements. The synthesized powders were then compacted into green bodies and sintered at 1000 ºC. Density test showed a linear change towards the different concentration on the zinc where zinc dopants improved the densification and microstructure of the calcium phosphate.

Keywords: calcium phosphate, zinc, mechanochemical, fourier transform infrared, X-ray diffraction.

INTRODUCTION

Calcium phosphate is commonly used for a number of biomedical applications in the forms of granules, blocks (Adzila *et al.* 2011 & 2013), coatings and dense bodies (Sopyan *et al.* 2007) (Sopyan & Kaur, 2009) for bone augmentation. Calcium phosphate has also been found useful for drug delivery and antibiotics. It exists naturally in human bone as crystals within collagen. The high strength is necessary for reliable implant in the body (Webster *et al.* 2004). Many improvements have been made to overcome the limitation of calcium phosphate mainly for hydroxyapatite (HA) in loading application by controlling microstructures via novel sintering techniques or utilization of nanopowders (Tang *et al.* 2009).

Development of dense HA ceramics with superior mechanical properties is possible if the starting powder is stoichiometric with improved powder properties such as crystallinity, agglomeration and morphology (Sopyan & Kaur, 2009). Because of its excellence in biocompability and bioactivity, calcium phosphate is by far the most suitable material for hard tissues substitution. The zinc cation (Zn) is one of the most important cations that can be incorporated in the Ca sites of HA atomic structure. This cation has been found to be very osteoconductive and can stimulate osteogenesis (Esfahani *et al.* 2014).

Mechanochemical ball milling has been used since 1922 wherein the materials components are synthesized by deformation process through ball particle, particle-wall, and particle-particle collisions (Adzila *et al.* 2013) at a particular time, leading to the chemical reaction between particles to form new nanosize composites or powders. It is a simple and low cost method compared to other techniques, and has recently received attention as an alternative route in preparing materials characterized by better biocompatibility with natural bone (Adzila *et al.* 2013) (Nasiri-Tabrizi *et al.* 2009). Synthesis of calcium phosphate through mechanochemical milling can be in either a wet medium (Mostafa, 2005) or under dry condition (Nasiri-Tabrizi *et al.* 2009).

In this study, zinc ion is doped into calcium phosphate through mechanochemical synthesis in a dry medium to study the effect of zinc ion in the synthesized calcium phosphate powder and to study the effect of zinc ion on the physical properties of sintered calcium phosphate.

METHODOLOGY

The main precursors used in this works are Calcium Hydroxide, Phosphoric Acid and Zinc Hydroxide (Fisher Scientific). All the precursors were mixed in the planetary ball mill (Fritsch, German). The milling speed and time were set at 300 rpm and 10 hours respectively. The equation of the chemical precursors used are as below:

$$5\text{-}XCa(OH)_2 + XZn(OH)_2 + 3H_3PO_4 \longrightarrow Ca_{5-x}\,Zn_x\,(PO_4)_3\,(OH)_2 + XH_2O$$

Where X = 0.1, 0.3, 0.5 molar concentration of zinc.

The phase existence in the synthesized powders was identified by using XRD. All the measurements performed at room temperature with the range of $2\theta = 10°$ to 40° at 2°/min scan speed. All the samples were analyzed by referring to the standards of the Joint Committee of Powder Diffraction Standards (JCPDS).

The functional group of the as synthesized powders were analyzed using FTIR spectrometer with 600 – 4000cm^{-1} scanning range with resolution of 4cm^{-1}. The sintering process used a temperature of 1000 °C at 5 °C/min heating and cooling rate in 2 hours.

The density of the sintered samples then were measured according to the Archimedes principle. In microstructure analysis, samples were prepared by polished under diamond paste and thermally etched at 950 °C for 30 minutes. The surface of the samples were analyzed under scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure-1 shows the XRD pattern of the undoped calcium phosphate and zinc-doped calcium phosphate with 0.1%, 0.3% and 0.5% mol concentrations. All the synthesized powders showed the similar peaks containing elements of calcium phosphate hydroxide and tricalcium phosphate with different peaks intensity. These peaks indicated that the reaction has occurred between calcium hydroxide and phosphoric acid.

