



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

by

**NOORAIZEDFIZA BINTI ZAINON  
(1240510802)**

A dissertation submitted in fulfillment of the requirements for the degree of  
Doctor of Philosophy

**School of Material Engineering  
UNIVERSITI MALAYSIA PERLIS  
2018**

## ACKNOWLEDGEMENT

Alhamdulillah, thanks to God Almighty for His blesses and strength that He has gave me to finish my research. Even though I had faced many challenges during my research that make my research progression becomes low as well as my motivation. However, thanks to Allah S.W.T and Prophet Muhammad S.A.W, finally I got strength to move on and capable to complete my research and thesis.

This thesis was dedicated to my late supervisor, Almarhumah Associated Professor Ir. Dr. Salmah Hussein Shah for her supervision over this work. Her encouragements and guidance have always helps me to grow in knowledge and passion for my study. I would like to express my deepest gratitude to my main and co supervisor, Dr. Rozyanty binti Rahman and Dr. Mohd Afian bin Omar for inputs and assistance in helping me to complete this research. I would like to take this opportunity to express my appreciation to the Dean of School of Materials Engineering, PM Dr. Khairul Rafizi Ahmad and Dean of School of Manufacturing Engineering, PM Dr, Khairul Azwan Ismail for their support in this study. My sincere thanks go to my friends and colleagues in School of Manufacturing Engineering and SIRIM AMREC for their supports and constructive discussions that aided me throughout the research. To Universiti Malaysia Perlis, I extend my gratitude for providing all the facilities and opportunity for me to pursue my doctoral degree.

Last but not least, I would like to thank my family members for their unfailing love and moral supports. They have never ceased to encourage me and motivate me all the time. Finally, I want to express my appreciations to my beloved family for their love and encouragement. Thanks you very much for supporting me every step of the way.

## TABLE OF CONTENTS

	<b>PAGE</b>
<b>THESIS DECLARATION</b>	i
<b>ACKNOWLEDGEMENT</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF FIGURES</b>	ix
<b>LIST OF TABLES</b>	xiv
<b>LIST OF ABBREVIATIONS</b>	xvi
<b>LIST OF SYMBOLS</b>	xviii
<b>ABSTRAK</b>	xx
<b>ABSTRACT</b>	xxi
<b>CHAPTER 1: INTRODUCTION</b>	
1.1 Metal injection molding	1
1.2 Magnesium development	2
1.3 Problem statement	3
1.4 Objectives	5
1.5 Novelty and Significant of the study	6
1.6 Scope of work	6
1.7 Structure of Dissertation	7
<b>CHAPTER 2: LITERATURE REVIEW</b>	
2.1 Introduction to Magnesium	9
2.1.1 Magnesium is Biomaterials	12

2.2	Powder Metallurgy	13
2.3	Background and Key Trend of Metal Injection Molding	14
2.4	Detail Process Outline	16
2.5	Powder Characteristics	18
2.6	Binders for Metal Injection Molding	20
2.7	Feedstocks Characterization	27
2.7.1	Critical Volume Powder Concentration and Optimum Loading by Torque Rheometry.	28
2.7.2	Flow Characteristics: Rheology as a Function of Shear Rate, Temperature, and Particle Attributes	31
2.8	Mixing	34
2.9	Injection Molding	36
2.9.1	Molding Parameters	38
2.10	Debinding Process	40
2.11	Sintering	43
2.12	Common Defects in Metal Injection Molding	44
2.13	The Differences of Current Process and Metal Injection Molding	48
2.14	Recent Development of Metal Injection Molding Material and Technology	49
2.15	Current Fabrication Method on Magnesium Parts	57
2.16	Potential Metal Injection Molding in Producing Magnesium Parts	57
2.17	Present Application and Future Opportunities for Magnesium Processing	59
2.18	Advantages and Limitations of Metal Injection Molding	61
2.19	Summary of literature reviews	64

