UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF SiO_2-Na_2O-CaO-P_2O_5-CaF_2 BIOGLASS/HYDROXYAPATITE COMPOSITE

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By

NOORFAUZANA BINTI ADNIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fullfillment of the Requirement for the Degree of Doctor of Philosophy

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May 2018

Chairman : Khamirul Amin Matori, PhD
Institute : Institute of Advance Technology

In spite of tremendous applications of bioactive glasses, their low mechanical properties such as low strength and high brittleness have limited their clinical applications as load-bearing implants. To overcome these limitation hence in this study, an alternative approaches proposed is by the development a novel composite of Bioglass (BG) and Hydroxyapatite (HA) via thermal treatment method. However, under such sintering conditions, the poor thermal stability of HA (dehydration and decomposition process) which occurred remarkably should be taken into account, since it declines the mechanical properties of the composite. Therefore, Calcium Fluoride (CaF_2) was incorporate into BG composition to improve the thermal stability of HA. In this research work, the purpose is to investigate the microstructure and mechanical properties and also their relationship of new BG-HA biocomposite with the incorporation of CaF_2 in BG system. Such observation is not documented in the literature in this scope of research since investigations on the microstructure, mechanical properties and also their relationship of based BG have remained pointing only towards the effect of heat treatment and liquid phase sintering (LPS), without considering the role of CaF_2 on the microstructure and mechanical properties of BG-HA composite. In addition, in this study, the observation of parallel relation of microstructure and mechanical properties of the BG-HA composites at each stages of sintering temperature was also elucidated.

SiO_2-Na_2O-CaO-P_2O_5-CaF_2 were prepared by conventional melt quenching method and were mixed with HA through solid state reaction, in proportion of 0, 10, 20, 30 and 40 wt% respectively. Each composition was sintered from 500 to 1000 °C with 50 °C increments. The samples were characterized by Thermal Gravimetric Analysis-Differential Scanning Calorimetry (TGA-DSC), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Field Effect Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (FESEM-EDAX), density, grain size, microhardness and compressive strength measurement. FTIR

analysis showed the evidence of non-bridging oxygens (NBO's) with the increase of the network-modifying species content (CaF_2), which responsible for the decrease in the volume of network structure thus increase the value of density. The XRD analysis indicated that BG with 10 wt% HA content sintered at 800 °C show high thermal stability by the presence of $Na_2Ca_3Si_2O_8$, $Na_4CaSi_3O_9$, $Na_2Ca_3Si_6O_{16}$, HA, FA and with the absence of β-TCP phases. FESEM micrograph illustrated increasing of grain size by the increasing of sintering temperature. The result shows that density, hardness and compressive strength improved from 500-800 °C sintering temperature. However, at 850-1000 °C sintering temperature the density, hardness and compressive strength significantly decreased. Finally, density of 2.95 g/cm^3, hardness of 250 HV and compressive strength value of 103 MPa has been attained for BG with 10 wt% HA content sintered at 800 °C. The superior mechanical strength was attributed to the improved densification by heat treatment, LPS and also by the improvement of HA thermal stability through the incorporation of CaF_2.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

