

SIMULATION AND EXPERIMENTAL CHARACTERIZATIONS OF  
POLYVINYL ALCOHOL-CASSAVA STARCH COMPOUND FOR INJECTION  
MOULDING APPLICATION

LEE TIN SIN

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Polymer Engineering)

Faculty of Chemical Engineering  
Universiti Teknologi Malaysia

OCTOBER 2010

## ACKNOWLEDGEMENT

First of all, the author would like to express his sincere gratitude to his parents for their unlimited support. Next, the author would also like to take this opportunity to thank his supervisors, Assoc. Prof. Dr Wan Aizan Wan Abdul Rahman and Assoc. Prof. Dr Abdul Razak Rahmat for their guidance, advice and knowledge imparted to the author throughout the course of doing this study. The authors are grateful for financial support from Ministry of Science, Technology and Innovations by Federal Government of Malaysia-Putrajaya under eScience Fund 03-01-06-SF0468 and the National Science Fellowship 1/2008. A very special thank to Assoc. Prof. Dr Zhao-Yan Sun from the State key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, China for providing the free-of-charge service of testing some of the samples. Last but not least, the author would like to express his genuine gratitude to all friends for their motivation, endless cooperation and the friendships that has been built for the past few years. Thank you.

## ABSTRACT

Polyvinyl alcohol (PVOH) blends with *cassava* starch (CSS) is a biodegradable polymer compound. This polymer compound is suitable to be used as biodegradable material to reduce the accumulation of synthetic petroleum-based polymer solid wastes. In this study, the fundamental blending characterizations of PVOH-CSS were investigated by molecular modeling to unveil the hydrogen bonding interactions among the blending components. In addition, infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were conducted to support the molecular modeling outcomes. The processability behaviour of the PVOH-glycerol-CSS compounds (PGCS) such as specific heat capacity, pressure-volume-temperature, and shear rate-viscosity were studied as well. These data were imported into Moldflow software for injection moulding simulation based on a name tag article design (NTA). Subsequently, the simulated outcomes were validated by actual injection moulding process using statistical analysis. The fundamental blending characterizations results showed that blending of PVOH and CSS are synergistically compatible. However, the incorporation of glycerol has weakened the genuine interactions between PVOH and CSS. Meanwhile, the processability study of PGCS showed that 40 wt.% and 50 wt.% CSS compounds are favourable to be injection moulded. Finally, the statistical outcomes have concluded that optimum processing can help to produce NTA with low volumetric shrinkages at acceptable variabilities. In conclusion, PVOH-CSS blend is a compatible polymer compound. It is also a high potential injection moulding processable biodegradable starch-based polymer compound.

## ABSTRAK

Adunan polivinil alkohol (PVOH) dan kanji ubi kayu (CSS) merupakan adunan polimer biodegradasi. Adunan polimer ini adalah sesuai digunakan sebagai bahan biodegradasi untuk tujuan mengurangkan pengumpulan bahan buangan polimer yang berasal dari sintetik petrolium. Dalam kajian ini, pencirian asas terhadap adunan dikaji dengan menggunakan permodelan molekul untuk melihat interaksi ikatan hidrogen diantara komponen adunan. Tambahan pula, teknik-teknik seperti spektroskopi infra-merah (FT-IR), kalorimeter imbasan kebezaan (DSC), dan analisa thermogravimetrik (TGA) dijalankan untuk menyokong keputusan permodelan molekul. Selain itu, kebolehan pemprosesan untuk adunan PVOH-gliserol-CSS (PGCS) seperti muatan haba tentu, tekanan-isipadu-suhu, dan kadar ricih-kelikatan juga dikaji. Data-data ini kemudian dimasukkan ke dalam perisian Moldflow untuk simulasi acuan suntikan dengan berdasarkan kepada rekabentuk tanda nama (NTA). Seterusnya, keputusan simulasi disahkan melalui proses suntikan acuan sebenar dengan menggunakan analisa statistik. Keputusan pencirian asas adunan menunjukkan bahawa adunan PVOH dan CSS adalah serasi secara sinergistik. Bagaimanapun, penambahan gliserol telah melemahkan interaksi asal antara PVOH dan CSS. Pada masa yang sama, kajian kebolehan pemprosesan PGCS menunjukkan bahawa CSS adunan 40 berat% dan 50 berat% adalah baik untuk diproses secara acuan suntikan. Akhirnya, keputusan statistik menunjukkan bahawa pemprosesan optimum boleh membantu menghasilkan NTA yang mempunyai penyusutan isipadu yang rendah pada kebolehubahan yang boleh diterima. Kesimpulannya, adunan PVOH-CSS ialah adunan polimer yang serasi. Adunan ini merupakan adunan biodegradasi berasaskan kanji yang berpotensi tinggi dan dapat diproseskan secara suntikan acuan.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>TITLE PAGE</b>	<b>i</b>
	<b>DECLARATION</b>	<b>ii</b>
	<b>ACKNOWLEDGEMENT</b>	<b>iii</b>
	<b>ABSTRACT</b>	<b>iv</b>
	<b>ABSTRAK</b>	<b>v</b>
	<b>TABLE OF CONTENTS</b>	<b>vi</b>
	<b>LIST OF TABLES</b>	<b>xi</b>
	<b>LIST OF FIGURES</b>	<b>xv</b>
	<b>LIST OF ABBREVIATIONS AND SYMBOLS</b>	<b>xxiii</b>
<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
	1.1 Background of Project	1
	1.2 Problems Statement	4
	1.3 Objectives	4
	1.4 Scope of Study	5
<b>2</b>	<b>LITERATURE REVIEW</b>	<b>9</b>
	2.1 Introduction	9
	2.2 Native Starch	10
	2.3 Polyvinyl Alcohol	12

