UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYHYDROXYBUTYRATE/POLY(LACTIC ACID)/MODIFIED MAGNESIUM ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

TEH SIEW NU

FS 2014 17

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By

TEH SIEW NU

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

May 2014

DEDICATIONS

I dedicate my dissertation work to my lovely family and friends. A word of appreciation and deepest affection is inadequate to my loving parents whose word of encouragement and push for tenacity in my ears. My sisters and brother who have been my constant source of inspiration, never left my side, and encourage me whenever I need them. I wish to dedicate this dissertation to my roommate and all my friends, for being there support and listen to me throughout the entire master program. They have given me the drive and discipline to tackle any task with enthusiasm and determination. Without their love and support, this project would not have been made possible.

Abstract of thesis presented to Senate of University Putra Malaysia in Fulfillment of the requirement for the degree of Master of Science

PREPARATION AND CHARACTERIZATION OF POLYHYDROXYBUTYRATE/POLY(LACTIC ACID)/MODIFIED MAGNESIUM ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

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May 2014

Chair : Prof. Mansor Ahmad, PhD

Faculty : Science

Arising concerns in environmental issues make the biodegradable polymers played increasing important role as environmental friendly materials. However, most biodegradable polymers like polyhydroxybutyrate (PHB) have poor properties which prohibit its commercial application. Therefore, the present work is aimed to modify and improve the properties of PHB to become nanocomposites. In this study, polyhydroxybutyrate/poly(lactic acid) (PLA)/modified magnesium aluminum layered double hydroxides (Mg/Al LDH) nanocomposites were prepared by solvent-casting method. Mg/Al layered double hydroxide (MALDH) was first synthesized via a co-precipitation method from nitrate salt solution and then modified with sodium stearate via an anion exchange process. The modification increased the interlayer spacing of the MALDH from 7.88 to 30.26 Å. This suggests that the intercalation of stearate ions into the interlayer of MALDH was success. The modified Mg/Al LDH (SMALDH) was then used in the preparation of the PHB/PLA nanocomposites.

The morphology, thermal, and mechanical properties of the PHB/PLA blends and nanocomposites were investigated using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analyzer (TGA), and mechanical measurement, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The PHB/PLA blends were prepared before preparing the nanocomposites by solvent casting method in order to find the optimum ratio of the blends. Blending of PLA to PHB enhances the mechanical properties of PHB. The optimum ratio between PHB/PLA investigated was 90% PHB and 10% PLA which gave the maximum tensile strength and tensile modulus of PHB to 28.73 MPa and 651.83 MPa, respectively. This suggested the good interfacial adhesion between

PHB and PLA. SEM of PHB/PLA blends show that the fracture surface of the PHB had been modified with the addition of PLA.

The mechanical properties of the polymer blends nanocomposites depend on the amount of the SMALDH added into the PHB/PLA blends. The addition of 1.5 wt% of SMALDH improved the tensile strength and tensile modulus of PHB/PLA blend by 23% and 13%, respectively. XRD result and transmission electron micrograph showed that the nanocomposites produced are of mixture intercalated/exfoliated types.

Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLIHIDROKSIBUTIRAT/POLI(ASID LAKTIK)/MAGNESIUM ALUMINIUM HIDROKSIDA BERLAPIS GANDA DIUBAH SUAI

Oleh

TEH SIEW NU

Mei 2014

Pengerusi: Prof. Mansor Ahmad, PhD

Fakulti: Sains

Kebimbangan yang timbul dalam isu alam sekitar menjadikan polimer terbiodegradasi memainkan peranan yang semakin penting sebagai bahan mesra alam sekitar. Walau bagaimanapun, kebanyakan polimer terbiodegradasi seperti polihidroksibutirat (PHB) mempunyai ciri-ciri lemah yang melarang penggunaan komersialnya. Oleh itu, kajian ini bertujuan untuk mengubah suai dan memperbaiki sifat PHB dengan penyediaan nanokomposit. Dalam kajian ini, nanokomposit polihidroksibutirat/poli(asid laktik)/Mg/Al hidroksida berlapis ganda telah disediakan melalui kaedah pelarut. Mg/Al hidroksida berlapis ganda (MALDH) disintesis terlebih dahulu melalui kaedah ko-pemendakan daripada larutan garam nitrat dan kemudiannya diubah suai dengan natrium stearat melalui process pertukaran anion. Pengubahsuaian tersebut meningkatkan ruangan antara lapisan dalam MALDH daripada 7.88 kepada 30.26 Å. Ini menunjukkan bahawa interkalasi ion stearat ke dalam ruangan antara lapisan MALDH telah berjaya. Mg/Al LDH yang diubahsuai (SMALDH) digunakan dalam penyediaan nanokomposit PHB/PLA.

