EFFECT OF AGING TIME, CALCINATION AND SINTERING TEMPERATURE TO β-TRICALCIUM PHOSPHATE (β-TCP)

HANNA BINTI BAKAR REDIN

UNIVERSITI SAINS MALAYSIA

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by

HANNA BINTI BAKAR REDIN

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Aging Time, Calcination and Sintering Temperature to β-Tricalcium Phosphate (β-TCP)**". I also declare that it has not been previously submitted for the award of any degree or diploma of similar title as this for any other examining body or university.

Name of student : Hanna binti Bakar Redin Signature:

Date : 7th August, 2019

Witness by

Supervisor : Dr Shah Rizal bin Kasim Signature:

Date : 7th August, 2019

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LIST OF SYMBOLS

mol	Moles
m	Millimeter
wt %	Weight percent
ºC	Degree Celcius
θ	Theta
º/min	Degree per minute
μm	Micrometer
Min	Minute
g	Gram
MPa	Mega pascal

LIST OF ABBREVIATIONS

α-TCP	α-Tricalcium Phosphate
β-TCP	β-Tricalcium Phosphate
Ca	Calcium
CaP	Calcium phosphate
Ca/P	Calcium to phosphorus ratio
DTS	Diametral tensile strength
FA	Fluoroapatite
FESEM	Field emission scanning electron microscopy
HA	Hydroxapatite
ICDD	International Centre of Diffraction Data
PSA	Particle size analysis
SBF	Simulated Body Fluid
TCP	Tricalcium phosphate
TCP-FA	Tricalcium phosphate- Fluoroapatite
TCP-HA	Tricalcium phosphate- Hydroxyapatite
TG-DSC	Thermogravimetric- Differential scanning calorimetry
XRD	X-ray diffraction

KESAN MASA PENUAAN, SUHU PENGKASINAN DAN PENSINTERAN TERHADAP Β-TRIKALSIUM FOSFAT (Β-TCP)

ABSTRAK

β-Trikalsium Fosfat (β-TCP) mempunyai kadar resapan yang tinggi dan ia dikenalpasti sebagai bahan biodegradasi yang membantu penumbuhan dan penggantian tulang. Melalui kajian ini, β-TCP telah disintesis menggunakan kaedah sol-gel. Objektif kajian ini ialah untuk menentukan kesan masa penuaan, suhu pengkalsinan dan pensinteran terhadap ciri-ciri β-TCP. Serbuk β-TCP disintesis dengan 0.0926 mol kalsium nitrat tetrahydrat $Ca(NO_3)_2.4H_2O$, 0.0926 mol asid sitrik monohydrat $C_6H_8O_7.H_2O$ dan 0.0617 mol di-ammonia fosfat $(NH_4)_2HPO_4$ sebagai bahan prapenanda. Parameter yang dikaji ialah 2 masa penuaan (24 dan 48 jam) dan 5 suhu pengkalsinan (500ºC, 600ºC, 700ºC, 800ºC dan 900ºC). Serbuk β-TCP dicirikan melalui TG-DSC, pembelauan sinar-X (XRD), mikroskop imbasan elektron pancaran medan (FESEM) dan FTIR. Sampel dengan pembentukan fasa β-TCP yang tertinggi dimampatkan menjadi bentuk palet dan disinter pada suhu 1000ºC dan 1100ºC masing-masing. Sampel tersinter diuji melalui ujian keliangan, analisa pengecutan, ujian mekanikal DTS dan ujian in-vitro cecair simulasi jasad (SBF). Dari analisis ini, serbuk yang telah dikalsin pada suhu 900ºC dengan masa penuaan 48 jam menghasilkan pembentukan β-TCP yang tertinggi (83.9 wt%) manakala pada suhu 500ºC dengan masa penuaan 24 jam menghasilkan pembentukan β-TCP yang terendah (41.2 wt%). Ini menunjukkan corak pembentukan fasa β-TCP meningkat dengan peningkatan suhu pengkalsinan. Lapisan apatit terbentuk pada keseluruhan permukaan pada hari ke-7 rendaman untuk palet yang telah disinter pada suhu 1100ºC penggantian didalam larutan SBF. Ini membuktikan β-TCP adalah bahan bioaktif dan bioserasi.