2.4	Thermoplastic Starch	14
2.5	Characteristics of Starch Filled LDPE and Starch Filled PVOH Blends	15
2.5.1	Starch Filled LDPE	17
2.5.2	Starch Filled PVOH	21
2.6	Molecular Modeling and Simulation	23
2.6.1	Intermolecular Interactions	23
2.6.2	Computational Chemistry and Molecular Modeling	24
2.6.3	Molecular Mechanics	25
2.6.4	Quantum Mechanics	26
2.6.5	Molecular Modeling in Polymers	28
2.7	Detection of Hydrogen Bonds	30
2.8	Rheology of Starch-Polymer Blends	32
2.9	Pressure-Volume-Temperature Behaviour of Polyvinyl Alcohol	36
2.10	Injection Moulding Volumetric Shrinkage	38
2.11	Injection Moulding Processing of Starch Based Compound	41
2.12	Injection Moulding Simulation	42
2.13	Design of Experiment- Full Factorial Design	44
<b>3</b>	<b>METHODOLOGY</b>	<b>47</b>
3.1	Materials	47
3.1.1	Polyvinyl Alcohol	47
3.1.2	Starch	48
3.1.3	Glycerol and Calcium Stearate	48
3.1.4	Phosphoric Acid	49
3.2	Molecular Modeling Strategy	50
3.3	Samples Preparation and Compounding	52
3.3.1	Solution Casting Method	52
3.3.2	Melt Blending Method	54

3.4	Materials Characterizations	55
3.4.1	Fundamental Characterizations	56
3.4.1.1	Detection of Hydrogen Bonds by FT-IR	56
3.4.1.2	Determination of Enthalpy of Melting by DSC	56
3.4.1.3	Determination of Thermal Decomposition Activation Energy by TGA	57
3.4.2	Macroscopic Properties Characterizations and Model Fittings	60
3.4.2.1	Determination of Rheology Properties by Capillary Rheometer and Model Data Fitting	60
3.4.2.2	Determination of Specific Heat Capacity by DSC	65
3.4.3	Determination of Pressure-Volume-Temperature and Model Data Fitting	67
3.5	Injection Moulding Simulation Analysis	70
3.6	Experimental Validation and Effects Identifications	73
<b>4</b>	<b>MOLECULAR MODELING AND FUNDAMENTAL CHARACTERIZATIONS</b>	<b>77</b>
4.1	Introduction	77
4.1.1	Binding Energies and Solubility Parameters Analysis of PVOH and Starch	78
4.1.2	Vibrational Frequency and Experimental FT-IR Analysis of Binary PVOH-Starch Blending System	85
4.1.3	FT-IR Analysis of Ternary PVOH-Glycerol-Starch Blending System	90
4.1.4	DSC Analysis of Binary PVOH-Starch Blending System	92
4.1.5	DSC Analysis of Ternary PVOH-Glycerol-Starch Blending System	96

