

**PROPERTIES OF BIOCOMPATIBLE
Mg-Zn/HYDROXYAPATITE COMPOSITES
FABRICATED BY DIFFERENT POWDER
MIXING TECHNIQUES**

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TECHNIQUES**

by

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LIST OF ABBREVIATIONS

Ar	Argon
bm	Ball mill
BPR	Ball-to-powder ratio
DSP	Double step processing
EDX	Energy dispersive x-ray
FESEM	Field emission scanning electron microscope
HCP	Hexagonal closed-pack
HBSS	Hanks' balanced salt solution
MA	Mechanical alloying
MM	Mechanical milling
PM	Powder metallurgy
pm	Planetary mill
Pt	Platinum
OM	Optical microscope
SCE	Saturated calomel electrode
SSP	Single step processing
SSP pm	Single step processing (planetary mill)
SSP bm	Single step processing (ball mill)
XRD	X-ray diffraction

LIST OF SYMBOLS

\AA	Angstrom
2θ	Diffraction angle
E_{corr}	Corrosion potential
e^-	Electron
a, c	Lattice parameter
HA	Hydroxyapatite
HV	Vickers hardness
i_{corr}	Corrosion current density
Mg	Magnesium
nm	Nanometers
Zn	Zinc

**SIFAT-SIFAT KESERASIAN BIO KOMPOSIT Mg-Zn/HIDROKSIAPATIT
DIFABRIKASI MELALUI TEKNIK CAMPURAN SERBUK YANG
BERBEZA**

ABSTRAK

Kajian ini bertujuan untuk mengkaji sifat mekanikal dan biodegradasi komposit magnesium-zink/hidroksiapatit (Mg-Zn/HA) yang difabrikasi melalui teknik-teknik campuran serbuk yang berbeza. Teknik campuran serbuk komposit tersebut dibahagikan kepada dua, iaitu pemprosesan langkah tunggal yang melibatkan teknik pengalioian mekanikal dan pengisaran mekanikal, sementara pemprosesan langkah berganda melibatkan gabungan pengalioian mekanikal dan pengisaran mekanikal. Sifat-sifat mekanikal dan biodegradasi komposit tersebut didapati mencapai tahap terbaik apabila serbuknya dihasilkan melalui teknik pengalioian mekanikal dengan masa pengisaran selama 4 jam dan kelajuan kisaran pada 220 putaran per minit. Komposit yang dihasilkan melalui kaedah pengalioian mekanikal kemudiannya dikisar dengan tempoh yang berbeza untuk mengkaji kesan masa kisaran kepada sifat komposit tersebut. Komposit Mg-Zn/HA yang difabrikasi melalui kaedah pengalioian mekanikal dan dikisar selama 6 jam mempunyai kombinasi terbaik dari segi penambahbaikan pada sifat kakisan dan sifat mekanikal, iaitu kadar kakisan terendah (0.1487 mm/tahun melalui pengutuban elektrokimia dan $0.34 \times 10^{-3} \text{ mm/tahun}$ melalui ujian rendaman) dan kekerasan mikro (64 HV) juga kekuatan mampatan (193 MPa) yang sesuai. Komposit biodegradasi yang difabrikasi melalui teknik pengalioian mekanikal selama 6 didapati sangat sesuai untuk aplikasi implan, berdasarkan kekuatan mekanikal dan ciri-ciri biodegradasi yang baik. Dari segi keserasian bio, secara keseluruhannya komposit Mg-Zn/HA mempamerkan sifat bioaktiviti melalui

ujian rendaman yang dijalankan, namun masa rendaman selama 24 jam didapati tidak mencukupi untuk menghasilkan komposit yang mempunyai bioaktiviti yang dapat memenuhi keperluan pemineralan awal tulang iaitu nisbah Ca:P daripada 1:1 kepada 1:1.67. Namun begitu, komposit Mg-Zn/HA yang dihasilkan melalui kaedah pemprosesan langkah tunggal pengisaran mekanikal (nisbah Ca: P sebanyak 1.76) didapati mempunyai bioaktiviti yang paling tinggi mengatasi komposit-komposit yang dihasilkan melalui kaedah pemprosesan langkah tunggal pengalioian mekanikal dan pemprosesan langkah berganda.

PROPERTIES OF BIOCOMPATIBLE Mg-Zn/HYDROXYAPATITE COMPOSITE FABRICATED BY DIFFERENT POWDER MIXING TECHNIQUES

ABSTRACT

This work aims to investigate the mechanical performance and biodegradation behaviour of magnesium-zinc/hydroxyapatite (Mg-Zn/HA) composite that was fabricated via different powder mixing techniques. The powder mixing techniques of the composite was mainly divided into two, the first one is single step processing which involved the mechanical alloying and mechanical milling techniques, while the second is double step processing which involved the combination of mechanical alloying and mechanical milling. The optimum mechanical properties and biodegradation behaviour of the composite was achieved when the powders were prepared using mechanical alloying technique with the milling time of 4 hours and milling speed of 220 rpm. The composite prepared through the mechanical alloying technique was then subjected to various milling time to investigate the effect of milling time towards the properties of the composite. Mg-Zn/HA composite which was fabricated through the mechanical alloying technique and milled for 6 hours attained the best combination of improved corrosion behaviour as well as mechanical properties which is due to lowest corrosion rate (0.1487 mm/year by electrochemical polarization and 0.34×10^{-3} mm/year by immersion test) and acceptable microhardness (64 HV) and compressive strength (193 MPa). Fabrication of the biodegradable composite through the mechanical alloying technique within the 6 hours milling time was found to be suitable for the implant application, due to good mechanical strength and biodegradation behaviour. In term of biocompatibility, generally Mg-Zn/HA

