UNIVERSITI TEKNIKAL MALAYSIA MELAKA

SYNTHESIS OF HYDROXYAPATITE POWDER FROM EGGSHELL WASTE FOR BIOCERAMIC PURPOSE

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials).

By

NOOR IDAYU AHMAD
B050810110

FACULTY OF MANUFACTURING ENGINEERING

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TOIBAH BINTI ABD RAHIM
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Fakulti Kejuruteraan Pembuatan
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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material) with Honours. The member of the supervisory committee is as follow:

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ABSTRAK

Hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$ telah berjaya dihasilkan dari kulit telur. Ia adalah suatu bahan yang penting dan ia adalah konstituen anorganik tetulang dan gigi. Ia juga digunakan sebagai penggantian injap-injap jantung, sendi-sendi pinggul dan implan lain dalam tubuh badan manusia. Dalam tugas ini, sisa kulit telur digunakan sebagai sumber kalsium supaya menghasilkan serbuk Hydroxyapatite. Sisa kulit telur merupakan sumber yang kaya dengan kalsium pada kuantiti yang banyak dalam industri makanan. Proses ini akan melibatkan pembersihan, pengeringan dan penguraian terma kulit telur yang mengandungi kalsium karbonat ke dalam kalsium oksida. Ia akan dipengaruhi oleh tindak balas hidroterma pada suhu yang rendah. Serbuk HA akan dianalisis dengan menggunakan X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) spektroskopi, Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) dan Particle Size Analyzer. Secara umumnya, proses pemanasan adalah penting untuk membentuk seramik. Walaubagaimanapun , adalah mustahil untuk mengawal permukaan bahan. Dengan menggunakan kaedah hidroterma HA, adalah berkemungkin akan dapat mengawal permukaan bahan dan komposisi kimia. Bahan ini akan sesuai seperti penghasilan tulang dan pembawa untuk sistem penyampaian dadah. Dalam kajian ini, TCP diperolehi ketika dipanaskan pada suhu yang tinggi dengan penghabluran yang meningkat. Spektrum FTIR juga menunjukkan had maksimum HA dipanaskan pada suhu 1000°C di antara 900 cm-1ke 1200. Ini menunjukkan bahawa penghabluran adalah sesuai dipanaskan pada suhu yang lebih tinggi. Pemerhatian mikrostruktur TCP dapat dilihat dengan menggunakan FESEM, zarah halus berbentuk bulat dan semi-bultan dapat dilihat dengan jelas. Saiz zarah serbuk menurun ketika suhu meningkat berbanding dengan persamaan sherrer XRD.

ABSTRACT

Hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$ was successfully produced by using eggshell waste. It is an important biomaterial and is the principal inorganic constituent of bones and teeth. It is also used as the replacement of heart valves, hip joints and other implants in the human body. In this work, eggshell waste is used as the source of CaO in order to produce hydroxyapatite powder. Eggshell waste represents a rich source of calcium is available in huge quantity from food industry. The process involved cleaning, drying and thermal decomposition of eggshell which contain calcium carbonate into calcium oxide. It followed by hydrothermal reaction at low temperature. The synthesized powder was characterized by using X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Field emission scanning electron microscope (FESEM), Thermal Gravimetric Analysis (TGA) and Particle Size Analyzer. In general, sintering process was indispensable to shape the ceramics. However, it is impossible to control the crystal face of materials surface. Using hydrothermal reactions for HA preparation, it is possible to control the crystal face and the chemical composition. This material will be suitable as scaffold for cultured bone and carrier for drug delivery system. In this researched, the TCP was obtained when calcined at high temperature with increase cristalinity. The FTIR spectra also shows the peaks of phosphate bands were observe in the synthesized HA at 1200 up to 900 cm-1. This evolution also indicates good crystallinity for the materials heated at higher temperatures. Microstructure Observation of TCP derived from Eggshell Waste by Using FESEM, fine particles with spherical and semi-spherical shapes were observed. The particle size of powder was decreases when temperatures increases compared with XRD sherrer equation.

