SUPERCRITICAL FLUID AIDED POLYLACTIC ACID BIOCOMPOSITE FILM WITH CINNAMON ESSENTIAL OIL FOR ACTIVE FOOD PACKAGING

BY

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A thesis submitted in fulfilment of the requirement for the degree of Master of Science (Materials Engineering)

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MAY 2019

ABSTRACT

The demand for food safety by consumers promotes continuous improvement of active packaging systems for food product and is recently increasing. The safety issues of food-packaging industries directed the attention towards biodegradable packaging applications. Therefore, this research aims to develop a polylactic acid (PLA) reinforced with durian skin fibre (DSF) biocomposite film for active food packaging. In the biocomposite, epoxidized palm oil (EPO) was added as a plasticizer and cinnamon essential oil (CEO) was added as an antimicrobial agent. Supercritical carbon dioxide ($SCCO_2$) method was employed as treatment to improve dispersion of DSF in the biocomposite. The effect of DSF content, EPO and CEO were studied in terms of thermal, structural, mechanical, and functional properties of the PLA biocomposite film. The PLA biocomposites were produced via solvent casting method. The process started with the optimization of DSF content, EPO, and CEO based on the tensile test. Design Expert software version 6.0.8 via response surface method (RSM) was used to analyse and determine the highest values of tensile strength and tensile modulus. The selected optimum values were at 3 wt % DSF, 5 wt % EPO, and 1 wt % CEO. The P-value of both responses was less than 0.05, while the coefficient, R^2, is nearly 1.0 which confirms that the tensile properties model is significant. Once optimized, the PLA biocomposites were treated by supercritical carbon dioxide. The conditions of CO_2 treatment on PLA biocomposite were conducted at 2 conditions under 40 ^oC temperature and at 100 bar and 200 bar pressure. Tensile properties of PLA-DSF biocomposite improved by about 5% after $SCCO_2$ treatment at condition 1 (40 ^oC; 100 bar). Scanning electron micrograph revealed that a porosity was induced in $SCCO_2$ treated PLA biocomposite. The elongation of treated PLA-DSF biocomposite increased with the addition of EPO and CEO. The presence of aldehyde as a functional group was evident in Fourier transform infrared (FTIR) analysis spectroscopy. From thermogravimetry analysis (TGA), the $SCCO_2$ treated biocomposite with the addition of DSF, EPO and CEO at condition 2 (40^oC; 200 bar) has resulted the lowest weight loss due to the degradation effect of thermal. Differential scanning calorimetry (DSC) analysis shows that the $SCCO_2$ treated biocomposite possessed the highest crystallinity as compared to untreated biocomposite. Similarly, tensile strength of the $SCCO_2$ treated biocomposite also possess high tensile strength. Water absorption test showed that the sample untreated with DSF of PLA biocomposite absorbs most water as compared to other compositions with 5.1%. This is due to the hydrophilic nature of fibre that easies to absorb water molecules. Soil burial test showed that the sample of treated PLA and DSF possessed the highest value of weight losses after 80 days with 97.8 %. Biocomposite with CEO demonstrated antimicrobial activity against both gram-positive and gram-negative bacteria. The treated PLA biocomposite is whiter, indicating the potential as an active food packaging material. The supercritical fluid treatment of PLA biocomposite is significant for active packaging industries to ensure the packaging meets the requirement by consumers and is eco-friendly.

