EVALUATION OF HYDROXYAPATITE (HA) FROM WASTE EGGSHELL STRENGTHENED WITH ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) BY USING INJECTION MOLDING PROCESS

THOUFEILI BIN TAUFEK

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Faculty of Mechanical and Manufacturing Engineering
Universiti Tun Hussein Onn Malaysia

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DEDICATION

To my beloved parents, Taufek Bin Omar and Mazura Binti Nasaruddin. My siblings, Tasha Erina Binti Taufek and Tirmidzi Bin Taufek. Last but not least, to my endless support from Saidatul Naseha Uyaina Binti Arshad and also to my fellow homies, The Yantra.

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ABSTRACT

This research presents the capability of the waste eggshell as a part of material improvement for the biomedical purpose. Hydroxyapatite ceramics (HA) has been investigated because of its excellent biocompatibility and tissue bioactivity properties. HA from the waste eggshell has been extracted under the calcination process and Tri-Calcium Phosphate (TCP) has been added to the eggshell solution. For the biomedical purposes, some standard should be met in order to implant certain material inside human body. Therefore, this research followed the standard of stoichiometric which has been set by US Food and Drug Administration (FDA) , due to its similarity with the mineral constituents of human bones and teeth which is Ca/P=1.67. HA was analysed under Energy-Dispersive Analysis X-ray system (EDX) in order to investigate the mineral constituent. The HA then was mixed with UHMWPE inside the brabender plastograph machine to form a feedstock. In order to support the process ability of injection molding, the flow ability of the feedstock during injection molding process should be in pseudoplastic form where the viscosity decreased when the shear rate increased [64]. The Taguchi's Method has been used as the Design of Experiment (DOE) in order to get suitable parameters for injection molding process when HA/UHMWPE were used as a feedstock. In this study, injection temperature, injection pressure, injection time and holding time have been investigated. It was found that, the result from Taguchi's Method, the optimized parameter for injection temperature, injection pressure, injection time and holding time were 220˚C, 0.6MPa, 7s and 5s respectively. Mixture of HA/UHMWPE again have been analysed by using EDX test and also obtained the value of stoichiometric Ca/P=1.71. The value of flow behaviour, *n* for each composition are less than 1. Hence, it showed that it was pseudoplastic.

ABSTRAK

Kajian ini mengkaji tentang keupayaan sisa kulit telur sebagai sebahagian daripada bahan penambahbaikan bagi tujuan biomedik. Hydroxyapatite ceramics (HA) telah dikaji oleh kerana kehebatannya di dalam biokompatibiliti dan sifat bioaktiviti terhadap tisu manusia. HA daripada sisa kulit telur telah diekstrak melalui proses pengkalsinan dan Tri-Calcium Phosphate (TCP) telah dicampurkan ke dalam campuran kulit telur. Bagi tujuan-tujuan biomedik, beberapa piawaian harus dicapai untuk memasukkan beberapa bahan ke dalam badan manusia. Oleh itu, kajian ini telah mengikut piawaian stoikiometri yang telah ditetapkan oleh US Food and Drug Administration (FDA), disebabkan kesamaannya dengan konstituen mineral bagi tulang dan gigi manusia iaitu Ca/P=1.67. HA telah dianalisa melalui Energy-Dispersive Analysis X-ray system (EDX) bagi mengenal pasti kandugan mineral. HA tersebut telah dicampurkan dengan UHMWPE di dalam mesin brabender plastograph untuk membentuk pengisi. Bagi membantu proses pengacuan suntikan, kebolehan aliran pengisi semasa pengacuan suntikan hendaklah berada dalam keadaan pseudoplastik dimana tahap kelikatan menurun apabila kadar ricih meningkat [64]. Kaedah Taguchi telah digunakan sebagai reka bentuk kajian bagi mendapatkan parameter yang sesuai untuk digunakan semasa proses pengacuan suntikan dimana HA/UHMWPE digunakan sebagai pengisi. Dalam kajian ini, suhu penyuntikan, tekanan suntikan, masa suntikan dan masa pegangan telah dikaji. Berdasarkan hasil kajian daripada kaedah Taguchi, parameter yang telah dioptimumkan bagi suhu penyuntikan, tekanan suntikan, masa suntikan dan masa pegangan adalah masing-masing bernilai 220˚C, 0.6MPa, 7s dan 5s. Campuran HA/UHMWPE telah dianalisa sekali lagi dengan menggunakan ujian EDX dan juga telah memperoleh nilai stoikiometri Ca/P=1.71. Nilai sifat aliran, *n* bagi setiap komposisi adalah kurang dari 1. Maka, ia menunjukkan bahawa ianya adalah pseudoplastik.

