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EFFECT OF SILICA IN CALCIUM PHOSPHATE MATERIAL FOR BIOMEDICAL APPLICATION

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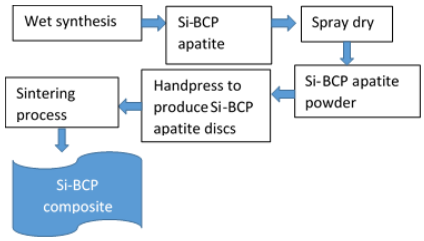
Graphical abstract



Abstract

Calcium phosphate bioceramic materials has been widely used in medical field due to their compounds which have similarities with natural bone and teeth. Despite of these materials, silica was introduced in order to improve bioactivity level of the material. In this paper, biphasic calcium phosphate (BCP) was synthesized using calcium hydroxide ($Ca(OH)_2$) and orthophosphoric acid (H_3PO_4) as chemical precursors at Ca/P ratio 1.60 via wet chemical technique. Additionally silicon dioxide (SiO_2) at 3 and 5 wt% was added into the mixture before proceeding with spray drying process. Apatite powder obtained after spray drying process was pressed into discs and sintered at 950°C to obtain biphasic mixture. Sintered Si-BCP discs were immersed in simulated body fluid (SBF) for predetermined time. Scanning Electron Microscope (SEM) images revealed that dissolution and precipitation of Si-BCP with 5% Si content occurred at day 3, while BCP without Si addition started at day 21. Formation of apatite crystal was observed on the surface of the samples. Due to this, Si-BCP has potential to be developed for quick healing medical application.

Keywords: Biphasic calcium phosphate, hydroxyapatite, tri-calcium phosphate, silica, degradation

1.0 INTRODUCTION

Load bearing components for artificial joints are made of bioinert alloys. Problems related to this component include loosening as a result of imflammatory process or aseptic loosening which caused by abrasion particles generated by the implants. Due to this, the coating surface is crucial for the fixation mechanism due to in direct contact with the bone and body fluid of implantation. Coating bioinert implants with bioactive calcium phosphate offers a potential for biological interaction between the bone and the coated implant. The main interest of calcium phosphate ceramic coating is osteoconduction and faster and better osteogenic cells spreading and bone onto the surface implant.

BCP which consists of hydroxyapatite (HA) and tri-calcium phosphate (TCP) has been developed and intended for implant material coating. HA is found to be more stable in body environment while TCP is found to be more soluble. Thus, through the combination of a balanced rate between HA and TCP, it is possible to formulate BCP with a controlled dissolution rate and different mechanical properties [1,2]. Attempts to improve the bioactivity of this ceramic includes the modification of its structure by incorporation of silica to obtain Si-BCP composite. Additionally, presence of silica in biocompatible and bioactive materials has been reported to improve osteoblast cell adhesion and proliferation [4]. This is resulted from silicon ions released from silica-substituted calcium phosphate materials which could positively influence osteoblasts.

Surface charge and structure of calcium phosphate is altered by Si substitution.

This current work focused on *in-vitro* study of Si-BCP in simulated body fluid (SBF). This study was conducted in order to observe the dissolution behavior and also to observe precipitation of calcium phosphate at different concentration of Si.

2.0 EXPERIMENTAL

Calcium phosphate slurry was prepared using calcium hydroxide (Fluka analytical, Sigma-Aldrich Germany) and phosphoric acid (Avantor Material Performance, Thailand) via wet synthesis technique. The mixture precursors was based on 1.60 Ca/P ratio. Phosphoric acid was added gradually into calcium hydroxide solution at 250 rpm using mechanical stirrer. Temperature during reaction of the mixture was controlled between 80-85°C and final pH of the suspension was set below 9.5 respectively. Silicon dioxide (SiO_2) was added into apatite slurry at different wt%. White gelatinous apatite slurry obtained at the end of the process as showed in Figure 1.

