UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF POLY(LACTIC ACID)/KENAF-DERIVED CELLULOSE WITH THERMALLY GRAFTED AMINOSILANE AND EPOXIDIZED PLANT OILS FOR POTENTIAL FOOD PACKAGING APPLICATIONS

TEE YEE BOND

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By

TEE YEE BOND

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

June 2015
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

DEVELOPMENT OF POLY(LACTIC ACID)/KENAF-DERIVED CELLULOSE WITH THERMALLY GRAFTED AMINOSILANE AND EPOXIDIZED PLANT OILS FOR POTENTIAL FOOD PACKAGING APPLICATIONS

By

TEE YEE BOND

June 2015

Chair: Rosnita A. Talib, PhD

Faculty: Engineering

Poly(lactic acid) (PLA) biocomposites aimed for food packaging applications were developed from the present research. Seventeen PLA blends were studied and one optimum ternary biocomposite was finalized to conclude the work. Kenaf-derived cellulose (C), 3-aminopropyltriethoxysilane (APS), epoxidized soybean oil (ESO), and epoxidized palm oil (EPO) were the core materials tested for reinforcement.

It is typical that natural fibers-filled plastic composites to report poor interfacial adhesion due to their distinct difference in polarity. To improve the interfacial adhesion, kenaf-derived cellulose was treated with silane coupling agent, APS prior to filling into PLA. Moreover, they were subjected to thermal treatment for permanent cross-linking upon acknowledging that desorption of chemicals is highly undesirable in food-related packaging. Also distinct to typical practices, C was thermally grafted with various silane concentrations (5, 8, and 11 wt%) and these silane-grafted cellulose (SGC) were termed as SGC5, SGC8, and SGC11. From investigation via Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), morphology analysis, size distribution, and density measurement, it was conclusive that (i) cellulose was derived from kenaf, and (ii) silane was effectively grafted onto the cellulose.
30 wt% of C, SGC5, SGC8, and SGC11 were respectively melt-compounded into PLA and hot-pressed into 0.3-mm sheets with the aim to develop biocomposite with optimum properties. With highest reinforcement in tensile strength, water resistance, dimensional stability, crystallinity, and oxygen barrier, PLA/SGC8 was concluded as the biocomposite for development towards packaging applications. Nonetheless, all biocomposites did not improve PLA’s brittle nature. Concurrently, they reduced the toughness. With sustainability in mind, EPO and commercialized ESO were plasticizers considered to reinforce these properties. Out of the analyses subjected, it is noteworthy that EPO can transition PLA to become ductile and tougher at lower concentration than ESO which denoted its competency as alternative bioplasticizer.

Comprehending EPO’s potential as reactive plasticizer, the research continued with EPO addition at various loadings (3, 5, and 10 wt%) into PLA/SGC8 composite. Peak shifts were observed in the FTIR spectra of PLA/SGC8/EPO blends which was absent in PLA/C/EPO. It was proposed that EPO could reactively interact with PLA and SGC which therefore functioned as a compatible layer between the interfaces. The proposed mechanism was validated from morphology analysis plus improvement in water resistance, mechanical, and thermal properties of PLA/SGC8/EPO blends. Of all ternary blends, PLA/SGC8/EPO5 reported optimum reinforcement in EAB and toughness. The oxygen and water vapour barrier of this optimized blend suggested potential as packaging material for salad mixes.

Conceding that the developed biocomposite can be impractical if it cannot be fabricated into functional product, PLA/SGC8/EPO5 together with PLA/EPO10, PLA/C/EPO5, and PLA (as reference) sheets were selectively subjected to thermoformability and overall migration test. While PLA/C/EPO5 failed both tests, PLA/SGC8/EPO5 was thermoformable and constituent migration was within the stipulated overall migration limit. These practical tests reasserted the competency of the presently developed biocomposite to be fabricated towards food packaging applications.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN POLI(ASID LAKTIK)/SELULOSA TERBITAN KENAF
YANG DIGRAFKAN SECARA TERMA DENGAN SILANA-AMINO DAN
MINYAK TUMBUHAN YANG DIEPOKSIKAN UNTUK POTENSI
APLIKASI PEMBUNGKUSAN MAKANAN

Oleh

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Biokomposit poli(asid laktik) (PLA) untuk aplikasi pembungkusan makanan telah dibangunkan dalam penyelidikan ini. Daripada tujuh belas campuran PLA yang dikaji, satu biokomposit dengan sifat-sifat optimum telah dimuktamadkan. Selulosa terbitan kenaf (C), ‘3-aminopropyltriethoxysilane’ (APS), minyak kacang soya yang diepoksikan (ESO), dan minyak kelapa sawit yang diepoksikan (EPO) adalah bahan utama yang dipilih untuk pengukuhan biokomposit.