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LIST OF SYMBOLS AND ABBREVIATIONS

FDA	-	Food & Drugs Administration
UHMWPE	-	Ultra High Molecular Weight Polyethylene
HA	-	Hydroxyapatite
CAD	-	Computer Aided Design
ASTM	-	American Society for Testing and Materials
HDPE	-	High Density Polyethylene
SEM	-	Scanning Electron Microscope
EDS	-	Energy Dispersive X-ray Spectroscopy
XRD	-	X-Ray Powder Diffraction
TGA	-	Thermogravimetric Analysis
DSC	-	Differential Scanning Calorimetry
JCPDS	-	Joint Committee on Powder Diffraction Standards
DOF	-	Design of freedom
Ca	-	Calcium
P	-	Phosphorus
FDM	-	Fused deposited machine
SF	-	Sisal fiber
GF	-	Glass fiber

LIST OF EQUATIONS

CHAPTER 1

INTRODUCTION

1.1 Research background

Injection molding is an important process in plastic industry, because of its high production rate and cost effectiveness. It can also produce complicated shape. Injection molding process is a process where molten plastic material is being injected at high pressure into a mold that will give a final product shape. Injection molding can produce a variety of products from the very tiny wire spools, bottle caps, to larger products such as car bumpers and even medical devices including plastic syringe and container. Powder Injection Molding (PIM) exhibits superior benefits to other conventional manufacturing techniques. PIM is a sustainable and rapidly advancing technology that is suitable for metals and ceramics and characterized by 3-D structure, dimensional accuracy, and cost-effective operational requirements [1]. Many attentions were directed towards the development of polymer composites for load-bearing orthopedic applications. The advantage of using a composite material for such application is due to the fact that by varying the amount and type of reinforcing material such as hydroxyapatite (HA), the mechanical and biological properties can be tailored for the specific application. Furthermore, the low processing temperature of the composites prevent phase and compositional changes of the HA. The issue to be highlighted here is to explore the potential of using hydroxyapatite (HA) as ceramic filler for biomaterial composite in injection molding process. This is by the fact that the earth has tons of eggshell (ES) being disposed every day and believe these waste can be converted into more valuable industrial products. These ES will end up as the waste product, therefore it is beneficial if the ES could be recycled. Among the wide choice of polymer matrices that have been widely promoted, ultra-height molecular weight polyethylene (UHMWPE) and its composites have been highlighted as having the potential for such application. UHMWPE is a high performance thermoplastic which is said to be associated with high performance devices, structural and load-bearing materials [2]. It is best suited for medium mechanical duties in water, oil hydraulics, pneumatics, and unlubricated applications. It has a good abrasion resistance but it is better suited for soft mating surfaces. In addition to its superior mechanical properties, UHMWPE also have other functional properties suitable for biomedical applications because UHMWPE are low friction coefficient, high resistance to wear, high impact resistance, high ductility and stability in the body [3]. Use of UHMWPE as a composite matrix has not achieved much success due to difficulties in processing. It's extremely high molecular weight makes it difficult to process by conventional thermoplastic processing techniques [4]. Furthermore, dispersion of HA particles in UHMWPE has been a serious challenge due to the high viscosity of UHMWPE.

