



**The Effect of Filler Content and Chemical Modification
On Properties of Polylactic Acid/Recycled Low Density
Polyethylene/*Nypa Fruticans* Husk Biocomposites**

by

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TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	x
LIST OF TABLES	xvi
LIST OF ABBREVIATIONS	xviii
ABSTRAK	xix
ABSTRACT	xx
CHAPTER 1: INTRODUCTION	
1.1 Research Background	1
1.2 Problem Statement	7
1.3 Research Objective	9
1.4 Organization of the Thesis	10
CHAPTER 2: LITERATURE REVIEW	
2.1 Polymer Biocomposites	12
2.1.1 Classification of Biocomposites	13
2.1.2 Classification of Biodegradable Polymers	14
2.2 Matrix	16
2.3 Polylactic Acid (PLA)	17
2.3.1 Polymerization of PLA	19
2.3.2 Properties of PLA	21

2.3.3 PLA Applications	22
2.4 Polyethylene	24
2.4.1 Low Density Polyethylene	26
2.4.2 Polymerization of LDPE	27
2.4.3 Recycled Low Density Polyethylene	28
2.4.4 PLA Blends	29
2.5 Filler	31
2.5.1 Classification of Filler	32
2.5.2 Filler-Matrix Interaction	34
2.5.2.1 Quantitative Evaluation of Interfacial Interaction	39
2.5.2 Effects of Reinforcement Filler	41
2.5.3 Factors Influencing the Performance of Biocomposites	42
2.6 Natural Fibers	42
2.6.1 Classification of Natural Fibers	44
2.6.2 Composition of Natural Fibers	46
2.6.2.1 Cellulose	46
2.6.2.2 Hemicellulose	47
2.6.2.3 Lignin	48
2.6.3 Advantages and Disadvantages of Natural Fibers	50
2.7 Nypa Fruticans Husk	51
2.8 PLA/Natural Fiber Biocomposites	54
2.9 Chemical Modification	59
2.9.1 Silane Coupling Agent	59
2.9.2 Compatibilizer	62
2.9.3 Methyl Methacrylate (MMA)	65

2.9.4 Enzyme Treatment	67
2.9.5 Chelator Treatment	70
2.10 Biodegradation	72
2.10.1 Mechanism of Biodegradation	73
2.10.1.1 Solubilization	74
2.10.1.2 Ionization	74
2.10.1.3 Hydrolysis	74
2.10.1.4 Microbial Degradation	75
2.10.1.5 Enzyme-Catalyzed Hydrolysis	75
2.10.2 Factors Affecting Polymer Degradation	76
2.10.2.1 Chemical Composition	76
2.10.2.2 Molecular Weight	77
2.10.2.3 Hydrophobic Character	77
2.10.2.4 Size of the Molecules	77
2.10.3 Biodegradation of PLA	78
2.11 Statistical Analysis in Biocomposites	80
 CHAPTER 3: METHODOLOGY	
3.1 Materials	83
3.1.1 Matrices	83
3.1.2 Filler	84
3.1.3 Chemical Modification	85
3.2 Chemical Modification of PLA/rLDPE/NFH biocomposites	87
3.3 Chemical Modification of PLA/rLDPE/NFH biocomposites with EDTA	87

3.4 Chemical Modification of PLA/rLDPE/NFH biocomposites with EDTA/Enzyme	87
3.5 Chemical Modification of PLA/rLDPE/NFH biocomposites with 3-APE/Enzyme	88
3.6 Preparation of PLA/rLDPE/NFH Biocomposites	88
3.7 Preparation of PLA/rLDPE/NFH Biocomposites with different compatibilizer and chemical modification	89
3.8 Preparation of PLA/rLDPE/NFH Biocomposites with ETDA/Enzyme and 3-APE/Enzyme	91
3.9 Tensile Testing	92
3.9.1 Filler Matrix Interaction	92
3.10 Enzymatic Biodegradation	93
3.11 Thermal Analysis	94
3.11.1 Differential Scanning Calorimetry (DSC)	94
3.11.2 Thermogravimetric Analysis (TGA)	94
3.12 Fourier Transform Infrared (FTIR)	95
3.13 Morphological Analysis	95
 CHAPTER 4: RESULT AND DISCUSSIONS	
4.1 Effect of NFH Content on Properties of PLA/rLDPE/NFH Biocomposites	96
4.1.1 Tensile Properties	96
4.1.2 Filler Matrix Interaction	101
4.1.3 Morphological Study	103
4.1.4 Differential Scanning Calorimetry Analysis	105
4.1.5 Thermogravimetric Analysis	108
4.1.6 Enzymatic Biodegradation	111