SIFAT STRUKTUR – MIKRO DAN MEKANIKAL KOMPOSIT SiO_2-Na_2O-CaO-P_2O_5-CaF_2 BIOGLASS/HYDROXYAPATITE

Oleh

NOORFAUZANA BINTI ADNIN

Mei 2018

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Walaupun kaca bioaktif mempunyai aplikasi yang menarik, sifat mekaniknya yang lemah seperti sifat kekerasan yang rendah dan kerapuhan yang tinggi telah membataskan aplikasi klinikalnya sebagai implan pembawa beban. Bagi mengatasi had tersebut, pendekatan alternatif yang dicadangkan adalah dengan penyediaan komposit baru iaitu Bioglass (BG) dan Hydroxyapatite (HA) melalui teknik rawatan haba. Walau bagaimanapun, di bawah pembabitan keadaan persinteran, kestabilan haba HA yang rendah (proses dehidrasi dan penguraian) yang belaku secara luar biasa harus dititik beratkan, memandangkan ianya menyebabkan kemerosotan sifat mekanikal komposit tersebut. Oleh itu, Calcium Fluorida (CaF_2) telah diperkenalkan dalam komposisi BG untuk meningkatkan kestabilan haba HA. Penyelidikan ini adalah bertujuan untuk menyiasat sifat struktur mikro dan mekanikal serta hubungan kait antara kedua sifat tersebut terhadap biokomposit BG-HA yang baru melalui pengenalan CaF_2 dalam sistem BG. Pemerhatian ini tiada dalam kesusasteraan bidang penyelidikan ini dan kajian mengenai sifat struktur mikro, mekanik dan juga hubungan kait antara keduanya terhadap BG hanya memberi tumpuan kepada kesan rawatan panas dan persinteran fasa cecair, tanpa mempertimbangkan peranan CaF_2 pada struktur mikro dan sifat mekanikal komposit BG-HA. Di samping itu, dalam kajian ini, pemerhatian terhadap hubungan struktur mikro dengan sifat mekanikal komposit BG-HA pada setiap peringkat suhu persinteran juga diperjelaskan.

SiO_2-Na_2O-CaO-P_2O_5-CaF_2 disediakan melalui kaedah kebiasaan iaitu pencairan pelindap kejutan dan dicampur dengan HA melalui tindak balas keadaan pepejal masing-masing dengan kadaran 0, 10, 20, 30 dan 40 wt%. Setiap komposisi disinter dari 500 hingga 1000 °C dengan kenaikan 50 °C. Sampel tersebut dicirikan oleh Pengukuran Haba Gravimetrik-Kalorimetri Pengesan Berbeza (TGA-DSC), Spektroskopi Inframerah Transformasi Fourier (FTIR), Pembelauan Sinar-X (XRD), Mikroskopi Elektron Pengesan Kesan Medan dan Spektroskopi Penyebaran Tenaga (FESEM-EDAX), pengukuran ketumpatan, saiz butiran, kekerasan mikro dan kekuatan mampatan. Analisis FTIR membuktian kewujudan oxygen yang tidak bersambung (NBO's) dengan peningkatan kandungan spesis rangkaian pengubahsuai (CaF_2), yang bertanggungjawab terhadap pengurangan isipadu struktur rangkaian lalu meningkatkan nilai ketumpatan. Analisis XRD menunjukkan bahawa BG dengan 10 wt% HA yang disinter pada 800 °C mempunyai kestabilan terma yang tinggi dengan pembentukan fasa $Na_2Ca_3Si_2O_8$, $Na_4CaSi_3O_9$, $Na_2Ca_3Si_6O_{16}$, HA, FA tanpa kehadiran fasa β-TCP. Mikrograf FESEM menunjukkan peningkatkan saiz butiran dengan peningkatan suhu persinteran. Keputusan ini menunjukkan bahawa ketumpatan, kekerasan dan kekuatan mampatan meningkat dengan suhu persinteran dari 500-800 °C. Walau bagaimanapun, pada 850-1000 °C ketumpatan, kekerasan dan kekuatan mampatan menurun. Akhirnya, nilai ketumpatan pada 2.95 g/cm^3, kekerasan pada 250 HV dan kekuatan mampatan pada 103 MPa dicapai oleh BG dengan 10 wt% HA, disinter pada 800 °C. Keunggulan kekuatan mekanikal adalah disebabkan oleh peningkatan ketumpatan oleh rawatan haba, sintering fasa cecair serta peningkatan kestabilan haba HA melalui pengenalan CaF_2.