Sering kali, komposit plastik yang diisi dengan fiber semulajadi mempunyai lekatan antara muka yang lemah atas perbezaan ionik yang ketara. Untuk mengatasi masalah tersebut, selulosa terbitan kenaf dirawat dengan silana APS sebelum diisi ke dalam PLA. Selain itu, mereka turut diberi rawatan terma supaya silana-amino digrafkan secara kekal ke atas C. Hal demikian kerana lesapan kimia adalah amat tidak diingini dalam aplikasi pembungkusan makanan. Juga berbeza dengan amalan tipikal, C digrafkan secara terma dengan silana-amino pada pelbagai kepekatan (5, 8, dan 11%) dan mereka dinamakan sebagai SGC5, SGC8, dan SGC11. Daripada kajian Spektroskopi Inframerah Fourier (FTIR), analisis Termogravimetri (TGA), analisis morfologi, taburan saiz, dan pengukuran ketumpatan, adalah disahkan bahawa (i) selulosa berjaya diterbitkan daripada kenaf, dan (ii) silana digrafkan ke atas selulosa dengan berkesan.
30% C, SGC5, SGC8, dan SGC11 dicampur ke dalam PLA dan ditekan secara terma untuk penghasilan kepingan komposit dengan ketebalan 0.3-mm. Ia bertujuan untuk membangunkan biokomposit dengan ciri-ciri optimum. Dengan peningkatan optimum dalam kekuatan tegangan, rintangan air, kestabilan dimensi, penghabluran, dan rintangan oksigen, PLA/SGC8 disimpulkan sebagai biokomposit untuk pembangunan ke arah aplikasi pembungkusan. Walau bagaimanapun, semua biokomposit tidak meningkatkan keboleh muluran PLA. Malah, kekuatan impaknya merosot. Disebabkan kemapanan sumbernya, EPO dan ESO yang telah dikomersialkan dipertimbangkan sebagai pemplastik (plasticizer) untuk mengukuhkan sifat-sifat tersebut. Daripada analisis-analisis yang dijalankan, EPO boleh meningkatkan kemuluran dan kekuatan impak PLA pada kepekatan yang lebih rendah daripada ESO. Hal demikian mengesahkan kecekapan EPO sebagai bio-pemplastik alternatif.

Setelah memahami potensi EPO sebagai pemplastik reaktif, penyelidikan diteruskan dengan penambahan EPO pada pelbagai kepekatan (3, 5, dan 10%) ke dalam komposit PLA/SGC8. Terdapat perubahan puncak dalam spektrum FTIR campuran PLA/SGC8/EPO yang tidak wujud dalam spektrum FTIR PLA/C/EPO. Justeru itu, adalah dicadangkan bahawa EPO boleh berinteraksi secara reaktif dengan PLA dan SGC. EPO mungkin boleh berfungsi sebagai lapisan keserasian antara PLA dan SGC. Mekanisme interaksi yang dicadangkan boleh disahkan daripada analisis morfologi serta peningkatan ketara pada rintangan air, mekanikal, dan sifat-sifat terma dalam campuran PLA/SGC8/EPO. Daripada sampel-sampel komposit yang dikaji, PLA/SGC8/EPO5 melaporkan peningkatan optimum kemuluran dan kekuatan impak. Daripada penyelidikan rintangan oksigen dan wap air, adalah dicadangkan bahawa biokomposit tersebut berpotensi untuk digunakan dalam pembungkusan campuran salad.

Atas pemahaman bahawa biokomposit yang dibangunkan boleh menjadi tidak praktikal jika ia tidak boleh dibentuk ke dalam produk berfungsi, PLA/SGC8/EPO5 bersama-sama dengan PLA, PLA/EPO10, dan PLA/C/EPO5 dipilih untuk ujian pembentukan plastik secara terma dan penghijrahan keseluruhan bahan. PLA/C/EPO5 gagal dalam ujian-ujian tersebut. Sementara itu, PLA/SGC8/EPO5 boleh dibentuk secara terma dengan baik dan penghijrahan bahan daripadanya berada dalam had penghijrahan yang dibenarkan. Ujian-ujian praktikal tersebut memberi sokongan kukuh ke atas kesesuaian biokomposit yang kini dibangunkan untuk difabrikasi ke arah aplikasi pembungkusan makanan.
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Last but not least, I owe a big thanks to my family especially my parents for their loving support, patience, and faith in me in pursuing this postgraduate study. For that, I dedicate this dissertation to my beloved parents, Tee Chong Seng and Yeow Meng Choo.
I certify that a Thesis Examination Committee has met on 30th June 2015 to conduct the final examination of Tee Yee Bond on his thesis entitled “Development of Poly(Lactic Acid)/Kenaf-Derived Cellulose with Thermally Grafted Aminosilane and Epoxidized Plant Oils for Potential Food Packaging Applications” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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# TABLE OF CONTENTS

| ABSTRACT | i |
| ABSTRAK | iii |
| ACKNOWLEDGEMENTS | v |
| APPROVAL | vi |
| DECLARATION | vii |
| LIST OF TABLES | xv |
| LIST OF FIGURES | xviii |
| LIST OF ABBREVIATIONS | xxvi |

## CHAPTER

### 1 INTRODUCTION

1.1 Statement and Significance of the Problem  
1.2 Research Aim and Objectives  
1.3 Significance of the Research  
1.4 Thesis Outline  

### 2 LITERATURE REVIEW

2.1 From Synthetic to Natural Fiber as Reinforcing Agent in Composites  
2.2 Biocomposite and Its Potential in the Packaging Field  
2.3 Natural Fibers for Biocomposites  
2.4 Cellulose, Hemicellulose, and Lignin in Natural Fibers  
2.5 Advantages and Disadvantages of Natural Fibers as Composite Fillers  
2.6 Kenaf and Its Development in Malaysia  
2.7 Kenaf-Derived Cellulose for the Present Research  
2.8 Effects of Alkali Treatment on Natural Fibers and Composites  
2.8.1 Chemical Properties  
2.8.2 Mechanical Properties  
2.8.3 Morphological Properties  
2.8.4 Condition Chosen for Alkali Treatment  
2.9 Silane Coupling Agent  
2.10 Activating Alkoxy Groups in Silane for Natural Fibers
2.11 Recognising Condition for Silanols-
2.12 Natural Fibers Binding Coupling Agent APS for the Present Research
2.12.1 Is APS Safe for Packaging Applications?
2.13 Chemically Grafting Prehydrolysed Silane Coupling Agent onto Cellulosic Fibers
2.14 Effects of Silane Coupling Agent
2.14.1 Chemical Properties
2.14.2 Mechanical Properties
2.14.3 Thermal Properties
2.14.4 Physical Properties
2.15 Bioplastic PLA
2.16 Plasticizer for PLA
2.17 Theoretical Assessment of Polymer-Plasticizer Miscibility
2.18 Effects of Plasticizers Addition in PLA
2.18.1 Chemical Properties
2.18.2 Mechanical Properties
2.18.3 Thermal Properties
2.18.4 Morphological Properties
2.19 Bio-Sourced Plasticizers for the Present Research
2.20 Chemical Structure of Epoxidized Oil
2.21 Permeation on a Molecular Scale Coefficient of Permeability for Packaging Film
2.22 Coefficient of Permeability for Packaging Film
2.22.1 Water Vapour Transmission Rate (WVTR)
2.22.2 Oxygen Transmission Rate (OTR)
2.23 Barrier Requirements for Food Packaging
2.24 Factors for Barrier Properties

