UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF POLYLACTIC ACID/HALLOYSITE NANOTUBES BIONANOCOMPOSITE FILMS AS FOOD PACKAGING FILMS

NAZRATUL PUTRI BINTI RISYON

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By

NAZRATUL PUTRI BINTI RISYON

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CHARACTERIZATION OF POLYLACTIC ACID/HALLOYSITE NANOTUBES BIONANOCOMPOSITE FILMS AS FOOD PACKAGING FILMS

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September 2017

Chair : Siti Hajar Othman, PhD
Faculty : Engineering

In this work PLA/HNTs bionanocomposite films at varying concentration of HNTs (0.0, 1.5, 3.0, 4.5 and 6.0 wt.%) were produced to replace the commercialized food packaging materials in industry that are usually made-up of non-biodegradable material.

Bionanocomposite films were prepared by casting method using polylactic acid (PLA) as biopolymer and halloysite nanotubes (HNTs) as the nanofiller producing PLA/HNTs bionanocomposite films. The neat PLA and PLA/HNTs bionanocomposite films were investigated regarding the dispersion of HNTs in the PLA films, chemical bonding between HNTs and PLA as well as molecular weight of PLA. The effects of HNTs concentrations on the mechanical, thermal, barrier and optical properties were investigated. Demonstration on the PLA films for food packaging application also conducted by studying the firmness and weight loss of tomato cherries that packaged with the films.

It was found that HNTs were well dispersed in 3.0 wt.% PLA/HNTs bionanocomposite films while agglomeration of HNTs occurred in 6.0 wt.% PLA/HNTs bionanocomposite films indicated by the particle distribution histogram and TEM images. Hydrogen bond was formed between HNTs and PLA as proven from TEM analysis. The weight of average molecular weight (Mw) of PLA film incorporated with 3.0 wt% HNTs were lower than PLA film incorporated with 6.0 wt.% HNTs while

number of average molecular weight (Mn) of 3.0 wt.% PLA/HNTs bionanocomposite films were higher than 6.0 wt.% PLA/HNTs bionanocomposite films. 3.0 wt.% PLA/HNTs bionanocomposite films were found able to exhibit the optimum mechanical properties in terms of tensile strength, yield strength and Young's modulus due to the well dispersion of HNTs in the PLA matrix thus forming a stable hydrogen bond between HNTs particles and PLA molecules. This condition also due to the high average molecular number (Mn) which was 3.97×10^4 and polydispersity index (PDI) which was 1.97. At 3.0 wt.% PLA/HNTs bionanocomposite films also exhibit the lowest water vapor permeability (WVP) and oxygen transmission rate (OTR) compared to other concentration of PLA/HNTs bionanocomposite films due to the formation of tortuous path resulted from well dispersed HNTs in the PLA matrix. Meanwhile, incorporation of 3.0 wt.% HNTs in PLA matrix resulted to the optimum improvement in heat stability of the films by increasing the resistance of the films towards phase changes when heat was applied. Films transparency analysis revealed that there was no significant ($p>0.05$) change in the transmittance of light of the films when HNTs was added into PLA matrix. Based on the obtained results, the optimum concentration of HNTs in PLA that resulted to improvement in mechanical, thermal and barrier properties was found to be at 3.0 wt%. Demonstration on the tomato cherries' firmness and weight loss indicated that the PLA film incorporated with HNTs able to extend the shelf life of the packaged tomato cherries due to improved mechanical, thermal and barrier properties of the film.

