SYNTHESIS AND CHARACTERIZATION OF POLYLACTIC ACID / PALM OIL BASED POLYURETHANE FOR BIODEGRADABLE PACKAGING MATERIALS

BY

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A dissertation submitted in fulfillment of the requirement for the degree of Master of Science (Biotechnology Engineering)

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DECEMBER 2017

ABSTRACT

Conventional packaging materials such as polystyrene (PS), polypropylene (PP) and polyethylene (PE) are produced by using petroleum-based substances but recently its non-biodegradability has created awareness towards people. Therefore, degradable plastics are highly sought in both commercial and also in research. Polylactic acid (PLA) is a type of biodegradable biopolymer which is brittle but has good mechanical strength. To improve its brittleness, polyurethane (PU) was tailored using PLA with incorporation of chain extender. Palm oil polyol (PO) was used as soft segments to improve the brittleness and flexibility of PLA and hexamethylene diisocyanate (HDI) was used as source of isocyanate. The objective of this study is to synthesize PLA/palm based PU using One-Shot Method. Followed by chemical structure, thermal and mechanical characterization of produced PU. Biodegradability is also evaluated using soil method. PLA/palm based polyurethane (PLAPOPU) is synthesized using One-Shot polymerization process. Fourier Transform Infra-Red (FT-IR) Spectroscopy is used to confirm the formation of urethane bond. The glass transition temperature (T_g) is analysed using Differential Scanning Calorimetry (DSC). The mechanical test showed enhanced elongation properties of PLAPOPU with the highest elongation of 360% for PLAPOPU 4. Biodegradability test also had proven PLAPOPU to be readily degradable as the significant weight loss can be seen starting from the end of the second month of the test. Mechanical properties of PLA in term of elongation can be seen to be improved in this project, together with the enhanced biodegradability compared to the pure PLA.

خلاصة البحث

يتم إنتاج مواد التغليف التقليدية مثل البولي سترين والبولي بروبيلين والبولي إيثيلين باستخدام مواد مشتقة من النفط (البترول)، ولكنّ عدم قابليتها للتحلل البيولوجي أدّى إلى خلق الوعي في الآونة الأخيرة. لذلك، أصبح البلاستيك القابل للتحلل غايةً في كلٍّ من مجال التجارة و الأبحاث. حمض عديد (بولي) اللاكتيك (PLA) هو نوع من المبلمرات الحيوية القابلة للتحلل وهو هش غير أنّه يتميز بقوة ميكانيكية. وللتحسين من هشاشته، تم تصميم البولي يوريثين (PU) باستخدام PLA مع دمج سلسلة مطوّلة. تم استخدام بولي أويل من زيت النخيل (PO) كشرائح لينة لتحسين هشاشة ومرونة PLA واستُخدِم هيكسامثيلين ثنائي أيزوسيانات (HDI) كمصدر لمركب الأيزوسيانات. وكان الهدف من هذه الدراسة هو توليف PU / PLA المشتق من النخيل باستخدام طريقة الدفعة الواحدة، تليها دراسة التركيب الكيميائي والتوصيف الحراري والميكانيكي لعينات PU المنتجة. كما تم تقييم قابلية التحلل البيولوجي باستخدام طريقة التربة. تمّ تصنيع PU / PLA المشتق من النخيل والمبني على البولي يوريثين (PLAPOPU) باستخدام طريقة البلمرة بالدفعة الواحدة. وتم توظيف مطياف الأشعة تحت الحمراء (FTIR) لتأكيد تكوّن روابط اليوريثين. تمّ تحليل درجة حرارة انتقال الزجاج (T_g) باستخدام مسعر المسح التبايني (DSC). وأظهر الاختبار الميكانيكي خصائص استطالة محسّنة لمركب PLAPOPU الناتج مع استطالة قصوى بقيمة 360% لمركب PLAPOPU 4. وقد أثبت اختبار التحلل البيولوجي أيضا أنّ PLAPOPU قابلٌ للتحلل بسهولة حيث ثبت ذلك من خلال فقدانٍ ملحوظ في الوزن ابتداءً من نهاية الشهر الثاني من الاختبار. ويمكن ملاحظة تحسّن الخواص الميكانيكية لمركب PLA من حيث الاستطالة في هذه الدراسة، جنباً إلى جنب مع تحسّن قابليته للتحلل البيولوجي بالمقارنة مع PLA النقي.

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 dissertation for the degree of Master of Science (Biotechnology Engineering).