4.2 Effect of Silane Coupling Agent on Properties of PLA/rLDPE/NFH Biocomposites	113
4.2.1 Tensile Properties	113
4.2.2 Filler Matrix Interaction	117
4.2.3 Morphological Study	119
4.2.4 Fourier Transform Infrared Analysis	120
4.2.5 Differential Scanning Calorimetry Analysis	122
4.2.6 Thermogravimetric Analysis	124
4.2.7 Enzymatic Biodegradation	127
4.3 Effect of Polyethylene grafted Maleic Anhydride on Properties of PLA/rLDPE/NFH Biocomposites	129
4.3.1 Tensile Properties	129
4.3.2 Filler Matrix Interaction	132
4.3.3 Morphological Study	134
4.3.4 Fourier Transform Infrared Analysis	136
4.3.5 Differential Scanning Calorimetry Analysis	137
4.3.6 Thermogravimetric Analysis	139
4.3.7 Enzymatic Biodegradation	142
4.4 Effect of Methyl Methacrylate (MMA) on Properties of PLA/rLDPE/NFH Biocomposites	143
4.4.1 Tensile Properties	143
4.4.2 Filler Matrix Interaction	146
4.4.3 Morphological Study	148
4.4.4 Fourier Transform Infrared Analysis	150
4.4.5 Differential Scanning Calorimetry Analysis	152
4.4.6 Thermogravimetric Analysis	153
4.4.7 Enzymatic Biodegradation	156

4.5 Effect of EDTA on Properties of PLA/rLDPE/NFH Biocomposites	157
4.5.1 Tensile Properties	157
4.5.2 Filler Matrix Interaction	160
4.5.3 Morphological Study	162
4.5.4 Fourier Transform Infrared Analysis	164
4.5.5 Different Scanning Calorimetry Analysis	166
4.5.6 Thermogravimetric Analysis	167
4.5.7 Enzymatic Biodegradation	170
4.6 Effect of EDTA/Enzyme on Properties of PLA/rLDPE/NFH Biocomposites	171
4.6.1 Tensile Properties	171
4.6.2 Filler Matrix Interaction	174
4.6.3 Morphological Study	176
4.6.4 Fourier Transform Infrared Analysis	178
4.6.5 Different Scanning Calorimetry Analysis	179
4.6.6 Thermogravimetric Analysis	181
4.6.7 Enzymatic Biodegradation	184
4.7 Effect of 3-APE/Enzyme on Properties of PLA/rLDPE/NFH Biocomposites	186
4.7.1 Tensile Properties	186
4.7.2 Filler Matrix Interaction	189
4.7.3 Morphological Study	191
4.7.4 Fourier Transform Infrared Analysis	193
4.7.5 Different Scanning Calorimetry Analysis	194
4.7.6 Thermogravimetric Analysis	196
4.7.7 Enzymatic Biodegradation	199

CHAPTER 5: CONCLUSIONS AND SUGGESTIONS	
5.1 Conclusion	200
5.2 Suggestions	201
REFERENCES	203
APPENDICES	227

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LIST OF FIGURES

NO.		PAGE
2.1	Classification of biocomposites	13
2.2	Classification of Biodegradable Polymers Base Biopolyester	15
2.3	Structure of PLA	18
2.4	Polymerization routes to polylactic acid	19
2.5	Schematic of PLA production via prepolymer and lactide	20
2.6	Non-solvent process to prepare polylactic acid	21
2.7	Chemical structure of polyethylene	24
2.8	Structure of LDPE	26
2.9	The mechanism of free radical polymerization of LDPE	27
2.10	Classification of Filler in Polymer	32
2.11	Classification of filler according to shape and size	33
2.12	Mechanism of adsorption and wetting	34
2.13	Mechanism of Inter-diffusion	37
2.14	Mechanism of electrostatic attraction	37
2.15	Mechanism of chemical bonding	38
2.16	Mechanism of mechanical bonding	39
2.17	Classification of natural fibres	45
2.18	Molecular structure of cellulose	46
2.19	Chemical structure of hemicelluloses	48
2.20	Structure of lignin	49
2.21	Various parts of the Nypa Palm	52
2.22	Scheme of interaction of silanes with natural fibers	60