4.1.6	Thermogravimetric Degradation and Activation Energy of Binary PVOH-Starch Blending System	100
4.1.7	Thermogravimetric Degradation and Activation Energy of Ternary PVOH-Glycerol-Starch Blending System	106
4.2	Conclusion	113
<b>5</b>	<b>MACROSCOPIC CHARACTERIZATIONS</b>	<b>114</b>
5.1	Introduction	114
5.2	Specific Heat Capacity Characterization	115
5.3	Rheology Characterization	121
5.4	Pressure-Volume-Temperature Characterization	125
5.5	Conclusion	130
<b>6</b>	<b>INJECTION MOULDING SIMULATION AND OPTIMIZATION</b>	<b>134</b>
6.1	Introduction	134
6.2	NTA Model Design Quality	135
6.3	Structural Defects of NTA in Injection Moulding	136
6.4	Injection Moulding Processability of PPV46 and PPV55 in NTA	140
6.4.1	Comparisons of PPV46 and PPV55 at Filling Stage	140
6.4.2	Comparisons of PPV46 and PPV55 at Packing Stage	146
6.5	Full Factorial Analysis and Actual Injection Moulding Process Validation	152
6.5.1	Analysis of Process Factors Affecting Volumetric Shrinkage of PPV46 and PPV55	153
6.5.2	Analysis of Process Factors Affecting Variability of Volumetric Shrinkage of PPV46 and PPV55	164



6.5.3 Comparisons of Simulation and Experimental Outcomes	168
6.6 Conclusion	169
<b>7 CONCLUSION AND RECOMMENDATIONS</b>	<b>171</b>
7.1 Overall Conclusion	171
7.2 Recommendation of Future Works	173
<b>REFERENCES</b>	<b>174</b>
APPENDIX A : Specific Heat Capacity of Sapphire (British Standards Institution, 2005c)	188
APPENDIX B : Publication 1 in <i>Materials Science and Engineering: C</i> (Impact Factor: 1.816)	190
APPENDIX C : Publication 2 in <i>Carbohydrate Polymers</i> (Impact Factor: 3.167)	191
APPENDIX D : Publication 3 in <i>Polymer</i> (Impact Factor: 3.573)	192
APPENDIX E : Publication 4 in <i>Carbohydrate Polymers</i> (Impact Factor: 3.167)	193
APPENDIX F : Publication 5 in <i>Carbohydrate Polymers</i> (Impact Factor: 3.167)	194
APPENDIX G : Publication 6 in <i>International Journal of Thermophysics</i> (Impact Factor: 0.702)	195
APPENDIX H : Publication 7 in <i>Pertanika Journal of Science and Technology</i> (Indexed in EBSCO)	196
APPENDIX I : Publication 8 in <i>Carbohydrate Polymers</i> (Impact Factor: 3.167)	197

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Infrared absorption bands of fully and partially hydrolyzed PVOH	14
2.2	Hildebrand solubility parameter of synthetic polymers	16
2.3	Physicomechanical properties of LDPE-starch films	19
2.4	Differences blending of PVOH in starch-glycerol (Mao <i>et al.</i> , 2000)	22
2.5	Comparisons of accuracy of semi-empirical methods to experiment CO <sub>2</sub>	28
2.6	OVAT analysis approach of a chemical process	44
2.7	Full factorial design analysis approach of a chemical process	45
3.1	PVOH specification of grade BF17-H	48
3.2	Computational modeling of the Glu-mPVOH complexes	50

3.3	Formulation of first block solution cast PVOH-starch	53
3.4	Formulation of second block solution cast PVOH-starch-glycerol	54
3.5	Composition of PPVOH	55
3.6	Composition of melt blended PGCS	55
3.7	Two-Domain Tait PVT model	69
4.1	Binding energies, $\Delta E$ (kcal/mol) at AM1 and PM3 of the complexes	79
4.2	Hansen solubility parameters, $\delta_H$ of the modeled species	84
4.3	Vibrational frequencies of hydroxyl group at AM1 and PM3 of the 1Glu-1mPVOH, 1Glu-2mPVOH, 1Glu-3mPVOH, and 1Glu-4mPVOH complexes with single hydrogen bond and their corresponding decrease in frequencies	86
4.4	Vibrational frequencies of hydroxyl group at AM1 and PM3 of the 1Glu-4mPVOH complex with double hydrogen bonds and their corresponding decrease in frequencies	87
4.5	Onset and end-point melting temperature, experimental ( $\Delta H_m$ ) and theoretical ( $\Delta H_{mi}$ ) enthalpy of melting of solution cast PVOH and starch films	94
4.6	Onset and end-point melting temperatures and enthalpy of melting ( $\Delta H_m$ ) of solution cast glycerol plasticized PVOH and starch films	97