Morfologi, sifat haba dan sifat-sifat mekanik dalam adunan PHB/PLA dan nanokomposit telah dikaji dengan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah Transform Fourier (FTIR), analisis termogravimetri (TGA), pengukuran ketegangan, mikroskopi pengimbasan elektron (SEM), dan mikroskopi transmisi elektron (TEM). Adunan PHB/PLA telah disediakan sebelum penyediaan nanokomposit dengan menggunakan teknik acuan pelarut untuk mencari nisbah optimum dalam campuran. Pengadunan PHB dengan PLA meningkatkan sifat-sifat mekanik PHB. Nisbah optimum antara adunan PHB/PLA diselidiki adalah 90% PHB dan 10% PLA yang memberikan kekuatan tegangan dan modulus tegangan yang maksimum. Kehadiran 10% PLA meningkatkan kekuatan tegangan dan modulus tegangan PHB masing-masing kepada 28.73 MPa dan 651.83 MPa. Ini mencadangkan lekatan antara muka yang baik antara PHB dan PLA. SEM adunan

PHB/PLA menunjukkan bahawa permukaan patah PHB telah diubahsuai apabila PLA diadun kepadanya.

Sifat-sifat mekanik polimer adunan nanokomposit bergantung kepada kuantiti SMALDH yang ditambahkan ke dalam adunan PHB/PLA. Penambahan 1.5 % berat SMALDH meningkatkan kekuatan tegangan dan modulus tegangan adunan PHB / PLA masing-masing sebanyak 23 % dan 13 %. Keputusan hasil XRD dan TEM menunjukkan bahawa nanokomposit yang dihasilkan adalah daripada jenis campuran diinterkalasi/'exfoliat'.

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I certify that a Thesis Examination Committee has met on 9th May 2014 to conduct the final examination of Teh Siew Nu on her thesis entitled "Preparation and Characterization of Polyhydroxybutyrate/Poly(lactic acid)-Modified Magnesium Aluminium Layered Double Hydroxides Nanocomposites 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:

Mohamed Ibrahim Mohamed Tahir, PhD
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Md Jelas Haron, PhD
Professor
Centre of Foundation Studies for Agricultural Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd Zaizi Desa, PhD
Associate Professor
Centre of Foundation Studies for Agricultural Science
Universiti Putra Malaysia
(Internal Examiner)

Ishak Ahmad, PhD
Associate Professor
School of Chemical Sciences and Food Technology
Faculty of Science and Technology
Univeristi Kebangsaan Malaysia
Malaysia
(External Examiner)

NORITAH OMAR, PHD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 July 2014

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:

Mansor Bin Ahmad, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Nor Azowa Binti Ibrahim, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Norhazlin Binti Zainuddin, PhD
Senior Lecturer
Department of Chemistry, Faculty of Science
Universiti Putra Malaysia
(Member)

Wan Md Zin Wan Yunus, PhD
Professor
Department of Chemistry, Centre for Defence Foundation Studies
National Defence University of Malaysia
(Member)

BUJANG KIM HUAT, PhD
Proffesor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date**:**

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Signature: ______________________
Name of Chairman of Supervisory Committee: Professor Dr. Mansor Ahmad

Signature: ______________________
Name of Member of Supervisory Committee: Dr. Nor Azowa Ibrahim

Signature: ______________________
Name of Member of Supervisory Committee: Dr. Norhazlin Zainuddin

Signature: ______________________
Name of Member of Supervisory Committee: Professor Dato' Dr. Wan Md Zin Wan Yunus

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LIST OF ABBREVIATIONS

Al	Aluminium
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetry
FTIR	Fourier Transform Infrared
LDH	Layered Double Hydroxides
MALDH	Unmodified Mg/Al LDH
Mg	Magnesium
$Mg(OH)_2$	Magnesium Hydroxides
Ni	Nickel
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
PDLLA	Poly(*d*,*l*- lactide)
PHB	Polyhydroxybutyrate
PHB30B	Composites of polyhydroxybutyrate and organically modified montmorillonites
PHBNa	Composites of polyhydroxybutyrate and sodium montmorillonites
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
SEM	Scanning Electron Microscopy
SMALDH	Stearate-Mg/Al LDH
TEM	Transmission Electron Microscopy
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
T_{max}	Maximum Degradation Temperature
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Polymer had existed in nature form and play important function in plant and animal life since life began. With the growth in polymer science and modern technologies, polymers play increasing role in human beings.