Figure 1 Apatite slurry obtained after synthesis

This gelatinous apatite slurry was then spray dried process to obtain dry apatite powder. Prior to spray the spray dryer inlet temperature is set to 280°C and an outlet temperature is not more than 120°C. The compressed air is turned on to -0.05 MPa to 0.3 MPa (-0.5-3 bar) and 50-70% air- on the flow meter. This is followed by turning on the feed pump (Brand Watson Marlow 505s) in the range of 20-45 rpm. To spray dry, double distilled dionized (DDI) water is slowly fed first into the atomizer until the required outlet temperature is stable ~85°-95°C. Then the feed pump is switched from distilled water to the gelatinous apatite slurry. The air pressure is kept constant inorder to obtain homogenous atomization. Once the spray drying process is completed, the spray dried apatite powder is collected from the glass-jar collector at the bottom of the spray dryer. Apatite powder derived from spray drying process was pressed into discs and sintered at 950°C to obtain silica-biphasic calcium phophate (Si-BCP). The samples were then characterized using X-ray diffractometer (Bruker, Germany)and Fourier transform infrared spectroscopy (FTIR). Generally, preparation of Si-BCP composite is as shown in Figure 2.

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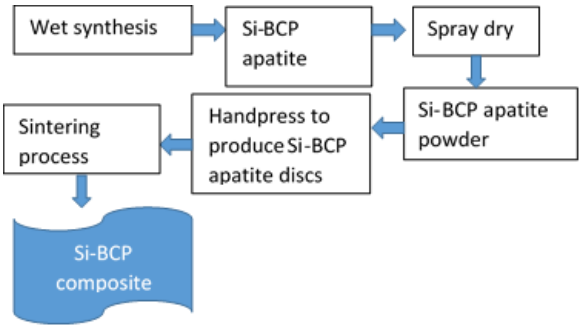

Figure 2 Work flow of Si-BCP composite preparation

For immersion process, SBF was prepared as described by Kokubo (Kokubo, 1992: Ohtsuki *et al*., 1992; Li *et al*., 1992). The appropriate amount of chemical reagents: NaCl, $NaHCO_3$, KCl, $K_2HPO_4.3H_2O$, $MgCl_2.6H_2O$, $CaCl_2$ and Na_2SO_4 were dissolved in ion-exchanged and distilled water. Then, the solution was buffered at the physiological pH of 7.4 using Tris(hydroxymethyl) aminomethane (Tris) and hydrocloric acid (1M).

Si-BCP with different wt% of Si discs (Φ~ 2cm) were soaked in SBF solution at 3, 7, 21 and 30 days respectively. Temperature of the solution was maintained at 37°C throughout the process in an incubator. The samples were then taken out at every time frame, washed using distilled water and dried out before characterized using SEM. Determination of pH and Ca^{2+} concentration were carried out in order to study the dissolution behaviour. For Ca^{2+} determination, complexometric titration method was carried out based on ISO 6058-1984 (E) on SBF solution prior to immersion process. Apart from that, compressive strength was also conducted using Universal Testing Machine (Instron 3369, Canton USA).

3.0 RESULTS AND DISCUSSION

3.1 Samples Preparation

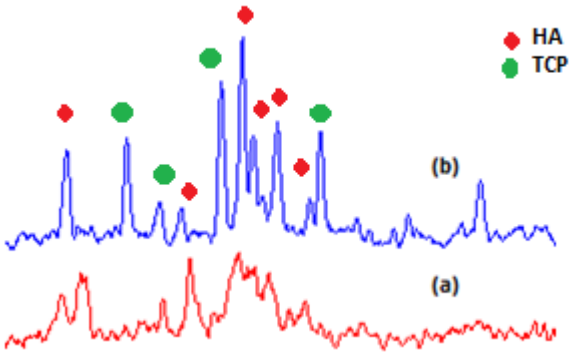

Figure 3 XRD spectrum of silica-BCP apatite (a) before sintering and (b) after sintering at 950°C

Sintering of silica apatite powder at 950°C resulted in improvement in crystallinity in terms of peak resolution compared to as-synthesised powder as in Figure 3. At this temperature, formation of both HA and TCP main peaks observed conforming the biphasic mixture.