## **CHAPTER 3: METHODOLOGY**

3.1	Flow of the Methodology	67
3.2	Material Characterization	69
3.2.1	Metal Powder	69
3.2.2	Binder	69
3.3	Critical Powder Volume Concentration (CPVC) and Optimal Loading Determination	71
3.3.1	Oil Absorption Test	71
3.3.2	Mathematical Models	72
3.3.3	Torque Measurement	73
3.4	Feedstocks Preparation	75
3.4.1	Composition and Variation of Formulation	75
3.5	Feedstock Characterization	79
3.5.1	Torque Rheometry	80
3.5.2	Capillary Rheology	80
3.5.3	Injection Molding	84
3.5.4	Properties Characterization of the Green Molded Parts	85
3.5.5	Solvent Debinding	87
3.5.6	Scanning Electron Microscopy (SEM)	90
3.6	Sintering	91
3.6.1	Density and porosity analysis	92
3.6.2	Morphology analysis	93

## **CHAPTER 4: RESULTS AND DISCUSSIONS**

4.1	Material Characterization	94
4.1.1	Metal Powder	94

4.1.2	Binder Constituent	97
4.1.2.1	Paraffin Wax (PW)	98
4.1.2.2	Palm Stearin (PS)	100
4.1.2.3	High Density Polyethylene (HDPE)	101
4.1.2.4	Waste Rubber (WR)	103
4.1.2.5	Waste Plastic (WP)	104
4.1.2.6	Stearic Acid (SA)	106
4.1.2.7	Zinc Stearate (ZS)	107
4.2	Critical Powder Volume Concentration (CPVC) and Optimal Loading	108
4.2.1	Oil Absorption Test on the Magnesium Powder	108
4.2.2	Relative Viscosity	112
4.2.3	Torque evolution curves for different powder loading	113
4.2.4	Torque Measurements on the Magnesium Feedstocks	115
4.2.5	Feedstocks Morphology	116
4.3	Rheology Properties of the Feedstocks at Different Powder Loading	118
4.3.1	Effect of shear rate on the Feedstocks Rheology	120
4.3.2	Yield stress of the Feedstocks	125
4.3.3	Melt Flow Rate (MFR) of the Feedstocks	127
4.3.4	Effect of temperature on the Feedstocks Rheology	128
4.3.5	Moldability index of the Feedstocks	133
4.4	Effect of Different Wetting Agent in the Binder Systems	134
4.4.1	Torque evolution curves of the Feedstocks Prepared with Different Wetting Agent	134
4.4.2	Capillary Rheometer test for the Feedstocks Prepared with Different Wetting Agent	137

4.4.3	Activation energy of the Feedstocks Prepared with Different Wetting Agent	142
4.4.4	Moldability index of the Feedstocks Prepared with Different Wetting Agent	146
4.5	Effect of Different Additives in the Binder Systems	148
4.5.1	Torque evolution curves of the Feedstocks Prepared with Different Additives	149
4.5.2	Capillary Rheometer test for the Feedstocks Prepared with Different Additives	152
4.5.3	Activation energy of the Feedstocks Prepared with Different Additives	160
4.5.4	Moldability index of the Feedstocks Prepared with Different Additives	162
4.6	Effect of Different Backbone Polymer in the Binder Systems	162
4.6.1	Torque evolution curves of the Feedstocks Prepared with Different Backbone Polymer	162
4.6.2	Capillary Rheometer test for the Feedstocks Prepared with Different Backbone Polymer	165
4.6.3	Activation energy of the Feedstocks Prepared with Different Backbone Polymer	170
4.6.4	Moldability index of the Feedstocks Prepared with Different Backbone Polymer	172
4.7	Summary of the Results for Rheology	173
4.8	Injection Molding of PWPEWPSA Feedstocks	175
4.8.1	Defect Occurs During Injection Molding	176
4.8.2	Density of the Molded part	180
4.8.3	Strength of the Molded part	182
4.8.4	Morphology of the Molded Part on Outer Surface and Fracture Surface	183
4.9	Solvent Debinding of the PWPEWPSA molded parts	185
4.9.1	Solvent Debinding Mechanism	187

4.9.2	Effect of Temperature and Immersion Time on the Solvent Debinding Rate	189
4.9.3	Effect of Surface Area to Volume Ratio ( $\psi$ ) on the Solvent Debinding Rate	193
4.9.4	Diffusion and Dissolution Stages Evaluation during Debinding	195
4.9.5	Activation Energy for Diffusion and Dissolution Stages during Debinding	198
4.9.6	Microstructure of Brown Parts	200
4.10	Sintering of PWPEWPSA Brown Parts	202
4.10.1	Morphology of the Magnesium Part Sintered at Various Temperature	202
4.10.2	Density and porosity of PWPEWPSA Sintered Parts	207
4.11	Summary of Chapter 4	207
<b>CHAPTER 5: CONCLUSION AND FUTURE WORK</b>		
5.1	Conclusion	211
5.2	Future Work	212
<b>REFERENCES</b>		213
<b>LIST OF AWARDS</b>		229
<b>LIST OF PUBLICATIONS</b>		230
<b>APPENDIX A</b>		231
<b>APPENDIX B</b>		232
<b>APPENDIX C</b>		233
<b>APPENDIX D</b>		234
<b>APPENDIX E</b>		235
<b>APPENDIX F</b>		236