Most of the polymers available in marketplace are rarely use by themselves without adding any additives due to their poor performance. Blending of the several types of materials or additives which are not green materials into the polymer are common way to enhance and modify polymers poor properties. Widely used of these polymers which are extremely durable and not environmental friendly created a long-term disposal problem and global pollution if not controlled well.

The environmental concerns bring opportunities in the development and commercialized of the biodegradable polymers from renewable resources. In the past two decades, biodegradable polymers have attracted much attention and played important role as green materials in order to preserve and protect environment, and the realization that our petroleum resources are finite and the shortage of landfill (Abdelwahab *et al*., 2012; Yu and Chen, 2009). Naturally occurring microorganisms such as bacteria can split biodegradable polymers into carbon dioxide and water. Park *et al.* (2005) stated that the biodegradable polymers are able to cleave into biocompatible byproducts through chemical or biological reactions.

Biodegradable polymer can be classified into natural polymers which obtain from natural resources and synthetic biodegradable polymers which are manmade polymer. The natural polymers such as protein, chitosan, polysaccharides, rubber, and cellulose had functioned in different way in their native settings. Synthetic biodegradable polymers can be derived from agricultural products like poly(lactic acid) (PLA) and fermentation of bacteria such as polyhydroxybutyrate (PHB).

Polyhydroxybutyrate is the simplest family of polyhydroxyalkanoates (PHA) which derived from bacteria fermentation. PHB is the linear polyester with melting point of 175 °C and glass transition temperature of around 4 °C. It is insoluble in water and resistant to hydrolytic degradation. PHB has good oxygen permeability and nontoxic. This hydrophobic polymer is brittle which is largely due to the presence of large crystals in the form of spherulites (Yu and Chen, 2009). The structure of PHB is shown in Figure 1.1.

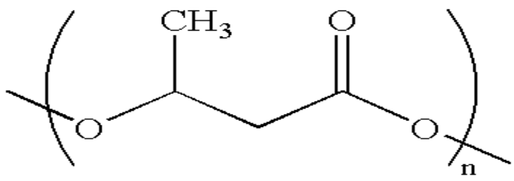

Figure 1.1: Structure of polyhydroxybutyrate.

Poly(lactic acid) is one of the aliphatic polyester. PLA can be derived from agricultural products like corn and sugar cane through fermentation and chemical process of lactic acid. The melting point of PLA is around 130 °C to 180 °C and the glass transition temperature of around 60 °C. The highly transparent PLA has good mechanical properties like high tensile strength and thermoplacticity (Yu and Chen, 2009). Figure 1.2 shows chemicals structure of PLA.

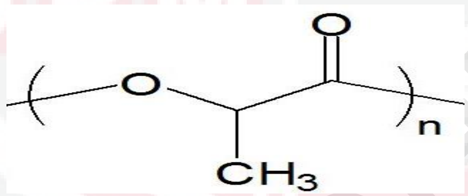

Figure 1.2: Structure of poly(lactic acid).

The materials that can exchange inorganic and organic ions in the interlayer are known as layered materials. Layered double hydroxides (LDH) are a type of layered materials which known as anionic or hydrotalcite-like clays. The hydrotalcite structure of LDH is shown in Figure 1.3. LDH has similar geometries like cationic layered silicate clays. Anions and water molecules are randomly located in the interlayer of LDH. The anions located in the interlayer of LDH neutralize the positive charge on the LDH layer which produces from the occupancy of a trivalent cation as reported by Kumar *et al*. (2012), Kovanda *et al*. (2009) and Newman and Jones (1998). Newman and Jones (1998) suggested that LDH layers made up from the infinite edge-sharing octahedral units that coordinated by hydroxyl groups.