EFFECT OF AGING TIME, CALCINATIONS AND SINTERING TEMPERATURE TO β-TRICALCIUM PHOSPHATE (β-TCP)

ABSTRACT

β-TCP has a higher resorption rate and it is normally considered as a biodegradable materials that allows bone growth and replacement. In this study, β-TCP was synthesized through sol-gel method. Thus, the objectives of this study were to determine the effect of aging time and calcination temperature towards the formation of β-TCP phase and effect of sintering temperature on the properties of β-TCP pallet. To synthesize β-TCP powder, 0.0926 mol of calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$, 0.0926 mol citric acid monohydrate $C_6H_8O_7.H_2O$ and 0.0617 mol of di-ammonium hydrogen phosphate $(NH_4)2HPO_4$ were used. Parameter that were studied include two aging time, 24 hours and 48 hours and five calcination temperature; 500ºC, 600ºC, 700ºC, 800ºC and 900ºC. Powder were characterized via thermogravimetric-differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and fourier transform infrared spectroscopy (FTIR). Powder with highest formation of β-TCP were pressed into pallet form and sintered at 1000ºC and 1100ºC. Final characterization and testing including bulk density and porosity test, shrinkage analysis, diametral tensile strength (DTS) test and simulated body fluid (SBF) test were performed on sintered pallet. From the analysis, powder calcined at 900ºC with 48 hour ageing time shows the highest formation of β-TCP (83.9 wt%) while 500ºC with 24 hours aging time shows the lowest β-TCP formation (41.2wt%). It shows that increasing trend of β-TCP phase with the increase of calcination temperature. Full surface area of apatite layer formed

after 7^{th} day immersion of sintered pallet at 1100 ºC in SBF solution. This prove that β-TCP is bioactive and biocompatible material.

CHAPTER 1

INTRODUCTION

1.1 Research background

Bone is the basic unit of the human skeletal system which provides the structural and bear the weight of the body, protects the important organs, support mechanical movement, hosts hematopoietic cells, and maintain iron homeostatis (Qin, 2013). It has a complex, varying arrangement of structures on broad length scales, which together enables diverse mechanical, biological and chemical functions. According to Wolff's law Burr and Allen, (2019) bone in a healthy person or animal will adapt to the loads under which it is placed. If loading on the bone increases, it will remodel itself over time to become stronger by first changing the internal architechture of the bone. In contrast, if the loading on the bone decreases, the bone will become less dense (a process known as osteopenia) due to the lack of the stimulus required for continued remodelling.

This unique manner in which bone can constantly undergo self-remodeling has created interesting clinical approaches to the healing of damaged bone. There are four common bone substitutes which are known as alloplast (synthetic bone substitute), xenograft (harvested from bovine bone or coral), allograft (harvested from one individual and implanted into patient of the same species) and autograft (bone tissue transferred from different part of the same individual) (Hench, 2013). Specifically, alloplast enables us to tailor its structure and material properties as desired (Ducheyne, 2017).

It is acknowledged that all of the above-mentioned bone substitutes contains traces of calcium (Ca) and phosphorus (P), as in our natural bone. They include ceramic type of material such as hydroxyapatite (HA), fluorapatite (FA), tricalcium

phosphate (TCP), TCP-HA composites and TCP-FA composites (Sakka et al., 2013). However, most of the alloplast bone graft being used are HA and TCP due to its osteoconduction, hardness and acceptability by bone (McCarthy and Frassica, 1998).

HA and β-TCP have a good biocompatibility and bioactivity properties Wang and Jain, (2010) due to the significant feature of these materials where they can construct direct chemical bond with bone tissue. HA exhibit close resemblance to chemical composition of natural bone; high biocompatibility characteristic that is needed in bone regeneration. Compare to HA, β-TCP also has remarkable properties; its chemical similarity to the mineral component of mammalian bone and teeth, excellent biocompatibility with living bodies, as well as biodegradable properties when replacing hard tissues (Sakka et al., 2013).

Despite from all the advantages, β-TCP also has it disadvantages such as the difficulties involved in full densification and discovering appropriate method to keep sintering temperatures low to avoid transformation to α-TCP (Elliott, 2013).When β-TCP is used as load bearing biomaterial, they depicts poor mechanical properties such as the material become brittle and low fatigue strength.

Different tricalcium phosphate (TCP) synthesis techniques have been developed in recent years. These techniques include mechanochemical synthesis and combustion preparation (Ghosh and Sarkar, 2016). Besides, various type of wet chemistry techniques such as direct precipitation, hydrothermal synthesis, emulsion or micro-emulsion routes and sol-gel procedures are also widely used. Among all method stated above, sol-gel synthesis of TCP has recently attracted much attention, due to its huge advantages, which include high purity product, homogenous composition and low synthesis temperature (Liu et al., 2001). Low temperature formation of the β-TCP phase have been the main contributions of the sol-gel process, in comparison with

conventional methods. For instance, temperatures higher than 1000ºC are usually required to sinter β-TCP prepared by wet precipitation method, whilst several hundred degrees celsius lower than above needed to densify β-TCP via sol-gel method (Hwang et al., 2000 and Nahar et al., 2017).