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I certify that a Thesis Examination Committee has met on 7 May 2018 to conduct the final examination of Noorfauzana binti Adnin on her thesis entitled "Microstructural and Mechanical Properties of SiO_2-Na_2O-CaO-P_2O_5-CaF_2 Bioglass/Hydroxyapatite Composite" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

BG	Bioglass
HA	Hydroxyapatite
β-TCP	Beta-tricalcium phosphate
α-TCP	Alpha-tricalcium phosphate
SiO_2	Silicon oxide
CaO	Calcium oxide
$CaCO_3$	Calcium carbonate
Na_2O	Natrium oxide
Na_2CO_3	Natrium carbonate
P_2O_5	Phosphorus pentoxide
CaF_2	Calcium fluoride
BG-HA	Bioglass-hydroxyapatite
LPS	Liquid phase sintering
Ca/P	Calcium/phosphate
OH	Hydroxyl
F	Fluorine
FA	Fluoroapatite
FHA	Fluorohydroxyapatite
Na	Natrium
TCP	Tricalcium phosphate
ZrO_2	Zirconia
Y-TZP	Yitrium-trizirconia phosphate
Mg	Magnesium

CNT	Carbon nanotubes
Co-Cr-Mo	Cobalt-chromium-molybdenum
PVA	Polyvinal alcohol
COL-BG	Collagen-bioglass
Al_2O_3	Aluminium oxide
SPS	Spark plasma sintering
45S5	45 wt% silicate, 24.5 wt% calcium oxide, 24.5 wt% natrium oxide and 6.0 wt% phosphate
SLS	Selective laser sintering
$Ca_2P_2O_7$	Calcium phosphate
H_2O	Water molecule
HA-BG	Hydroxyapatite-bioglass
K_2O	Potassium oxide
ZnO	Zinc oxide
Zn	Zinc
Ca	Calcium
MgO	Magnesium oxide
SrO	Strontium
CAD	Computer-aided design
CPT	Camptothecin
SLS	Soda lime silica
CS	Clam shell
Ti	Titanium
Co-Cr	Cobalt-chromium
C	Carbon

CaP	Calcium phosphate
A-W	Apatite-wollastonite
S53P4	53 wt% silicone oxide, 4 wt% phosphate, 23 wt% natrium oxide and 20 wt% calcium oxide
SiO	Silicone monoxide
HCA	Hydroxycarbonated apatite
MPa	Mega pascal
SiO_4	Silica
NBO	Non bridging oxygens
$Ca_{10}(PO_4)_6F_2$	Fluoroapatite
β-$Ca_3(PO_4)_6$	Beta-tricalcium phosphate
$Ca_{10}(PO_4)_6(OH)_2$	Hydroxyapatite
HIV	Human immunodeficiency virus
BSE	Bovine spongiform encephalopathy
HCl	Hydrochloric acid
P	Phosphorus
pH	Power of hydrogen
Mpa.m	Mega pascal. meter
Cm	Centimeter
N/A	Not applicable
Nm	Nanometer
PO_4	Phosphate
Cl	Chlorine
Co	Cobalt
PO_4^{3-}	Phosphate ion

GPa	Giga pascal
N.mm	Newton millimetre
SrF_2	Strontium fluoride
MgF_2	Magnesium fluoride
NaF	Sodium fluoride
KF	Potassium fluoride
H^+	Hydrogen ion
O^{-2}	Oxygen ion
µm	Micrometer
J	Joule
$Na_2Ca_2Si_3O_9$	Natrium calcium silicate
g	Gram
$Ca_{10}(PO_4)_6O$	Oxygen phosphorite
$CaNaPO_4$	Calcium natrium phosphate
$Ca_3(PO_4)_2$	Calcium phosphate
wt	Weight
rpm	Revolutions per minute
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
FESEM	Field effect scanning electron microscope
HV	Hardness vickers
EDAX	Energy dispersive analysis x-ray
T_g	Transition temperature