However, tricalcium phosphate (TCP) has a majority amount existed compared to calcium phosphate hydroxide which also known as hydroxyapatite (HA). Zn elements were not exhibited between these peaks. It might be hindered or already substituted into the calcium (Ca) lattice. The effect of Zn substitution into Ca lattice can be detected by the decrease of TCP and HA peaks with the increase of Zn mol concentration.

Figure-2 shows the FTIR spectra of the synthesized undoped CP and Zn-doped CP at various concentrations. All the samples showed the bands corresponding to the HA structure. The spectra shows the characteristic bands of absorbed water, hydroxyl and phosphate species. The broad band at 2500–3700cm^{-1} and a small band at about 1635cm^{-1} are due to absorbed water. The shoulder located approximately at 3572cm^{-1} corresponds to the stretching vibration of the hydroxyl group. The absorption band at about 632cm^{-1} corresponds to the OH− vibrational mode. The bands with shoulder at 962–1105cm^{-1} was assigned to the P–O stretching vibration of the phosphate groups $(PO4)_3$− (Stanic *et al.* 2010). The presence of carbon ion C-C in the synthesized powders might be due from the synthesis process which was handled in air environment.

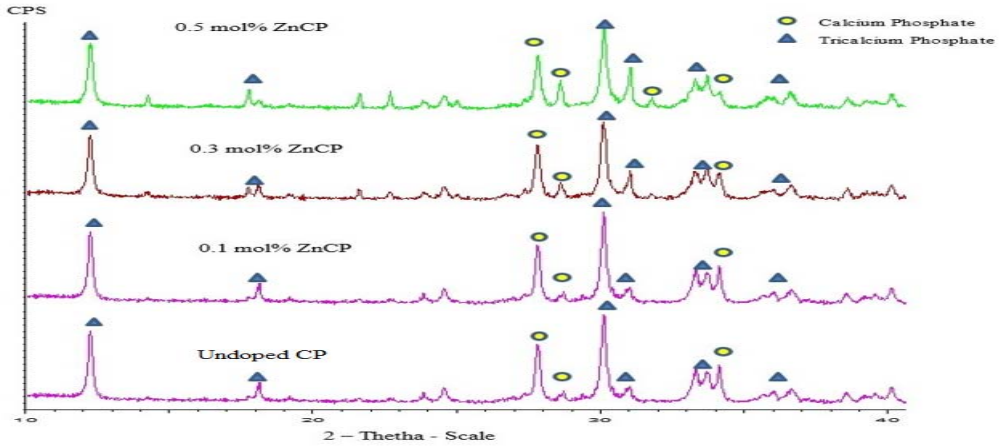

Figure-1. XRD Pattern of Undoped Calcium Phosphate and Zn-doped Calcium Phosphate at Various Concentrations.