3 THERMALLY GRAFTING AMINOSILANE ONTO KENAF-DERIVED CELLULOSE AND THEIR EFFECTS AS REINFORCING FILLERS IN PLA/SGC COMPOSITES
3.1 Introduction
3.2 Experimental
3.2.1 Materials
3.2.2 Preparation of Cellulose from Kenaf Bast Fibers
| 3.2.3 | Cellulose Sizing | 59 |
| 3.2.4 | Preparation of Silane-Grafted Cellulose | 59 |
| 3.2.5 | Preparation of Composite Pellets | 60 |
| 3.2.6 | Preparation of Composite Sheets | 61 |
| 3.2.7 | Sheet Thickness | 62 |
| 3.2.8 | Storage of Sample Sheets | 62 |
| 3.2.9 | FTIR Spectra Analysis | 62 |
| 3.2.10 | Thermogravimetric Analysis (TGA) | 62 |
| 3.2.11 | Differential Scanning Calorimetry (DSC) | 63 |
| 3.2.12 | Tensile Test | 63 |
| 3.2.13 | Notched Izod Impact Test | 63 |
| 3.2.14 | Oxygen Permeability | 63 |
| 3.2.15 | Water Vapour Permeability | 64 |
| 3.2.16 | Density | 65 |
| 3.2.17 | Water Absorption and Dimensional Stability | 65 |
| 3.2.18 | Morphological Analysis | 66 |
| 3.2.19 | Statistical Analysis | 66 |

### 3.3 Results and Discussion

**3.3.1 Properties of KBF, C, SGC5, SGC8, and SGC11**

- 3.3.1.1 FTIR Spectra
- 3.3.1.2 Fiber Size Distribution and Aspect Ratio
- 3.3.1.3 Morphology Analysis
- 3.3.1.4 Density of C, SGC5, SGC8, and SGC11
- 3.3.1.5 Thermogravimetric Analysis

**3.3.2 Properties of PLA/SGC Composites**

- 3.3.2.1 Melt-Compounding Analysis
- 3.3.2.2 Density of PLA Composites
- 3.3.2.3 FTIR Spectra
- 3.3.2.4 Mechanical Properties
- 3.3.2.5 Thermogravimetric Analysis
- 3.3.2.6 Differential Scanning Calorimetry Analysis
3.3.2.7 Water Absorption and Dimensional Stability 99
3.3.2.8 Barrier Properties 105
3.3.2.9 Morphology Analysis

3.4 Summary 109

4 EFFECTS OF ADDING BIO-SOURCED PLASTICIZERS IN PLA AND PLA COMPOSITES 111
4.1 Introduction 111
4.2 Experimental 111
4.2.1 Materials 112
4.2.2 Preparation of Composite Pellets 112
4.2.3 Thermogravimetric Analysis 112
4.3 Results and Discussion 113
4.3.1 Melt-Compounding Analysis 113
4.3.2 Density 115
4.3.3 FTIR Spectra 117
4.3.4 Mechanical Properties 124
4.3.5 Thermogravimetric Analysis 132
4.3.6 Differential Scanning Calorimetric Analysis 138
4.3.7 Water Absorption and Dimensional Stability 143
4.3.8 Barrier Properties 147
4.3.9 Morphology Analysis 151
4.4 Summary 158

5 THERMOFORMABILITY AND OVERALL MIGRATION TEST 160
5.1 Introduction 160
5.2 Experimental 160
5.2.1 Materials 160
5.2.2 Vacuum Forming 160
5.2.3 Overall Migration Test 162
5.2.3.1 Exposure to Food Simulant 162
5.2.3.2 Preparation of Dishes 163
5.2.3.3 Evaporation of Simulant 163
5.3 Results and Discussion 163
5.3.1 Thermoforming Temperature 163
5.3.2 Physical Observation of Thermoformed Articles 165
5.3.3 Overall Migration Test 167
6 CONCLUSIONS AND RECOMMENDATIONS 111
6.1 Conclusions 170
  6.1.1 Thermally Grafting Aminosilane onto Kenaf-Derived Cellulose 170
  6.1.2 Effects of SGC as fillers in PLA 170
  6.1.3 Effects of EPO and ESO as Plasticizers in PLA 171
  6.1.4 Effects of EPO as Plasticizer in PLA Composites 171
6.2 Recommendations for Future Research 172