1.2 Problem statement

Nowadays, people do not see any benefit that can be found in waste ES and they just throw it away until it becomes wastage. Waste ES contains HA that can be used for biomedical application such as dental, orthopaedic and surgery. In this study, the calcination process has been used as method to extract the ES. Failing to extract HA from the ES will affect the valuable trace ions which play a crucial role in the bone regeneration process and also known to speed up the bone formation process [5]. It has been established that HA must meet the minimal requirements described by the US Food and Drug Administration (FDA). By not following the FDA standard, it can affect the bioactivity and also the durability of the material inside the human body. By not selecting the right method on how to extract HA from the ES, different value of stoichiometric such as crystallinity and calcium phosphorus ratio (Ca/P ratio) will affect the mechanical properties of the implant such as cohesive and bond strenght of the implant [6]. As for UHWMPE and HA, the absorption between melts and the wall of the die is very strong. Moreover, UHMWPE also has a high molecular weight and very tight chain entanglement. Thus, a marked pressure vibration and unusual flow of their melts by extrusion will occur and it will affect the processablity during the injection molding process [7]. A large standard deviation indicates inhomogeneous feedstock mixing, which can result in density gradients within the molded part and causing distortions. Lastly, for the parameters of the injection molding, the injection temperature, injection pressure, injection time and holding time plays an important role for the process. Failing to optimize those parameters will gives defect on the sample after the injection molding process.

1.3 Objectives

The objective of this research are;

i. To extract HA from waste eggshell by using calcination process.
ii. To obtain the value of stoichiometric near to Ca/P = 1.67 in order to meet the standard requirement by US Food and Drug Administration (FDA).
iii. To investigate the flowability between HA and UHMWPE.
iv. To optimize the injection molding parameter by using Taguchi Method.

1.4 Scopes of research

i. Calcination method that has been used to extract hydroxyapatite powder from the raw ES.
ii. The Ca/P ratio of extracted HA from waste ES have been investigated under Energy Dispersive X-Ray Spectroscopy (EDX) test.
iii. The flowability of the feedstock has been investigated under capillary rheometer.
iv. The parameters for injection molding process consist of injection temperature, injection pressure, injection time and holding time when HA/UHMWPE as a feedstock have been investigated under Design of Experiment. Taguchi's Method has been selected.

1.5 Significant of research

Bioactive apatite, such as HA, [$Ca_{10}(PO_4)_6(OH)_2$] has been extensively investigated for biomedical applications due to its excellent biocompatibility and tissue bioactivity properties. Its bioactivity provides direct bonding to the bone tissue, therefore promotes rapid bone growth that has particular benefit to orthopaedic and dental applications. Due to its similarity in chemical composition to the inorganic matrix of bone, HA is widely used as implant materials for bone. Unfortunately, because of its poor mechanical properties, this bioactive material is not suitable for load bearing applications. On the other hand, composite blending with a polymeric material such as UHMWPE introduces new improvement possibilities, hence the mechanical and biological properties of bio-composites can be tailored to meet specific clinical requirements. Furthermore, the use of UHMWPE as a composite matrix has been explored with various fillers, such as carbon and metals. This study is intended to explore the potential of using waste-derived hydroxyapatite ceramic composite as biomedical material, where it can contribute to the sustainability of the earth and reduces the environmental pollution.

CHAPTER 2

LITERATURE REVIEW

Nowadays, the development of new biomedical material for an orthophaedic implant in human body have been explored widely. Orthophaedic implant is one of biomedical applications that many researchers tend to study their functional and possibility to help tissues and bone growth in human body. Implant is a kind of medical process where the ideology is to replace or substitute the missing biological structure inside human body. In order to make a part for biomedical applications, some of the standards by Food and Drugs Administration (FDA) must be followed in order to ensure the biomedical materials used for orthopaedic implant can be considered as biocompatible inside human body. Some materials used for orthophaedic implant such as titanium alloy, stainless steel and metal cannot help the bone growth and also for the tissues regeneration. Due to the limitations as stated before, researchers have found a new way to invent a new technology where the ceramic powder has been used for implant. Due to the organic behavior of certain materials that can help the bone growth and also the tissues development, powder injection molding (PIM) has been used in order to produce parts that can contribute to biomedical purposes. During mixing, ceramic powder is blended with binders to form a homogeneous compound. Furthermore, binders provide viscosity to the powder, thereby simplifying the process of filling feedstock into molds during injection molding process [8]. Many types of binder have been tested for biomedical purposes such as high density polyethylene (HDPE), polyethylene glycol (PEG) and also polypropylene (PP). Despite the substantial effort made in studying PE and PP binders. Their usage often leads to processing issues such as insufficient initial pore formation and weak internal transport mechanisms within the green parts [9].