DEDICATION

For my lovely family especially my father and my mother that give their support and always with me……….

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LIST OF ABBREVIATIONS

Al_2O_3	-	Alumina Oxide
CaCO3	-	Calcium Carbonate
CaO	-	Calcium Oxide
Ca	-	Calcium
FESEM	-	Field emission scanning electron microscope
FTIR	-	Fourier Transform Infrared spectroscopy,
HA	-	Hydroxyapatite
HCA	-	Hydroxyl Carbonate Apatite
P	-	Phosphorus
TGA	-	Thermo gravimetric analysis
TCP	-	Tri-Calcium Phosphate
UTEM	-	University Technical Malaysia Melaka
XRD	-	X-Ray Diffraction
ZrO_2	-	Zirconia
ºC	-	Celcius
(Sr,Ca) CO_3	-	Strontium Calcium Carbonate
nm	-	nanometer
µm	-	micronmeter

CHAPTER 1

INTRODUCTION

1.1 Background

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH_2)$) is among of the few materials that are classified as bioactive, meaning that it will support bone ingrowths and asseointegration when used in orthopedic, dental and maxillofacial applications. Coating of HA is often applied to metallic implants, especially stainless steels and titanium alloys to improve the surface properties. HA may be employed in form such as powders, porous blocks and hybrid composites to fill bone defects or voids. These may arise when large sections of bone have had to be removed or when bone augmentations are required (e.g. dental applications) (Gergely *et al.* 2010).

HA is a particularly attractive material for bone and tooth implants since it closely resembles human tooth and bone mineral and has proven to be biologically compatible with these tissues. Since HA was applied for first time in 1981 for periodontal lesion filling, its use in the medical field has expanded to solid blocks, solid components and films for dental implants. Many studies have shown that HA ceramics show no toxicity, no inflammatory response, no pyrogenetic response, no fibrous tissue formation between implant and bone, and the ability to bong directly to the host bone (Ibrahim *et al.* 2006).

The properties of HA can be influenced by control of particle size, chemical composition and morphology and can be synthesize by a variety of methods such as hydrothermal methods, sol gel method, hydrolysis methods, wet methods and etc. In the hydrothermal methods, the synthesis conditions consist of the application of high temperature and pressure to aqueous solutions to induce the precipitation of well crystallize apatite's. The hydrothermal method is becoming one of the most tools for advanced materials processing, particularly owing to its advantages in the processing (Earl *et al*. 2006).

Several methods of chemical synthesis have been developed to produce HA powder from various natural sources such as eggshells, seashells (Gergely *et al*. 2010), cockle shell, body fluids (Gergely *et al*. 2010) and many more. All these natural sources represents a rich of calcium in preparing the HA powder. An eggshell is constituted, structurally speaking, by a three layers structure, namely the cuticle, spongeous layer and lamellar layer. The cuticle layer represents the outermost surface and it consists of a number of proteins. Spongeous and lamellar layers form a matrix constituted by protein fibers bonded to calcite (calcium carbonate) crystals in the proportion of 1:50 (Rivera *et al*. 1999).

In this research project, hydrothermal process is used to produce hhdroxyapatite powder into a highly pure any crystalline state from calcium carbonate that contains in the eggshell waste. It is a simple method, inexpensive and easy to be carried out.

1.2 Problem Statement

Previously, the synthesize HA in terms of structure, composition, crystalline, solubility, biological reactivity and other physical and mechanical properties and focus to produce HA with suitable chemical, physical and biological properties that can be apply in the biomaterial application. Considering the numerous applications of HA in biomedical fields, development of various synthesis methods is a major issue now and obviously, a simple cost effective procedure is highly desirable to the researchers. A number of synthesis techniques using various sources of calcium (Ca) and phosphorus (P) are develop which includes hydrothermal method, wet chemical method, thermal deposition and solid state reaction.