خلاصة البحث

شجع طلب المستهلكين على سلامة الأغذية على التحسين المستمر لأنظمة التعبئة والتغليف النشط للمنتجات الغذائية، ولايزال التزايد مستمراً. كما وجهت قضايا السلامة الخاصة بصناعات تغليف الأغذية الانتباه إلى تطبيقات التغليف القابل للتحلل البيولوجي. ولذلك، يهدف هذا البحث إلى تطوير عديد حمض اللاكتيك (PLA) المعزز بغشاء حيوي biocomposite من ألياف قشر الدوريان (DSF) للتغليف النشط للمواد الغذائية. مع زيت القرفة (CEO) كعامل مضاد للميكروبات. تمّ إضافة زيت النخيل (EPO) إلى biocomposite كمادة ملدّنة و زيت القرفة كعامل مضاد للميكروبات (CEO). أُستخدمت تقنية (Supercritical) بواسطة ثاني أكسيد الكربون ($SCCO_2$) لمعالجة تبدّد (DSF) في عينة biocomposite. أعقب ذلك دراسة محتوى كلّ من DSF، EPO و CEO من حيث تأثيرها على الخصائص الحرارية والبنائية والميكانيكية والوظيفية لفيلم PLA-DSF biocomposite. بدايةً، تم إنتاج PLA biocomposite بتقنية صب المذيب. أعقب ذلك دراسة التحسين optimization لمحتوى كلٍ من DSF، EPO و CEO استنادًا إلى نتائج خصائص الشد. تم استخدام برنامج Design Expert من خلال أسلوب response surface (RSM) لتحليل وتحديد أعلى قيم لقوة الشد ومعامل الشد. وكانت القيم المثلى المختارة عند 3% وزناً لـ DSF، 5% وزناً لـ EPO، و 1% وزناً بالنسبة لـ CEO. كانت قيمة P العددية لكل من الاستجابتين أقلّ من 0.05 ، في حين كانت قيمة معامل التحديد R^2 مايقارب 1.00 مما يؤكد دلالة نموذج خصائص الشد. وبعد التحسين optimization، تمت معالجة PLA biocomposite بواسطة ثاني أكسيد الكربون (Supercritical). تم إجراء معالجة CO_2 في حالتين: الحالة الأولى عند 40 درجة مئوية وضغط 100 بار، والثانية عند 40 درجة مئوية وَ 200 بار. أظهرت خصائص الشد تحسناً في PLA-DSF biocomposite بنحو 5 % بعد المعالجة بطريقة $SCCO_2$ في الحالة الأولى(40 درجة مئوية، ضغط 100 بار). كما كشف المجهر الإلكتروني الماسح ازدياد المسامية في PLA biocomposie المعالجة بتقنية $SCCO_2$. كذلك زادت استطالة PLA-DSF biocomposie مع إضافة كلٍ من EPO وCEO. وبالإضافة إلى ذلك، ثبت وجود الألدهيد كمجموعة وظيفية بواسطة التحليل الطيفي للأشعة تحت الحمراء (FTIR). وبناءً على نتيجة تحليل Thermogravimetric (TGA) ، فإن biocomposie المعالج بتقنية $SCCO_2$ بإضافة DSF ، EPO وCEO في الحالة الثانية (40 درجة مئوية، ضغط 200 بار) خسرت أقل قدر من وزنها بسبب التحلل الحراري. تُظهر نتائج المسح التفريقي DSC أن عينة biocomposie المعالجة بتقنية $SCCO_2$ تمتلك أعلى درجة من التبلور مقارنةً بنظيرتها غير المعالجة. وبالمثل ، فإن قوة الشد الخاصة بعينة biocomposie المعالجة بـتقنية SCCO2 تمتلك أيضًا قوة شد عالية. يظهر اختبار امتصاص الماء أن عينة PLA biocomposite غير المعالجة بإضافة DSF تمتص معظم كمية الماء مقارنة بالتراكيب الأخرى بنسبة 5.1% ، مايعود إلى طبيعة الألياف المحبة للماء والتي تمتص جزيئات الماء بسهولة. كما أظهر اختبار Soil burial أن عينة biocomposite المعالجة بكلّ من PLA و DSF أظهرت أكبر قيمة لفقدان وزنها بعد 80 يوماً بنسبة 97.8%. أظهر متراكب biocomposite مع CEO نشاطاً مضاداً للميكروبات ضد كل من البكتيريا موجبة الجرام وسالبة الجرام. كما أنّ PLA biocomposite المعالج أكثر بياضاً، مما يشير إلى إمكانية استخدامه كمادة نشطة لتعبئة المواد الغذائية. وأخيراً فإنّ تقنية المعالجة السائلة supercritical للمبلمر PLA biocomposite تُعَدّ أمرًا بالغ الأهمية بالنسبة لصناعات التغليف الفعالة لضمان تلبية حاجات المستهلكين وكذلك كونها صديقة للبيئة