In this chapter, a review of the concept of PIM process by using injection molding and its cycle, and also the process of injection molding that have been made by researches before, which include the PIM parameters. Besides that, this chapter discuss about the rheological behavior HA/UHMWPE acts as a feedstock for injection molding process in order to find the information about the suitable parameters by using the theory of Taguchi's method.

2.1 Powder injection molding (PIM)

Powder injection molding (PIM) is an efficient method for the high volume production of shaped components from powders. PIM is a derivative of ceramic injection molding and it uses much of the same technology, along with batch sintering processes used in powder metallurgy and ceramic processing. The methods for PIM similar to metal injection molding (MIM) which compatible for the making of syntactic foams made from high-melting point like steel [10]. The process is cost effective and also have near net-shape forming process of small intricate and precise part [11]. PIM includes four processing stages including mixing, injection molding of the feedstock, debinding, and sintering. Among the four processing steps, the sintering process is the most important because it affects the final quality of the parts including the final density, mechanical, and chemical properties [12]. Furthermore, some of the research are using the magnetic PIM process. On the other hand, the magnetic PIM process enables a high precision replication of a magnetic part and producing the geometrical complexity or microscale structures [13]. This technology can be directly applied to relevant manufacturing industries for production and commercialization of micro magnetic parts. On the other hand, PIM also gives benefit to good economy growth around the world. Because of the near net shape and the material from the wastage can be used as a feedstock in order to produce parts from PIM process, it will contribute to the environment by using the recycle materials from wastage. While there are many micro electro mechanical system (MEMS) related products in the automotive sector, the biomedical branch shows the largest amount of growth and the greatest potential for further increases [14]. Thus, it will affect the economy growth of the world in a good way. Lastly, PIM lets the fast cycle time and low cost production of small-sized complex components consistently with high dimensional accuracy [15].

2.2 Binder

Binder is one of the most important part in injection molding process. Binder must have a characteristic to incorporate with fine metal or ceramic powder. For metal injection molding process, partially water-soluble binder system with surfactant addition was used to mix with either stainless steel 316L or yttriastabilized zirconia nano-powder to form feedstock to avoid the agglomeration of fine powder and environmentally hazardous organic binder [16]. Thian et al. [17], produced HA/Ti6Al4V composite using PIM with commercial binder. Results showed that some of the cracks and void are observed on certain places. One of the objective in PIM is to get reasonable strength after the process for some applications, thus the selection of binder have to be chosen wisely. Polyoxymethylene (POM) is an engineering polymer that has also found applications as a binder material in powder injection moulding (PIM), which is a versatile mass production method for small, complex shaped components of metal or ceramic. According to Gutierrez, J. N. et al. [18] in PIM, PIM acts as a carrier medium for metal or ceramic powders during the injection moulding process and it is later removed to obtain a metallic or ceramic piece after sintering. The main advantage of PIM in powder injection moulding comes from the instability of acetal linkages, which results in rapid hydrolysis. Lastly, having a suitable binder system is a major factor in obtaining feedstock with good rheological properties and good mechanical properties in the final products. According to Thavanayagam, G. et al. [19], in general, a binder system is composed of at least three components: a backbone polymer that retains the shape of a moulded part during debinding and sintering, a low viscosity polymer that gives the feedstock suitable viscosity and which can be easily extracted during solvent debinding, and an additive that improves wettability of powder particles. Thus, a good binder system must have good flow characteristics, be comparatively low cost, have good interactions with metal powders, enable easy debinding, and easily disposed for the benefit of environment.