In conclusion, the well dispersed of HNTs in PLA matrix, stable hydrogen bond between HNTs and PLA as well as high Mn and low Mw of PLA improved mechanical, thermal and barrier properties of PLA/HNTs bionanocomposite film. Addition of HNTs in PLA film able to prolong the shelf life of tomato cherries packaged with PLA/HNTs bionanocomposite film. Molecular weight analysis and demonstration of the PLA/HNTs bionanocomposite film is considered as the novelties of this work.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENCIRIAN KEATAS FILEM POLYLACTIC ACID/HALLOYSITE NANOTUBES BIONANOCOMPOSITE SEBAGAI FILEM PEMBUNGKUS MAKANAN

Oleh

NAZRATUL PUTRI BINTI RISYON

September 2017

Pengerusi: Siti Hajar Othman, PHD
Fakulti: Kejuruteraan

Dalam kerja ini, Filem bionanokomposit PLA/HNTs dengan kepekatan HNTs yang pelbagai (0.0, 1.5, 3.0, 4.5 and 6.0 wt.%) dihasilkan untuk menggantikan bahan pembungkus makanan komersil dalam industry yang biasanya diperbuat daripada bahan yang tidak boleh dilupuskan.

Filem bionanokomposit dihasilkan dengan cara acuan menggunakan polilaktik asid (PLA) sebagai biopolimer dan halloysite nanotubes (HNTs) sebagai bahan pengisi nano dan terhasillah filem PLA/HNTs bionanokomposit. Filem PLA ditambahkan dengan 1.5, 3.0, 4.5 dan 6.0 HNTs. Filem PLA sahaja dan filem PLA/HNTs bionanokomposit tersebut dikaji mengenai taburan HNTs dalam filem PLA, pencantuman kimia antara HNTs dan PLA serta berat molecular PLA. Kesan daripada kepekatan HNTs (0.0, 1.5, 3.0, 4.5 and 6.0 wt.%) terhadap ciri-ciri mekanikal, haba, perintang dan penghantaran diujikaji. Demonstrasi terhadap filem PLA untuk dijadikan sebagai pembungkus makanan dijalankan dengan mengkaji kepejalan dan kehilangan berat tomato ceri yang dibungkus menggunakan filem tersebut.

Ia menunjukkan taburan sekata berlaku pada HNTs yang ditambah sebanyak 3.0 wt.% ke dalam matrik PLA manakala penggumpalan HNTs berlaku pada HNTs yang ditambah sebanyak 6.0 wt.% kedalam matrik PLA yang ditemui melalui histogram

taburan butiran yang mana pencantuman hidrogen berlaku antara HNTs dan PLA. Berat untuk purata berat molekul (Mw) untuk filem PLA yang ditambah 3.0 wt.% HNTs lebih rendah berbanding filem PLA yang ditambah 6.0 wt.% HNTs manakala bilangan untuk purata berat molekul (Mn) filem PLA yang ditambah 3.0 wt.% HNTs lebih tinggi berbanding filem PLA yang ditambah 6.0 wt.% HNTs. Didapati bahawa penambahan 3.0 wt.% HNTs ke dalam PLA mampu menghasilkan filem PLA/HNTs bionanokomposit yang mempunyai ciri-ciri mekanikal yang optimum yang mana menghasilkan kekuatan tegangan, kekuatan alah dan Young's modulus yang tertinggi disebabkan taburan HNTs yang sekata didalam matrik PLA dan menghasilkan penghubung hidrogen yang stabil antara HNTs dan PLA juga kerana nilai Mn yang tinggi iaitu 3.97 x 10^4 g/mol dan PDI yang tinggi iaitu 1.97. Filem PLA/HNTs bionanokomposit dengan penambahan sebanyak 3.0 wt.% HNTs menghasilkan WVP dan OTR yang paling rendah dibandingkan dengan filem PLA/HNTs bionanokomposit yang lain disebabkan terhasilnya laluan yang berliku-liku oleh taburan HNTs yang sekata di dalam matrik PLA. Manakala, penambahan 3.0 wt.% HNTs ke dalam matrik PLA menghasilkan meningkatan yang optimum kepada ketahanan haba untuk filem dengan menambah daya tahan filem terhadap perubahan fasa apabila haba disalurkan. Analisis kelutsinaran filem mendedahkan bahawa tiada perubahan yang ketara ($p>0.05$) terhadap kelutsinaran filem apabila HNTs ditambah ke dalam matrik PLA. Demonstrasi terhadap kepejalan dan kehilangan berat tomato ceri menunjukkan bahawa filem PLA yang ditambah dengan HNTs mampu untuk memanjangkan jangka hayat tomato ceri yang dibungkus tersebut.