4.7	Temperatures at 20 % weight loss in thermogravimetry test at heating rates of 20, 25, 30, 35 and 40 °C/min for PVOH and starch blend films	102
4.8	Temperatures at 20 % weight loss in thermogravimetry test at heating rates of 20, 25, 30, 35 and 40 °C/min for PVOH, glycerol and starch blend films	108
5.1a	Specific heat capacity, $C_{sp}$ of PPV, PPV28 and PPV37	119
5.1b	Specific heat capacity, $C_{sp}$ of PPV46 and PPV55	120
5.2	Data fitted Cross-WLF viscosity model of PPV46 and PPV55	123
5.3	Data fitted Two-Domain Tait PVT model of PPV46 and PPV55	133
6.1	Injection moulding simulation parameters for PPV46 and PPV55	140
6.2	Process factors and their respective levels	152
6.3	Measurement of volumes of AFNT filled by PPV46	154
6.4	Measurement of volumes of AFNT filled by PPV55	155
6.5	Volumetric shrinkage of AFNT filled by PPV46	156
6.6	Volumetric shrinkage of AFNT filled by PPV55	157
6.7	Volumetric shrinkages of verification experiments	164

6.8	Comparison of experimental and simulation outcomes	168
-----	--	-----

**LIST OF FIGURES**

<b>FIGURE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Stereochemistry of starch amylose portion	11
2.2	Stereochemistry of starch amylopectin portion	11
2.3	Hydrogen bonding formed between hydroxyl groups of PVOH and starch	17
2.4	Schematic diagram of weak adhesion region in LDPE-starch blend causes reduction in physicommechanical properties and migration of solvents	20
2.5	Lennard-Jones potential model	24
2.6	Formation of hydrogen bond of hydroxyl functional groups	31
2.7	Shear rate-viscosity of PVOH-starch (w/w): 1.0/1.0 at moisture content 36.0 % (Wang <i>et al.</i> , 1995)	33
2.8	Shear rate-viscosity of PVOH-starch (w/w): 1.0/1.0 at temperature 110 °C and various moisture contents (Wang <i>et al.</i> , 1995)	34

2.9	Influences of starch types on viscosity of blends containing 50 wt.% starch measured at temperature 150 °C. (A = 30 % amylopectin, B = 70 % amylopectin, C = 100 % amylopectin) (Villar <i>et al.</i> , 1995)	35
2.10	Influences of poly(ethylene-co-vinyl alcohol) contents on viscosity for blends containing native corn measured at temperature 150 °C. (A = 100 % starch, B = 70 % starch, C = 50 % starch, D = 30 % starch, E = 0 % starch) (Villar <i>et al.</i> , 1995)	36
2.11	PVT diagram of fully hydrolyzed PVOH (Zoller and Walsh, 1995)	38
2.12	(a) Pareto plot (b) Interaction plot (c) Cube plot (d) Surface plot	46
3.1	Thermogravimetry curve at increasing heating rates, ( $\alpha$ = degree of conversion, $\beta$ = heating rate, $T$ = temperature) (British Standard Institution, 2005a)	58
3.2	Heating rates versus the reciprocal of the absolute temperature ( $\alpha$ = degree of conversion, $\beta$ = heating rate, $T$ = temperature) (British Standard Institution, 2005a)	59
3.3	Gottfert® Rheograph 75 capillary rheometer	61
3.4	Schematic Bagley plot for capillary dies (British Standard Institutions, 2005b)	62
3.5	Welsenberg Rabinowitsch correction for true shear rate (ASTM International, 2008)	63

3.6	DSC diagram for determination specific heat capacity of sample – 1 is the blank run, 2 is the calibration run and 3 is the sample run (British Standards Institution, 2005c)	66
3.7	Drawing and dimensions of NTA (measurement in mm)	71
3.8	(a) NTA drawing with hidden lines (b) NTA in shaded drawing	72
3.9	Injection moulding machine Demag EL-EXISE 60/370 at 60 tonnes	74
3.10	(a) Male mould of NTA (b) Female mould of NTA (c) NTA mould set	75
4.1	Geometrically optimized structures of single hydrogen bond Glu-1mPVOH at (a) AM1 and (b) PM3	80
4.2	Geometrically optimized structures of single hydrogen bond Glu-2mPVOH at (a) AM1 and (b) PM3	80
4.3	Geometrically optimized structures of single hydrogen bond Glu-3mPVOH at (a) AM1 and (b) PM3	81
4.4	Geometrically optimized structures of single hydrogen bond Glu-4mPVOH at (a) AM1 and (b) PM3	82
4.5	Geometrically optimized structures of double hydrogen bonds Glu-4mPVOH at (a) AM1 and (b) PM3	83