T_c	Crystallization temperature
Cu	Copper
Kg	Kilogram
F	Force
N	Newton
ATR	Attenuated total reflection
ZnSe	Zinc selenide
Ge	Germanium
IR	Infrared light

LIST OF SYMBOLS

α	Alpha
β	Beta
wt%	Weight percentage
°C	Degree celsius
$<$	Less than
a, b and c	Lattice parameter
%	Percentage
γ	Specific surface (interface) energy
A	Total surface (interface) area
γA	Total interfacial energy of a powder compact
Δγ	Change in interfacial energy
r_1 and r_2	Radii of curvature
σ	Effective stress on the atoms under the surface
μ	Diffusion potential
Ω	Atomic or molar volume
ϒ	Vacancy
°C/min	Heating/cooling rate
d	Spacing between the lattice planes in the crystals
θ	Angle of diffraction
n	Order of diffraction (an integer)
λ	Wavelength of the x- ray (0.154nm)
W_{air}	Weight of pellet in air
W_{water}	Weight of pellet in water

ρ	Density
ρ_{water}	Density of water (1 g cm^{-3})
ρ_{xrd}	Theoretical density from XRD density
ρ_r	Relative density
P	Amount of porosity
Z	Number of molecules per unit cell
M	Molecular weight of a sample
N_a	Avogadro's number (6.022140857 x 10^{23})
V	Volume of the crystal structure
ρ_{exp}	Experimental density
136°	Interfacial angle of pyramid shape indenter
d_1 and d_2	Average of the two diagonals
a.u	Arbitrary unit
2θ	2 theta degree
Å	Angstrom (10^{-10}m)
(h, k, l)	Miller indexes
(α, β, ϒ)	Angle between lattice parameter in crystal structure
P	Pressure
σ	Compressive strength

CHAPTER 1

INTRODUCTION

1.1 Introduction

In this chapter, the author's motivation for embarking upon research into the specific area is introduced and explained. Background and research topic is presented first, followed by selection of materials, problems statement, objectives of study and outline of the thesis.

1.2 Background of Study

Over the last several decades, an increase in longevity and life expectancy has raised the average age of the world's population. It is projected that by 2050 there will be more than 1 billion people alive on earth aged 60 years old or older (Gunduz and Oktar, 2014). Currently, there are a large number of older people aged at 70 and 80 years old compared to previous years. This improvement may be related to better nutrition and improvement in medical care, improved vaccinations, drugs and water treatment. Moreover, in the light of human life expectancy up to 90 years, the improvements in life care and the increase of accidents, due to sport activities and car accidents, the need for effective and inexpensive biomaterials available to everyone such as those produced from biologically derived HA and BG, is in great demand. This has resulted in an urgent need for improved biomaterials and processing technologies for implants, more so for orthopaedic and dental applications.

Owed to this, implants or transplants can be utilized to preserve human's quality of life due to illnesses disorder and accidents. Bone and joint degenerative and inflammatory problems affect millions of people worldwide. In fact, they account for half of all chronic disease in people over 50 years in developed countries. In addition, it is predicted that the percentage of person over 50 years of age affected by bone diseases will double up by 2020. The number of treated skeletal defiencies steadily increases in a global state. Effective ways for bone replacements and enhancement of bone formation together with research directed to find ideal biomaterials for grating purposes, which will feature biocompatibility and productive simplicity and economy are required.

Medical technologies benefit the lives of people in many ways. Through the use of biomaterial technologies, people can live healthier, more productive and independent life. Many individuals who previously may have been chronically ill, disabled, or suffering chronic pain can now look forward to leading normal or close to normal life. Worldwide health care problem are including defects and functional disorder of bone (Carrington, 2005). With the increasing of aging people and illness, bone repair has turn out to be the main clinical and socioeconomic necessity (Cancedda et al., 2003). Research into novel materials for biomedical applications is ever increasing as the medical community look to improve their way in which disorders and trauma are treated. Many new materials have been developed in an attempt to address these concerns but there are still issues surrounding the appropriateness of their mechanical properties, the ability of degradable materials to retain their properties once implanted and the ability to form the material in situ to the requirements of the surgeon.