2.23	Structure of Maleic anhydride grafted polyethylene	63
2.24	The reaction of cellulose fibers with MAPE copolymers	64
2.25	Structure of methyl methacrylate	65
2.26	Structure of Ethylenediaminetetraacetic acid (EDTA)	71
2.27	Proposed degradation mechanism of polylactic acid (PLA) in the bulk state	79
4.1	Effect of NFH content on tensile strength of PLA/rLDPE/NFH biocomposites	98
4.2	Scanning electron micrograph of <i>Nypa fruticans</i> husk	98
4.3	Effect of NFH content on elongation at break of PLA/rLDPE/NFH biocomposites	100
4.4	Effect of NFH content on Young's modulus of PLA/rLDPE/NFH biocomposites	101
4.5	Reduced tensile strength of PLA/rLDPE/NFH biocomposites plotted in linear form	102
4.6	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE	104
4.7	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite (20 php NFH)	104
4.8	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite (40 php NFH)	105
4.9	DSC curve of PLA/rLDPE and PLA/rLDPE/NFH biocomposites	107
4.10	TGA curves of NFH, PLA/rLDPE and PLA/rLDPE/NFH biocomposites	109
4.11	DTG curves of NFH, PLA/rLDPE and PLA/rLDPE/NFH biocomposites	110
4.12	Weight loss of PLA/rLDPE and PLA/rLDPE/NFH biocomposites on enzymatic biodegradation	112
4.13	Effect of NFH content on tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites	114
4.14	Effect of NFH content on elongation at break of untreated and treated PLA/rLDPE/NFH biocomposites	115
4.15	Effect of NFH content on Young's modulus of untreated and treated PLA/rLDPE/NFH biocomposites	117

4.16	Reduced tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites plotted in linear form	118
4.17	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with 3-APE (20 php NFH)	119
4.18	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with 3-APE (40 php NFH)	120
4.19	FTIR Spectra of untreated and treated NFH with 3-APE	121
4.20	Schematic reaction between NFH with 3-APE and PLA/rLDPE	122
4.21	DSC curves of untreated and treated PLA/rLDPE/NFH biocomposites with 3-APE	123
4.22	TGA curves of PLA/rLDPE, untreated and treated PLA/rLDPE/NFH biocomposites with 3-APE	125
4.23	DTG curves of untreated and treated PLA/rLDPE/NFH biocomposites with 3-APE	127
4.24	Weight loss of untreated and treated PLA/rLDPE/NFH biocomposites on enzymatic biodegradation	128
4.25	Effect of NFH content on tensile strength of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites	130
4.26	Effect of NFH content on elongation at break of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites	131
4.27	Effect of NFH content on Young's modulus of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites	132
4.28	Reduced tensile strength of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites plotted in linear form	133
4.29	Scanning electron micrograph of tensile fracture surface of compatibilized PLA/rLDPE/NFH biocomposite with PEMA (20 php NFH)	135
4.30	Scanning electron micrograph of tensile fracture surface of compatibilized PLA/rLDPE/NFH biocomposite with PEMA (40 php NFH)	135
4.31	FTIR spectra of uncompatibilized and compatibilized PLA/rLDPE/NFH with PEMA biocomposites	136
4.32	Schematic reaction of NFH with PEMA and PLA/rLDPE	137
4.33	DSC curves of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites with PEMA	138

4.34	Thermogravimetric analysis curves of uncompatibilized and compatibilized PLA/rLDPE/NFH with PEMA biocomposites	140
4.35	DTG curves of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites with PEMA	141
4.36	Weight loss of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites on enzymatic biodegradation	142
4.37	Effect of NFH content on tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites	144
4.38	Effect of NFH content on elongation at break of untreated and treated PLA/rLDPE/NFH biocomposites	145
4.39	Effect of NFH content on Young's modulus of untreated and treated PLA/rLDPE/NFH biocomposites	146
4.40	Reduced tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites plotted in linear form	147
4.41	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with MMA (20 php NFH)	149
4.42	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with MMA (40 php NFH)	149
4.43	FTIR spectra of untreated and treated NFH with MMA	150
4.44	Schematic reaction of NFH with MMA and PLA/rLDPE	151
4.45	DSC curves of untreated and treated PLA/rLDPE/NFH biocomposites with MMA	152
4.46	TGA curve of untreated and treated PLA/rLDPE/NFH biocomposites with MMA	154
4.47	DTG curve of untreated and treated PLA/rLDPE/NFH biocomposites with MMA	155
4.48	Weight loss of untreated and treated PLA/rLDPE/NFH biocomposites on enzymatic biodegradation	156
4.49	Effect of NFH content on tensile strength of PLA/rLDPE/NFH biocomposites with and without EDTA	158
4.50	Effect of NFH content on elongation at break of PLA/rLDPE/NFH biocomposites with and without EDTA	159