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering)

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DECLARATION

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ACKNOWLEDGEMENTS

First and foremost, I would like to express my appreciation and wholehearted sense of gratitude to my supervisor Associate Professor Dr. Hazleen Anuar for her enthusiastic guidance, valuable suggestions and persistent supervision which were indispensable for the completion of this research work. I would also like to record my deep appreciation to my co-supervisor Dr Yose Fachmi Buys for his supports. My special thanks go, lab technician Bro. Hairi and Bro. Ibrahim for their help and excellent advice on my work.

I wish to extend my gratitude to all MME Female Postgraduate members (Kak Wani, Kak Seha and Kak Salwa), colleagues and friends (Munirah, Zahra and Kak Raihana) for their continuous support, happy moments together and wonderful friendship.

I am also thankful to Ministry of Higher Education Malaysia for the financial support provided throughout my Master.

Special dedication to Mak (Hasmah Mat Ali), Ayah (Mohd Apandi Sidek), and my siblings (Kak Long, Abang Ngah, Abang doh and Adik) for their unconditional love along with their support and encourages me. Most special thanks to my future husband, Mualim Md Salleh for your endless support throughout my ups and downs in making this research success.

TABLE OF CONTENT

Abstract i
Abstract in Arabic ii
Approval Page iii
Declaration iv
Copyright v
Acknowledgements vi
List of Tables x
List of Figures xi

CHAPTER ONE: INTRODUCTION 1
1.1 Background 1
1.2 Problem Statement And Its Significance 5
1.3 Research Objective 7
1.4 Research Scope 7
1.5 Thesis Organization 8

CHAPTER TWO: LITERATURE REVIEW 10
2.1 Introduction 10
2.2 Biodegradable Polymer 11
2.2.1 Poly (Lactic Acid) (PLA) 12
2.2.2 Advantage and Disadvantages of PLA 13
2.3 Natural Fiber Reinforcement 15
2.3.1 Advantages and Disadvantages of Natural Fiber 17
2.3.2 Durian Skin Fibre (DSF) 18
2.4 Composite Materials 19
2.4.1 Natural Fiber Reinforced Biocomposites 20
2.5 Preparation of Natural Fibre Reinforced Biocomposites 22
2.5.1 Melt-Blending 22
2.5.2 Polymer Solution Casting 24
2.6 Plasticizer 26
2.6.1 Synthetic Plasticizer 27
2.6.2 Natural Plasticizer 28
2.5.2.1 Epoxidized Palm Oil (EPO) as Plasticizer Agent 30
2.7 Biodegradable Food Packaging 31
2.7.1 Active Packaging 33
2.7.2 Intelligent Packaging 34
2.8 Antimicrobial Agent 36
2.8.1 Plant Based Antimicrobial Agent 37
2.8.2 Cinnamon Essential Oil (CEO) as Antimicrobial Agent 38
2.9 Supercritical Impregnation (SSI) 42
2.9.1 Supercritical Carbon Dioxide ($SCCO_2$) 44
2.9.2 Supercritical Water 48
2.10 Functional Properties of Food Packaging 49
2.10.1 Environmental Degradation 49

2.10.1.1 Water Absorption..50
2.10.1.2 Soil Burial Exposure..52
2.10.2 Optical Properties..53
2.10.3 Gas Chromatography (GC) Analysis...54
2.11 Summary 56