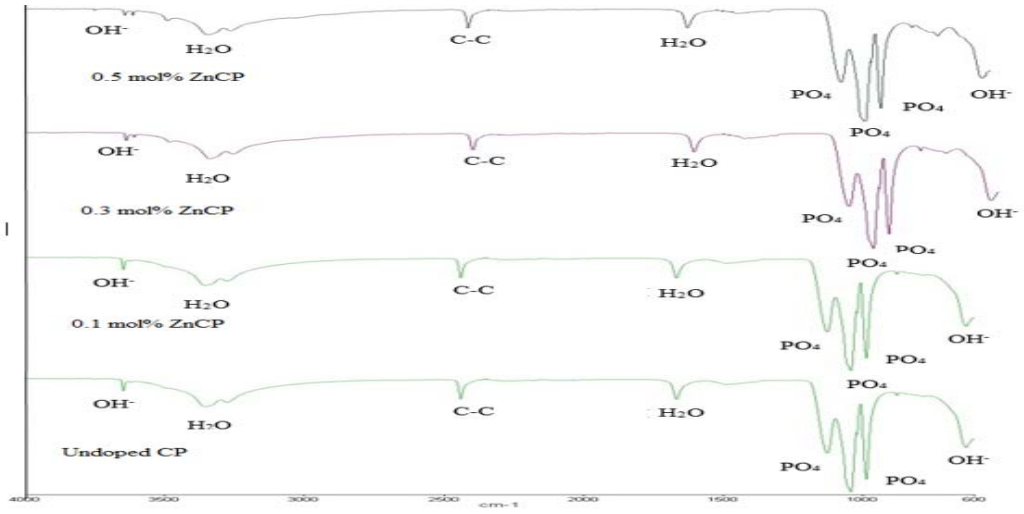

Figure-2. IR-Spectra for Undoped CP and Zn-doped CP at various concentration.

The densification of the sintered samples at 1000 ^{o}C were measured through density test based on the Archimedes principle. Based on Figure-3, a linear increase of density was observed from the undoped CP, 76.8% until 0.3 mol% ZnCP, 99.4%. However, the density dropped at 0.5 mol% ZnCP with 86.2%. Generally Zn ion increased

the density of CP where the maximum value was achieved at 99.4% in 0.3% ZnCP.

Compared from the previous study by Kalita & Bhatt (2007), the maximum density of about 95 % was achieved at 1250 °C in 1.0 wt. % of Zn doped HA. The increase amount of dopant also decreased the densities. Yeong *et al.* 2001 worked on nanocrystalline HA powder of size 25 nm via mechanochemical processing and achieved sintered density equivalent to 98.2% theoretical density at 1200 °C for 2 h.

Figure-4 shows the SEM micrograph of the samples surface for the undoped CP and Zn-doped CP (0.1 mol% - 0.5 mol%). The porosities are exhibited in all the samples where they were decreased with the increase of Zn concentration. The particle size generally also decreased with the increase of Zn concentration as we can see that the particles melted and cover almost of the porosities in 0.5% ZnCP. This result was in line with the relative density graph shown in Figure-3. The density of the undoped CP is enhanced by Zn dopants. Zn ion decreased the particles size as well as the porosities which lead to the high densification of CP.

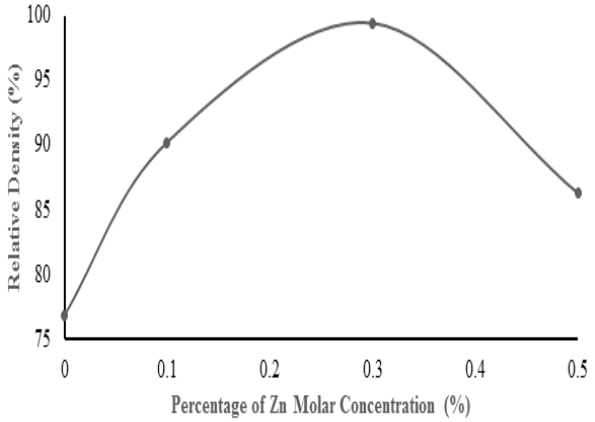

Figure-3. Relative Density of the Undoped CP and Zn-Doped CP at Various Concentrations.

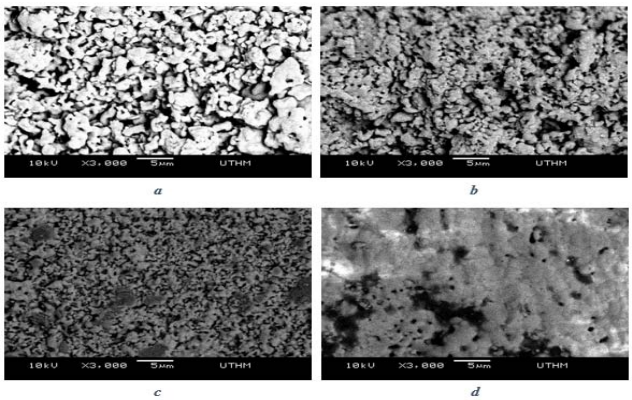

Figure-4. SEM micrograph of the samples surface sintered at 1000 °C: (a) Undoped CP (b) 0.1 mol% ZnCP (c) 0.3 mol% ZnCP and (d) 0.5 mol% ZnCP.