4.51	Effect of NFH content on Young's modulus of PLA/rLDPE/NFH biocomposites with and without EDTA	160
4.52	Reduced tensile strength of PLA/rLDPE/NFH with and without EDTA biocomposites plotted in linear form	161
4.53	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite with EDTA (20 php NFH)	163
4.54	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite with EDTA (40 php NFH)	163
4.55	FTIR spectra of NFH with and without EDTA	164
4.56	Schematic reaction of treated NFH with EDTA	165
4.57	DSC curves of PLA/rLDPE/NFH biocomposites with and without EDTA	166
4.58	TGA curves of PLA/rLDPE/NFH biocomposites with and without EDTA	168
4.59	DTG curve of PLA/rLDPE/NFH biocomposites with and without EDTA	169
4.60	Weight loss of PLA/rLDPE/NFH biocomposites with and without EDTA on enzymatic biodegradation	170
4.61	Effect of NFH content on tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	172
4.62	Effect of NFH content on elongation at break of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	173
4.63	Effect of NFH content on Young's modulus of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	174
4.64	Reduced tensile strength of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme plotted in linear form	175
4.65	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite treated with binary modification using EDTA/Enzyme (20 php NFH)	177
4.66	Scanning electron micrograph of tensile fracture surface of PLA/rLDPE/NFH biocomposite treated with binary modification using EDTA/Enzyme (40 php NFH)	177

4.67	FTIR spectra of untreated and treated NFH with binary modification using EDTA/Enzyme	179
4.68	DSC curve of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	180
4.69	TGA curves of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	182
4.70	DTG curves of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	184
4.71	Weight loss of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme on enzymatic biodegradation	185
4.72	Effect of NFH content on tensile strength of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	187
4.73	Effect of NFH content on elongation at break of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	188
4.74	Effect of NFH content on Young's modulus of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	189
4.75	Reduced tensile strength of PLA treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme plotted in linear form	190
4.76	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with 3-APE/Enzyme (20 php NFH)	192
4.77	Scanning electron micrograph of tensile fracture surface of treated PLA/rLDPE/NFH biocomposite with 3-APE/Enzyme (40 php NFH)	192
4.78	FTIR spectra of untreated and treated NFH with 3-APE/Enzyme	194
4.79	DSC curve of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	195
4.80	TGA curves of treated PLA/rLDPE/NFH treated biocomposites with 3-APE and 3-APE/Enzyme	197
4.81	DTG curve of treated PLA/rLDPE/NFH treated biocomposites with 3-APE and 3-APE/Enzyme	198
4.82	Weight loss of treated PLA/rLDPE/NFH treated biocomposites with 3-APE and 3-APE/Enzyme on enzymatic biodegradation	199

LIST OF TABLES

NO.		PAGE
1.1	Natural Fibers as filler in PLA	3
1.2	Blends of PLA	5
2.1	Chemical composition of various parts of Nypa Palm	53
3.1	Properties of Polylactic Acid	83
3.2	Properties of recycled Low Density Polyethylene	84
3.3	Chemical composition of <i>Nypa fruticans</i> husk	84
3.4	Properties of Polyethylene grafted Maleic Anhydride	85
3.5	Properties of 3-Aminopropyltriethoxysilane	85
3.6	Properties of Methyl Methacrylate acid	86
3.7	Properties of Ethylenediaminetetraacetic acid disodium salt-2-hydrate	86
3.8	Properties of Lipase	86
3.9	Formulation of PLA/rLDPE/NFH biocomposites with different NFH content	89
3.10	Formulation of uncompatibilized and compatibilized PLA/rLPDE/NFH biocomposites	90
3.11	Formulation of untreated and treated PLA/rLPDE/NFH biocomposites with different chemical modification	90
3.12	Formulation of treated PLA/rLPDE/NFH biocomposites with EDTA/Enzyme and 3-APE/Enzyme	91
4.1	Statistical Analysis of Variance (ANOVA) for NFH Content	103
4.2	DSC Data of PLA/rLDPE/NFH biocomposites	107
4.3	TGA data of PLA/rLDPE/NFH biocomposites	109
4.4	Statistical Analysis of Variance (ANOVA) for treated biocomposites	118
4.5	DSC data of untreated and treated PLA/rLDPE/NFH biocomposites with 3-APE	124