REFERENCES 174
APPENDICES 203
BIODATA OF STUDENT 254
LIST OF PUBLICATIONS 255
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Microfibril size and chemical constituent of kenaf bast and core.</td>
</tr>
<tr>
<td>2.2</td>
<td>Characteristic frequencies in FTIR spectra corresponding to the main functional group of natural fibers.</td>
</tr>
<tr>
<td>2.3</td>
<td>Silane coupling agents typically used for the targeted polymer matrices in natural fiber/polymer composites.</td>
</tr>
<tr>
<td>2.4</td>
<td>Characteristic frequencies in FTIR spectra corresponding to silane treatment on natural fibers.</td>
</tr>
<tr>
<td>2.5</td>
<td>Glass transition temperature ($T_g$) and melting temperature ($T_m$) of PLA at different L- and D-lactide ratio.</td>
</tr>
<tr>
<td>2.6</td>
<td>Characteristic frequencies in FTIR spectra corresponding to addition of plasticizers into plastics and composites.</td>
</tr>
<tr>
<td>2.7</td>
<td>Structure of fatty acids in triglyceride and the typical fatty acid composition of soybean oil.</td>
</tr>
<tr>
<td>2.8</td>
<td>WVTR and OTR requirements for several food products.</td>
</tr>
<tr>
<td>3.1</td>
<td>Properties of the PLA resin from PLA 2003D Datasheet.</td>
</tr>
<tr>
<td>3.2</td>
<td>Pressing condition for hot and cold press machine.</td>
</tr>
<tr>
<td>3.3</td>
<td>Aspect ratio (L/D) of the composite fillers.</td>
</tr>
<tr>
<td>3.4</td>
<td>Weight losses (%) of KBF, C, SGC5, SGC8, and SGC11 at various temperatures.</td>
</tr>
<tr>
<td>3.5</td>
<td>Data extracted from torque and stock temperature curves of PLA and PLA.</td>
</tr>
</tbody>
</table>
composites during melt-compounding.

3.6 Mechanical properties of PLA and PLA composites with fixed matrix/filler loading of 70/30.  

3.7 Weight losses (%) of PLA and PLA composites at various temperatures.  

3.8 DSC results for PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.  

3.9 OTR, OP, WVTR, and WVP of PLA and PLA composites with fixed matrix/filler loading of 70/30.  

4.1 Properties of ESO and EPO from theDatasheets.  

4.2 The amount of PLA and PLA composites blends per batch of melt-blending.  

4.3 Data extracted from torque and stock temperature curves of PLA and PLA added with various additives during melt-compounding.  

4.4 Mechanical properties of PLA and various PLA composite blends.  

4.5 TGA and DTG results for PLA and PLA plasticized with EPO and ESO at various loadings.  

4.6 DSC results for PLA and various PLA composite blends.  

4.7 Water absorption (%) and thickness swelling (%) of PLA and plasticized PLA at various plasticizers loadings after 20 days of water immersion.  

4.8 OTR, OP, WVTR, and WVP of PLA and various PLA composite blends.  

5.1 Observation of vacuum formed articles.  

xvi
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Overall migration from samples into food simulant (distilled water) after 10 days at 40 °C.</td>
</tr>
<tr>
<td>A-1</td>
<td>Physical, mechanical, and, chemical properties of natural fibers as compared to glass and wood.</td>
</tr>
<tr>
<td>A-2</td>
<td>WVTR values of polymers normalized to 0.25 mm thickness.</td>
</tr>
<tr>
<td>A-3</td>
<td>OTR values of polymers normalized to 0.25 mm thickness.</td>
</tr>
<tr>
<td>A-4</td>
<td>Mechanical properties of PLA from various literatures.</td>
</tr>
<tr>
<td>A-5</td>
<td>Tensile and flexural strengths (TS and FS) of thermoplastics reinforced with (silane treated and untreated) fillers from various literatures.</td>
</tr>
<tr>
<td>A-6</td>
<td>Tensile and flexural modulus (TM and FM) of thermoplastics reinforced with (silane treated and untreated) fillers from various literatures.</td>
</tr>
<tr>
<td>A-7</td>
<td>Elongation at break (EAB) of thermoplastics reinforced with (silane treated and untreated) fillers from various literatures.</td>
</tr>
<tr>
<td>A-8</td>
<td>Impact strength (IS) of thermoplastics reinforced with (silane treated and untreated) fillers from various literatures.</td>
</tr>
<tr>
<td>A-9</td>
<td>Tensile properties of thermoplastics added with plasticizers from various literatures.</td>
</tr>
<tr>
<td>A-10</td>
<td>Impact strength of thermoplastics added with plasticizers from various literatures.</td>
</tr>
<tr>
<td>A-11</td>
<td>Tensile properties of plasticized composites from various literatures.</td>
</tr>
<tr>
<td>A-12</td>
<td>Impact strength of plasticized composites from various literatures.</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.1</td>
<td>Process flow chart (*more than one formulation).</td>
</tr>
<tr>
<td>2.1</td>
<td>Classification of natural fibers used as fillers for composite.</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic drawing of cellulose and microfibril structure.</td>
</tr>
<tr>
<td>2.3</td>
<td>The chemical structure of cellulose with cellubiose repeat unit.</td>
</tr>
<tr>
<td>2.4</td>
<td>The structure of a wood fiber.</td>
</tr>
<tr>
<td>2.5</td>
<td>(a) Kenaf plant and (b) cross section of kenaf stalk.</td>
</tr>
<tr>
<td>2.6</td>
<td>Interaction of silane with natural fiber via hydrolysis.</td>
</tr>
<tr>
<td>2.7</td>
<td>The possible siloxane structures from self-condensation of silanol molecules.</td>
</tr>
<tr>
<td>2.8</td>
<td>Adsorption and chemical grafting of prehydrolysed silane with natural fiber.</td>
</tr>
<tr>
<td>2.9</td>
<td>Illustration of the silane structure on the cellulose.</td>
</tr>
<tr>
<td>2.10</td>
<td>Formation of PLA from lactic acid or lactide dimer.</td>
</tr>
<tr>
<td>2.11</td>
<td>Three diastereomeric structures of lactide.</td>
</tr>
<tr>
<td>2.12</td>
<td>Glass transition and melting temperatures of PLA and other thermoplastics.</td>
</tr>
<tr>
<td>2.13</td>
<td>Possible chemical structures of (a) triglyceride; and (b) its epoxidized form.</td>
</tr>
<tr>
<td>2.14</td>
<td>Permeation through a film.</td>
</tr>
</tbody>
</table>
2.15 Diffusion of permeant through (a) polymer film, and (b) nanocomposite film with exfoliated clay platelets.