1.3 Selection of Materials

To date, with the advancement of medicine, biology and materials science, metal, polymers and natural materials have been utilized as biomedical implant. Nevertheless, some of them are bioinert materials (stainless steel, titanium alloy and aluminium ceramics) which restricted their clinical applications owing to their non-active bond with human tissue (Younger and Chapman, 1989). Therefore, selection of appropriate bioceramics is significantly important. Among various kinds of materials, bioactive ceramics such as BG and HA are considered as the most promising biomaterials, due their ability to form direct bonds with living bone and afterwards implantations in bone defects (Liu, 2012). Consequently, in the previous decades BG and HA has turn into research hotspot for bone repair.

BG ceramics open up new possibilities for medical treatment and constitute a new area of research in the natural science and medicine. Owing to their widely variable combinations of properties, BG ceramics can be more easily adapted to suit medical requirements that can customary implant. BG extensively used in various ways as in replacement of hips, knees, tendons and ligaments due to the appropriate such us compatibility, chemical stability and high wear resistance. Bioactive glass-ceramics are establish to have superior mechanical properties corresponding to bending strength, fracture toughness and young’s modulus, allowing to be used in load bearing applications (Hashmi et al., 2013). Bioactive glass-ceramics has been used successfully in more than 60,000 clinical cases including vertebral replacement and iliac creast repair.

In 2016, a research team from University of Milano-Bicoccu and Imperial Collage of London have developed BG, a material that mimics the properties of natural cartilage and might support its regrowth to benefit persons suffering severe pain due to osteoarthritis. The material can be formulated to be shock absorbent and also imitates the load bearing quality of real cartilage. Engineering synthetic cartilage disc implants from BG would be the alternative to conventional treatment. The BG would act similarly to real cartilage without the need for metal or plastic devices employed at present. These achievements thus demonstrate that it is possible to design bioactive glass-ceramics with improved microstructure and mechanical properties that should be possible to use clinically as load bearing applications. Glass ceramics obtained by sintering process and it is well documented that during the incident of crystallization and densification, the parent glass microstructure’s shrinks, hence reducing the porosity and the solid structure improves in mechanical strength. Brittleness as well as low fracture toughness continues as main problem of these materials. Due to this drawback, bioactive glass is limited in use as implant devices for load bearing applications.

Numerous techniques have been investigated in attempts to improve the mechanical properties of BG ceramics, by formation of BG composites reinforced with other bioactive ceramics which is HA. Owed to it structural and compositional resemblance to the mineralized matrix of natural bone, HA was identified as unique bioceramics for implants, The bone bonding capacity of HA may help cementless fixation of orthopaedic prosthesis. Despite this criteria, it is also known for its simulating effect of bone formation, termed as osteoconductive (Natasha et al., 2011). HA was identified as the ultimate stable calcium phosphate (Sinha et al., 2008) and have been comprehensively studied for its numerous potential in medical applications. The main reason for developing and producing composite materials is to achieve a combination of properties not achievable by any of the elemental materials alone. Approaches to achieving enhanced mechanical properties including the incorporation of CaF_2 into the BG composition. In recent years, increasing interest has been shown in sintering of BG with HA. Such composites come to retain their useful bioactive properties whilst providing more suitable mechanical properties for load bearing application.

1.4 Problem Statement

The enormous progress made in the field of medicine over the past few decades has been partly due to the introduction of new instruments but also a result of the use of new materials. It is impossible to imagine modern medicine without bioceramic materials. BG ceramics open up new possibilities for medical treatment and constitute a new area of research in the natural science and medicine. Owing to their widely variable combination of properties, BG ceramics can be more easily adapted to suit medical requirements that can customize implants. BG on the other hand, exhibit excellent biocompatibility, but their poor mechanical properties (low strength, toughness and high brittleness) are a significant hindrance for load-bearing applications.