CHAPTER THREE: RESEARCH METHODOLOGY 57
3.1 Introduction 57
3.2 Materials Preparation 58
3.2.1 Poly (Lactic Acid) (PLA)..58
3.2.2 Preparation of Durian Skin Fibre (DSF) 59
3.2.3 Epoxidized Palm Oil (EPO)..60
3.2.4 Cinnamon Essential Oil (CEO) 60
3.2.5 Chloroform...60
3.3 Experimental Method..60
3.3.1 Optimization Using Design of Experiment (DOE) 60
3.3.2 Preparation of PLA Biocomposite Film via Solution Casting 61
3.3.3 Preparation of Pla Biocomposite Film via Supercritical Impregnation (SSI)..63
3.4 Mechanical Characterization...64
3.4.1 Tensile Test 64
3.5 Thermal Characterization..65
3.5.1 Differential Scanning Calorimetry (DSC) 65
3.5.2 Thermogravimetric Analysis (TGA) 66
3.6 Degradability Testing..66
3.6.1 Water Absorption Test...66
3.6.2 Soil Burial Test..67
3.7 Functional Characterization 68
3.7.1 Fourier Transform Infrared (FTIR) Spectroscopy............................68
3.7.2 Optical Analysis 68
3.7.3 Dimension Change...69
3.7.4 Antimicrobial Preparation...69
3.7.4.2 Culture Preparation 70
3.7.4.3 Antimicrobial Activity: Agar Diffusion Method...................71
3.7.5 Gas Chromatography Time-of-Flight/ Mass-Spectrometer (GC-TOF/MS)...72
3.8 Surface Morphology Characterization 72
3.8.1 Scanning Electron Microscopy (SEM) 72
3.9 Summary 73

CHAPTER FOUR: RESULT AND DISCUSSION 74
4.1 Introduction 74
4.2 Design of Experiment 74
4.3Tensile Properties 84
4.3.1 Tensile Strength..84
4.3.2 Tensile Modulus 88
4.3.3 Stress-Strain Curve 91
4.4 Differential Scanning Calorimetry (DSC) Analysis. 94
4.5 Thermal Stability of PLA Biocomposite...99

4.6 Fourier Transform Infrared (FTIR) Analysis 103
4.7 Water Absorption Test 106
4.8 Soil Burial Degradation Test 110
4.8.1 Weight Loss...110
4.8.2 Physical Appearance..114
4.8.3 Surface Morphology 118
4.9 Appearance And Dimension Change of PLA Biocomposite 120
4.9.1 Optical Analysis 120
4.9.2 Dimension Change...125
4.10 Antimicrobial Activity 127
4.11 Summary 134

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION 134
5.1 Conclusion..134
5.2 Recommendation 136

REFERENCES 138

APPENDIX A: LIST OF PUBLICATIONS AND AWARDS.................................151
APPENDIX B: LIST OF EQUIPMENT'S AND INSTRUMENTS 153

LIST OF TABLES

Table 2.1 Several studies on its reinforced composites 27

Table 2.2 The chemical constituent of pure CEO in different part of cinnamon 44

Table 2.3: Several studies on the CEO effect as antimicrobial on biocomposite 45

Table 2.4: Several studies on the supercritical carbon dioxide method 51

Table 2.5: Several studies on supercritical $SCCO_2$ on PLA biocomposites 51

Table 3.1: The amount of composition in each sample 67

Table 4.1: Tensile properties value of PLA-DSF biocomposites 81

Table 4.2: The result of ANOVA response surface quadratic model for tensile strength 88

Table 4.3: The result of ANOVA response surface quadratic model for tensile modulus 89