4.6	(a) FT-IR spectra of solution cast film of neat PVOH (PV), starch (ST) and PVOH-starch blends (W28, W37, W46 and W55), (b) Wavenumber shift of –OH peak in solution cast film of neat PVOH (PV), starch (ST) and PVOH-starch blends (W28, W37, W46 and W55)	89
4.7	(a) FT-IR spectra of glycerol added solution cast film of neat PVOH (PVG), starch (STG) and PVOH-starch blends (WG28, WG37, WG46 and WG55), (b) Wavenumber shift of –OH peak in glycerol added solution cast film of neat PVOH (PVG), starch (STG) and PVOH-starch blends (WG28, WG37, WG46 and WG55)	91
4.8	DSC thermograms of solution cast PVOH and starch films	93
4.9	Plot of experimental ( $\Delta H_m$ ) and theoretical ( $\Delta H_{mi}$ ) enthalpy of melting of solution cast PVOH and starch films	95
4.10	DSC thermograms of solution cast glycerol plasticized PVOH and starch films	97
4.11	Plot of experimental ( $\Delta H_m$ ) and theoretical ( $\Delta H_{mi}$ ) enthalpy of melting of solution cast glycerol plasticized PVOH and starch films	99
4.12	Thermogravimetry curves of W28 at heating rates 20, 30, and 40 °C/min	101

4.13	Logarithm of the heating rates, $\log \beta$ against the reciprocal of absolute temperature, $1/T$ for 20 wt.% mass loss of PVOH and starch blend films. Activation energy, $E_a$ (kJ/mol) is calculated from the slope ( $-0.4567 E_a/R_c$ ). $R_c$ is the gas constant 8.314 J/mol.K and R is the regression of the linear graphs.	103
4.14	Thermogravimetry curves of solution cast PVOH and starch blend films recorded at a heating rate of 20 °C/min	104
4.15	Plot of activation energy ( $E_a$ ) to the amount of PVOH in starch blend films	105
4.16	Thermogravimetry curves of WG55 at heating rates 20, 30 and 40 °C/min	107
4.17	Logarithm of the heating rate, $\log \beta$ against the reciprocal of absolute temperature, $1/T$ for 20 wt% mass loss of PVOH, glycerol and starch blend films. Activation energy, $E_a$ (kJ/mol) is calculated from the slope ( $-0.4567 E_a/R_c$ ). $R_c$ is the gas constant 8.314 J/mol.K and R is the regression of the linear graphs	109
4.18	Thermogravimetry curves of solution cast PVOH, glycerol and starch blend films recorded at heating rate of 20 °C/min blend films	110
4.19	Plot of activation energy ( $E_a$ ) to the amount of PVOH-glycerol in starch	112
5.1	DSC thermograms of PGCS, PPVOH, reference sapphire, and empty aluminum pan	116

5.2	Specific heat capacity, $C_{sp}$ of the PPV and PGCS compounds	118
5.3	Shear rate-viscosity of PPV and PGCS compounds at 190 °C	122
5.4a	Shear rate-viscosity data fitted into Cross-WLF model of PPV46	124
5.4b	Shear rate-viscosity data fitted into Cross-WLF model of PPV55	124
5.5a	PVT diagram of PPV	127
5.5b	PVT diagram of PPV55	127
5.5c	PVT diagram of PPV46	128
5.5d	PVT diagram of PPV37	128
5.5e	PVT diagram of PPV28	129
5.6	Combination of PVT diagram of PPV and PGCS compounds at 500 bar	129
5.7a	Comparisons of experimental and modeling fitting into Two-Domain Tait model for PPV46 (Parentheses are the regression)	131
5.7b	Comparisons of experimental and modeling fitting into Two-Domain Tait model for PPV55 (Parentheses are the regression)	132

6.1	NTA design (a) before meshing (b) after meshing	137
6.2	NTA dual cavity design with runner, sprue, and gate included	138
6.3	Air traps found in dual-cavity of NTA	139
6.4	Weld lines in dual-cavity of NTA	139
6.5	Filling simulation screen outputs of (a) PPV46 at injection pressure of 9 MPa (b) PPV55 at injection pressure of 10 MPa	142
6.6	Filling time illustrations of (a) PPV46 at injection pressure of 9 MPa (b) PPV55 at injection pressure of 10 MPa	143
6.7	Filling simulation screen output of PPV55 at injection pressure of 9 MPa	144
6.8	FLFE illustrations (a) PPV46 (b) PPV55 at injection pressure of 9 MPa	145
6.9	FLFE illustration of PPV55 at injection pressure of 10 MPa	146
6.10	Volumetric shrinkage illustrations of (a) PPV46 (b) PPV55	148
6.11	Frozen layer fraction (FLFT) of PPV46 corresponds to moulding period	150

6.12	Frozen layer fraction (FLFT) of PPV55 corresponds to moulding period	151
6.13	AFNT filled by PPV46 (a) Normal probability plot (b) Pareto chart	159
6.14	AFNT filled by PPV55 (a) Normal probability plot (b) Pareto plot	161
6.15	Interaction plot of AFNT filled by PPV55	162
6.16	Volumetric shrinkage cube plots for AFNT (a) PPV46 (b) PPV55	163
6.17	(a) Pareto chart (b) Cube plot of AFNT filled by PPV46	166
6.18	(a) Pareto chart (b) Cube plot of AFNT filled by PPV55	167
6.19	Injection moulded NTA final product	170