However, among these methods, hydrothermal is short synthesis time, easiness of controlling silica or metal ratio, possibility of continuous synthesis (Sayari, A. and Jaroniec, M. 2008). Depending on the feeding egg shell contains about (94-97) % $CaCO_3$ while rest of the percentage is organic matter and egg pigment. Egg shell is a waste material after the usage of egg. Hence, utilisation of egg shell will benefit in two ways: which are egg shell derivated HA will be cost-effective bioceramic material for biomedical applications, and the second one is utilisation of egg shell will be an effective material-recycling technology for waste management (Samina, A. and Mainul, A. 2008).

1.3 Objective of the Research

The aim of this research is to produce hydroxyapatite biomaterial with adequate strength, high purity good physical properties and biocompatibility. The main objectives of this study are:-

i. To synthesize hydroxyapatite using eggshell via hydrothermal method.
ii. To conduct physical and chemical characterization on the synthesized powder using Field emission scanning electron microscope (FESEM), Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD) and Particle size analyzer.

1.4 Scope of Study

In general, the research was being described in more detail in Chapter 3. It is to studied and synthesized HA powder by using hydrothermal method from eggshell waste material. This technique is selected due to the simple process, availability of the equipments and also easily adjustable parameters with potentially good results. In this research, the effect of stirring speed and calcinations condition will be studied. The amount of carbonate addition is varied in order to study the formation of carbonate in carbonated hydroxyapatite, while pH and temperature are maintained at constant value. The characterization of the product powders are carried out using XRD, FTIR, FESEM , TGA and the Particle size analyzer.

CHAPTER 2
LITERATURE REVIEW

2.1 Biomaterials

A biomaterial is a non-viable materials used in a medical devices intended to interact with biological systems. They may be distinguished from other materials in that they possess a combination of properties, including chemical, mechanical physical and biological properties that render them suitable for safe, effective and reliable use within a physiological environment (Williams, 1987). Put simply it is a non-living (non viable) which is intended to have close contact with biological tissue which has appropriate mechanical and physiological properties for its application (i.e. meets the required strength and safety for its usage). Biomaterials are used in many of today's medical devices, including, artificial skin, artificial blood vessels, total artificial hearts, pacemakers, dental fillings, wires plates and pins for bone repair, total artificial joint replacements.

The success of biomaterials in the body depends on factors such as the material properties, design and biocompatibility of the material used. Biocompatibility involves the acceptance of an artificial implant by the surrounding tissues and the body as whole (Park and Bronzino. 2003). The compatibility characteristics which may be important in the function of an implant device made of biomaterials include adequate mechanical properties such as strength, stiffness and fatigue and biological characteristics of the material (Schwartz *et al*. 1999). Biomaterials can be broadly categorized under the four categories which are metal, polymer, ceramic, and composite. Each material have their own benefits. Metallic biomaterials have mechanical reliability that other class of biomaterials could not succeed. Ceramic biomaterials have excellent biocompatibility while implanted in the body. On the other hand, polymer biomaterials are easy to manufacture to produce various shapes with reasonable cost and desired mechanical and physical properties. Composite biomaterials offer a variety of advantages in compare to homogeneous materials (Lakes, 2003). The advantages and disadvantages of each category of biomaterials are briefly explained in Table. 2.1.

2.2 Classification of Biomaterials

The general classification of biomaterials, which finds immense applications in the field of medicine are given as follows:

i. Metals and alloys
ii. Polymers
iii. Composites
iv. Glass and ceramics

Sometimes, a single material mentioned above cannot fulfill the complete requirements imposed for specific applications. In such case, combinations of more than one material are required (Rejendran, 2009).

Table 2.1: Class of materials used as biomaterials (Park and Lakes, 2007).