3.1 (a) Pellets arranged onto the Mylar® sheets and (b) metal plates sandwiching the pellets and the sheets.

3.2 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for KBF, C, and SGC at various silane concentrations in the FTIR region from 600 to 4000 cm\(^{-1}\).

3.3 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for KBF, C, and SGC at various silane concentrations in the FTIR region from 3200 to 3500 cm\(^{-1}\).

3.4 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for KBF, C, and SGC at various silane concentrations in the FTIR region from 1600 to 1700 cm\(^{-1}\).

3.5 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for (a) C; and (b) SGC8 in the FTIR region from 1000 to 1100 cm\(^{-1}\).

3.6 Distribution of the diameter for composite fillers after sieving with 125-µm test sieve.

3.7 VPSEM micrographs at 1300x magnification of (a) kenaf bast fiber; and (b) cellulose.

3.8 VPSEM micrographs at 4500x magnification of (a) C; (b) SGC5; (c) SGC8; and (d) silane-grafted cellulose. Density.

3.9 Density of cellulose, SGC5, SGC8, and SGC11.

3.10 TGA curves for KBF, C, SGC5, SGC8, and SGC11.

3.11 DTG curves for KBF, C, SGC5, SGC8, and SGC11.

3.12 Torque and stock temperature curves during
the melt-compounding of PLA and PLA composites at adjusted temperature 170 °C.

3.13 Density of PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.

3.14 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for C, PLA, PLA/C, and PLA/SGC at various silane concentrations in the FTIR region from 600 to 4000 cm\(^{-1}\).

3.15 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for C, PLA, PLA/C, and PLA/SGC at various silane concentrations in the FTIR region from 3200 to 3500 cm\(^{-1}\).

3.16 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for C, PLA, PLA/C, and PLA/SGC at various silane concentrations in the FTIR region from 1700 to 1800 cm\(^{-1}\).

3.17 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for C, PLA, PLA/C, and PLA/SGC at various silane concentrations in the FTIR region from 1000 to 1250 cm\(^{-1}\).

3.18 Proposed chemical interactions (intramolecular hydrogen bonding) between silane-grafted cellulose and PLA.

3.19 TGA curves for PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.

3.20 DTG curves for PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.

3.21 DSC curves for PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.

3.22 Water absorption of PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.

3.23 Thickness swelling of PLA and PLA composites with fixed matrix/filler weight ratio of 70/30.
3.24 VPSEM micrographs at 250x magnification of tensile fracture surfaces of (a) PLA; (b) PLA/C; (c) PLA/SGC5; (d) PLA/SGC8; and (e) PLA/SGC11.

3.25 VPSEM micrographs at 500x magnification of tensile fracture surface of (a) PLA/C; (b) PLA/SGC8; and (c) PLA/SGC11.

4.1 Density of PLA and PLA/plasticizer blends at various loadings.

4.2 Density of PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.3 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO and ESO in the FTIR region from 600 to 4000 cm\(^{-1}\).

4.4 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO, PLA, and PLA/EPO at various EPO concentrations in the FTIR region from 600 to 4000 cm\(^{-1}\).

4.5 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for ESO, PLA, and PLA/ESO at various ESO concentrations in the FTIR region from 600 to 4000 cm\(^{-1}\).

4.6 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO and EPO-plasticized PLA composites at various EPO concentrations in the FTIR region from 600 to 4000 cm\(^{-1}\).

4.7 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO, PLA/C, PLA/C/EPO5, PLA/SGC8, and PLA/SGC8/EPO5 in the FTIR region from 3000 to 2800 cm\(^{-1}\).

4.8 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO, PLA/C, and PLA/C/EPO5 in the FTIR region from 1800 to 1700 cm\(^{-1}\).
4.9 Normalized absorbance as a function of wavenumber (cm\(^{-1}\)) for EPO, PLA/SGC8, and PLA/SGC8/EPO5 in the FTIR region from 1800 to 1700 cm\(^{-1}\).

4.10 Proposed chemical interactions (intramolecular hydrogen bonding) among EPO plasticizer, silane-grafted cellulose, and PLA.

4.11 Tensile strength (MPa) of plasticized PLA at various EPO and ESO wt%.

4.12 Tensile modulus (GPa) of plasticized PLA at various EPO and ESO wt%.

4.13 Elongation at Break (%) of plasticized PLA at various EPO and ESO wt%.

4.14 Post tensile deformed strips of (a) PLA; (b) PLA/EPO5; and (c) PLA/ESO15.

4.15 Impact strengths (J/m) of PLA and PLA plasticized with EPO and ESO at various loadings.

4.16 Effect of EPO content (wt%) on tensile properties of PLA/SGC8 composites.

4.17 Impact strengths (J/m) of PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.18 TGA curves for raw materials at 170 °C.

4.19 TGA curves for post-mixed pellets at 160 °C.

4.20 TGA curves for PLA and PLA/EPO at various EPO loadings.

4.21 DTG curves for PLA and PLA/EPO at various EPO loadings.

4.22 TGA curves for PLA and PLA/ESO at various ESO loadings.

4.23 DTG curves for PLA and PLA/ESO at various
4.24 TGA curves for PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.25 DTG curves for PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.26 DSC curves for PLA and PLA plasticized with EPO and ESO at various loadings.

4.27 DSC curves for PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.28 Water absorption of PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.29 Thickness swelling of PLA composites with fixed matrix/filler weight ratio of 70/30 and varying plasticizer loadings.