Table 4.4: Thermal properties of PLA biocomposite 102

Table 4.5 TGA result of PLA biocomposite 106

Table 4.6 Optical properties of PLA biocomposite 128

Table 4.7 Dimension change of PLA biocomposite 131

Table 4.8: GC component 143

LIST OF FIGURES

Fig 2.1: Chemical configuration of PLA polymer plastic 15

Fig. 2.2: The classification of natural fibre 19

Fig 2.3: Production of biomass waste from durian 22

Fig. 2.4: Process to produce polymer bicomposites film 30

Fig. 2.5: Chemical configuration of epoxidized palm oil 35

Fig. 2.6: Phenolic chemical configuration in CEO 45

Fig. 2.7: The major and minor of chemical compounds of CEO 46

Fig 2.8: Pressure-temperature phase diagram of supercritical fluids 49

Fig. 2.9: The effect of water molecule on biocomposite 63

Fig.3.1 Research methodology flowchart 63

Fig. 3.2: process to produce micro size of durian skin fibre (DSF) 64

Fig. 3.3: The preparation of sample film 68

Fig. 3.4: The equipment for supercritical carbon dioxide ($SCCO_2$) 69

Fig. 3.5: The schematic diagram of supercritical carbon dioxide equipment 69

Fig 3.6: Dimension of sample according to ASTM D882 70

Fig 3.7: The sample were immersed in distilled water. 72

Fig. 3.8: Preparation of Luria-Bertani (LB) agar 75

Fig. 3.9: Tested bacteria after cultured 77

Fig. 4.1: The 2-D contour design of the response surface on the tensile strength. 86

Fig 4.2: The 2-D contour design of the response surface on the tensile modulus 88

Fig.4.3: Tensile strength for untreated and treated $SCCO_2$ of PLA biocomposite 91

Fig. 4.4: SEM micrographs of PLA biocomposite before and after treatment 94

Fig. 4.5:Tensile strength for untreated and treated SCCO2 of PLA biocomposite 95

Fig. 4.6: Stress strain for untreated and treated SCCO2 of PLA biocomposite 99

Fig. 4.7: DSC thermogram of PLA biocomposite 101

Fig. 4.8: TGA thermogram of PLA biocomposite before and after treatment 106

Fig. 4.9: FTIR spectra of PLA biocomposite 110

Fig. 4.10: Water absoption of PLA biocomposite 113

Fig. 4.11: Weight loss of PLA biocomposite for 80 days 118

Fig. 4.12: Physical apperance of PLA biocomposite after burial in soil 121

Fig. 4.13: The surface morphology for PLA biocomposite without $SCCO_2$ treatment 125

Fig. 4.14: The surface morphology for PLA biocomposite with $SCCO_2$ treatment 126

Fig. 4.15: The L-value of PLA biocomposite 130

Fig. 4.16: Visual appreance of PLA biocomposite 130

Fig. 4.17: The thickness behaviour of PLA biocomposite 132

Fig. 4.18: The inhinbition zone of PLA biocomposite 135

Fig. 4.18: The inhinbition zone of PLA biocomposite 140

LIST OF ABREVIATION

CEO	Cinnamon
CO_2	Carbon dioxide
DBP	di-n-butylphthalate
DOE	Design of Experiment
DSC	Differential Scanning Calorimetry
DSF	Durian skin fibre
EPO	Epoxidized palm oil
FDA	Food and Drug Administration
FTIR	Fourier Transform Infrared
H_2O	Water
ISO	International Organization for Standardization
KF	Kenaf fibre
LDPE	Low-density polyethylene
Mw	Moecular weight
MT	Metric ton
HDPE	High-density polyethylene
PBS	Polybutylene succinate
PCL	Poly(γ-caprolactone)
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PHA	Polyhydroxyl alkanoate
PLA	Polylactic acid

PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
$SCCO_2$	Supercritical carbon dioxide
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
WPO	World Packaging Organization

CHAPTER ONE

1 INTRODUCTION

1.1 BACKGROUND

Food packaging is known as a coordinated system of providing food for carriage, distribution, packing, trade and end-use to fulfil the consumer expectations. Consumer requirements for secure, environment-friendly and high-quality packaging materials have been increased, and therefore technical development for the garbage disposal problems are being resolved (Anuar et al., 2017). Due to renewability, biodegradability and commercial viability, development of biodegradable materials is interesting in the food packaging sector, since it provides a replacement to the usage of synthetic products (Nur Aimi et al., 2014). Other than that, production of biopolymer products can be an initiative income in the agriculture industry.

