



UNIVERSITI PUTRA MALAYSIA

***PREPARATION AND CHARACTERIZATION OF BIOCOMPOSITE FILMS
FROM KENAF- DERIVED CELLULOSE FIBERS AND POLYLACTIC ACID***

SITI HAJAR ABD RAHMAN

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**PREPARATION AND CHARACTERIZATION OF BIOCOMPOSITE FILMS
FROM KENAF- DERIVED CELLULOSE FIBERS AND POLYLACTIC
ACID**

By

SITI HAJAR ABD RAHMAN

**Thesis Submitted to the School of Graduates Studies, Universiti Putra Malaysia,
in fulfillment of the Partial Requirement for Degree of Master of Science**

May 2012

DEDICATION

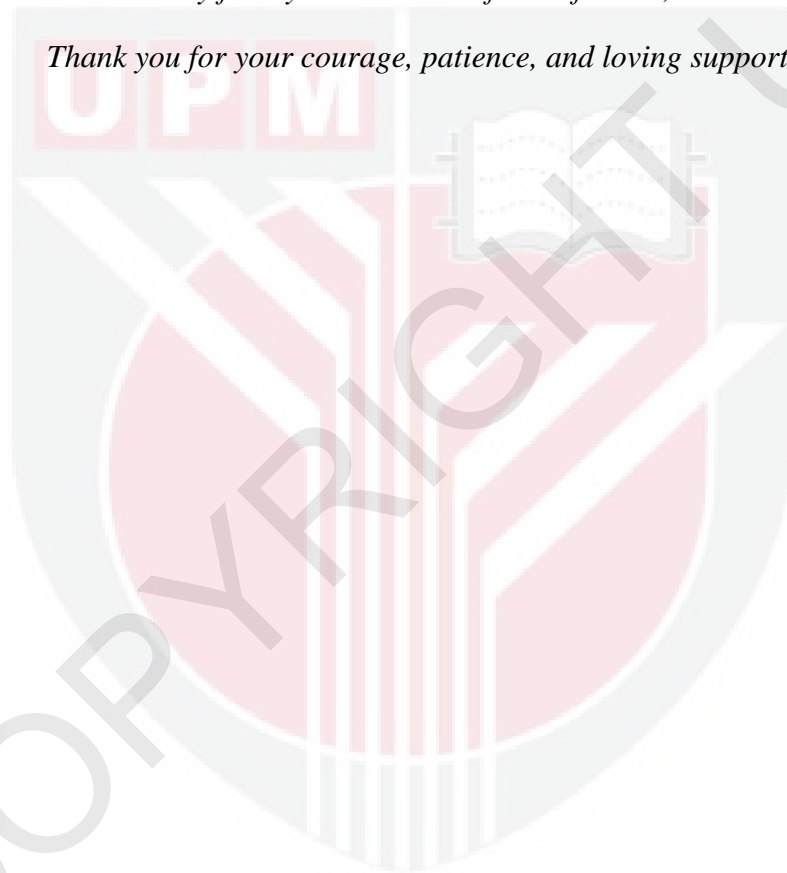
My better half, Megat Izzuddin;

My dear mother Fatimah Abd Ghani;

My siblings Zali Armi, Norrul Suhada, and Nor Mukminatun;

My family members and fellow friends,

Thank you for your courage, patience, and loving support.



Abstract of this thesis presented to the Senate of Universiti Putra Malaysia in the fulfillment of the partial requirement for the degree of Master of Science

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Chairman : Rosnita A. Talib, PhD

Faculty : Engineering

The aim of this study was to produce kenaf derived cellulose-poly(lactic acid) (KDC-PLA) biocomposites and characterize its properties relevant to potential packaging application such as thermal properties and barrier properties against oxygen and water vapor. Other important biocomposite properties in the development of packaging material such as tensile and morphological analysis were also carried out. Kenaf bast fiber is a fiber which was used to derive cellulose via chlorination and mercerization processes. It was then designated as kenaf derived cellulose (KDC).