**LIST OF ABBREVIATIONS AND SYMBOLS**

AFNT	-	Approximated flat slab name tag article
AM1	-	Austin Model 1
ANOVA	-	Analysis of variance
CaS	-	Calcium stearate
CED	-	Cohesive energy density
ChemSW	-	ChemSW® Molecular Modeling Pro
CNDO	-	Complete Neglect of Differential Overlap
CSS	-	<i>Cassava</i> starch or commonly known as starch in this study
DOE	-	Design of experiment
DSC	-	Differential scanning calorimetry
FLFT	-	Frozen layer fraction
FLFE	-	Frozen layer at end fill
FT-IR	-	Fourier transform infrared spectroscopy
Glu	-	D-glucose
H Bond	-	Hydrogen bond
Hyperchem	-	Hyperchem® Professional 8.0
IP	-	Injection pressure
IR	-	Infrared spectroscopy
IS	-	Injection speed
IT	-	Injection temperature
LDPE	-	Low density polyethylene
MINDO	-	Modified Intermediate Neglect of Differential Overlap
Moldflow	-	Moldflow® Plastics Insight 5.0
mPVOH	-	Polyvinyl alcohol repeating unit

NDO	-	Neglect of Differential Overlap
NMR	-	Nuclear magnetic resonance
NTA	-	Name tag article
OVAT	-	One-variable-at-a-time
PEL	-	Percentage elongation
PES	-	Potential energy surface
PGCS	-	Polyvinyl alcohol-glycerol-starch melt blended compound
PM3	-	Reparameterized Austin Model 3
PP	-	Packing pressure
PPVOH	-	Glycerol plasticized polyvinyl alcohol
PVOH	-	Polyvinyl alcohol
PVT	-	Pressure-volume-temperature
SEM	-	Scanning electron microscope
TG	-	Thermogravimetry
TGA	-	Thermogravimetry analysis
TNDO	-	Typed Neglected Differential of Overlap
TS	-	Tensile strength
TPS	-	Thermoplastic starch
V.F.	-	Vibrational frequency
VPSO	-	Velocity/pressure switch over
WLF	-	Williams-Landel-Ferry
ZINDO	-	Zerner's Intermediate Neglect of Differential Overlap
$\Delta E$	-	Binding energy
$E_a$	-	Activation energy
$C_{sp}$	-	Specific heat capacity
$R_c$	-	Gas constant 8.314 J/mol.K
$R^2$	-	Coefficient of determination
$T$	-	Temperature
$P$	-	Pressure
$V^{LJ}$	-	Lennard-Jones potential
$\alpha$	-	Degree of conversion
$\beta$	-	Heating rate
$\eta$	-	Melt viscosity

$\delta_H$	-	Hansen solubility parameter
$\tau$	-	Shear stress
$\Psi$	-	Wave function
$\dot{\gamma}$	-	Shear rate
$\phi$	-	Number of repeating unit



## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Project**

Plastics are extensively used in nearly all areas of daily life and their productions and fabrications are major worldwide industries. They become materials of choice for many applications because of light weights, cheap, durable and easily being processed to desired forms. However, people tend to exploit the usage of plastics by producing easy-disposable products. Synthetic polymeric materials such as polyethylene, polypropylene, polystyrene, polyvinyl chloride are non-degradable when being exposed in natural environment. Petroleum-based synthetic polymers require hundreds of years to fully degrade into harmless substances. The disposals of synthetic polymer materials have caused diminish of landfill. Living lives are prone to expose of toxic chemicals leakages due to contamination of groundwater. Meanwhile, the incineration is sometimes considered to be a good alternative to manage polymeric wastes. However, toxic gases emissions such as benzene, toluene, polychlorinated biphenyls can cause severe health problems (Rowat, 1999). One of

the alternatives to reduce harmful impacts of synthetic polymer is through substitution of petroleum-based polymers by natural biodegradable polymers. Biodegradable polymers can easily decompose into harmless substances when exposed to natural environment. Currently, there are several types of biodegradable polymer materials available in the market such as polylactic acid, poly( $\epsilon$ -caprolactone), polyvinyl alcohol (PVOH), starch polymers and oxo-additive petroleum based synthetic polymer (Bohlmann, 2005). Biodegradable polymers or its compounds do not degrade during the application period. These polymers will only begin to decompose rapidly when being exposed under the action of microbial and enzymes for digestion into fully harmless substances (Zee, 2005).