4.30 VPSEM micrographs at 500x magnification of tensile fracture surface of (a) PLA/EPO3; (b) PLA/EPO5; (c) PLA/EPO10; (d) PLA/EPO15; (e) PLA/ESO3; (f) PLA/ESO5; (g) PLA/ESO10; and (h) PLA/ESO15.

4.31 VPSEM micrographs at 500x magnification of tensile fracture surface of (a) PLA/EPO5; and 250x magnification of tensile fracture surface of (b) PLA/ESO15.

4.32 VPSEM micrographs at 125x magnification of tensile fracture surface of (a) PLA/SGC8; (b) PLA/C/EPO5; (c) PLA/C/EPO5; (d) PLA/SGC8/EPO3; (e) PLA/SGC8/EPO5; and (f) PLA/SGC8/EPO10.

4.33 VPSEM micrographs at 500x magnification of impact fracture surface of (a) PLA/C/EPO5; (b) PLA/SGC8/EPO3; (c) PLA/SGC8/EPO5; and (d) PLA/SGC8/EPO10.
4.34 VPSEM micrographs at 500x magnification of the cross-section of (a) PLA/C/EPO5; (b) PLA/SGC8/EPO3; (c) PLA/SGC8/EPO5; and (d) PLA/SGC8/EPO10 composites after 20 days of water immersion.

5.1 Experimental setup of a basic vacuum forming test.

5.2 The order of procedure for vacuum forming from (i) to (iv).

5.3 Samples preparation for overall migration test.

5.4 Temperature profiles at different settings of heatgun.

5.5 Vacuum formed articles of (a) PLA; (b) PLA/EPO10; (c) PLA/C/EPO5; and (d) PLA/SGC8/EPO5.

5.6 Food simulant-exposed articles of (a) PLA; (b) PLA/EPO10; (c) PLA/C/EPO5; and (d) PLA/SGC8/EPO5.

5.7 The difference in colour of food simulant from overall migration test with articles (a) PLA/SGC8/EPO5; and (b) PLA/C/EPO5.

C-1 Torque and stock temperature curves during the melt-compounding of PLA and PLA-plasticizers blends at adjusted temperature 170 ºC.

C-2 Torque and stock temperature curves during the melt-compounding of PLA-plasticizers-fillers blends at adjusted temperature 170 ºC.

D-1 (a) Kenaf bast fibre; (b) (ground and sieved) kenaf-derived cellulose; and (c) silane-grafted cellulose.

D-2 ~0.3 mm thick sheets of (a) PLA; (b) PLA/ESO5; (c) PLA/EPO5; (d) PLA/C; (e) PLA/SGC8; (f) PLA/C/EPO5; and (g) PLA/SGC8/EPO5.
D-3  Setup for (a) water bath during chlorination of KBF; and (b) Soxhlet extraction during ethanol washing of SGC.

D-4  (a) Grinder; (b) test sieve; and (c) stereo microscope (digital analyser).

D-5  (a) Internal mixer; (b) mixing chamber of internal mixer; and (c) hot and cold press machine.

D-6  Water immersion test for all 17 samples with each strip dimension of 20.0 mm x 10.0 mm x 0.3 mm.

D-7  (a) Oxygen Permeability Analyser (MOCON Inc., OpTech®-O₂ Platinum, US) and (b) the preparation of sample sheet for OTR test.