composite possessed good bioactivity characteristics through the immersion test, however immersion time of 24 hours was found to be insufficient to produce composites that can satisfy the initial bone mineralization which the Ca:P ratio in the range of 1:1 to 1:1.67. However, Mg-Zn/HA composite that was fabricated through single step processing of mechanical milling (Ca:P ratio of 1.76) was found to have the highest bioactivity over the other two composites that was fabricated through single step processing of mechanical alloying and double step processing.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Biomaterials are defined as artificial or natural materials used to replace the lost or injured biological structure, with aims to restore its form and function. It is used in different parts of the human body as stents in blood vessel, artificial valves in heart, replacement implants in knees, hips, elbows, shoulders, ears and orodental structures (Geetha et al., 2009). Along with the advancement in the medical technology, several types of materials such as metals, ceramics, polymers and composites have been extensively utilized for implants into human body (Adeosun et al., 2014).

Biomaterial implants can either be used to replace a diseased part or to promote healing process. Implants are usually divided into two types, degradable or permanent implant, based on how long the implants are required to remain present in human body (Manivasagam et al., 2016). Permanent metallic implants available in the medical market such as titanium alloys, stainless steel 316L and cobalt-chromium alloys always require the implants to stay permanently in the body. In situations where the permanent implant is just required until the healing process is complete, the implant is no longer useful, thus conducting the secondary surgery is crucial to remove the implant (Park & Bronzino, 2003). The development of biodegradable implants clearly can obviate the need of secondary surgery, thus reduces the cost of health care and patient morbidity.

There is a wide variety of biomaterials introduced, mainly ceramics-based, polymers-based and metallic-based. Each of these three classes of materials possess their own unique characteristics to fit into the application of biomaterials. Ceramics-

based biomaterials, such as widely used calcium phosphate-based bioceramics, is acknowledged for its superior bioactivity (an ability of the implant material that allow the adherence and proliferation of bone cells on its surface and pores) and osseointegration (ability of the implant to be structurally and functionally bonded to the living bone (Bose et al., 2012; Parithimarkalaignan & Padmanabhan, 2013). Despite of the qualities of bioceramics, it exhibited poor mechanical properties and brittleness, which is strictly limits their application in load-bearing implants (Ibrahim et al., 2017).

As for polymer-based biomaterials, the major concern is the possibility of local inflammation due to the polymer itself or through its degradation products. The biodegradation and resorption process of the polymer begins once implanted in human body, and the process also caused the acidic by-products to be released, thus results in inflammatory reactions (Sheikh et al., 2015). Inherent poor mechanical properties of polymer and maintaining its mechanical strength until the bone is completely healed also becoming one of the major challenges faced in the researches of polymeric-based biodegradable implants, in addition to design an implant that slowly degrade in body environment (Cheung et al., 2007; Adeosun et al., 2014). These problems caused the application of polymer-based biomaterials to be limited to be used for load-bearing applications. Contrast to metal-based biomaterials, this class possess the sufficient mechanical compatibility, with excellent biocompatibility such as titanium and its alloys, cobalt-based alloys, stainless steels and new generation of biodegradable magnesium. From a perspective of biological, numerous researches reported that more new bone is formed when using bioceramics and magnesium alloys as bone fixation devices compared to polymers. This can be associated to the osteoconductive and osseoinductive of the ceramics and biocompatibility behaviour of magnesium alloys

(Sheikh et al., 2015).

The use of permanent or non-biodegradable metal-based implants such as titanium and its alloys, stainless steels and cobalt-based alloys are very dominant in the medical market due to their excellent mechanical performance and bioinertness. The use of metal-based medical implants can be traced back in 1920's, which stainless steel alloy was used as implant materials owing to its superior corrosion resistance. Since the discovery, researchers starting to focus on developing high corrosion resistant materials for medical application. This was the era of glorious findings of 316L stainless steels, cobalt-based alloys and titanium alloys, which all of the materials were proved to have excellent mechanical properties and also good biocompatibility in human body (Ibrahim et al., 2017). Even though these types of metals are predominant in the orthopaedic market, every materials possess their own advantages and disadvantages. The most highlighted issues associated with the use of these permanent implant are stress shielding problem and the needs of performing secondary surgery to remove the implant after healing process is completed (Chen & Thouas, 2015). These issues quickly becoming the driving forces to the development of new generation of biodegradable metals.

The challenge of developing the biodegradable metals explored three types of most promising metals, such as iron based alloy (Li et al., 2014), zinc based alloy (Mostaed et al., 2016) and magnesium based alloy (Witte et al., 2008; Feyerabend, 2014). The use of biodegradable metal as biomaterials has been discovered since 200 A.D. in Europe, which Fe dental implant was found to be properly integrated into bone (Zheng et al., 2014). Since Fe was reported to experience slower degradation rate based on animal experiments, surgeons have diverts the use of Fe to Mg and its alloy for countless clinical applications, for almost 100 years (Zhen et al., 2013; Li et al., 2014).