Kesimpulannya, HNTs yang merebak secara rata di dalam PLA, sambungan hidrogen yang stabil antara HNTS dan PLA serta Mn yang tinggi dan Mw yang rendah meningkatkan ciri-ciri mekanikal, kepanasan, dan rintangan filem PLA/HNTs bionanokomposit. Penambahan HNTs di dalam filem PLA mampu memanjangkan jangka hayat tomato ceri yang dibungkus dengan filem PLA/HNTs bionanokomposit.

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I certify that a Thesis Examination Committee has met on 6 November 2017 to conduct the final examination of Nazratul Putri binti Risyon on her thesis entitled "Characterization of Polylactic acid/Halloysite Nanotubes Bionanocomposite Films as Food Packaging Films" 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

Rosnah binti Shamsudin, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Mohd Nazli Naim, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Ishak bin Ahmad, PhD
Associate Professor
Universiti Kebangsaan Malaysia
Malaysia
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 29 January 2018

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Siti Hajar Othman, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Roseliza Kadir Basha, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Rosnita A. Talib, PhD
Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Name of Chairman of
Supervisory Committee: Siti Hajar Othman_

Signature: ____________________
Name of Member of
Supervisory Committee: Roseliza Kadir Basha

Signature: ____________________
Name of Member of
Supervisory Committee: Rosnita A. Talib

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LIST OF ABBREVIATIONS

CO_2	Carbon dioxide
CH_4	Methane
H_2O	Water
PCL	Polycaprolactone
PBS	Poly(butylenes succinate)
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
FDA	US Food and Administration
GRAS	General Recognized As Safe
MMT	Montmorillonite nanoclay
HNTs	Halloysite nanoclay
PET	Polyethylene terephthalate
HDPE	High-density polyethylene
N_2O	Nitrous oxide
HFCs	Hydrofluorocarbons
PFCs	Perfluorocarbons
SF_6	Sulphur hexafluoride
PVC	Polyvinyl chloride
LDPE	Low-density polyethlene
PP	Polypropyrene
PS	Polystyrene
$CH_3CHOHCOOH$	2-hydroxypropionic acid
$CHCl_3$	Chloroform
TiO_2	Titanium dioxide
Ag	Silver
$Al_2Si_2O_5(OH)_4H_2O$	Aluminium nanoclay
ZnO	Zinc oxide
FESEM	Field Emission Scanning Electron Microscope
TEM	Transmission Electron Microscope
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
Mw	Average molecular weight
Mn	Average molecular number
WVP	Water vapor permeability
OTR	Oxygen transmission rate
Mz+1	Higher weight average molecular weight
PDI	Polydispersity index
EAB	Elongation at break

CHAPTER 1

INTRODUCTION

1.1 Background

Food packaging materials play an important role to preserve, protect, market and distribute food to consumer. Characteristics and properties of food packaging materials such as mechanical, thermal and barrier properties as well as optical properties particularly transmittance of light are indicators that determine shelf life and demand of consumers towards the packaged food and packaging materials themselves. Apart from that, application of food packaging is also dependent on the mechanical, thermal, barrier and optical properties of the food packaging material. For application, the food packaging materials need to exhibit good mechanical, thermal, barrier and optical properties in order to function effectively. The materials utilized to produce food packaging play an important role in determining whether the food packaging can be functioning well.