D-8  (a) Water Vapour Permeability Analyser (Permatran W3/31, MOCON Inc., US) and (b) the preparation of sample sheet for WVTR test.
LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGM</td>
<td>Acetyl glycerol monolaurate</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
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<tr>
<td>AOTD</td>
<td>Advance Oleochemical Technology Division</td>
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<tr>
<td>APS</td>
<td>3-aminopropyl triethoxysilane</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society of Testing and Materials</td>
</tr>
<tr>
<td>ATBC</td>
<td>Acetyl(tributyl citrate)</td>
</tr>
<tr>
<td>BBP</td>
<td>Butylbenzylphthalate</td>
</tr>
<tr>
<td>C</td>
<td>Cellulose</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstract Service</td>
</tr>
<tr>
<td>CES</td>
<td>Cyanoethyltrimethoxy silane</td>
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<tr>
<td>COPP</td>
<td>γ-(2,3-cyclopropoxy)-propyltrimethoxy Silane</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>DBS</td>
<td>Dibutyl sebacate</td>
</tr>
<tr>
<td>DEHP</td>
<td>Di-(2-ethylhexyl) phthalate</td>
</tr>
<tr>
<td>DOA</td>
<td>Bis(2-ethylhexyl) adipate</td>
</tr>
<tr>
<td>DOP</td>
<td>Dioctyl phthalate</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>DTG</td>
<td>Differential Thermogravimetry</td>
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<tr>
<td>ECER</td>
<td>East Corridor Economic Region</td>
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<td>EHO</td>
<td>Epoxidized hemp oil</td>
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<tr>
<td>ELO</td>
<td>Epoxidized linseed oil</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>EPO</td>
<td>Epoxidized palm oil</td>
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<tr>
<td>ESO</td>
<td>Epoxidized soybean oil</td>
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<tr>
<td>FCM</td>
<td>Food contact material</td>
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<td>FCS</td>
<td>Food contact substance</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>GPA</td>
<td>Giga Pascal</td>
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<tr>
<td>GPS</td>
<td>3-glycidoxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>GRAS</td>
<td>Generally recognised as safe</td>
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<tr>
<td>GTA</td>
<td>Glyceryl triacetate</td>
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<tr>
<td>HAP</td>
<td>Hydroxyapatite</td>
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<tr>
<td>HDI</td>
<td>Hexamethylenediisocyanate</td>
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<tr>
<td>HIPS</td>
<td>High-impact polystyrene</td>
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<tr>
<td>HPMC</td>
<td>Hydroxypropyl methylcellulose</td>
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<tr>
<td>ICKAF</td>
<td>International Conference on Kenaf and Allied Fibers</td>
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<tr>
<td>INTROP</td>
<td>Institute of Tropical Forestry and Forest Product</td>
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<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
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<tr>
<td>KBF</td>
<td>Kenaf bast fiber</td>
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<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
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<tr>
<td>MA</td>
<td>Maleic anyhridride</td>
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<td>MAP</td>
<td>Modified atmosphere packaging</td>
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<tr>
<td>MCC</td>
<td>Microcrystalline cellulose</td>
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<tr>
<td>MFC</td>
<td>Microfibrillated cellulose</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>MGST</td>
<td>Maleic anhydride-grafted starch</td>
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<tr>
<td>MMT</td>
<td>Sodium montmorillonite</td>
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<tr>
<td>MPa</td>
<td>Mega Pascal</td>
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<tr>
<td>MPOB</td>
<td>Malaysian Palm Oil Board</td>
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<tr>
<td>MPS</td>
<td>3-methacryloxypropyltrimethoxysilane</td>
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<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
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<tr>
<td>OLA</td>
<td>Oligomeric lactic acid</td>
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<tr>
<td>OML</td>
<td>Overall migration limit</td>
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<tr>
<td>OPEFB</td>
<td>Oil palm empty fruit bunch</td>
</tr>
<tr>
<td>OTR</td>
<td>Oxygen transmission rate</td>
</tr>
<tr>
<td>PBOH</td>
<td>Poly(1,3-butanediol)</td>
</tr>
<tr>
<td>PBS</td>
<td>Poly(butylene succinate)</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactone</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PF</td>
<td>Phenolformaldehyde</td>
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<tr>
<td>PHA</td>
<td>Polyhydroxyalkanoates</td>
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<tr>
<td>PHB</td>
<td>Poly(hydroxybutyrate)</td>
</tr>
<tr>
<td>PHBV</td>
<td>Poly(hydroxybutyrate-valerate)</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly(lactic acid)</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPG</td>
<td>Poly(propylene glycol)</td>
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<td>PS</td>
<td>Polystyrene</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>PVC</td>
<td>Polyvinyl carbonate</td>
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<tr>
<td>RSF</td>
<td>Rice straw fiber</td>
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<tr>
<td>SGC</td>
<td>Silane-grafted cellulose</td>
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<tr>
<td>SML</td>
<td>Specific migration limit</td>
</tr>
<tr>
<td>TBAC</td>
<td>Tributyl O-acetylcitrate</td>
</tr>
<tr>
<td>TEC</td>
<td>Triethyl citrate</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TOR</td>
<td>Threshold of Regulation</td>
</tr>
<tr>
<td>USFDA</td>
<td>United States Food and Drug Administration</td>
</tr>
<tr>
<td>v%</td>
<td>Volume fraction</td>
</tr>
<tr>
<td>VPSEM</td>
<td>Vapour Pressure Scanning Electron Microscopy</td>
</tr>
<tr>
<td>VTS</td>
<td>Vinyltrimethoxysilane</td>
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<tr>
<td>wt%</td>
<td>Weight Fraction</td>
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<tr>
<td>WVTR</td>
<td>Water vapour transmission rate</td>
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CHAPTER 1

INTRODUCTION

1.1 Statement and Significance of the Problem

There is always a vast interest in developing new bio-based products. The cumulative concern from the depleting petroleum, the increasing social and environmental concern, and the stringent government regulations especially in Asian and European countries have made the need for "greener" products more vital than ever. The packaging industry is among the most obvious target for these efforts as the usage of packaging materials has shown continuous increase over time (Johansson et al., 2012).

In terms of plastic production, the technology development of petroleum-based plastics are more long-standing as compared to the latterly developing bioplastics such as polyhydroxylalkanoates (PHAs) and poly(lactic acid) (PLA). Mechanical and physical performance limitations as well as high costs from low-volume production became barriers for the widespread acceptance of these bioplastics (Mohanty et al., 2000). To empower these biomaterials as the wave of the future, the incorporation of inexpensive natural fibers can be done in which they do not only decrease in production cost, but they may offer additional sustainability advantages.

Acknowledging that PLA made the utmost impact in the packaging industry and as much as 60 % of packaging was used in the food and beverage sector, it is aimed to develop a PLA biocomposite suitable for food packaging applications (Johansson et al., 2012). When food related packaging is in concern, it is crucial to incorporate only substances that are approved for food contact and personal care. For safety measures, in addition to cross-checking with the international standards for approved chemical substances, it is decided to emphasize on the usage of bio-sourced materials in the present composite development. Cellulose was derived from local crop kenaf and was added into PLA as fillers. However, one major drawback of using natural fibers as composite fillers is their marked hydrophilicity nature and highly polar character. This limits their compatibility with the polymeric matrices which are mostly hydrophobic and non-polar (Xie et al., 2010). Among other chemical treatments, many researchers treated the natural fibers with silane coupling agent to improve the filler-matrix interfacial adhesion. Similar treatment was also applied in the present work. However, foreseeing the possible reverse hydrolysis of the chemical compound and leaching from the cellulose fillers which are highly undesirable in food packaging, it was brought a
step further with thermal grafting to permanently cross-link the silanol and siloxane polymer networks onto the cell walls. The effectiveness of the thermal treatment and its influence on the fillers’ and composites’ characteristics were discussed.