CONCLUSIONS

Calcium phosphate and Zn-doped calcium phosphate were successfully synthesized through mechanochemical synthesis. The substitution of Zn element in calcium phosphate was indicated by the different peaks intensity and the bands showed in the XRD and FTIR respectively. Hence, the inclusion of Zn improved the density and the microstructure of calcium phosphate where the maximum density of 99.4% was obtained in 0.3% ZnCP sintered at 1000 °C. This result was supported by SEM analysis where the porosities and the particles size of 0.3% ZnCP were reduced respectively. Further study will be continue with Inductively coupled plasma (ICP) analysis to determine the amount of Zn substitution after synthesis and mechanical performance of sintered samples with Vickers hardness test.

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REFERENCES

[1] Adzila S., Sopyan I., Hamdi M. and Ramesh S. 2011. Mechanochemical synthesis of nanosized hydroxyapatite powder and its conversion to dense bodies. Materials Science Forum, 694, pp.118-122.

[2] Adzila S., Sopyan I., Tan C. Y., Ramesh S., Wong Y., H., Purbolaksono J. and Hamdi M. 2013. Mechanochemical synthesis of nanohydroxyapatite bioceramics. Indian Journal of Chemistry, 52A, pp.1570-1575.

[3] Esfahani H., Salahi E., Tayebifard A., Rahimipour M. R. and Keyanpour-Rad M. 2014. Influence of zinc incorporation on microstructure of hydroxyapatite to characterize the effect of pH and calcination temperatures. Journal of Asian Ceramic Societies, Vol. 2, pp.248–252.

[4] Kalita S., J. and Bhatt H. A. 2007. Nanocrystalline hydroxyapatite doped with magnesium and zinc: Synthesis and characterization. Materials Science and Engineering C, Vol. 27, pp.837–848.

[5] Mostafa N. Y. 2005. Characterization, thermal stability and sintering of hydroxyapatite powders prepared by different routes. Materials Chemistry and Physics, Vol. 94, pp. 333–341.

[6] Nasiri-Tabrizi B., Honarmandi P., Ebrahimi-Kahrizsangi R., and Honarmandi P. 2009. Synthesis of nanosize single-crystal hydroxyapatite via mechanochemical method. Materials Letters, Vol. 63, pp.543–546.

[7] Sopyan I., Mel M., Ramesh S. and Khalid K. A. 2007. Porous hydroxyapatite for artificial bone applications. Science and Technology of Advanced Materials, Vol. 8, pp.116-123.

[8] Sopyan I. and Kaur J. 2009. Preparation and characterization of porous hydroxyapatite through polymeric sponge method. Ceramics International, Vol. 35, pp.3161-3168.

[9] Stani´c V., Dimitrijevi´c S., Stankovi´c J., A., Mitri´c, M., Joki ´c B., Ple´ca˘s I. B. and Rai˘cevi´c S. 2010. Synthesis, characterization and antimicrobial activity of copper and zinc-doped hydroxyapatite nanopowders. Applied Surface Science, Vol. 256, pp. 6083–6089.

[10] Tang C. Y., Uskokovic P. S., Tsui C. P., Veljovic D., Petrovic R. and Janackovic D. 2009. Influence of microstructure and phase composition on the nanoindentation characterization of bioceramic materials based on hydroxyapatite. Ceramics International, Vol. 35, pp.2171-2178.

[11] Webster T. J., Massa-Schlueter E. A., Smith J. L. and Slamovich E. B. 2004. Osteoblast response to hydroxyapatite doped with divalent and trivalent cations. Biomaterials, Vol. 25, pp. 2111-2121.

[12] Yeong K. C. B., Wang J. and Ng S. C. 2001. Mechanochemical synthesis of nanocrystalline hydroxyapatite from CaO and $CaHPO_2$. Biomaterials, Vol. 22, pp.2705-2712.