Current development shows that starch based biodegradable polymers have gained broad academic and industrial interests (Mani and Bhattacharya, 1998; Raj *et al.*, 2004; Cyras *et al.*, 2006; Wang *et al.*, 2006; Novamont, 2007; Schlemmer *et al.*, 2007; Plantic, 2007; Liu *et al.*, 2009; Chung *et al.*, 2010; Yu *et al.*, 2010). Starch is a mixture of natural ingredients- amylose and amylopectin. Both amylose and amylopectin are consisted of  $D$ -glucose repeating unit (Wade, 1999; Liu *et al.*, 2009). Starch is polar substance with vast amount of hydroxyl (-OH) groups present in the molecules. As a result, polar polymers such as PVOH, polyethylene oxide and polyethylene vinyl acetate possess polar pendant groups are compatible with starch. When blending of polar polymers and starch together, hydrogen bonds are very likely to form in between the polar side groups of the polymers and the starch molecules. Cenovese and Shanks (2001) reported that the presence of hydrogen bonding in polymeric material is able to enhance morphological and structural properties of the blending. In spite of that, blending of polar polymers with starch can overcome the existing physical limitations of thermoplastic starch (TPS) such as water solubility, poor mechanical properties and brittleness while retaining its biodegradable property (Mao *et al.*, 2000).

It is known that blending of starch with synthetic polymer helps to improve biodegradability. However, starch is a polar substance. Blending starch with non-polar synthetic polymer such as polyethylene is not compatible. Jagannath *et al.* (2006) reported that starch filled low density polyethylene showed deterioration in mechanical properties. In order to overcome this problem, it is better to blend an inherent polar polymer with starch, so that the compatibility of the blending complex will not be disrupted. Hence, in this study, polar polymer PVOH was blended with starch. To date, little study has been performed on the molecular level and processing behaviour of PVOH-starch blending complex. Most of the works are limited to mechanical properties and biodegradability of PVOH-starch compounds.

A thorough study of molecular level and macroscopic properties of PVOH-*cassava* starch (written in abbreviation as CSS in particular term or starch in common term) was performed to ensure the compounds can be widely applied across the plastic industries. Besides that, this study was also aimed to reveal the processability of PVOH-starch using injection moulding technology. Since most of the injection moulding facilities is mainly used for production of petroleum-based polymer products, the industrial practitioners are unwilling to shift their well setup production lines to novel starch-based biodegradable polymer materials which tend to cost them a lot of efforts when implement new production procedures. Thus, in this study, the processing behaviour of PVOH-starch was studied also with the aids of injection moulding simulation analysis. The shear rate-viscosity and PVT characteristics of PVOH-starch compounds were modeled and embedded into Moldflow® program for injection moulding simulation analysis. The simulation analysis outcomes helped to predict the injection moulding processing parameters of PVOH-starch compounds as well as reducing cost and time spent on the online trial-and-error production (Sapuan, 2005). These outcomes are not only favorable for industrial implementation, but it also helps to encourage further development and improvement of biodegradable starch-based polymer compounds.

## 1.2 Problem Statements

Based on the lack previous studies about the genuine interactions of PVOH-starch blends as well as the processability of PVOH-starch compound, therefore, the following problems have been identified:

1. What are the differences of binding energy, vibrational frequency of hydroxyl (-OH) group and the solubility parameters of PVOH-starch and their original components? What are the percentage combinations of PVOH-starch to produce the best theoretical stability?
2. What are the thermal stability and extent of hydrogen bonds formation in PVOH-starch blends? Do the experimental results agree with theoretical computational modeling outcomes?
3. What are the pressure-volume-temperature (PVT), thermal properties and rheology shear rate-viscosity of melt blended PVOH-glycerol-starch compounds (PGCS)?
4. What are the optimum processing parameters to produce PGCS articles by injection moulding technology?

## 1.3 Objectives

The main objective of this project is to develop a molecular stable biodegradable PVOH-starch compound and this compound can be well processed by injection moulding technology. Actually, the application of starch-polymer blend is not limited to biodegradable packaging material but also apply in advance biomaterial field as tissue engineering scaffold (Neves *et al.*, 2005; Sinha *et al.*, 2007), hydrogels for use as bone cements or drug-delivery carriers (Zhai *et al.*, 2002),

and protein immobilization (Melo-Junior *et al.*, 2008). Therefore, the main objective was not limited to obtain an individual starch based biodegradable product, but the results will also help to explore the fundamental interactions of polymer-starch system. This will lead towards further development of the starch based polymer compounds applications in the future. In order to achieve this objective, the following sub-objectives were identified.