PLA is one of the most promising candidates among the renewable source-based products, due to its availability, biocompatibility, excellent tensile strength, good processability and biodegradability, which is a significant benefit from an environmental perspective. Biodegradable films produced from starch crops are defined as odour-free, flavourless, neutral and non-toxicity (Yussuf et al., 2010). Presently, in food packaging sector, PLA is used in wraps for bakery and confectionary products, disposable food service tableware items, packaging for fresh products and water bottles. Despite the benefit features, mechanical properties of PLA are unsatisfactory for packaging applications due to brittleness. The reinforced PLA matrix with fiber is believed to improve its mechanical performance (Gunti et al., 2016). Advance technology driver is the development of biocomposite technology, which also promotes new potentials for biopolymers plastics. The production of biocomposites is considered to be beneficial in various industries, as biocomposites application is gradually increasing and gaining significance through alternative synthetic-based materials, making them suitable primarily for packaging purposes.

Worldwide, natural fibers are more environmentally friendly and can decrease the environmental problems due to the biodegradable properties compared with synthetic fibers. In order to produce bio-composites while preserving the green features, biopolymers plastics must be reinforced with natural fiber (Kumar et al., 2010). The development of biocomposite materials by using durian skin waste can be one of the beneficial approaches for increasing and enhancing the utilization of agricultural wastes. Durian skin fiber (DSF) has best features to be used in reinforcing filler for PLA biopolymer (Wan Nazri et al., 2014). Durian or, it scientific name, Durio zibethinus Murray can be found in Southeast Asian countries such as Malaysia, Thailand, Indonesia and Philippines. To preserve the green environment, the durian skin waste can be used to produce durian skin fiber (DSF). This attempt could finally decrease environment pollution by decreasing the amount of organic wastes.

Besides, the processability of films can be increased with plasticizers that contribute to decreasing the glass transition temperature (T_g) and enhance the polymer chain flexibility (Ali et al., 2016). Some researchers acknowledge that the natural plasticizers are better, which can be found naturally extracted from animals, vegetable fats and plants oil (Silverajah et al., 2012; Chieng et al., 2014). Among the natural plasticizer, epoxidized palm oil (EPO) is favourable plant oil due to its characteristics like inexpensive, non-toxicity and availability as a renewable agriculture resource.

Nowadays, the safety issues of food are utterly worrisome in the world. Handling food packaging safety is just significant at the consumer level because many of them have contaminated on food (Souza et al., 2013). These big issues may distract many researchers involved in plastic manufacturing. Due to the problems highlighted, there is a necessity to produce food packaging with an anti-microbial agent and preventing food contamination. Demand in the application of active packaging systems for food production has increased lately. Bacteria and fungi are examples of active microorganisms which may have migrated through direct interaction between food and packaging material or via gas phase diffusion from inside packaging layer to the food surface (Qin et al., 2015). Most of these living organisms may cause undesirable responses which can damage organoleptic and nutritional value of food. Hence, PLA biocomposite displays potential as a biodegradable packaging material in the presence of antimicrobial functionality (Debiagi et al., 2014).

Active packaging materials in the presence of antimicrobial agents like essential oil may be considered as the contemporary advancement of functional packaging. This antimicrobial agent in biocomposite films can avoid almost all bacteria activities that affect the food contamination (Erdohan et al., 2013). Essential oils' characteristics are volatile, natural and have a strong odour, extracted from different sections of plants such as leaves, stems or roots. The production of essential oil can be exploited as natural antimicrobials agent and can be used as one of the additives for food (Anuar et al., 2017). The incorporation of essential oil in biocomposite material as secure antimicrobials is expected to be non-harmful for food product and human application. Cinnamon has been used as a spice long time ago. The combination of essential oils into viscous biocomposite solvents via solvent casting has some disadvantages mostly due to hydrophobic oil behavior by EPO and CEO which make it difficult to become a homogeneous film. Therefore, supercritical carbon dioxide (SCCO_2) treatment is introduced in this study to employ PLA biocomposite films as the plasticizing agent.