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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ACKNOWLEDGEMENTS

In the name of Allah, the most Merciful and the most Compassionate.

Alhamdullilah, all praise to Allah for His blessings, I am able to complete this research work.

I wish to express my sincere appreciation and gratitude to my supervisors, Dr. Fathilah Ali for her invaluable inputs and encouragement throughout this study. Thank you for giving me lots of motivation to accomplish this project. I would like to also thank Prof. Ibrahim Ali Noorbatcha for his commitment and constructive suggestions.

I appreciate all the support from staffs in the Department of Biotechnology Engineering; especially to Bro Hafizul, Bro Aslan, Bro Iznan and Haji Tukiman. I would like to take this opportunity to express my gratitude to my colleagues, in particular Bro Noor, Bro Shukri, and Bro Ibrahim for their wise suggestions and moral supports.

Last but not least, special thanks go to my family for their inspiration, du'a and blessings especially to my mother, Jemilah binti Mahmood and my father, Ismail bin Mahmud. This work will be impossible without their innumerable supports, both financially and emotionally during the course of this study.

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LIST OF ABBREVIATIONS

PLA	Polylactic acid
PO	Palm oil polyol
PU	Polyurethane
TPU	Thermoplastic polyurethane
PLAPOPU	PLA/palm based polyurethane
HDI	Hexamethylene diisocyanate
TDI	Toluene diisocyanate
MDI	Methylene diphenyl diisocyanate
PS	Polystyrene
PP	Polypropylene
PE	Polyethylene
PCL	Polycaprolactone
PEG	Polyethylene glycol
PLGA	Poly(lactic-co-glycolic) acid
UTM	Universal testing machine
DSC	Differential scanning calorimetry
FTIR	Fourier Transfer Infrared Spectroscopy
T_g	Glass Transition Temperature
PLAHDI	PLA/HDI Polyurethane
PLAPOPU	PLA/PO/HDI Polyurethane
PET	Polyethylene terephthalate
PMMA	Poly (methyl) methacrylate
EDA	Ethylenediamine
BDA	Butanediamine
HMDA	Hexamethylenediamine
PDO	Propanediol
SA	Succinic acid
DFA	Dimmer fatty acid
DFAPA	Dimmer fatty acid polyamide
RBD	Refined bleached deodorized
DEG	Diethylene glycol
CNC	Cellulose nanocrystal

LIST OF SYMBOLS & UNIT

Kg	Kilogram
MPa	Megapascal
KPa	Kilopascal
Mol	Molar
KN	Kilonewton
^{o}C	Celcius

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

One of the biggest challenges faced by many developing countries is the solid waste management. The rapid development of economical state in developing countries leads to an increase in amount of solid wastes produced. Among many other countries, Malaysia is one of the countries that are struggling with this matter. In 2012, Malaysia with over 29 million populations was estimated to produce approximately 25,000 metric tonnes of domestic wastes per day. The average amount of solid wastes produced by Malaysian per capita is estimated at 0.8 k_g/person/day, but it also depends on the economic and geographical nature of the cities. For big cities with compact population such as Kuala Lumpur, the waste generated per capita is estimated to be 1.5 k_g/person/day. Figure 1.1 shows the composition of wastes at peninsular Malaysia (Zainu et al., 2015).

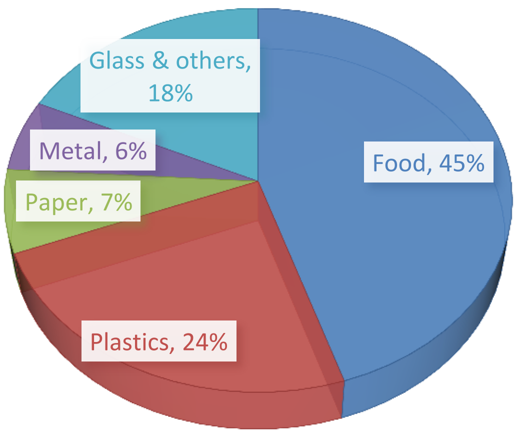

Figure 1.1 Waste composition generated per day in Peninsular Malaysia (Zainu et al., 2015)

From Figure 1.1, the highest contributor of wastes come from the food waste. This is inevitable as the population increases, the food wastes generated will also increase. Besides that, hotels and restaurants will also generate higher amount of food waste as the city become more compact with customers. The second largest waste generated is plastic wastes. This includes packaging materials such as bottle and plastic bags. Unlike food waste that will decomposed after several days, most of the commercial plastic materials that are used today are non-degradable, which means that the wastes probably will remain physically unchanged for years and consequently will take major space at the landfill. Knowing that these plastics are used as packaging materials, it is very crucial to develop better packaging materials which are degradable.