1. To determine the differences of binding energy, vibrational frequency of hydroxyl (-OH) groups, and solubility parameters of PVOH-starch and their components by quantum mechanics computational method.
2. To investigate decomposition activation energy, enthalpy of melting and infrared spectroscopy of PVOH-starch. The results were compared with simulation outcomes for validation.
3. To characterize the PVT, thermal properties and rheology shear rate-viscosity of PGCS for injection moulding simulation analysis.
4. To identify the optimum injection moulding processing parameters of PGCS articles by Moldflow® simulation and verified by actual injection moulding process.

#### **1.4 Scope of Study**

In general, this project was divided into five sections: molecular interactions simulation, samples compounding, fundamental and macroscopic properties characterizations, injection moulding simulation analysis, and validation-optimization of actual injection moulding process.

### **a) Molecular Interaction Simulation**

The molecular interactions simulation of PVOH-starch was conducted by HyperChem® Professional 8.0 (Hyperchem) and ChemSW® Molecular Modeling Pro (ChemSW). The investigations were limited to obtain binding energies, vibrational frequency of hydroxyl (-OH) group by quantum mechanics calculation (Hypercube, 2002) using Hyperchem. Meanwhile, the solubility parameters of the components were obtained using ChemSW. Since PVOH and starch are macromolecules with high molecular weights, thus PVOH and starch molecules were modeled into rather simple repeating unit basis. Basically PVOH were modeled into vinyl alcohol repeating unit and starch was represented by D-glucose unit. Vibrational analysis of molecules has provided a clear visualization about bending and stretching of the chemical bonds when subjected to infrared irradiation in virtual computer environment.

### **b) Samples Compounding**

Blending of PVOH and starch were carried out by solution casting and melt blending methods. Solution casting samples were used for fundamental characterizations of PVOH-starch binary system and PVOH-glycerol-starch ternary system. The amount of glycerol added in this study was limited to 30 wt.%. This is the amount of glycerol needed to produce extrudable PVOH (Famili *et al.*, 1991; Marten *et al.*, 1991; Marten *et al.*, 1992; Famili *et al.*, 1994). 30 wt.% of glycerol was used in solution casting of PVOH-glycerol-starch ternary system so that it can generate analysis outcomes approaching the actual melt blending samples. Solution cast samples were used for fundamental characterization because this sample preparation method only involved moderate temperatures to dissolve and blending of

PVOH, starch, and glycerol together. Unlike melt blending of PVOH-starch which used a twin screws extruder, it required incorporation of lubricants and some additives to encourage mixing at relative higher temperatures as compared to solution casting method. Incorporation of additives would disturb the genuine interactions of PVOH-starch. In addition, high processing temperature also induce side-reaction to occur which would create disturbance to the fundamental properties study. Therefore, melt blending samples were used for macroscopic characterizations such as thermal and rheology properties of PVOH-starch compound. Meanwhile, solution casting samples was used to characterize the decomposition activation energy, enthalpy of melting and detection of hydrogen bonds by Thermogravimetry Analysis (TGA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared Spectroscopy (FT-IR), respectively.

### **c) Fundamental and Macroscopic Properties Characterizations**

PVOH-CSS blends were divided into fundamental and macroscopic characterizations.

#### **I. Fundamental characterizations for solution cast samples**

- i. Detection of hydrogen bonding effects (shifting of O–H stretching wavenumber) by FT-IR.
- ii. Determination of thermal decomposition activation energy at 20% mass losses by TGA.
- iii. Determination of enthalpy of melting by DSC.

## **II. Macroscopic characterization for melt blending samples**

- i. Shear rate-viscosity analysis by capillary rheometer.
- ii. PVT analysis by SWO PVT apparatus.
- iii. Specific heat capacity analysis by DSC.

### **d) Injection Moulding Simulation**

Injection moulding simulation analysis was conducted by Moldflow® Plastics Insight 5.0 (Moldflow). Name tag article (NTA) was designed by SolidWorks®. The simulation included flowing and packing analyses. Data obtained in macroscopic characterizations were embedded into Moldflow database. Shear rate-viscosity relationship of PVOH-starch was modeled into Cross-WLF equation. Meanwhile, PVT data were modeled into Two-Domain Modified Tait equation.

### **e) Validation-Optimization in Actual Injection Moulding Process**

The outcomes generated from Moldflow injection moulding simulation analysis were validated and optimized in actual injection moulding machine. Basically, four process factors were studied at 2-levels full factorial design method. The four process factors were injection temperature, injection pressure, injection speed and packing pressure. The response of interest of the experiment was volumetric shrinkage of the NTA.