The SCCO_2 process can present an effective and beneficial medium for polymer processing. The major benefits of polymer treatment with SCCO_2 include processing at low temperatures, allowing a large amount of CO_2 into different kinds of a polymer including synthetic and biopolymer and rapidly complete solvent elimination from the final product (Souza et al., 2013). Besides its greener characteristics, SCCO_2 is chemically inert, inexpensive, easily purchased, non-flammable and highly pure. CO_2 gas is a suitable solvent for non-polar constituents and dissolves in most polymer compounds (Milovanovic et al., 2017). This facilitates the incorporation of substances that can be used as organic solvents, plasticising agent and impregnation medium in specimens processing. The thermal properties are affected by the SCCO_2 process as the CO_2 solvent generates a molecular like lubricant (Souza et al., 2014; Adamovic et al., 2018).

In short, SCCO_2 offers regulated product quality and safety as well as efficient time and energy management. The mould and die industry is a rapidly growing industry with high demands especially in the aerospace and automotive parts. For this industry, improving production and at the same time providing the best quality of products is essential. To fulfil these criteria, conventional machining is less favourable compared to high-speed machining thus making the latter more relevant in today's fast-moving world.

1.2 PROBLEM STATEMENT AND ITS SIGNIFICANCE

Worldwide, the rising awareness concern on environment problems has cause excessive research on the development of greener technology. Despite the high cost of plastic waste disposal and the effect of hazardous productions on living organisms, the demand for the utilization of bio-based products is increasing rapidly. The application of bio-based composite showed a great performance since past few years for numerous reasons such as the abundance of material, low cost, environment preservation, renewable source and ease of production. From this strategic concept, it assists to support the industry and more concentration on the main issues where the value of bioplastics is that of a resource.

PLA is the most recommended material as it has excellent properties in compostability, biodegradability, transparency and safety. Despite these outstanding features, high brittleness of PLA causes limited application (Mekonen et al., 2013). Thus, PLA matrices cause many disadvantages in the packaging industry. Improvement of biocomposite materials for food packaging by using PLA and DSF can be one of the alternative approaches to solve energy and environmental problems, but long-term experimental exposure will affect the durability and flexibility of biocomposite film. Agricultural crops are abundant and available. This problem also leads to ecological crisis due to extreme burning in open air. Therefore, by utilising agriculture waste, this environmental problem could be reduced. Durian skin waste is also one of the crops which can easily be obtained everywhere in the market. Durian skin fiber (DSF) was selected to be used as reinforcement with the matrix material. Nur Aimi et al. (2015) already reported in their study that DSF has great potential when embedded with polymer matric due to its lignocelluloses characteristics. In addition, the behaviour of polymer matrices may be modified by adding DSF as reinforcement. However, there are also drawbacks reinforced natural fiber into polymer matrix. The incompatibility between hydrophobic polymer matrix and hydrophilic fibers can lead to poor mechanical properties of the specimen (Layth et al., 2015). In this study, mechanical and functional tests of PLA reinforced DSF biocomposite were carried out along with the thermal behavior of the biocomposite film.

Many researchers experimented the addition of plasticizer and fiber to improve the mechanical properties of polymer matrices (Ali et al., 2016). For this study, epoxidized palm oil (EPO) as a plasticizer was used to improve the flexibility and processability of PLA biocomposite. The natural plasticizer is preferred by industries as well as consumers due to the safety of the packaging material. Other than that, the increasing demand of consumers and manufacturers for antimicrobial food packaging product in order to ensure food safety is guaranteed. Microorganisms or bacteria can be formed due to the surrounding or due to the long period. So, the addition of cinnamon essential oil (CEO) can avoid the growth of living organisms over food inside food packaging of a product. To deal with this problem, the development of food packaging which incorporates antimicrobial properties was fabricated to improve the package functionality. Supercritical carbon dioxide ($SCCO_2$) method was used as treatment in this study. Other study reported $SCCO_2$ impregnation was employed to improve the processability (Souza et al., 2014). PLA biocomposite film derived from supercritical carbon dioxide ($SCCO_2$) method due to it being environment-friendly, high purity, low plasticization effect and no microbial activity. With these benefits, it is expected that the PLA/DSF-EPO filled cinnamon essential oil (CEO) has the potential for active food packaging application.

