INVESTIGATION ON THE PHYSICAL PROPERTIES OF MAGNESIUM FEEDSTOCKS FOR METAL INJECTION MOULDING

by

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LIST OF ABBREVIATIONS

2C-PIM	Two Color Powder Injection Molding
AAHDPE	Acrylic Acid Grafted High Density Polyethylene
CBVC	Critical Binder Volume Concentration
CPVC	Critical Powder Volume Concentration
DSC	Differential Scanning Calorimetric
ECAP	Equal Channel Angular Pressing
HDPE	High Density Polyethylene
HIP	Hot Isotactic Pressing
MFR	Melt Flow Rate
Mg	Magnesium
Mg-Ca	Magnesium Calcium Alloy
MIM	Metal Injection Molding
MIM-SH	Metal Injection Molding-Space Holder
PEG	Polyethylene Glycol
PF	Powder Forging
PGA	Polyglycolic Acid
PIM	Powder Injection Molding
PLA	Polylactide Acid
PM	Powder Metallurgy
PS	Palm Stearin
PVT	Pressure-Volume-Temparature
PW	Paraffin Wax

SA	Stearic Acid
SEM	Scanning Electron Micrograph
TGA	Thermal Gravimetric Analysis
TTQ	Totalized Torque
UPM	Ultrasonic Powder Machine
UTM	Ultimate Tensile Machine
Vol.%	Volume Percent
WP	Waste Plastic
WR	Waste Rubber
Wt.%	Weight Percent
XRD	X-Ray Diffraction
ZS	Zinc Stearate
K	Constant indicating the viscosity of the melt flow

LIST OF SYMBOLS

E_a	Flow Activation Energy
T_b	Beginning Temperature
ρ	Density
Q	Flow Rate
Q_b	Activation energy for Diffusion/Dissolution
P	Force
E_{frict}	Friction Energy
R	Gas Constant
H	Homogeneity
H_o	Initial Mixture Homogeneity
R^2	Linear Correlation Coefficient
m	Mass
M	Mean
α	Moldability Index
η_o	Reference Viscosity
η_r	Relative Viscosity
γ	Shear Rate
n	Shear Sensitivity/ Flow Index/ Power Law Index
τ	Shear Stress
T_a	Softening Temperature
E_{sp}	Specific Energy

c_{feed}	Specific Heat
s	Speed
ψ	Surface Area per Volume Ratio
T_{oh}	Temperature Overheat
η	Viscosity
V	Volume
w	Weight
E_t	Work Energy
σ	Yield Strength

Siasatan Terhadap Sifat-Sifat Fizikal Bahan Mentah Magnesium untuk Suntikan Logam Beracuan