Materials	**Advantages**	**Disadvantages**	**Examples**
Polymers (nylon, silicone, rubber, polyester, etc)	Resilient, easy to fabricate	Not strong, deforms with time, may degrade	Sutures, blood vessels, other soft tissues, hip Socket
Metals (Ti and its alloys, Co-Cr alloys, Au, Ag, stainless steel, etc)	Strong, tough, ductile	May corrode, dense, difficult to make	Joint replacements, dental root implants, bone plates and screws
Ceramics (alumina, zirconia, calcium phosphates including hydroxyapatite, carbon)	Very biocompatible	Brittle, not resilient, weak in tension	Dental and orthopaedic implants
Composites (carbon-carbon, wire- or fiber-reinforced bone cement)	Strong, tailor-made	Difficult to make	Bone cement, dental and resin

2.2.1 Metals and Alloys

Metals were among the first orthopedic biomaterials and are commonly used to this day. Currently, most orthopedic implants are made from either stainless steel, titanium or one of its alloys, or a cobalt-chrome alloy, although tantalum and nitinol metals have also been used (Herman, 2010).

2.2.2 Polymers

Most of the biodegradable polymeric products on the market are made from only a few polymers, many of which were first used in sutures. The most common suture materials are the polylactic and glycolic acid polymers and copolymer, the trimethylene carbonate copolymers and polydioxanone. The advantages of the biodegradable polymeric products include the following, they disappear, so long-term stress shielding is not a concern; there are no long-term device or materials problems and no second operation is required for removal. The biodegradable polymeric products can be used for drug delivery (Herman, 2010).

2.2.3 Composites

The use of composite technology has led to a wide range of new biomaterials, namely, biocomposite materials that offer a great promise to improve the quality of life of many people. The ceramic materials alone do not possess the required mechanical properties of the artificial materials to replace natural bone. Therefore, in order to increase the strength of the artificial material, reinforcement (bioactive glass) to matrix (polymer) leads to biocomposite materials. The stiffness of the biocomposite materials is very close to that of bone and hence, finds wide applications in industries.

A hydroxyapatite-polyethylene composite has been developed for use in orthopedic implants. The material knits together with bone, maintains good mechanical properties and can be shaped or trimmed during surgery using a scalpel (Herman, 2010).

2.2.4 Glass and ceramics

Bioactive glasses and glass ceramics have occupied an important role as bone repairing materials in the medical field. This is possible as they provide a compatible chemical and mechanical environment for bone tissue attachment. All bioactive glasses and glass ceramics bond with the living bones through the formation of apatite layer which is formed on the surface of the living bones. The surface forms a biologically active hydroxyl carbonate apatite (HCA) layer, which provides the bonding interface or biocompatibility with natural tissues. Therefore, the essential condition required for an artificial material to bond with the living bone is the formation of the apatite layer on its surface in the body. Materials such as glasses, glasses ceramics, metals, polymers and composite cements can form the HCA layer and hence, bond with living and are known as bioactive materials (Rajendran, 2009).

2.3 Bioceramics

Bioceramics are produced in a variety of forms and phases and serve any different functions in repair of the body. In many applications ceramics are used in the form bulk materials of a specific shape, called implants, prostheses, or prosthetic devices. Bioceramics are also to fill space while the natural repair processes restore function. In general, bioceramics show better biocompatibility with tissue response compared to polymer or metal biomaterials (Hench and Wilson, 1993). Based on their excellent biocompatibility, they are used as implants within bones, joints and teeth in the form of bulk materials of specific shape. They are also used as coatings on a substrate or in conjunction with metallic core structure for prosthesis (Desai *et al.*2008). In other situations the ceramics is used as a coating on a substrate, or as a second phase in a composite, combining the characteristics of both into a new material with enhanced mechanical and biochemical properties. Ceramic structures can also be modified with varying porosity for bonding with the natural bones (Hench and Wilson, 1993).

Bioceramics are made in many different phases. They can be single crystals (Sapphire), polycrystalline (Alumina or HA), glass (Bioglass), glass-ceramics (glass-ceramic), or composites (polyethylene-HA). The phase or phases used depend on the properties and function required. For example single crystal sapphire is used as a dental implant