The incorporation of KDC presents an alternative approach to achieve the intended properties. Thus, in this work, KDC loadings ranging from 0-60% were incorporated in the KDC-PLA biocomposite films. The KDC was found to be less thermal stable than the kenaf bast fiber. X-Ray Diffraction (XRD) spectrum revealed that the cellulose has relatively higher crystallinity index as compared to kenaf bast fiber

which led to this phenomenon. In the case of biocomposite's thermal stability, 6% lower degradation temperature was demonstrated when maximum 60% KDC incorporated in PLA matrix. The thermal properties of KDC-PLA biocomposite showed no major changes with KDC addition. This reflected by nearly unmodified crystallization temperature (T_c) of KDC-PLA biocomposite films. The additional loading of cellulose also shifted the melting temperature (T_m) value to the higher temperature. It means that by incorporating KDC into the PLA matrix have increases the melting point of biocomposite while percent of crystallinity ($\%X_c$) showed no particular trend with additional loadings of KDC in biocomposite. With the additional KDC loading, the oxygen gas permeability was significantly reduced by 85% (shown by decrease in permeability value) but the water vapor permeability was increased by 91% for the highest KDC loading (60%). However the water vapor permeability is still acceptable as the value is within moderate water vapor permeability (50-100 g/m²/day). Composite properties on tensile strength and elongation at break were found reduced as compared to the neat PLA while tensile modulus was found increased showing that the stiffer biocomposite is produced with higher KDC loading. Proven with Environmental Scanning Electron Microscope (ESEM) micrograph, the reduced in tensile strength was due to weak interfacial adhesion between PLA matrix and KDC. Significant reduction in elongation at break suggested that a lower interfacial interaction effect and/or lack of optimum dispersion of KDC in biocomposite. This resulted biocomposite possibly has the potential application in the fruits and vegetables packaging field that require low oxygen gas permeability and moderate water vapor permeability.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi sebahagian daripada keperluan untuk ijazah Master Sains

**PREPARATION AND CHARACTERIZATION OF BIOCOMPOSITE FILMS
FROM KENAF- DERIVED CELLULOSE FIBERS AND POLYLACTIC
ACID**

Oleh

SITI HAJAR ABD RAHMAN

Mei 2012

Pengerusi : Rosnita A. Talib, PhD

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Tujuan kajian ini adalah untuk menghasilkan biocomposit selulosa kenaf -polylactic asid (KDC-PLA) dan mencirikan sifat yang berkaitan dengan aplikasi pembungkusan yang berpotensi seperti sifat haba dan ketelapan terhadap oksigen dan wap air. Lain-lain sifat bicomposit penting dalam pembangunan bahan pembungkusan seperti analisis tegangan dan morfologi juga telah dijalankan. Serat kulit kenaf adalah serat yang telah digunakan untuk memperolehi selulosa melalui proses pengklorinan dan *mercerization*. Ia kemudian dinamakan sebagai selulosa perolehan kenaf (KDC). Gabungan KDC ini memaparkan pendekatan alternatif untuk mencapai sifat-sifat seperti yang dikehendaki. Oleh itu, dalam kajian ini, kandungan KDC antara 0-60% telah digabungkan dalam filem biokomposit KDC-PLA. KDC itu didapati mempunyai sifat haba yang kurang stabil berbanding gentian kulit kenaf. Melalui spektrum pembelauan Sinar-X (XRD) didapati bahawa selulosa mempunyai penghabluran indeks yang lebih tinggi berbanding gentian kulit kenaf telah