4.6	TGA data of untreated and treated PLA/rLDPE/NFH biocomposites with 3-APE	126
4.7	Statistical Analysis of Variance (ANOVA) for compatibilized biocomposites	134
4.8	DSC data of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites with PEMA	139
4.9	TGA data of uncompatibilized and compatibilized PLA/rLDPE/NFH biocomposites with PEMA	140
4.10	Statistical Analysis of Variance (ANOVA) for treated biocomposites	148
4.11	DSC data of untreated and treated PLA/rLDPE/NFH biocomposites with MMA	153
4.12	TGA data of untreated and treated PLA/rLDPE/NFH biocomposites with MMA	154
4.13	Statistical Analysis of Variance (ANOVA) for biocomposites with EDTA	162
4.14	DSC data of PLA/rLDPE/NFH biocomposites with and without EDTA	167
4.15	TGA data of PLA/rLDPE/NFH biocomposites with and without EDTA	168
4.16	Statistical Analysis of Variance (ANOVA) for biocomposites with EDTA/Enzyme.	176
4.17	DSC data of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	181
4.18	TGA data of untreated and treated PLA/rLDPE/NFH biocomposites with binary modification using EDTA/Enzyme	183
4.19	Statistical Analysis of Variance (ANOVA) for biocomposites with 3-APE/Enzyme.	191
4.20	DSC data of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	196
4.21	TGA data of treated PLA/rLDPE/NFH biocomposites with 3-APE and 3-APE/Enzyme	197

LIST OF ABBREVIATIONS

3-APE	3-aminopropyltriethoxysilane
ASTM	American society testing method
ATR	Attenuated total reflectance
CO ₂	Carbon dioxide
DP	Degree polymerization
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared
HDPE	High density polyethylene
LDPE	Low density polyethylene
MMA	Methyl methacrylate
NFH	<i>Nypa Fruticans</i> husk
PEMA	Polyethylene grafted Maleic Anhydride
php	Part per hundred polymer
PLA	Polylactic acid
rLDPE	Recycled low density polyethylene
SEM	Scanning electron microscopy
T _c	Crystallization temperature
T _g	Glass transition temperature
TGA	Thermogravimetry analysis
T _m	Melting temperature
X _c	Degree of crystallization
ΔH _f	Heat fusion of polymer biocomposites
ΔH _f ^o	Heat fusion of 100% crystalline matrix

Kesan Kandungan Pengisi dan Modifikasi Kimia Keatas Sifat-Sifat Polilaktik Asid/Polietilena Ketumpatan Rendah Kitar Semula/Serat Nipa Fruktikan Biokomposit