3.2 Dissolution Behaviour

Figure 4 and 5 show the suface of silica BCP discs before and after 21 days of immersion respectively. From the SEM images, macro and microporosities observed on the surface of BCP composites. Morphology of samples before immersion were found to be denser with less porosity observed resulted from handpressing and sintering process. BCP with silica were found to be coarser compared to BCP without Si. After 3 weeks of immersion, it can be seen that BCP with Si samples appered to be covered by precipitation of apatite layer. Apart from that, larger porosity observed for Si-BCP samples with higher silica content that maybe resulted from faster dissolution process as compared to samples without Si addition.

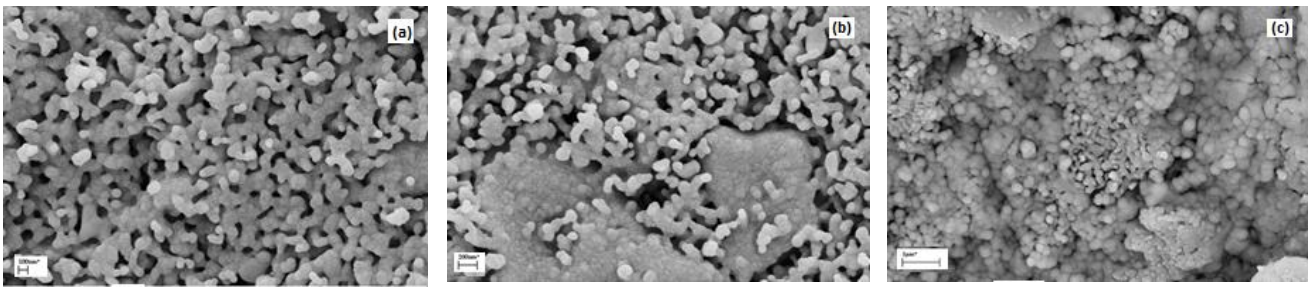

Figure 4 SEM images of BCP discs with (a) 0 wt% silica, (b) 3 wt% silica and (c) 5 wt% silica before immersion

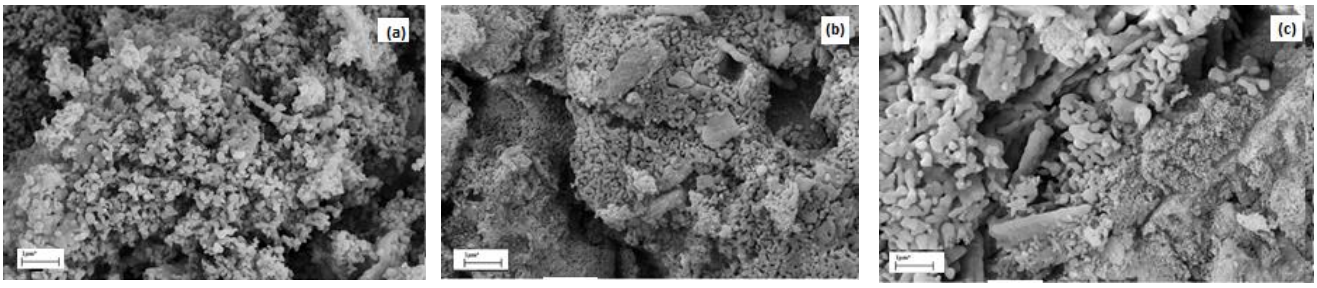

Figure 5 SEM images of BCP discs with (a) 0 wt% silica, (b) 3 wt% silica and (c) 5 wt% silica after 21 days immersion

3.3 pH and Ca2+ Ion Concentration Study

Figure 6 shows pH reading of BCP sample at different silica concentration. From the result, sample with higher silica content showed higher pH reading which corresponded on Ca^{2+} concentration released in SBF as showed in Figure 7. The release of high concentration of Ca^{2+} levels to the microenvironment results in pH changes, promotes a mild inflammatory response and favours fibrous tissue formation [3]. In addition, the release of controlled levels of Ca^{2+} over time favors the formation of apatite layer which is necessary for bioactivity [4]. From the result, BCP without silica addition was found to have decreased in Ca^{2+} release over time while BCP with silica displayed stable release of Ca^{2+}.