## LIST OF FIGURES

NO.		PAGE
2.1	Schematic diagram of metal injection molding.	18
2.2	Comparison in torque rheometers of homogenous and inhomogeneous feedstock.	36
2.3	Real/possible applications of biodegradable magnesium implants summarized by Chen et al (2014). (a) Cardiovascular stents, Germany; (b) MAGNEZIX screw, Europe; (c) microclip for laryngeal microsurgery; (d) biodegradable orthopedic implants; (e) wound closing devices.	61
3.1	Flow of the methodology.	67
3.2	The dimensions of the green molded part that need to be recorded.	86
3.3	Diagrammatic of solvent debinding.	88
3.4	Sintering profile for Mg feedstocks.	91
3.5	Set up of the sample for the sintering process.	92
4.1	The morphology of the magnesium powder.	95
4.2	The distribution of powder particle size	95
4.3	EDS image of the powder particles	96
4.4	Distribution composition chart for magnesium powder	97
4.5	DSC curve for paraffin wax.	99
4.6	DTG curve for paraffin wax.	99
4.7	DSC curve for palm stearin.	100
4.8	DSC curve for HDPE.	102
4.9	TGA curve for HDPE.	103
4.10	DTG curve for waste rubber.	104
4.11	The DSC curve for waste plastic.	105
4.12	TGA curve for waste plastic.	106

<b>NO.</b>		<b>PAGE</b>
4.13	DSC curve for stearic acid.	107
4.14	Mixing torque versus time at the various levels of oleic acid addition of Mg feedstock.	110
4.15	Torque and temperature of Mg feedstock for different oleic acid volume.	111
4.16	Torque evolution curve of Mg feedstock at different powder loading.	114
4.17	SEM observation of Mg feedstock with different formulation (a) F1, (b) F2, (c) F3, d) F4, and (e) F5.	117
4.18	Softening and beginning temperature of Mg feedstocks.	119
4.19	The viscosity versus shear rate of Mg feedstock at (a) T= 120 °C, (b) T= 130 °C, and (c) T=140 °C.	122
4.20	Log viscosity versus log shear rate of Mg feedstocks at different temperature (a) T= 120 °C, (b) T= 130 °C, and (c) T= 140 °C.	124
4.21	Shear stress versus shear rate of Mg feedstocks at 140 °C.	126
4.22	MFR for Mg feedstocks as a function of temperature at different powder loading.	128
4.23	Ln viscosity versus absolute temperature of Mg feedstock with different loading at shear rate of 1000 s <sup>-1</sup> .	129
4.24	Determination of powder loading region.	131
4.25	Torque evolution curves during compounding of Mg feedstocks with different wetting agent at various formulation.	135
4.26	Average on mixing torque for different wetting agent.	137
4.27	Average deviation on mixing torque for different wetting agent.	137
4.28	Log shear stress versus log shear rate of Mg feedstocks prepared with different wetting agent for 65 vol% powder loading at different temperature.	139
4.29	Log viscosity versus log shear rate of Mg feedstocks prepared with different wetting agent for 65 vol% powder loading at different temperature.	141