Nowadays, most of the commercialized food packaging in industry is made-up of non-biodegradable material such as petroleum which resulted to disposal problem and environmental issue for example increase in amount of municipal solid waste. The municipal solid waste is commonly discarded at surrounding area and landfill area (Kumar et al., 2010) to be degraded by natural microorganisms (bacteria, actinomycetales, fungi, algae and protozoa) (Aislabie et al., 2013) and enzymes (*Proteinase K, pronas* and bromelain) (Kolstad et al., 2012; Premraj and Doble, 2005). However, some of the commercialized food packaging municipal solid waste could not be degraded for hundreds or thousands of years (Souza et al., 2012). To solve this environmental issue, studies have been directed towards development of biodegradable materials for food packaging applications such as those made from biopolymer.

Biopolymer can be decomposed into carbon dioxide (CO_2), methane (CH_4), water (H_2O), inorganic compounds or biomass by the enzymatic actions of microorganisms (Torres-Pacheco, 2006). There are various types of biopolymers that have been used to produce food packaging material such as polycaprolactone (PCL), poly (butylenes succinate) (PBS), polyhydroxybutyrate (PHB) and polylactic acid (PLA) (Othman, 2014; Rhim et al., 2013). Among them, PLA is the most promising biopolymer to be used in all applications related to food packaging because it has been approved by US Food and Administration (FDA) as well as classified as General Recognized As Safe (GRAS) material (Molinaro et al., 2013). PLA is also cost effective (Endres and Siebert-raths, 2011).

However, the application of biopolymer as food packaging material is limited because it exhibits low mechanical, thermal and barrier properties (Peelman et al., 2013). The biopolymer is still not satisfactory to be used in food packaging application due to the brittleness of biopolymer, low heat distortion temperature, high gas and vapour permeability (Rhim et al., 2013). Thus, enhancement in the properties of biopolymer for food packaging applications has to be explored to develop materials that have potential to be used in variety of food packaging application such as for processed meats, cheese, confectionery, cereals, boil-in-bag foods, fruits and vegetables (Rhim et al., 2013). One of the ways to improve these properties is by application of nanotechnology.

Nanotechnology is defined as creation or utilisation of structures, devices or materials that have at least one dimension with 1-100 nm in length (Duncan, 2014). In the vast field of nanotechnology, polymer matrix based nanocomposite is becoming an important area of research and development (Paul and Robeson., 2008). Bionanocomposite is a multiphase material that formed by two or more elements that have continuous phase or matrix particularly biopolymer and discontinuous phase or nanofiller (<100nm) (Othman, 2014). The incorporation of nanofillers in biopolymer might increase the biodegradability of the biopolymer (Silvestre et al., 2011). Thus, bionanocomposite has the ability to solve the food packaging municipal waste problem, as well as contributes to decrease of CO_2 emissions (Silvestre et al., 2011) which will reduce the greenhouse effect.

Furthermore, bionanocomposite is an innovative solution to improve the performance of food packaging material in terms of mechanical, thermal and barrier properties. The incorporation of nanofillers into food packaging material will form an excellent interfacial interaction between biopolymer and nanofillers by hydrogen bonding (Bhuvana and Prabakaran, 2014) which improve mechanical properties of the polymer. Studies by Bhuvana and Prabakaran (2014) and Silve et al. (2014) show that, the amount of nanofillers in biopolymer also influences the mechanical properties of the bionanocomposite food packaging (Othman, 2014). Tensile strength and modulus are usually increase but elongation at break is usually decrease with the increase in amount of nanofillers until optimum concentration of nanofillers is achieved. When the amount of nanofiller exceeded optimum concentration, mechanical strength and modulus decreased and elongation at break increased due to agglomeration of HNTs particles (Azizi et al., 2014; Sadegh-hassani and Nafchi, 2014; Rhim et al., 2013).