There are many types of packaging materials such as metal container, glass, paper and plastics. Some of these materials are not biodegradable or contain very low biodegradability and even may pollute the land. For example, metals and chemical substances can leach from the packaging materials, while iron and tin are examples of ion which may migrate from metal container especially corroded metal (Catala & Gavara, 2009). Among factors that should be taken into account when producing packaging materials are product characteristics, products and packaging interactions, shelf life, cost and environmental impacts. From environmental aspect, biodegradability should be emphasized in packaging materials as these materials are usually dumped into the landfill without being reused by the user (Catala & Gavara, 2009).

There are many biodegradable polymers such as aliphatic polyesters, aromatic copolyester, polyamides and poly-esteramides and also polyurethanes (Zhang, 2015). Polyurethane (PU) is a polymer synthesized from three constituents which are diisocyanate, polyol and a chain extender. PU can be categorized into two groups, which are the petroleum-based polyurethane and bio-based polyurethane. Researchers try to reduce the use of petroleum-based PU because it is non-biodegradable, unlike its counterpart, bio-based PU is readily biodegradable. The biodegradability of PU depends on the polyol used, usually combinations of polyols are used to produce high molecular weight PU to meet certain properties and requirement for certain usage (Vroman & Tighzert, 2009).

Over recent years, green products are considered by consumer as preferable products as awareness of environment and nature increases. Packaging materials are one of the areas where emergence of green products can be really much appreciated. Green packaging material can be described as safe, environmental-friendly, renewable material-derived and manufactured using clean technology (Herrmann & Rong, 2009). Polylactic acid (PLA) is a natural derived polymer usually from a starchy materials, is a suitable polymer to be used as green product due to its biodegradability. However, brittleness and poor ductility seems to limit its applications, especially when it involves mechanical toughness. There are a lot of methods used to improve the mechanical drawbacks of PLA, such as addition of plasticizer (Silverajah et al., 2012), blending (Pawar & Purwar, 2013) and production of composites (Xiong et al., 2013).

Using PLA to produce polyurethane is one of the ways used to improve the brittleness of PLA. In order to develop desirable PLA-based PU, other polyol is combined with PLA. Polyol derived from vegetable oil is becoming popular among researchers as this polyol is not only biodegradable and environmental friendly but also cheaper in price. Castor oil (Li et al., 2016), linseed oil (Zhang et al., 2015) and palm oil (Pawlik & Prociak, 2012) are among the vegetable oils used in the production of PU. Numerous methods are used to produce vegetable oil PU, the most common methods are one-shot method and pre-polymerization method. Many studies had been reported to produce blends and composites using PLA and vegetable oil such as reinforced epoxidized linseed oil plasticized polylactic acid nanocomposite (Alam et al., 2014), PLA/Starch/epoxidized soybean oil composites (Xiong et al., 2013) and PLA/epoxidized palm olein blend (Silverajah et al., 2012). All of these composites were studied to improve the brittleness of PLA and production of PLA-vegetable oil based PU is seen to be one of the ways.

1.2 PROBLEM STATEMENT

Commercial polymers that usually used as packaging materials are polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and poly (methyl methacrylate) (PMMA). Despite their low degradability, these materials are still preferred to be used as packaging material because of its flexibility. However, low degradability of commercial plastics contributes to environmental problems.

Polylactic acid (PLA) is used for various applications such as medical, packaging, textile fibres and also for 3D printer. PLA exhibits good strength and degradability but its brittleness is among its disadvantages. In order to improve the properties of PLA, other polymers are combined with PLA. Ali et.al (2014) had reported the synthesis of thermoplastic PU using PLA and polycaprolactone (PCL), the resulting PU produced was high in molecular weight and most importantly high in elongation-at-break. PLA had been blended with vegetable oils to improve its brittleness, however production of PU from PLA and vegetable oil as the chain extender still have not been widely studied.

Vegetable oil seems to be one of promising ingredient to produce PU. The natural biodegradability of vegetable oil opens the possibility of biodegradable material even wider (Xia & Larock, 2010). The uses of vegetable oil in production of PU is not something new, a lot of research had been done on various types of vegetable oil. Palm oil is used to produce PU in many research, especially in the production of flexible PU foam (Chuayjuljit & Sangpakdee, 2007). The sustainability of palm oil makes it a suitable candidate for a commercialized biodegradable and flexible PU.