In the synthesis of β-TCP powder, there are many factors that affect the composition and characteristics of the final products, including pH, aging time, calcination temperature, sintering temperature and and soaking time, initial reagent purity and ratios, have been investigated Brinker and Scherer, (2013). All of these factors may cause the results obtained to differ and have distinct chemical and physical characteristics, such as porosity, crystal size, grain size and roughness (Sakka et al., 2013). These characteristics can cause consequent effects on their functionality for bone regeneration application (Le Nihouannen et al., 2007).

1.2 Problem statement

β-Tricalcium Phosphate (β-TCP) is one of calcium phosphate compound that frequently used as a bone graft subtitute. It has a higher resorption rate than HA and it is normally considered as a biodegradable materials that allows bone growth and replacement (Han et al., 2009). Thus, β-TCP have an important position among other biomaterials because it is considered to be fully biocompatible with living bodies when replacing hard tissues. TCP bioceramic powders can be synthesized by using several techniques such as direct precipitation or acid-base titration from aqueous solutions that contain calcium nitrate ($Ca(NO_3)_2$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (Sahoo, 2014).

β-TCP can be synthesized by different chemical routes, as reported in the literature including direct precipitation, sol-gel route Oh et al., (2006),

mechanochemical synthesis Kumar et al., (2010) and hydrothermal method Zhang et al., (2009). The various synthesis methods have a varying effect on the particle size, crystallite size, densification behaviour, shrinkage and morphology of final products. Sol-gel method is preferred due to its simplicity of experimental operations, excellent homogenous molecular mixing, comparatively low synthesis temperature, and high yields of pure products (Brinker and Scherer, 2013). Moreover, the high reactivity of the sol-gel powder allows a reduction of processing temperature and any degradation phenomena occuring during sintering (Liu, 2001). But the major limitation of the sol-gel technique application is the high cost of the raw materials and often the precursor formed is extremely moisture sensitive (Nor, 2009).

Previous work have much information on the synthesis and characterization of β-TCP powder, such as the influence of processing parameters to the powder. But so far the study about aging time, low calcination temperature and sintering behaviour of dense β-TCP are less in the literature. Low calcination temperature were rarely being reported and the phase changes were rarely discussed. Nevertheless, still a few study being done investigating on the phase changes in β-TCP powder that were calcined at low temperature. Nor et al., (2009) reported that formation of β-TCP at 600ºC thus indicate formation of β-TCP started at this range of temperature.

Calcination temperature does determine the phase composition as well as morphology of the product. Transformation of HA to β-TCP take places when it is being subjected up to a certain degree of calcination temperature. According to Kokubo, (2008) HA will transform to β-TCP when it is being calcine up to 850ºC. As reported by Ghosh and Sarkar, (2016) increase in calcination temperature will increase the grain growth. A lot of studies regarding β-TCP powder that were subjected to high calcination temperature Mehdikhani et al., (2012), which is above 900ºC providing a

clear information on phase changes but only a few studies available for β-TCP at low calcination temperature. Therefore, calcination process influence the morphological features, chemical and surface properties while sintering process greatly influence the features of final products.

Feng et al., (2005) have shown that cross-linked structures of the molecules would increase as the aging time increase. But further work would required to understand this synthesis parameter via this method. Sintering temperature depends on the composition and crystalline phase of bioceramics, reported by Kokubo, (2008). Densification process will proceed rapidly as sintering temperature increase. As a result, strong chemical bonds are formed. Studies have shown that to densify β-TCP up to 95% calcium pyrophosphate doping is done which also prevents transformation of β-TCP to α-TCP at 1200ºC making it denser (Ryu, 2002). However, the pyrophosphate phase has a harmful effect due to the enlargement of the grain of sintered material which is detrimental to mechanical properties and generates significant cracking.

Thus, the study planned to focus on the synthesis of β-TCP via sol-gel method and fabrication of dense bodies from the synthesized calcined powders. The effect of aging time and calcination temperature on the phase evolution, morphology of the calcined powder are studied. As well as, the various effects on the densification, shrinkage, microstructure of the sintered β-TCP.

1.3 Research objectives

There are two objectives for this research work:

1. To determine the effect of aging time and calcination temperature to the formation of β-Tricalcium Phosphate (β-TCP) phase via sol-gel method.

2. To investigate the effect of sintering temperature to the properties β-TCP pallet.

1.4 Scope of research

This study consists of two stages. First stage, which involved synthesis of β-TCP powder via sol-gel method. The effect of aging time were used: 24 hours and 48 hours was studied while to evaluate the effect of calcination temperature, five temperature were selected, 500ºC, 600ºC, 700ºC, 800ºC and 900ºC and characterized through various characterization method; thermogravimetric-differential scanning calorimetry (TG-DSC) to determine the thermal behaviour of β-TCP powder, X-ray diffraction (XRD) to detect the presence of β-TCP phase, field emission scanning electron microscope (FESEM) to study the morphology of β-TCP powder and fourier transform infrared spectroscopy (FTIR) to identify chemical bonds in a molecule.