membawa kepada fenomena ini. Dalam kes kestabilan terma biokomposit, suhu degradasi yang menurun sebanyak 6% telah dihasilkan apabila maksimum 60% KDC digabungkan bersama PLA matriks. Sifat-sifat terma biokomposit KDC-PLA tidak menunjukkan perubahan besar dengan tambahan selulosa. Ini dicerminkan oleh suhu penghabluran (T_c) yang hampir tidak berubah. Filem biokomposit dengan kandungan KDC yang lebih tinggi telah mengubah suhu lebur (T_m) nilai kepada suhu yang lebih tinggi. Ia bermaksud bahawa dengan menggabungkan KDC ke matriks PLA mempunyai meningkatkan takat lebur daripada biokomposit manakala peratus penghabluran ($\%X_c$) tidak menunjukkan trend tertentu dengan pertambahan KDC ke dalam biokomposit. Dengan pertambahan kandungan KDC, kebolehtelapan gas oksigen telah berkurang sebanyak 85% tetapi kebolehtelapan wap air telah meningkat sebanyak 91% dengan kandungan KDC tertinggi (60%). Walau bagaimanapun kebolehtelapan wap air masih diterima sebagai nilai dalam kebolehtelapan air sederhana wap ($50-100 \text{ g/m}^2/\text{hari}$). Sifat komposit pada kekuatan tensile dan pemanjangan pada takat putus didapati berkurangan berbanding PLA kosong manakala modulus tegangan didapati meningkat menunjukkan bahawa biokomposit yang lebih tegang dihasilkan dengan muatan KDC yang lebih tinggi. Terbukti dengan pengimbasan mikroskop elektron (ESEM) mikrograf, pengurangan dalam kekuatan tegangan adalah disebabkan oleh lekatan antara muka yang lemah antara PLA matriks dan KDC. Pengurangan signifikan dalam pemanjangan pada takat putus mencadangkan bahawa kesan interaksi antara muka yang lebih rendah dan/atau kurang daripada penyebaran optimum KDC dalam biokomposit. Maka biokomposite ini didapati mempunyai potensi untuk diaplikasikan dalam bidang pembungkusan buah-buahan dan sayur-sayuran yang memerlukan kebolehtelapan gas oksigen rendah dan kebolehtelapan wap air sederhana.

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APPROVAL SHEET

I certify that a Thesis Examination Committee has met on 29 May 2012 to conduct the final examination of Siti Hajar Abd Rahman on her thesis entitle “Preparation and Characterization of Biocomposite Films From Kenaf- Derived Cellulose Fibers And Polylactic Acid” in accordance with Universities and University Colleges Act 1971 and the Constitution of Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously, and not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

SITI HAJAR BINTI ABD RAHMAN

Date: 31 May 2013



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LIST OF ALPHABETS

| | |
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| AFM | Atomic Force Microscopy |
| ASTM | American Society for Testing and Materials |
| CI | crystallinity index |
| CNSL | cashew nut shell liquid |
| CNT | carbon nanotube |
| DSC | Differential Scanning Calorimetry |
| DTA | differential thermal analysis |
| DTG | Derivative Thermogravimetric |
| E | Elongation at Break |
| ESEM | Environment Scanning Electron Microscope |
| EFB-PP | empty fruit bunch-polypropylene |
| KDC | kenaf derived cellulose |
| LDPE | low density poly-ethylene |
| LKTN | Lembaga Kenaf dan Tembakau Negara |
| MAP | modified atmosphere packaging |
| MCC | microcrystalline cellulose |
| MFC | microfibrillated cellulose |
| MFC | microfibrillated cellulose |
| MPP | maleated polypropylene |
| NaOH | Sodium Hydroxide |
| NBKP | Needle-leaf Bleached Kraft Pulp |
| NMMO | N-methylmorpholine-N-oxide |
| NR/LLDPE | natural rubber/low-density polyethylene |
| OPC | oxygen permeability coefficients |
| OPEFB | oil palm empty fruit bunch |
| OTR | Oxygen Transmission Rate |
| PA | polyamide |
| PCL | Polycaprolactone |
| PE | polyethylene |