ABSTRAK

Magnesium dan aloinya didapati amat bioserasi dan mempunyia sifat-sifat yang serupa dengan tulang semulajadi. Ini menjadikan mereka sebagai bahan yang menarik untuk bahagian-bahagian yang terbiodegredasi seperti implan bioperubatan. Memandangkan implan-implan bioperubatan adalah kecil dan berbentuk rumit, teknik pengacuanan suntikan logam (MIM) dilihat sebagai amat sesuai untuk bahagian-bahagian yang mempunyai bentuk hampir dengan produk akhir. Kajian ini mengkaji tentang sifat-sifat fizikal bahan mentah magnesium untuk proses penyuntikan acuan logam. Kajian terperinci bagi kelakuan bahan mentah yang telah dijalankan adalah termasuk penentuan muatan kritikal, kinetik pencampuran, pembelajaran reologi, sifat-sifat magnesium teracuan, penyahikatan larutan, dan pensinteran. Pengikat yang digunakan dalam kajian ini adalah lilin parafin (PW), sterin sawit (PS), asid sterik (SA), stearate zink (ZS), polietilena berketumpatan tinggi (HDPE), sisa getah (WR), dan sisa plastik (WP). Kepekatan kritikal isipadu serbuk (CPVC) ditentukan melalui ujian serapan minyak pada suhu bilik. Dalam kajian ini, sifat-sifat dan kelakuan reologi bagi bahan mentah magnesium untuk penyuntikan acuan disiasat dengan menggunakan reometer kapilari. Selepas suntikan pengacuanan, ketumpatan, kekuatan hijau dan morfologi bahagian yang diacuankan telah dinilai menggunakan konsep ketumpatan Archimedes, ujian pembengkokak 3 titik, dan mikrograf pengimbasan elektron (SEM). Kesan masa dan suhu larut lesap terhadap proses penyahikatan larutan bagi bahagian yang telah diacuan disiasat. Dalam proses ini, molekul-molekul bagi lilin parafin dan asid sterik disingkirkan daripada magnesium teracuan dengan kaedah merendam ke dalam larutan heptana. Kemudian, kadar penyahikatan larutan disiasat di bawah keadaan yang berbeza seperti masa, suhu, dan nisbah luas permukaan terhadap isipadu. Peratusan kadar kehilangan jisim bagi lilin parafin dan asid sterik dikira dan struktur pori-pori dianalisa menggunakan SEM. Proses pensinteran telah dijalankan dalam 2 kitaran iaitu kitaran penyahikatan dan kitaran pensinteran. Untuk kitaran penyahikatan, suhu yang digunakan adalah 450 ºC dengan kadar pemanasan 1K/min dan masa rendaman adalah 1 jam. Manakala bagi kitaran pensinteran suhu yang ditetapkan adalah 640 ºC dengan kadar pemanasan 5K/min selama 8 jam. Keputusan CPVC yang diperolehi adalah 69 vol.% dan muatan serbuk optimum adalah 65 vol.%. Keputusan reologi menunjukkan bahawa bahan mentah magnesium berkelakuan pseudoplastik dan mencadangkan bahawa bahan mentah yang mengandungi PWPEWPSA dalam sistem pengikatnya sebagai bahan mentah yang terbaik. Suhu yang optimum adalah 60 °C dengan masa rendaman 360 minit. Kemeresapan efektif adalah tinggi bagi peringkat pembubaran berbanding peringkat penyebaran. Tenaga pengaktifan pembubaran adalah sekitar 3-5 kali lebih tinggi berbanding tenaga pengaktifan penyebaran. Ketumpatan bahagian tersinter yang diperolehi adalah 1.134 g/cm^3.

Investigation on the Physical Properties of Magnesium Feedstocks for Metal Injection Moulding

ABSTRACT

Magnesium and its alloy are found to be extremely biocompatible and have similar properties to natural bone. This makes them an attractive material for the manufacture of biodegradable parts such as biomedical implant. As biomedical implants are rather small and complex in shape, the metal injection moulding (MIM) technique seems to be well suited for the near net shape mass production of such parts. This research investigated the physical properties of the magnesium feedstocks for metal injection moulding process. The detail study on the feedstocks behavior was conducted including critical loading determination, mixing kinetics, rheology study, green molded properties, solvent debinding process, and sintering. The binder used in this study were paraffin wax (PW), palm stearin (PS), stearic acid (SA), zinc stearate (ZS), high density polyethylene (HDPE), waste rubber (WR), and waste plastic (WP). The critical powder volume concentration (CPVC) of Mg powder was conducted using oil absorption test at room temperature. In this study, the rheological properties and behaviors of magnesium metal injection moulding feedstock was investigated using capillary rheometry. After injection moulding, the density, strength, and morphology of the green molded part was investigated using Archimedes density concept, 3 point bending test, and scanning electron micrograph, respectively. The effect of the leaching time and temperature on the solvent debinding process of Mg metal injection moulding (MIM) green part has been investigated. In this study, both soluble binder, paraffin wax and stearic acid molecules were removed from the Mg green part by immersing compact parts in heptane solution. Then, the solvent debinding rate has been investigated under the conditions of different leaching time, temperature, and surface area to volume ratio. The weight loss percentages of paraffin wax and stearic acid were calculated and the pores structure was analyzed by scanning electron micrograph. The effective diffusivity and activation energy of the soluble binder have also been studied. Sintering process has been carried out in 2 cycles which are debinding cycle and sintering cycle. For debinding cycle, the temperature was 450 °C with heating rate 1K/min and soaked for 1 hour. While the sintering cycle was set at 640 °C with heating rate of 5K/min and sintered for 8 hours. The result obtained for CPVC was 69 vol.% and the optimum powder loading was at 65 vol.%. The rheological results exhibited the pseudoplatic behavior and suggested feedstocks containing PWPEWPSA in the binder system as the best feedstocks. The optimum temperature was 60 ºC with immersion time of 360 minutes. Effective diffusivity was higher at dissolution stage as compared to diffusion stage. The dissolution activation energy (Q) was about 3-5 times higher than diffusion activation energy. The density of obtained sintered part was 1.134 g/cm^3.