The second stage of the research involved optimum parameter which achieved the highest formation of β-TCP from the first stage, pressed into pallet form and proceed with two sintering temperature, 1000ºC and 1100ºC, lastly followed by final characterization and testings.

For characterization and testing of β-TCP pallet, X-ray diffraction (XRD) was used to determine the crystallinity of β-TCP phase. The morphology of sintered pallet was evaluated using field emission scanning electron microscope (FESEM). Simulated body fluid (SBF) test was used to investigate the formation of bone-like apatite layer on the β-TCP surface pallet through in-vitro test. Several testing method including bulk density and porosity test, shrinkage analysis and diametral tensile strength (DTS) test were done to determine the properties of sintered β-TCP pallet.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Looking back at the history, many implantations had failed because of infection or lack of knowledge about the toxicity of the selected materials. However, within last few decades bone repair by bioceramic materials has gained such a popularity as a research subject due to their biocompatible, biodegradable and bioactive properties for bone formation (Karageorgiou and Kaplan, 2005). Bioceramics can be divided into two main groups, which are bioactive and bioinert. Bioactive ceramics provide direct and strong chemical bond with tissues and it is used in the skeletal system for fixation of implants. Among the example would be glass ceramic and dense non-porous glasses. Whereas, bioinert ceramics have the capability to conserve their physical and mechanical properties as they placed in the host. Bone plates, bone screw, and femoral heads are example of typically used as structural-support implants. One of the well-known example is alumina (Al_2O_3); which has been widely used in the femoral head of a hip implant and implant coating (Kokubo, 2008).

Bioceramics have been widely used as implant material, because it is considered to be fully biocompatible with living bodies when replacing hard tissues. This demand for bioceramics as implant material has captured the interest of researchers in the study of calcium phosphates (CaP) materials for tissue engineering. According to Dorozhkin and Epple, (2002) CaP has the same chemical composition that majorly occur human bone. Compund such as tricalcium phosphate ($Ca_3(PO_4)_2$, TCP), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) and calcium tetraphosphate ($Ca_4P_2O_9$) are among calcium phosphate family group with different atomic ratio. Among these

bioceramics, HA and β-TCP are extensively used as they encourage osteogenesis and form tight bonds with bone tissues.

Tricalcium phosphate (TCP) bioceramics powders can be synthesized by using techniques such as wet-precipitation or acid-base titration. Other than that, synthesis techniques such as mechanochemical synthesis and electrochemical deposition, combustion preparation, hydrothermal synthesis and sol-gel procedures have been developed. Among all of the methods stated above, sol-gel synthesis has recently engage a lot of attention, due to advantages for example; high purity product, homogeneous composition and low synthesis temperature.

The purpose of writing this chapter is to provide further understanding about the bone composition, structure and grafting, the chosen bioceramics, classes of calcium phosphate (CaP) and advantages of of β-tricalcium phosphate. This chapter will also elaborate more on the synthesis method of CaP, advantages and drawback of these synthesis method.

2.2 Bone

Bone are living tissue which has its own blood vessels and cell that helps them to grow and recondition itself when subjected to injuries. It also can be defined as a mineralized dense connective tissue which include proteins and vitamins. Among function of bone system are to provide the framework of the body, attaching muscles and tendons, permits movement of our body, manufacture blood cells and protecting our internal organs (Yuan et al., 2017). It is one of a set of vertebrate mineralized tissues that uses some version of calcium phosphate as their mineral.

2.2.1 Bone composition

Bone is a composite of mineral, collagen, non-collagenous proteins, other organics and water. Bone's organic material is about 90% by mass collagen type I. The other organics are various non-collagenous proteins and glycoproteins. The function of these other organis is the subject of intense research. Some of them have biological functions; for instance, bone sialoprotein and bone morphogenetic protein have roles in the intiation and control of mineralization and it has been suggested that a glycoprotein is necessary for the determination of apatite nucleation sites.

Table 2.1: Mineral compositions of bone (Combes et al., 2016)

Element	**Chemical Formula**	**Weight percentage (wt%)**
Calcium	Ca	25
Phosphorus	P	12
Magnesium	Mg	0.37
Potassium	K	0.7
Zinc	Zn	0.009
Copper	Cu	0.0005
Sodium	Na	0.53
Cobalt	Co	0.0000025
Iron	Fe	0.0076
Strontium	Sr	0.05
Carbonates	CO_3^{2-}	5.6