| | |
|----------------|------------------------------------|
| PET | Polyethylene Terephthalate |
| PF | phenol formaldehyde |
| PHA | Polyhydroxyalkanoates |
| PHA | polyhydroxyalcanoates |
| PHB | Polyhydroxybutyrate |
| PLA | Polylactic Acid |
| PP | polypropylene |
| PS | polystyrene |
| PTT | poly (trimentylene terephthalate) |
| PVA | polyvinyl alcohol |
| PVC | Polyvinylchloride |
| PVOH | Polyvinyl Alcohol |
| RH | Relative Humidity |
| RN | ramie nanocrystallites |
| RNCF | Recycled newspaper cellulose fiber |
| SEM | Scanning Electron Microscope |
| T _c | Crystalline Temperature |
| TEM | Transmission Electron Microscope |
| T _g | glass transition temperature |
| TG | Thermogravimetric |
| TGA | Thermogravimetric Analysis |
| TM | Tensile Modulus |
| T _m | Melting Temperature |
| TS | Tensile Strength |
| WAXD | Wide-angle X-ray diffraction |
| WF | wood fiber |
| WVP | water vapour permeability |
| WVTR | Water Vapour Transmission Rate |
| XRD | X-Ray Diffraction |

CHAPTER 1

INTRODUCTION

1.1 Background

Increasing number of non-degradable waste, non-sustainable landfill, depletion of petroleum source have driven great responsibilities for producers and manufacturers to develop new eco-friendly materials and products based on natural fibers and biopolymers. Polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) are examples of petrochemical based polymers extensively used as packaging materials due to their large availability, low cost, and good mechanical performance such as high strength, good oxygen and water vapor barrier, and heat sealability. Some countries, however, have restricted or even banned the usage of some of these materials to limit these non-degradable wastes in their landfill which give rise to environmental concerns among consumers (Rosenthal 2008). This factor has further escalated the interest to use natural fibers with biopolymer as they are biodegradable, renewable and low cost.

Polylactic Acid (PLA), Polyvinyl Alcohol (PVOH), Polycaprolactone (PCL), and Polyhydroxyalkanoates (PHA) are among the example of biodegradable polymers according to their material class basis. Despite of having comparable properties to petrochemical based plastics, the main limitation of biopolymers is their high cost which is due to low volume production. Thus to still maintain the application of biodegradable polymers and to increase their applicability, biopolymers are reinforced with various types of fillers to reduce their cost and to gain new unique properties that are somehow even better than their neat biopolymer.

Natural fibers provide a lot more advantages over conventional reinforcing fibers like glass fibers and carbon fibers as they can reduce tool wear, enhanced energy recovery and biodegradability (Avella *et al.*, 2009).

Biodegradability is usually associated with the ability of the material to be broken down by natural processes. The definition of biodegradable plastic as developed in ASTM is based on the definition for a degradable plastic; “a degradable plastic is a plastic designed to undergo significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification” (Swift, 1992). Biodegradation occurs with enzymatic action involving living microorganisms. Microbial degradation is mostly carried out by both fungi and bacteria. For the case of natural fibers embedded in biopolymer matrix, the microorganisms’ activities will change the cellulose unit into digestible unit that eventually weaken the composite strength (Mohanty *et al.*, 2000). Thus, in this current study, the resulted biocomposite from KDC and PLA is considered as biodegradable although the biodegradability and biocompatibility studies were not conducted.

Biocomposite consisted of biopolymer as matrix material whereas biofibers acted as reinforcing materials (Mohanty *et al.*, 2000). Biofibers that are derived from natural resources reinforced into thermoplastic or thermoset matrix has a positive impact on environment with respect to ultimate disposability and material utilization (Rowell *et al.*, 1992). A number of applications on natural fibers reinforced biopolymer composites in packaging application has been found (Zampaloni *et al.*, 2007; Rhim and Ng 2007; Mohanty *et al.*, Drzal 2002; Sanchez-Garcia *et al.*, 2008). Despite of having diverse advantages over conventional

reinforcing materials, the main drawback of natural fibers is their hydrophilic nature that limits their compatibility with biopolymer matrix that is mostly hydrophobic during composite fabrication. Moreover, natural fibers tend to degrade at lower temperature to restrict the processing temperature of biocomposite below 200 °C (Tawakkal *et al.*, 2010).