Strength and biodegradability are clearly advantages of using PLA, while palm oil on the other hand has a good reputation in a production of flexible polymer. Flexibility and biodegradability are both important characteristics of packaging materials (Murariu & Dubois, 2016). However, there is no research have been done on the PU produced using combination of PLA diol and palm oil based polyol. Therefore, production of PU using PLA incorporated with palm oil polyol as chain extender is expected to fulfil these qualities.

1.3 RESEARCH OBJECTIVES

The objectives are as follows:

1. To synthesize polyurethane using PLA and palm oil polyol as constituents of soft and hard segment using one-shot method.
2. To characterize the chemical structure, thermal and mechanical properties of PLAPOPU.
3. To evaluate the biodegradability of PLAPOPU.

1.4 SCOPE OF STUDY

This study covered synthesis of PU using PLA and PO as main ingredient. Firstly, both one-shot and prepolymerization methods were used to synthesize the stated PU, method that produced PU with desirable physical properties was then used for the remaining project (i.e. Characterizations). Isocyanate compound that was used throughout the project was determined between hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI), whichever contributed to the desired PU was chosen as a suitable isocyanate compound. PU produced were undergone characterization such as chemical properties using Fourier transform infrared spectroscopy (FTIR), thermal behavior (i.e glass transition temperature, T_g) using differential scanning calorimetry (DSC), mechanical properties specifically for elongation at break using Universal Tensile Machine, UTM and also biodegradability test. Effects of parameters such as reaction time, stirring speed and reaction temperature were not studied in this project.

1.5 THESIS ORGANIZATION

This thesis has been divided into five chapters. **Chapter One** discusses the background of the study, introduces commercial packaging materials and its drawbacks. This chapter also introduces polylactic acid (PLA) with its advantages and disadvantages. Besides that, this chapter also includes problem statements, research objectives, and scope of the study.

Chapter Two covers the literature review related to this research. This chapter discusses Polyurethane (PU) in general, method of synthesis and also related researches pertaining polyurethane. This chapter also includes in-depth introduction to PLA and its composites, including PLA based PU. Besides that, this chapter also reviews vegetable oil and its application in PU.

Chapter Three discusses the research methodology. This chapter covers the methodology of the whole research from synthesis to the characterization of PLA/Palm based PU (PLAPOPU).

Chapter Four covers the result of the research together with the discussion. This includes result from synthesis process, chemical structure analysis, thermal analysis, tensile analysis and also biodegradability test.

Chapter Five presents the conclusion of this study. All conclusions derived from the result analyses in the previous chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Polyurethane (PU) is produced by series of reactions that determine the properties and types of the PU produced. Basically, PU is synthesized by reacting diisocayanate with hydroxyl-containing compound, polyol, common example such as polyether and polyester polyol. Different from the time when PU was first discovered on the year of 1937 by Otto Bayer and his co-worker where the focus was mainly on the PU produced from an aliphatic diisocyanate and diamine, now there are varieties of poly-isocyanate and polyol available commercially to be used in the research and production of PU (Sharmin & Zafar, 2012). There are several methods used to synthesize PU, the frequently used method in most research and for many applications are one-shot method and also the prepolymerization method. In one shot method, all of the ingredients such as polyol, isocyanate, chain extender and other additives such as catalyst and blowing agent are mixed together. While in the prepolymerization method, chain extender such as diol or water are added last after the reaction of polyol and isocyanate that produces the urethane polymer is completed (Wong, 2012). Selection of materials and pathways to produce PU has resulted in different types of PU with various characteristics and properties, especially in term of its physical and also chemical behavior. Hence, the application of PU has also increased, especially in automotive, medicine, construction, insulation and as packaging materials.