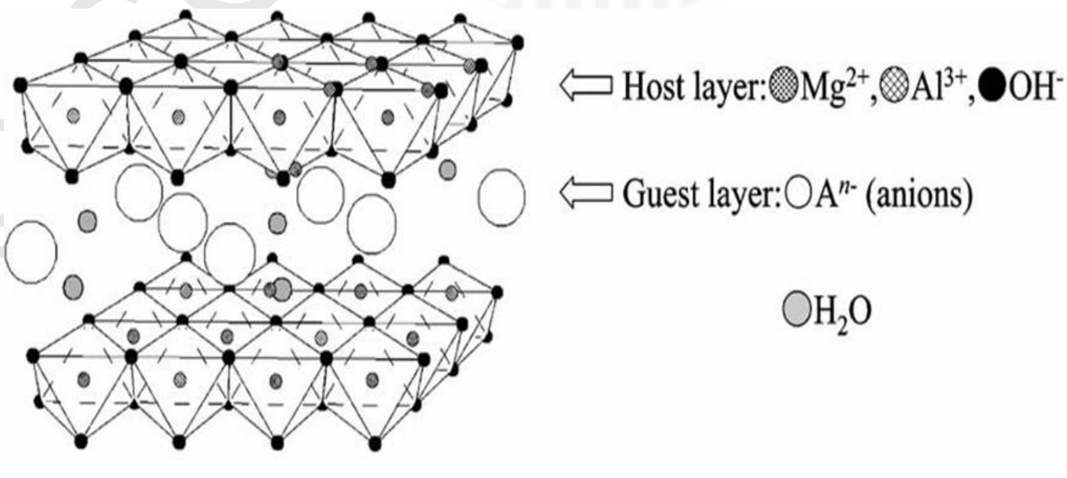

Figure 1.3: Hydrotalcite structure of LDH (Palmer *et al*., 2009).

1.2 Problem Statement

The biodegradable polymers had aroused considerable interest in research. PHB is a biodegradable polymer that derived from fermentation of bacteria. PHB has received extensively attention research as green or eco-friendly material. The chemical structure and physical properties of PHB is comparable to certain petrochemical-derived thermoplastic like polypropylene. For that reason, PHB is potential biodegradable polymers that can be used to replace certain traditional and non-biodegradable polymers (Chen and Luo, 2009). PLA is typical biodegradable aliphatic polyesters which can be produced from renewable resources. The good tensile strength properties, film transparency, biocompatible and processability has make PLA as commercially interesting polymer.

Both PHB and PLA are biodegradable polymers which are well known with their biocompatibility, sustainability, and similar thermal and mechanical properties to those certain conventional polymers. Thus, they have attracted many interests in order to explore their physical and processing properties for potential applications. Nevertheless, the poor processing properties and brittleness of both PHB and PLA at room temperature are noteworthy (Zhang *et al*., 2006). There have been many reports on the efforts to enhance the mechanical and processing properties of PHB and PLA. It is essential to reduce the crystallinity and process ability of PHB and PLA by incorporating other monomeric units into polymers chains or blending with other polymers. The easier and faster way to modify the properties of polymer is by blending compare to the copolymerization method.

Zhang *et al*. (1996) had blended PHB with Poly(d,l-lactide) (PDLLA) which is an amorphous polymer obtained from a mixture of D- and L-lactic acid through solvent casting method. They found out that PDLLA can be used to improve the elongation at break of PHB. Previous studies were focusing on using PHB as second polymer to improve the properties of PLA. However, there are few studies reported using PHB as primary polymer and blended with PLA to study their mechanical properties. Most of the researchers focused their studies in terms of structure, dispersibility, miscibility, and crystallinity of the blends but not mechanical properties.

According to Yang and Qiu (2010), combination of biodegradable polymers with economical organic or inorganic fillers are the alternative way to modify the biodegradable polymers, reduce cost and enhance the properties of the polymer which preserve the acceptable ductility at the same time. The organized two-dimensional arrays of organic species between the interlayers can result in novel functions that are different to the typical functions of the individual organic species. Kumar *et al*. (2012) and Tsai *et al*. (2006) reported that LDH become an attractive choice as nanofillers to improve various properties of the polymer matrices due to its high anion exchange capacities and layered structure which enables the incorporation into polymer become easier to form better nanocomposites. There had been large number of studies of polymer/LDH nanocomposites that showed enhancement in mechanical properties as reported by Du *et al*. (2006) and Ray and Okamoto (2003).

Therefore, PHB/PLA blend was blended with LDH in order to create a new type of environmental friendly nanocomposites and investigate the effect of LDH on the mechanical, thermal and morphology in the nanocomposites.

1.3 Objectives

The main objectives of this project are as follows:

1. To prepare polyhydroxybutyrate/poly(lactic acid) blends and PHB/PLA/Modified Mg/Al LDH nanocomposites at various compositions by solution casting method.

2. To study the mechanical and thermal properties and morphology of PHB/PLA blends.

3. To investigate the effect of LDH on the mechanical, morphology and thermal properties of PHB/PLA blends.

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