Bionanocomposite food packaging material also exhibits improved thermal properties thus producing more stable food packaging material towards heat. The thermal properties improved due to addition of well distributed nanofiller in biopolymer matrix that form tortuous path which delay the transfer of oxygen thus prolong burning time of biopolymer (Lecouvet et al., 2012). The nanofiller that added into biopolymer also acts as nucleating agent which able to increase the stability of biopolymer from phase changes when heat is applied to the biopolymer (Shi et al., 2013).

Apart from that, bionanocomposite food packaging material exhibits enhanced barrier protection to gases and light from penetrating to the food packaged (Silvestre et al., 2011). Good dispersion of nanofillers in biopolymer matrix will create tortuous path in the matrix thus increases the barrier of food packaging towards water vapour and gases (Dias et al., 2014). Nanofillers reduce the penetration of water and gas into the food packaging film and maintain moisture content and respiration rate of the packaged food (Othman, 2014). This is advantageous for food or drinks that require a high barrier towards gas particularly oxygen to prevent oxidation and high barrier towards water vapour to extend shelf life of the food such as bakery products, chips, carbonated beverage, fruits and vegetables (Duncan, 2014; Rha, 2012). Other than that, the usage of nanofillers to produce bionanocomposite also has economic advantage because only small amount of nanofillers are needed to increase performance of the material.

Variety types of nanofillers can be utilized to produce bionanocomposite material for food packaging application such as natural biopolymers, metal, metal oxide and clay (Othman, 2014). Among them, bionanocomposite material comprises of biopolymer and nanoclay is the most favourable because clay is a naturally occurring mineral that is safe for food packaging application, cost effective and commercially available (Souza et al., 2012). Besides, nanoclay has the ability to increase the mechanical, thermal and barrier properties of food packaging by forming exfoliated structure when dispersed well in the biopolymer matrix (Peelman et al., 2013).

There are many types of nanoclay that can be utilized to produce bionanocomposite material for food packaging application such as montmorillonite nanoclay (MMT), bentonite nanoclay, kaolinite nanoclay and halloysite nanotubes (HNTs). Among them, HNTs are the most promising due to its unique properties. HNTs are natural, non-toxic, biocompatible and excellent in dispersion (Liu et al., 2015; Silva et al., 2014; Kamble et al., 2012). The natural and non-toxic characteristics of HNTs make HNTs safe to be used for food packaging applications. Besides, HNTs also exhibits high capability in cation exchange thus HNTs have high possibility to form hydrogen bond by attracting hydrogen atom from PLA to combine with oxygen atom on HNTs (Kamble et al., 2012). These make HNTs as attractive candidate to support biopolymer matrix such as PLA (Rawtani and Agrawal, 2012). HNTs incorporated into PLA biopolymer films will produce bionanocomposite known as PLA/HNTs bionanocomposite films. HNTs also exhibit excellent dispersion in the PLA matrix (Kamble et al., 2012) which is an important behaviour to improve the mechanical, thermal and barrier properties of the PLA/HNTs bionanocomposite films. For potential commercialization, the usage of HNTs as nanofiller in food packaging film is promising because HNTs is cheap compared to other nanofiller such as carbon nanotbes (CNTs) and montmorillonite (MMT). Market size of PLA in food packaging, textile, transportation and electronics industry is expected to reach $5.2 billion by 2020 due to limited fossil fuel resources and increasing petrochemical price. Other than that, the usage of PLA in industry is an alternative to conventional polymer, the raw materials also sustainable, and low production cost (Dommermuth et al., 2013).Other than that, PLA and HNTs are materials which harmless to human thus can be applied as food packaging materials (Molinaro et al., 2013; Kamble et al., 2012). However, mechanical, thermal and barrier properties of the PLA/HNTs bionanocomposite films are significantly dependent on the concentration of nanofillers. Thus, optimum concentration of nanofiller particularly HNTs are needed to be determined in order to produce effective PLA/HNTs bionanocomposite films for food packaging application.