2.1.1 Polyol and Chain extender

Polyol is a hydroxyl-containing compound that will shape the properties of the PU. This is because PU consists of long chains of hard and soft segments that are alternate to each other. Polyether-based and polyester-based polyols usually are chosen to be the soft segment, while chain extender and isocyanate forming the hard segment of the PU. Biodegradability is now a topic for many researches as people are going for biodegradable products as concern to the environment. In PU, segments of the polymer affect the biodegradability, therefore selection of polyol is very important. Polyether based polyol is not favorable if the required characteristic of the PU is its biodegradability, in such cases researchers will opt for polyester based polyol as it is readily biodegradable. Examples of polyester are polylactide (PLA), poly-lactide-glycolide (PLGA) and also polycaprolactone (PCL). Polyester-based polyol can be produced by condensation polymerization method, such as condensation polymerization of lactic acid and 1,4-butanediol to produce PLA diol (Vroman & Tighzert,2009; Ali et al., 2014)

Shen et al. (2015) in their study of synthesis and characterization of biodegradable polyurethane for hypopharyngeal tissue engineering using PLA and polyethylene glycol (PEG) as the main components showed good result in biodegradability of the materials. By the 50th day of the biodegradability test, the material was degraded by more than 50% of its weight. Besides that, compatibility of the material is also good, showing the promotion of hypopharyngeal fibroblasts growth. While in another study conducted by Brzeska et al. (2015), PLA was used as a material to be blended with PU. In this study, it is also shown that PLA promoted and improved the biodegradability of the PU by reduction of molecular weight of polymer samples after incubation in phosphate buffer. From these study, it can be suggested that PLA based polyol can be used as a main ingredient in a biodegradable PU (Brzeska et al., 2015).

Chain extender plays a vital role in improving the properties of hard segment and determining the characteristics of the PU. Biodegradability and mechanical properties can be affected by selection of chain extenders. As studied by Ali et al. (2014), polycaprolactone-diol (PCL-diol) was used as a chain extender for PLA-PCL PU. PCL improved the elongation at break with high modulus using the suitable ratio of PLA and PCL. Extender commonly used is polyol or amine. -NH from amine will react with isocyanate group to yield urea. According to study conducted by Negim et al. (2013), decreasing chain length of amine-based extenders produced PU with increasing tensile strength, tear strength and also hardness. Besides that, PUs also had been studied using Poly (oxytetramethylene) glycol (PTMG) and varieties of amine chain extenders such as ethylenediamine (EDA), Butanediamine (BDA) and Hexamethylenediamine (HMDA) (Khatib et al., 2013).

Natural oil-based polyols are seen to be a great prospect to improve and promote a biodegradable and environment-friendly PU. In nature, vegetable oils such as palm oil, sunflower oil and rapeseed oil are non-reactive as it lacks the hydroxyl functional group (-OH) that is used in PU synthesis, except for castor oil that naturally contain this specific group in its chemical structure (Gayki & Thorat, 2015). To functionalize vegetable oil with –OH, there are several methods that can be used such as hydroformylation, epoxidation followed by ring opening and also hydrolysis. For palm oil, as reported by Zamiah and Ismail (2002), it can be functionalized to polyol by epoxidation, followed by introduction of polyhydric alcohol. Vegetable oil based polyol known to be used in many PU researches producing many types of PUs such as foam and film. Palm olein-based polyol was known to produce rigid PU as reported by Arniza et al. (2015). Palm olein based polyol also blended with petrochemical-based polyol and reacted with diphenylmethaneisocyanate. The experiment resulted to the production of medium-density rigid PU with good insulation properties compared to the standard density rigid PU foam (Zamiah & Ismail, 2002), (Arniza et al., 2015). Epoxidized palm olein had been reported by Silverajah et al. (2012), to be blended with PLA. Blend produced shown high flexural strength and flexural modulus, 77 MPa and 3237.2 MPa, compared to the neat PLA which was reported to be 64.2 MPa and 3003.6 MPa (Silverajah et al., 2012).

2.1.2 Isocyanate (-NCO)

Poly-isocyanate or di-isocyanate compound is the main ingredient in production of PU. PU produced by the reaction of isocyanate(-NCO) and polyol(-OH) which resulted in urethane (-NH-COO-) (Acero, 2014). There are many commercially available isocyanate compounds used in a production of PU, such as methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI). Selections of these compounds are important in order to yield a PU with desirable properties such as higher elongation and good biodegradability. Bond interaction between –OH and –NCO result from reaction between polyol and isocyanate determines the properties of the PU, in term of its rigidity, mechanical and also tensile properties. The structure of the isocyanate compounds is crucial to be considered because it affects the reactivity of the isocyanate towards polyol. For example, TDI and MDI is an aromatic type of isocyanate compounds, which consist of benzene ring. But TDI is known to produce a more rigid and higher tensile strength PU compared to MDI (Mizera & Ryszkowska, 2016). Both Isocyanate group (-NCO) in TDI attached directly to the same phenyl ring which provides it with more rigid