CHAPTER 1

INTRODUCTION

1.1 Metal injection moulding

Metal injection moulding (MIM) is a process by which powder is shaped into complex components using tooling and injection moulding machines that are very similar to those used in plastic injection moulding. MIM combines the versatility and high productivity of the injection moulding with the powder metallurgy technique of sintering (German and Bose, 1997). Then, since the sintering of a compacted powder is alike for a part obtained by injection or press moulding, the key points in MIM turned out to be how to make the metal flow into the mold and how to retain the shape of the molded part until it begins the sintering. The problem is commonly solved by dispersing the powdered metal into a binder to form a paste that flows at high temperature and becomes room temperatures. Consequently, the molded part retains its shape after injection moulding and may be handled and processed safely.

In MIM process, the metallic powders are injected into a mold. Plasticity and fluidity of the powder is essential for this to take place and this is achieved by the use of binder material. All binder systems are based on two important major groups of ingredients, polymers and waxes with minor additions of lubricants, surfactants or coupling agents. After injection moulding, the binders are then removed in a process known as debinding and the remaining “brown” part is then sintered at elevated temperatures to achieve a densified parts (Sidambe et al., 2012).

Homogeneous feedstock is produced from an appropriate mixture of metal powder and an ideal binder system. Up to now, there are various binder systems have been developed for use in practice of the MIM such as wax (Weich, 1983) thermoplastic (Lin et al., 1990), thermosetting-based binder (Strivens, 1960), solid polymer solution (SPS), and water based system (Anwar et al., 1995; German and Bose, 1997). Development of a new binder system is not an easy task, therefore, a good understanding of binder attributes and the associated powder characteristics are very critical. Since MIM is still new in Malaysia, the opportunity to further develop this method is very promising (Subuki, 2010).

This process begins by mixing selected powders and binders. The mixture is then granulated and injection molded into the desired shape. The polymer imparts viscous flow characteristics to the mixture to aid forming, die filling and uniformity of packing. After moulding, the binder is removed and the remaining powder structure was sintered. The product may then be further densified, heat treated, or machined to complete the fabrication process. The sintered products has the desirable complex shape and high precision as plastic injection moulding but is made of materials capable of performance levels unattainable with pure or filled polymers.

1.2 Magnesium development

Magnesium has high potential as a biomedical part. The critical advantage of Mg is its biodegradability. After a patient's injuries have healed, additional surgery for the removal of an implant could be avoided. Thus, both inconvenience and risk for the patient, as well as costs, can be reduced significantly. Standard implant materials such as titanium or stainless steel still suffer from stress shielding problems, causing bone desorption and implant loosening. On the other hand, degradable polymers, such as polyglycolic acid (PGA) or polylactide acid (PLA), are less suitable for load bearing applications due to their inferior mechanical properties. In contrast, novel Mg-Ca alloys show material properties matching those of cortical bone and are able to degrade fully into nontoxic elements essential for the human body (Wolff et al., 2012). Nevertheless, biomedical magnesium alloy require appropriate mechanical properties, suitable degradation rate in physiological environment, and what is most important, biosafety to human body (Li & Zheng, 2013). Metal Injection Moulding (MIM) possesses a high potential for the economic production of such implants. Moreover, the MIM processing route enables the establishment of both nearly dense as well as porous structures, helpful for tissue in-growth into the degrading implant (Osseo integration).

Interestingly, the density of Mg is slightly less than natural bone which ranges from 1.8 to 2.1 g/cm^3, while the elastic modulus of pure magnesium is 45 GPa and human bone varies between 40 and 57 GPa (Razavi et al., 2010; Feng & Han, 2010; Li et al., 2004). However, the conventional processing of magnesium is limited by multi manufacturing steps and their complexity contributes to significantly higher cost of the final product. The economy factor represents the downside of many non-conventional manufacturing techniques such as powder metallurgy. Thus, there is a continuous quest for a technology that would allow reducing cost and at the same time improving the properties application (Czerwinski, 2008).

1.3 Problem statement

In recent day, magnesium and its alloy are found to be extremely biocompatible and have similar properties to natural bone. This makes them an attractive material for