ABSTRAK

Biokomposit serat *Nipa fruktikan* (SNF) terisi polilaktik asid (PLA)/polietilena ketumpatan rendah kitar semula (PKRKS) telah disediakan menggunakan Brabender Plastikorder EC PLUS pada suhu 180 °C dan kelajuan rotor 50 rpm. Kesan kandungan SNF dan jenis-jenis modifikasi-modifikasi kimia yang berbeza ke atas sifat-sifat tensil, morfologi, sifat-sifat terma dan biosotan biokomposit PLA/PKRKS telah dikaji. Pelbagai jenis-jenis modifikasi-modifikasi kimia seperti polietilena dicantum maleik anhidrida (PEMA), 3-aminopropiltrioksisilana (3-APE), asid metil metakrilat (AMM), asid etilenadiaminatetraasetik garam-2-hidrat (AEDT), dan enzim telah digunakan, berturut-turut. Keputusan menunjukkan bahawa penambahan SNF kedalam PLA/PKRKS telah mengurangkan kekuatan tensil, pemanjangan pada takat putus, dan darjah penghabluran (X_c), dimana modulus Young dan kestabilan terma meningkat. Kesan α -amilase terhadap biosotan biokomposit PLA/PKRKS/SNF menunjukkan dengan peningkatan kandungan SNF, meningkatkan kadar biosotan biokomposit. Morfologi permukaan patahan tensil telah menunjukkan bahawa interaksi yang lemah terjadi diantara SNF dengan matrik PLA/rLDPE. Modifikasi-modifikasi kimia menghasilkan kesan positif ke atas sifat-sifat tensil dan terma biokomposit PLA/PKRKS/SNF. Kehadiran PEMA, 3-APE, AMM, AEDT, AEDT/Enzim dan 3-APE/Enzim telah meningkatkan kekuatan tensil, modulus Young, darjah penghabluran dan kestabilan terma biokomposit. Biokomposit terawat PLA/PKRKS/SNF dengan 3-APE/Enzim mempunyai kekuatan tensil, modulus Young, dan kestabilan terma yang paling tinggi berbanding biokomposit dengan modifikasi-modifikasi kimia yang lain. Walaubagaimana, biokomposit PLA/PKRKS/SNF terawat dengan AMM mempunyai darjah penghabluran yang tertinggi. Sementara, biokomposit PLA/PKRKS/SNF terawat dengan AEDT menunjukkan kadar biosotan yang paling tinggi. Interaksi antara muka yang lebih baik diantara SNF yang terawat dan matrik PLA/PKRKS telah dibuktikan melalui kajian SEM. FTIR spektra menunjukkan bahawa perubahan-perubahan kumpulan berfungsi biokomposit yang terawat.

The Effect of Filler Content and Chemical Modification On Properties of Polylactic Acid/Recycled Low Density Polyethylene/*Nypa Fruticans* Husk Biocomposites

ABSTRACT

Nypa fruticans husk (NFH) filled polylactic acid (PLA)/recycled low density polyethylene (rLDPE) biocomposites had been prepared using Brabender Plasticoder EC PLUS at temperature 180°C and rotor speed 50 rpm. The effect of NFH content and different types of chemical modifications on tensile properties, morphology, thermal properties and biodegradation of PLA/rLDPE/NFH biocomposites were studied. The various types of chemical modifications such as Polyethylene grafted maleic anhydride (PEMA), 3-Aminopropyltriethoxysilane (3-APE), Methyl methacrylate acid (MMA), Ethylenediaminetetraacetic acid disodium salt-2-hydrate (EDTA), and enzyme were used, respectively. The results showed that the addition of NFH reduced the tensile strength, elongation at break and degree of crystallinity (X_c), whereas the Young's modulus and thermal stability of biocomposites increased. The effects of α -amylase on the enzyme biodegradation of PLA/rLDPE/NFH biocomposites showed that the increased of NFH content has increased the biodegradation rate of the biocomposites. The morphology tensile fracture surface of PLA/rLDPE/NFH biocomposites indicates that poor interaction occurred between NFH and PLA/rLDPE matrix. The chemical modifications of NFH resulted positive effect on tensile and thermal properties of PLA/rLDPE/NFH biocomposites. The presence of PEMA, 3-APE, MMA, EDTA, EDTA/Enzyme and 3-APE/Enzyme have increased the tensile strength, Young's modulus, degree of crystallinity and thermal stability of biocomposites, whereas the elongation at break decreased. The treated PLA/rLDPE/NFH biocomposites with 3-APE/Enzyme have highest tensile strength, Young's modulus, and thermal stability compared to other chemical modifications of biocomposites. However, PLA/rLDPE/NFH biocomposites treated with MMA has highest degree of crystallinity. Meanwhile PLA/rLDPE/NFH biocomposites treated with EDTA exhibited highest rate of biodegradation. The better interfacial interaction between treated NFH and PLA/rLDPE matrix was proven by SEM study. The spectra FTIR indicated that the changes of functional group of treated biocomposites.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The growing environmental concern and increasing scarcity of fossil fuel resources have proven an intensive demand for biomass with controllable properties, with the desire to reduce petroleum consumption and mitigate pollution (Lu & Oza, 2013; Zhang & Sun, 2004). Biodegradable polymers have received much attention recently with growing pressure on the world resources as well as concern about disposal of plastics and commercial activity. Biodegradability, greenhouse, gas emission and renewability are the environmental benefits offered by biopolymer (Rajesh & Prasad, 2014).