Another concern with PLA is the brittle nature which limits its’ processability and the range of product development. Addition of silanized-cellulose could have increased the tensile strengths and moduli of the PLA; however it does not contribute in toughening it. Researchers have used plasticizers such as triacetin and poly(ethylene glycol) (PEG) onto PLA/natural fibers composites (Ibrahim et al., 2010; Masirek et al., 2007). However, these manmade plasticizers were unable to provide PLA/natural fibers composites an effective brittle-toughness transition. Recently, several authors have tested plant oils as plasticizers for PLA/starch composites and reported possible reaction between the modified starch and the plant oils and toughen the composites (Xiong et al., 2014; 2013c; 2013b; 2013a). Acknowledging that this could be a new path for fabricating an entirely bio-sourced composite, the present composites were plasticized with a novel local product, which is the epoxidized palm oil. Considering the compatibility and the ability of epoxidized palm oil as a reactive plasticizer for the PLA/silanized-cellulose composites, enhancement in the overall properties of the biocomposites is anticipated.

Generally with the right technique and combinations, PLA/natural fiber composites with good improvements can be achieved. However, there must be a critical cost-efficiency consideration. It is acknowledged that natural fiber composites will succeed more in the markets when they cost less than conventional composites for similar resolution (Thamae and Baillie, 2007). For the current research, with extraction of cellulose method adapted from standards similar to extracting cellulose from wood for pulp and paper production, using a comparatively small concentration of silane coupling agent to treat the fillers, and the use of sustainable and safe plant oil as reactive plasticizers, it is envisage that the novel biocomposite engineered can be economically viable.

1.2 Research Aim and Objectives

The aim of this research is to modify cellulose that was derived from kenaf bast fibers and use epoxidized palm oil as a novel plasticizer for poly(lactic acid) (PLA)/kenaf-derived cellulose biocomposite reinforcement to widen its window of application specifically in packaging food products. To achieve the aim, several objectives were set as listed below:
To improve the compatibility between the kenaf-derived cellulose and PLA via thermally grafting coupling agent 3-aminopropyltriethoxy silane (APS) onto cellulose.

2 To evaluate the plasticizing effect of epoxidized soybean oil (ESO) and epoxidized palm oil (EPO) on PLA matrix.

3 To determine the reinforcing mechanism(s) involved with various loadings of silane used to treat kenaf-derived cellulose and various loadings of EPO added in PLA/kenaf-derived cellulose composites.

4 To evaluate EPO as a novel reactive plasticizer in the PLA/kenaf-derived cellulose composite system.

5 To characterize the fillers and composites in terms of chemical, mechanical, physical, thermal, barrier, and morphological properties.

1.3 Significance of the Research

1 A novel research on the interaction between plant-derived cellulose that was silane-grafted thermally and bio-sourced plastic, PLA.

2 Testing the potential of Malaysia’s bio-sourced product, EPO as an alternative plasticizer.

3 A novel study on the interaction mechanism involved for EPO to reinforce the properties of PLA/kenaf-derived cellulose composites.

4 Development of a novel biocomposite suitable for food packaging applications.

1.4 Thesis Outline

The thesis consists of 6 chapters. Chapter 1 served as an introduction to the research which includes the statement and significance of problem, aim and objectives, as well as the significance of the research.

Chapter 2 presented the literature review on PLA polymer, natural fibers and their modifications, plasticizers, plastic packaging, and composites development in various areas. This chapter also reviewed previous findings on plastic-related composites in terms of chemical, mechanical, physical, thermal, barrier, and morphological properties.

Chapters 3 to 5 are the working chapters where the methodologies, results, and discussions were conveyed accordingly to the objectives set
in Section 1.2. The objectives in Chapter 3 were (i) to improve compatibility between kenaf-derived cellulose and PLA via thermal grafting aminosilane onto the cellulose prior to filling; followed by (ii) the determination of the reinforcing mechanism involved via various loadings of silane used for treatment. Analyses on properties of kenaf bast fibers (KBF), kenaf-derived cellulose (C), and silane-grafted cellulose (SGC) at various silane wt% were done. This was followed with the studies of binary composites, namely PLA/C and all PLA/SGC blends. To conclude, a PLA/SGC formulation with optimum characteristics was chosen for further modification as continued in Chapter 4.

Chapter 4 initiated with the evaluation of epoxidized palm oil (EPO) as alternative bio-plasticizer via the comparison with PLA plasticized with commercialised epoxidized soybean oil (ESO). This was followed by the addition of EPO at various loadings into PLA/SGC composites to evaluate the reinforcing mechanisms among the constituents. To conclude, a PLA/SGC/EPO formulation with optimum characteristics was determined.

As the final working chapter, Chapter 5 presented important practical evaluation on the optimized PLA/SGC/EPO blends along with some of the prepared samples in terms of their thermoformability and overall migration from the blend. Their applicability and suitability for food packaging were discussed. Finally, Chapter 6 presented the overall conclusions of the research and recommendations for future research. The process flow chart for the research methodology is as shown in Figure 1.1.
Figure 1.1: Process flow chart (*more than one formulation).
REFERENCES


García, M. A., Martino, M. N., and Zaritzky, N. E. 2000. Lipid addition to

182


Johansson, C., Bras, J., Mondragon, I., Nechita, P., Plackett, D., Simon,


Luz, S. M., Del Tio, J., Rocha, G. J. M., Gonçalves, A. R., and Del’Arco


Masirek, R., Kulinski, Z., Chionna, D., Piorkowska, E., and Pracella, M.


Mohanty, A. K., Misra, M., and Hinrichsen, G. 2000. Biofibres,


Pei, A., Zhou, Q., and Berglund, L. A. 2010. Functionalized cellulose
nanocrystals as biobased nucleation agents in poly(L-lactide) (PLLA) - Crystallization and mechanical property effects. *Composites Science and Technology* 70(5): 815-821.


Xiong, Z., Li, C., Ma, S., Feng, J., Yang, Y., Zhang, R., and Zhu, J. 2013c. The properties of poly (lactic acid)/starch blends with a functionalized plant oil: Tung oil anhydride. *Carbohydrate Polymers* 95(1): 77-84.