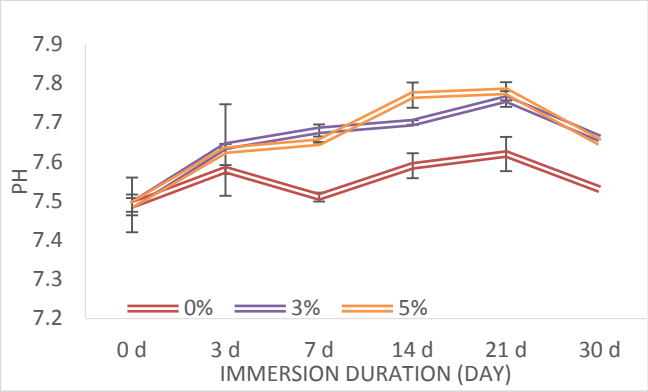

Figure 6 pH reading of different silica BCP samples

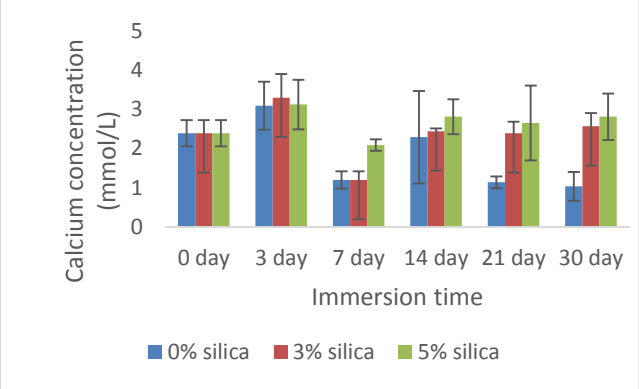

Figure 7 Calcium ions concentration released in SBF during immersion

The compressive strength of BCP samples was showed in Figure 8. From the result, compressive strength of BCP with 3 wt% and 5 wt% were initially lower compared to BCP sample without silica addition.

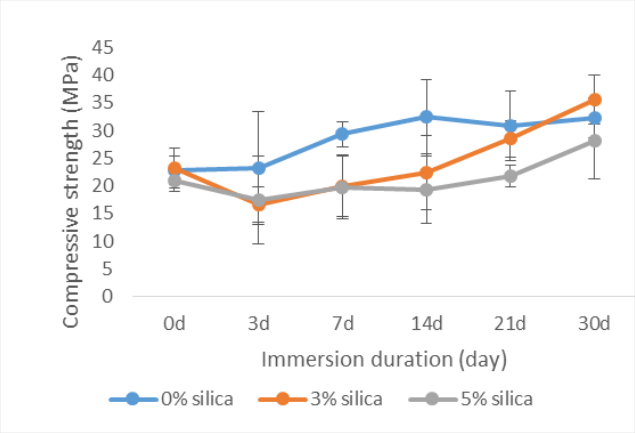

Figure 8 Compressive strength of BCP samples after immersion in SBF

As immersion time incresed, there was slight increased in compressive strength of Si-BCP sample while sample without silica it was slight decreased over time (Figure 8). This maybe due to formation of apatite layer which influenced the compressive strength of the samples.

The result revealed that the higher Si content contributed to faster dissolution rate thus, influenced its mechanical properties. Formation of apatite layers as showed in SEM results maybe contributed to this properties.

4.0 CONCLUSION

From this work, silica addition in biphasic calcium phosphate samples could facilitated dissolution and precipitation of apatite layer in SBF.It also increased calcium ion concentration released compared to BCP without Si sample. Overall, Si could possibly introduced into calcium phosphate materials since it has demonstrated potential use in medical application. However, further study needs to be conducted to investigate its properties *in-vitro* in terms of cytotoxicity and cell viability .

Acknowledgement

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