Poly (lactic acid) (PLA) made from renewable agriculture raw materials which are fermented to lactic acid, has been considered to be a type of commercial available and fully biodegradable polymers (Duhovic et al., 2009; Koronis et al., 2013; Lu et al., 2014; Qu et al., 2010). PLA is now one of the most promising biodegradable polymers for industrial plastic application, which served as an alternative to conventional synthetic polymer (Pantani & Sorrentino, 2013). Because of the demand of biodegradable based products in recent years, PLA based products are manufactured

commercially in many countries. Their application include film, food packaging, textiles, disposal bottle and table ware (Auras et al., 2004; Jia et al., 2014). In order to make them appropriate in many technical applications, the mechanical properties of PLA can be improved by using reinforcement (A et al., 2015; Akbari et al., 2015; Iwata, 2015; Shukor et al., 2014).

Nowadays, natural fibers exhibit many advantages over the synthetic fibers such as low density, low cost , high strength, high specific modulus and especially their recyclability (Salleh et al., 2014; Yu et al., 2014). The reinforcement of PLA with natural fibers seems to be a logical alternative in order to increase their mechanical performance as well as keeping the final material environmentally friendly. Some researchers have reported the natural fibers or fillers as reinforcement of PLA as shown in Table 1.1.

Table 1.1 : Natural Fibers as filler in PLA.

Natural Fiber	Reported by researcher
Kenaf	Huda et al., 2008; Ochi, 2008
Hemp	Baghaei et al., 2013; Oza et al., 2014; Sawpan et al., 2011
Ramie	Chen et al., 2015; Yu et al., 2010; Zhou et al., 2012
Rice straw	Qin et al., 2011; Zhao et al., 2011
Abaca	Bledzki et al., 2009; Reddy & Yang, 2015
Jute	Arao et al., 2015; Ma & Joo, 2011; Memon & Nakai, 2013; Rajesh & Prasad, 2014
Bamboo	Kumar et al., 2013; Lu et al., 2014; Young et al., 2014
Oil palm	Jaffar Al-Mulla et al., 2013; Koutsomitopoulou et al., 2014
Flax	Manshor et al., 2014; Nassiopoulos & Njuguna, 2015; Zhu et al., 2013
Cordenka	Bax & Müssig, 2008
Wood	Csizmadia et al., 2013; Peltola et al., 2014
Lignin	Spiridon et al., 2015

Nypa fruticans is a monoecious palm with special characteristics. Contrast to usual palms like coconut and oil palm, it thrives in river estuaries and brackish water environment in which salt and fresh water mingle. *Nypa fruticans* are a major source which are extensively used as thatching materials but most parts of the *Nypa fruticans* are left to decompose at its habitat (Rahman, 2000). Therefore, *Nypa fruticans* is an abundance resource that can be found throughout the year. *Nypa fruticans* consisting of frond, shell, husk and leaf. The total chemical composition showed that the cellulose

and hemicellulose contents were in the range of 28.9–45.6 wt% and 21.8–26.4 wt%, respectively. The lignin content was 19.4–33.8 wt% with the highest lignin content found in leaf. Besides the main chemical components, starch, protein and extractives were also present in significant amounts from 2 to 8 wt%. Additionally, the ash content was high from 5.1 to 11.7 wt% (Tamunaidu & Saka, 2011). In overall, each part of the *Nypa fruticans* has its individual superior characteristics and could be exploited as lignocellulosic resources for biocomposites.

On the other hand, PLA was chosen for its high biocompatibility and biodegradability. It has become an alternative to traditional commodity plastics for everyday applications as an environmental friendly polymer due to its some unique properties such as high strength, high stiffness and resistance to fats and oil (Hamad et al., 2011b). However, brittleness and other properties such as low viscosity, low thermal stability, high moisture sensitivity, medium gas barrier properties, high cost (comparing with PE, PP, PS, etc) and low solvents resistance (e.g., against water) are often insufficient for many applications. Therefore, blending can aid in the development of new biocomposite products with better performance (Akbari et al., 2015; Ebadi-Dehaghani et al., 2015; Hamad et al., 2011b; Ouchiar et al., 2015; Yu et al., 2006; Zhou et al., 2015).

The properties of PLA can be modified by polymer blending techniques, where it was blended with several synthetic and biopolymers in efforts to enhance its properties and also to obtain novel materials as shown in Table 1.2. PLA have been blended with different polymers to obtain materials with lower cost and improved properties.