1.2 Problem Statement

There is environmental issue regarding the usage of non-biodegradable food packaging material whereby the usage increases the dumping of municipal waste in landfill. Thus, this study is directed towards developing biodegradable material for potential food packaging application from biopolymer material particularly PLA. However, the application of PLA biopolymer for potential food packaging material is limited due to low mechanical, thermal and barrier properties (Peelman et al., 2013). Nonetheless, these properties can be improved by incorporation of nanofiller such as HNTs. The improvement is related to dispersion of HNTs in PLA, chemical bonding between HNTs and PLA as well as average molecular weight of PLA because well distribution of HNTs, strong chemical bonding between HNTs and PLA as well as high average molecular weight improve the properties of PLA film. Apart from that, HNTs concentration also plays an important role in determining the mechanical, thermal and barrier properties of the biopolymer.

To the best of knowledge, there was limited researches regarding PLA/HNTs bionanocomposite films for food packaging application (Othman et al., 2016; Silva et al., 2014; Stoclet et al., 2014). Although there were several studies explored the effect of HNTs concentration on the properties of PLA biopolymer films for food packaging application, the studies are not comprehensive and only focus on selected properties. Moreover, the studies did not demonstrate the application of their produced PLA/HNTs bionanocomposite film for food packaging application. Study on average molecular weight of PLA incorporated with HNTs is also uncommon to find in literature. Investigation is needed to fill in the literature gap in order to produce efficient PLA/HNTs bionanocomposite films as food packaging.

Therefore, demonstration on the application of PLA/HNTs bionanocomposite films as food packaging and study on the average molecular weight of PLA incorporated with HNTs are highlighted as the novelty of this research.

1.3 Objectives

This thesis reports a comprehensive study of the dispersion, chemical bonding and molecular weight of PLA/HNTs bionanocomposite films. The work also includes characterization and demonstration of the PLA/HNTs bionanocomposite films. There are two primary objectives of the present work:

1. To investigate dispersion and chemical bonding of HNTs in PLA matrix as well as molecular weight of neat PLA and PLA/HNTs bionanocomposite films to determine the mechanism that affect the changes in properties of bionanocomposite films.

2. To characterize mechanical, thermal, barrier and optical properties (transmittance) of neat PLA and PLA/HNTs bionanocomposite films incorporated with different concentration of HNTs in order to determine the optimum concentration of HNTs in PLA film as well as to demonstrate the application of the films as food packaging material particularly for tomato cherries packaging.

1.4 Thesis Outline

This thesis consists of five chapters. Chapter 1 is an introduction which begins with an overview of the issue surrounding the usage of non-biodegradable material, application of nanotechnology to biopolymer in order to solve the issue, nanofillers, and properties of the bionanocomposite films particularly PLA/HNTs films. Problem statement regarding the usage of non-degradable food packaging materials and poor properties of biopolymer are then highlighted followed by the objectives of the research.

Chapter 2 covers the literature review that consists of critical reviews of previous work that related to biopolymer, nanofiller, bionanocomposite and properties of PLA/HNTs bionanocomposite films. The properties of bionanocomposite films include mechanical, thermal, barrier and optical properties. The review provides the basis for the experimental and analysis sections of the thesis.

Chapter 3 covers methodology which consists of materials and methods that were used to prepare the neat PLA and PLA/HNTs bionanocomposite films by solvent casting method. This chapter also details the materials and methods used to investigate the dispersion, chemical bonding and average molecular weight of PLA/HNTs bionanocomposite films and to characterize on mechanical, thermal, barrier and optical properties (transmittance); and to demonstrate the application of PLA/HNTs bionanocomposite film as food packaging.

Chapter 4 presents the results and discussion on the findings of the present work including analysis and interpretation of the results. The results and discussions presented in Chapter 4 are structured according to the two main objectives of the present work.

Chapter 5, the final chapter covers the overall conclusion from the results discussed in Chapter 4 as well as some recommendations for potential future work.

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