Although there are numerous researches on the performances of the PLA biocomposite, there is still a gap for further studies and investigation on their properties and performance. The studies can vary from the method of biocomposite production and use of different natural fibers to investigate with different types of tests and experiments.

1.3 RESEARCH OBJECTIVE

The main objective of this research is to develop the application of PLA-DSF biocomposite packaging that can offer optimum properties as reinforcement material for PLA polymer matrices. In order to achieve these main objectives, several specific objectives need to be addressed as below:

i. To determine the optimum content of durian skin fiber (DSF), epoxidized palm oil (EPO) and cinnamon essential oil (CEO) based on tensile properties of PLA biocomposite.
ii. To investigate the effects of SCCO2 treatment on the tensile properties, functional gropu, degradation, morphology snd antimicrobial activity.

1.4 RESEARCH SCOPE

In this research, the optimum composition of PLA biocomposite was obtained using the design of experiment through the at different parameter (1, 3 and 5 wt%). EPO (0, 5 and 10 wt%) was added as a stabilise between PLA matrix and DSF reinforcement. CEO (0, 1, and 3 wt%) were incorporated as an antimicrobial agent in order to fabricate active food packaging from this biocomposite film. Biocomposite with composition of PLA, :DSF, :EPO, :CEO of 91, :3, :5, 1: which recorded highest result of tensile properties from DOE was selected for produce PLA films in this experiment. For sample preparation, the raw materials underwent solvent casting and supercritical carbon dioxide ($SCCO_2$) processes so as to improve dispersion and the plasticising behavior of biocomposite films. However, there is few study on $SCCO_2$ treatment on PLA/DSF-EPO with an antimicrobial agent as food packaging application. Thus, in this research, further testing on the effect of SCCO2 on PLA biocomposite was investigated in comparison to the other common biocomposite analysis (mechanical, thermal as well as morphological analysis).

1.5 THESIS ORGANIZATION

In this research,there are five chapter, each chapter contains each introduction and description in order to identify respective objectives of this research. In Chapter 1, the introduction and overview of the research is briefly discussed. This includes the problems and significance of the research, as the novel development of PLA biocomposite film as packaging and $SCCO_2$ treatment on film which never been reported before, are all disscused. The PLA biocomposite procedure from solution casting and treated under $SCCO_2$ has bright prospect in the industry, which is consisely explained in the introductory part. Suggestions and ideas to overcome such problems are also stated in this section. Moreover, the objectives to develop PLA biocomposite is briefly stated. This will be followed up n Chapter 2, which describes the historical aspects of PLA as well as physicals and chemical properties of PLA matrices, DSF, EPO and CEO. This chapter also explained the theoretical background for each step used to produce the treated $SCCO_2$ PLA biocomposite.

Chapter 3 describes, in detail, the experimental set-up, analytical procedures and treatment process involved, through the aid of flow charts, tables and figures for a better understanding. This chapter comprises the types of materials used as well as the equipment and apparatus. the analytical approaches are also revealed in this chapter, used to determine composition of material used which are PLA, DSF, EPO, and CEO and characterisation test for PLA biocomposite also presented.

The outcomes of this research are presented in Chapter 4. This chapter covers several different tests to assess the mechanical, thermal and functional properties of the PLA biocomposite. The results achieved, are discussed comprehensively with the provides support of different reference sources. Finally, Chapter 5 concludes the whole study and specify recommendations for future research works.