2.3 Powder

Powder in injection molding is used to produce from small component to complex component by using PIM. In recent years, with the development of computer aided design and computer aided manufacturing technologies (CAD/CAM), all ceramic systems have been widely interested and the limitation on producing complex geometry can be reduced. From the investigation made by He, J. et al. [20], stated that TZ- 3YS-E zirconia obtained a sintering density of 6.05 g·cm^3 and a hardness of 1300 HV0.5 with a small fluctuation sintered at 1475℃. This is due to the homogeneity in the region away from gate was superior to the nearer gate region based on evaluation of density, hardness, flexural strength and observation of microstructure, as well as the simulation of the mold filling of the feedstock. According to Radulović, J. [21], a good overall property profile usually have good processing characteristics, high dimensional stability, high rigidity and good warm strength. It makes polyacetals that preferred material in demanding applications. The advantage of this material in the molding phase can also be utilized in the powder injection molding. Other than that, the size of HA powder and density also have been investigated by Salleh, F. M. et al. [22], stated that particle size of the calcined HA powder in agglomeration flake shape was measured using the Malvern particle size analyser. The distribution on the particle size and density for the HA powder average is 5.3 μm and 3.3008 g/cm^3, respectively. The fabrication of HA/Ti6Al4V composite using PIM is rarely reported. HA/Ti6Al4V composite using PIM with commercial binder showed that some of the cracks and void are observed on certain places. In the sintered part, cracks that originate from the Titanium (Ti) particles are formed, which is attributed to the varying thermal expansions, thereby inducing residual stress on the composite [23]. The effects of powder characteristic, solid loading, debinding atmosphere and heating rate on the compact deformation affected by particle size, irregular particle shape and high solid loading and the distortion in PIM products. According to Mukund, B. N. et al. [24], based on the results of tolerance control and compact distortion in tensile, rectangular, disc shaped and complex shape specimens 68 vol.% was selected as the optimum loading.

2.4 Feedstock

PIM engages mixing stages of either metal or ceramic powder with binder to produce a feedstock. During injection moulding stages, the feedstock flows into the mold cavities under pressure to form a green part. The binders have two main roles that provide feedstock fluidity and strength in holding powder particle together until the sintering process. According to Salleh, F. M. et al. [25], palm stearin (PS) binder have been carried on its capability to provide capillary route for an ease of processing and shape retention, the contamination effects of PS to the part, and feasibility of PS binder to produce Ti-6Al-4V/HA composite part. Rheological characterization was performed to evaluate the flowability of the feedstocks for injection molding and the feedstocks exhibited a pseudoplastic behavior which is suitable for injection molding process. According to Jamaludin, M. I. et al. [26], selected metal powder at certain size (µm) and binders are mixed together at appropriate volumetric ratio to synthesize a homogenous feedstock. Binder system plays a main role to provide lubrication during injection molding flow by uniformly coating the metal powder and filling all gaps between the powder particles. Other than that, it is important to predict the flow behavior of feedstock otherwise poor flowability and high viscosity lead toward molding defects. Thus, lower value of flow behaviour index is desirable to produce the complex geometry parts because of high degree of shear sensitivity of feedstock. In turn, higher value of flow behaviour index exhibits the better rheological stability of feedstock and provides a good retention of shape of parts [27]. One of the representative problems in the PIM process is powder binder separation which arises from various phenomena, including the spatially different shear rates and viscosities of feedstock. According to Park, D. Y. et al. [28], changes in flow direction during injection molding also lead to powder binder separation, because the powder and binder with high and low densities are separately accumulated due to the different centrifugal forces induced by the difference in density. Thus, the powder binder separation results in various defects, such as distortion or cracking. During debinding or sintering, inhomogeneously distributed powder in a green part leads to non-uniform densification caused by the anisotropic shrinkage during sintering.

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