Recently, several attempts have been made to combine bioactive glasses with HA of different composition, in order to develop composites with improved mechanical performance. Unfortunately, the production of such composite systems implies in several drawbacks, including decomposition of HA phase/ or reactions between the constituent phases and also crystallization of the original phase, with non-trivial consequences in terms of microstructure and mechanical properties of the final samples. In addition, poor thermal stability of HA in the sintered composite induced a weaker mechanical strength of BG-HA composite as implant for load-bearing applications.

Therefore, research is in development on the preparation, microstructure and mechanical characterization of BG-HA composites and it is essential to prepare new biocomposites using every potential compositional changes and changes of preparation parameter since microstructure and mechanical properties of this composite are identified to be critically influenced by these significant variations. Instead of the influence of sintering temperature and LPS, it is also possible to enhance the microstructure and mechanical properties of the composite by thermal stability improvement of HA through the incorporation of CaF_2 into BG composition. Furthermore, it is expected that the composites have superior microstructure and mechanical properties, could be attributed by sintering the composites at low temperature, and hence much reduces the porosity.

Since there were only little studies on the effect of HA additions on BG composition, the exact role of "CaF_2" incorporation in BG and how it can improve the microstructure and mechanical properties of the composite have not yet been clarified. Moreover, most of the work has been devoted to heat treatment and LPS effect in order to improve the microstructure and mechanical properties, while no reports can be found on the role of CaF_2 in BG-HA composite. Also, in spite of many investigation carried out on BG, investigation concern about the parallel relation of microstructure and mechanical properties of the BG-HA composites at each stages of sintering temperature has not been sufficiently elucidated.

Based on the problem statement, the hypothesis of this research project is the observation of high densification, less porosity and small grain size microstructure would result in the increase of mechanical properties in the samples. Nevertheless, the existence of pores, large and abnormal grain size would deteriorate the microstructure and mechanical properties. The microstructure and mechanical properties would be enhanced due to the sintering at relatively low sintering temperature and the influences of LPS as well as major improvement of HA thermal stability with low tendency of HA thermal decomposition, resulting less formation of pores and small grain size observed in the sample. Another hypothesis of this research project is the observations of microstructure changes would greatly influence the mechanical properties of BG-HA composites at each stage of sintering temperature. It is also expected that the incorporation of CaF_2 would be remarkable in terms of microstructure and mechanical properties improvements for BG-HA composites in this study.

1.5 Objective of Study

In this present research work, five different compositions of SiO_2-Na_2O-CaO-P_2O_5-CaF_2 BG/HA composite with eleven sintering temperatures were performed. The aim of this research is to investigate the microstructure and mechanical properties of novel BG/HA composite with the inclusion of CaF_2 in the BG composition. With the main aim of this research, the following objectives are:

i. To investigate the microstructure properties of BG-HA composites.
ii. To evaluate the mechanical properties of BG-HA composites.
iii. To study the relationship between microstructure and mechanical properties of BG-HA composites.

1.6 Outline of Thesis

This thesis is divided into six chapters. Chapter 1 provides general introduction about biomaterials and also the importance of this significant study in our lives. Chapter 2 reviews related literature which is compulsory to understand the objective of the project. This chapter associates with previous work and gives motivation for the work performed in this thesis. Chapter 3 concentrates on the basic concepts and theory of biomaterials. This chapter focuses more on process, reaction, properties, application and further details about materials involved in this study. Chapter 4 describes the methodology used in the design of the experiments. It also includes the characterization techniques and instruments used in this research field. Chapter 5 present the findings of the study in the order of the specific problem as stated in the problem of statement. This chapter also discussed the significance of the results. Finally, chapter 6 summarizes a brief, generalized statement to answer the general and each of the specific sub-problems and presents an outlook for future work.

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