In packaging application, the packaging materials are expected to protect the product from physical damage and environmental damage (Hanlon *et al.*, 1998). In order to perform these functions, it is important for the biocomposite packaging materials to be tailored to have suitable mechanical and barrier properties. As suggested by Mohanty *et al.*, (2002), biocomposites that are produced from incorporation of natural fibers like kenaf, pineapple leaf fiber, hemp, and even local grasses with bioplastics will be resulted in biocomposites having superior performance materials highly applicable for rigid packaging. Several studies have discovered the potential of biocomposite material to be applied in packaging field (Auras *et al.*, 2004; Pilla 2011). Recycled newspaper cellulose fiber (RNCF) reinforced poly lactic acid (PLA) could be a promising composite in rigid packaging (Huda *et al.*, 2005) while scallop shell powder reinforced PLA was found to has high potential for fresh produce packaging application (Basha *et al.*, 2011).

The application of biocomposite materials in packaging need further knowledge in understanding the materials respond to several environments or atmosphere since packaging is the barrier between packaged product and environment. This will need certain conformation on materials' behavior when they are subjected to certain temperature, humidity, pressure, lighting condition and so on. The research to date tended to characterize the biocomposites based on their mechanical, physical, and chemical properties. When the application is narrowed down to smaller scale, it is important to further analyse the thermal and barrier

properties of biocomposite as this will define the real limitation of Kenaf derived cellulose - poly lactic acid (KDC-PLA) biocomposite with a range of and applicability of the material in packaging field. This study aimed to modify the permeability of KDC-PLA biocomposite against water vapor and oxygen gas with enhanced thermal properties such as melting and degradation temperature by incorporation of various KDC loadings. It is expected that this biocomposite film will present as a good candidate for further application in packaging field.

1.2 Problem Statement

Extensive studies have been done on the mechanical, thermal and degradation behavior of natural fiber but rarely literature are found on their thermal and barrier properties. These properties are considered as crucial because it represent the bicomposomposite performance when used as packaging materials. The raw and processed material is wildly, but the production technology is difficult and the equipment of it is not mature, the price of product is higher, so how to reduce the price, look out the best technology to the best mixture material of biobased materials is urgent need.

1.3 Objectives

The following specific objectives have been set to achieve this aim:

1. to compare the thermal properties between kenaf bast fiber and its derived KDC.
2. to evaluate the performance properties of KDC-PLA biocomposite films in terms of tensile, thermal and barrier against oxygen and water vapor.

1.4 Scope of Study

Thermal properties of kenaf bast fiber and kenaf derived KDC are investigated. Research is conducted on the effect of KDC loadings into polylactic acid (PLA) biopolymer on the thermal, tensile and barrier properties against oxygen and water vapor. The results are compared with the neat PLA.

1.5 Outline Of Thesis

The introductory chapter will briefly review the background of studies including the environmental issues arise due to non-degradable plastics materials and how the usage of biodegradable materials could be applied in packaging field.

A literature review on previous research work in various areas which is relevant to this research is presented in Chapter 2. The literature started with a comprehensive literature survey on the biocomposite materials and their application in packaging. A review of the raw materials being used in this study is also included in this chapter. This chapter also reviewed previous findings related to the natural fiber treatment and their properties, and also the properties of natural fiber reinforced biocomposites.

The methodology of the study is described in Chapter 3. This chapter presents techniques to determine the thermal, mechanical, morphological and barrier properties of kenaf bast fiber, KDC and biocomposite films. It also includes the techniques of the preparation of the KDC-PLA biocomposite films.

Chapter 4 is the results and discussion on the thermal properties of the kenaf bast fiber, KDC and KDC-PLA biocomposites films. The mechanical properties under tensile tests, oxygen and water vapor permeability, and Scanning electron microscopic (SEM) study of KDC-PLA biocomposites have also been analyzed and discussed in this chapter. Finally, in chapter 5 the conclusions and recommendations for the further works have been presented.



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