<b>NO.</b>		<b>PAGE</b>
4.30	Ln viscosity versus absolute temperature of Mg feedstocks with different wetting agent at various powder loading under fixed shear rate.	143
4.31	Correlation of activation energy and powder/binder content of Mg feedstocks.	146
4.32	Moldability index of Mg feedstocks containing different wetting agent in the binder system at different temperature.	148
4.33	Torque evolution curves during compounding the Mg feedstocks prepared with different additive components.	150
4.34	Average on mixing torque for Mg feedstocks prepared with different additive components.	151
4.35	Average deviation on mixing torque for Mg feedstocks prepared with different additives.	152
4.36	Log shear stress versus log shear rate of Mg feedstock prepared with different additive component for 65 vol.% powder loading at different temperature.	153
4.37	Log shear stress versus log shear rate of Mg feedstocks prepared with different additive components at temperature 140 °C.	154
4.38	Log viscosity versus log shear rate of Mg feedstocks prepared with different additive components for 65 vol.% powder loading at different temperature.	156
4.39	Log viscosity versus log shear rate of Mg feedstocks prepared with different additive components at temperature 140 °C.	157
4.40	Ln viscosity versus absolute temperature for Mg feedstock with different additive components at various powder loading under fixed shear rate (1000 s <sup>-1</sup> ).	159
4.41	Moldability index of Mg feedstocks containing different additive components in the binder system at different temperature.	161
4.42	Torque evolution curves during compounding the Mg feedstocks prepared with different backbone polymer.	163
4.43	Average on mixing torque for Mg feedstock prepared with different backbone polymer.	164
4.44	Average deviation on mixing torque for Mg feedstock prepared with different backbone polymer.	165

<b>NO.</b>		<b>PAGE</b>
4.45	Log shear stress versus log shear rate of Mg feedstocks prepared with different backbone polymer for 65vol.% powder loading at different temperature.	166
4.46	Log shear stress versus log shear rate of Mg feedstocks prepared with different backbone polymer for various powder loading at temperature 140 °C.	167
4.47	Log viscosity versus log shear rate of Mg feedstocks prepared with different backbone polymer for 65vol.% powder loading at different temperature.	168
4.48	Log shear stress versus log shear rate of Mg feedstocks prepared with different backbone polymer for various powder loading at temperature 140 °C.	168
4.49	Ln viscosity versus absolute temperature of Mg feedstocks with different backbone polymer at various powder loading under fixed shear rate (1000 s <sup>-1</sup> ).	169
4.50	Moldability index of Mg feedstocks containing different backbone polymer in the binder system at different temperature.	173
4.51	Green molded part.	176
4.52	Flow mark defect.	178
4.53	Powder/binder separation defect.	178
4.54	Shrinkage on the green molded parts at different dimensions for various powder loading.	180
4.55	Graph of density of green molded parts for various powder loading.	181
4.56	Scanning electron micrograph of fracture surface and outer surface of green molded parts containing different powder loading.	184
4.57	The schematics of solvent debinding process.	188
4.58	The relation of extracted temperature and immersion time on the amount of binder extracted ( $\psi = 1.01$ ).	190
4.59	Temperature influence on the debinding rate for molded parts with different surface area to volume ratio.	191
4.60	Defects occurs during solvent debinding at 80 °C.	192

<b>NO.</b>		<b>PAGE</b>
4.61	Total soluble binder extracted at temperature of 60 °C.	194
4.62	Schematics of the solvent pathway in the molded part during early stage of debinding process for a) $\psi = 0.95$ , b) $\psi = 1.01$ , and c) $\psi = 1.03$ .	195
4.63	Variation of $\ln(1/F)$ with immersion time over square of shape factor at different temperature as a function of surface area to volume ratio (a) $\psi = 0.95$ , (b) $\psi = 1.01$ , and (c) $\psi = 1.03$ .	197
4.64	The plots of $\ln$ diffusion coefficient versus absolute temperature Mg molded parts.	199
4.65	The SEM on fracture surface of Mg molded parts as a function of extraction time (a) $t = 10$ minutes, (b) $t = 60$ minutes, (c) $t = 180$ minutes, (d) $t = 360$ minutes.	201
4.66	Fracture surface of the Mg part after sintering at 450 °C.	203
4.67	Fracture surface of the Mg part after sintering at 550 °C.	203
4.68	Fracture surface of the Mg part after sintering at 640 °C.	204
4.69	Two sphere sintering model for mass transport mechanism (a) initial point of contact, (b) surface transport mechanism, and (c) bulk transport mechanism.	206

## LIST OF TABLES

NO.		PAGE
2.1	Properties of pure magnesium.	10
2.2	The physical and mechanical differences between bone and metals.	12
2.3	Defects frequently found in molding.	46
2.4	Defects frequently found in debinding process.	47
2.5	Comparison of MIM attributes with other fabrication techniques.	49
2.6	The potential components in automotive sector.	59
3.1	Mathematical model developed by several researchers.	73
3.2	Compounding conditions of the feedstocks based on different wetting agent in the binder system.	76
3.3	Compounding condition of the feedstock with different additives in the binder system.	77
3.4	Compounding condition of the feedstocks prepared with different backbone polymer.	78
3.5	Injection molding parameter.	84
4.1	Characteristics of magnesium powder.	96
4.2	Characteristics of the binders.	98
4.3	Torque recorded at each addition of oleic acid.	110
4.4	The relative viscosity of the Mg feedstocks.	113
4.5	Torque rheology parameter of Mg MIM feedstock.	116
4.6	The flow behavior index ( $n$ ) of the Mg feedstocks at temperature of 140 °C.	125
4.7	Yield stress of Mg feedstocks at 140 °C.	127
4.8	Values of $\eta_0$ , $E_a$ , and $R^2$ of Mg feedstocks with different powder loading at shear rate of 1000 s <sup>-1</sup> .	130

<b>NO.</b>		<b>PAGE</b>
4.9	Moldability index value for Mg feedstocks at reference shear rate of $1000\text{s}^{-1}$ .	132
4.10	The weight of the components in the Mg feedstocks.	133
4.11	The values of $n$ and $K$ of Mg feedstocks prepared with different wetting agent.	142
4.12	The value of $\eta_0$ , $E_a$ and $R_2$ for WPESA and SPESA Mg feedstocks.	144
4.13	The weight of the components in the Mg feedstocks.	149
4.14	The values of $n$ and $K$ for Mg feedstocks with different additive components.	158
4.15	The values of $\eta_0$ , $E_a$ , and $R_2$ for WPESA and WPPEZN Mg feedstocks.	160
4.16	The weight of the component in the Mg feedstocks.	162
4.17	The values of $n$ and $K$ of Mg feedstocks containing HDPE, HDPE/WP, and HDPE/WR as a backbone polymer.	169
4.18	The values of $\eta_0$ , $E_a$ , and $R_2$ for feedstocks with HDPE, HDPE/WP and HDPE/WR as a backbone polymer.	171
4.19	The summary of flow behavior index, activation energy, and moldability index of Mg feedstocks at various formulation.	174
4.20	The dimensions of the green molded parts for various powder loading.	179
4.21	The density, porosity and density reduction for the green molded parts.	181
4.22	The 3 point bending test results of molded parts with various powder loading.	182
4.23	The density, volume, and surface area to volume ratio of the molded parts for different powder loading.	186
4.24	Efficient diffusivity of the soluble binder at different temperature.	198
4.25	The activation energy of the Mg molded part at dissolution and diffusion stage.	199

## 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	Poly lactide Acid
PM	Powder Metallurgy
PS	Palm Stearin
PVT	Pressure-Volume-Temperature
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

©This item is protected by original copyright

## LIST OF SYMBOLS

$E_a$	Flow Activation Energy
$T_b$	Beginning Temperature
$\rho$	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
$\alpha$	Moldability Index
$\eta_o$	Reference Viscosity
$\eta_r$	Relative Viscosity
$\gamma$	Shear Rate
$n$	Shear Sensitivity/ Flow Index/ Power Law Index
$\tau$	Shear Stress
$T_a$	Softening Temperature
$E_{sp}$	Specific Energy

$c_{feed}$	Specific Heat
$s$	Speed
$\psi$	Surface Area per Volume Ratio
$T_{oh}$	Temperature Overheat
$\eta$	Viscosity
$V$	Volume
$w$	Weight
$E_t$	Work Energy
$\sigma$	Yield Strength

©This item is protected by original copyright

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

### ABSTRAK

Magnesium dan aloinya didapati amat bioserasi dan mempunyai sifat-sifat yang serupa dengan tulang semulajadi. Ini menjadikan mereka sebagai bahan yang menarik untuk bahagian-bahagian yang terbiodegradasi 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 diacuan 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 °C dengan kadar pemanasan 1K/min dan masa rendaman adalah 1 jam. Manakala bagi kitaran pensinteran suhu yang ditetapkan adalah 640 °C 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. Kemerresapan 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<sup>3</sup>.

# 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 pseudoplastic behavior and suggested feedstocks containing PWPEWPSA in the binder system as the best feedstocks. The optimum temperature was 60 °C 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<sup>3</sup>.

## 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 ingrowth 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<sup>3</sup>, 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