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SYNTHESIS AND CHARACTERIZATION OF JATROPHA OIL-BASED POLYURETHANE FROM JATROPHA OIL-BASED POLYOL

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By

AHMAD SYAFIQ BIN AHMAD HAZMI

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

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Dedications

This thesis has been written in the spirit to discover which long had energized other far reaching and greater scientists. Some of what we have come across in the following excerptions:

"He is Allah, the Creator, the Inventor of all things, the Bestower of forms. To Him belong the Best Names. All that is in the heavens and the earth glorify Him. And He is the All-Mighty, the All-Wise." - Al-Quran (59:24)

"*This most beautiful system of the sun, planets, and comets could only proceed from the counsel and dominion of an intelligent and powerful Being.*" - Isaac Newton

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

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A new vegetable oil-based polyol has been successfully functionalized for polyurethane fabrication. Starting with the crude jatropha oil, the double bonds are functionalized by introducing epoxy groups and followed by ring opening step to produce hydroxyl groups. This method effectively produced solvent-free epodixidized jatropha oil at rapid reaction kinetic with maximum oxirane oxygen content of 4.3%. This chemical synthesis scheme provides low viscosity and moderate functionality polyol with easier route to produce flexible film of vegetable-based polyurethane at reasonable material properties with hydroxyl number of 171 - 180 mg KOH/g, viscosity of 0.92 - 0.98 Pa.s and functionality of 5.

The jatropha oil-based polyol is then reacted with aromatic diisocyanate to produce jatropha oil-based polyurethane in the present of catalyst dibutyltin dilaurate. Three distinct regions have been observed in the reactivity test of polyurethane formation corresponding to reaction of hydroxyl and isocyanate groups and branching processes. The glass transition temperature of -55 to -45 ^{o}C suggested that existence of majority flexible/soft segments and exhibited rubber-like behavior in stress-strain measurement with tensile stress at break between 2 - 6 MPa and elongation at break of 110 - 193%. Fractography evidence by SEM showed relatively flat surface with ridges and V-shaped "chevron" marking. Jatropha oil-based polyurethane is thermally stable with the onset for thermal degradation is in the range of 233 - 277 ^{o}C followed by char formation. Pseudo-plastic flow behavior with index of 0.09 - 0.24 is observed in dynamic mechanical analysis. However high amount of acid (> 0.1 mg KOH/g) in the polyol is detrimental to the branching processes with evidence of relatively low glass transition temperature (-50 ^{o}C) and mechanical strength (2 MPa).

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

SINTESIS DAN PENCIRIAN POLIURETENA BERASASKAN MINYAK POKOK JARAK DARIPADA POLIOL BERASASKAN MINYAK POKOK JARAK

Oleh

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Sejenis poliol baru berasaskan tumbuh-tumbuhan telah berjaya difungsikan untuk penghasilan poliuretena. Bermula dengan minyak pokok jarak mentah, ikatan alkena telah difungsikan dengan memasukkan kumpulan berfungsi epoksi diikuti oleh pembukaan cincin epoksi untuk menghasilkan kumpulan hidroksida. Cara ini telah menghasilkan secara efektif minyak pokok jarak terepoksida tanpa menggunakan pelarut dengan tindakbalas kinetik pantas pada nilai maksimum kandungan oksigen oksiran 4.3%. Cara sintesis baru ini juga menghasilkan poliol yang mempunyai kelikatan rendah dan kefungsian sederhana di mana lebih mudah untuk menghasilkan filem boleh lentur daripada poliuretena berasaskan tumbuh-tumbuhan pada sifat-sifat yang munasabah iaitu nombor hidroksida 171 -180 mg KOH/g, kelikatan 0.92 - 0.98 Pa.s, dan kefungsian 5.

Kemudiannya poliol berasaskan minyak pokok jatropha bertindakbalas dengan dwi-isosianida aromatik untuk menghasilkan poliuretena berasaskan minyak pokok jarak di dalam kehadiran pemangkin dibutiltin dilaurat. Tiga zon berbeza telah kelihatan semasa ujian kelikatan pembentukkan poliuretena yang berkaitan dengan tindak balas kumpulan hidroksida dan diisosianida dan proses percabangan. Suhu peralihan kaca yang rendah pada -55 hingga -45 ^{o}C menyarankan majoriti adalah segmen bahagian boleh lentur dan memberikan sifat seakan getah berdasarkan penentukuran tegasan-terikan dengan tegasan semasa putus pada 2 - 6 MPa dan pemanjangan semasa putus adalah 110 - 193%. Bukti fraktografi oleh SEM menunjukkan permukaan rata dengan tanda rabung dan bentuk-V "chevron". Poliuretena berasaskan minyak pokok jarak mempunyai kestabilan terma dengan permulaan penguraian terma pada 233 - 277 ^{o}C diikuti dengan pembentukkan arang. Sifat mengalir pseudo-plastik dengan indeks 0.09 - 0.24 diperhatikan dalam analisis dinamik mekanikal. Walau bagaimanapun, kandungan asid yang tinggi (> 0.1 mg KOH/g) dalam poliol telah menjejaskan proses percabangan yang terbukti dengan suhu peralihan kaca (-50 ^{o}C) dan kekuatan mekanikal (2 MPa) yang rendah.

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Ahmad Syafiq

August 2012

I certify that an Examination Committee has met on **December 19, 2012** to conduct the final examination of Ahmad Syafiq bin Ahmad Hazmi on his Master of Science thesis entitled "Synthesis and Characterization of Jatropha Oil-Based Polyurethane From Jatropha Oil-Based Polyol" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the (Name of relevant degree).

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DECLARATION

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

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AHMAD SYAFIQ BIN AHMAD HAZMI

Date: 30 AUGUST 2012

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LIST OF ABBREVIATIONS

ASTM	ASTM International
ATR	Attenuated total reflectance
Brookfield viscosity	Viscosity measured by using Brookfield viscometer
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimeter
DTG	Degradation Temperature, First Derivative of TGA curve
E	Modulus
E’	Storage Modulus
E”	Loss Modulus
E_a	Activation energy
EW	Equivalent weight
FTIR	Fourier Transform Infrared
G	Shear modulus
GPC	Gel permeation chromatography
gram/eq	Gram per equivalent

M_c	Molecular weight between crosslink
MDI	Diphenylmethane diisocyanate
M_e	Molecular weight between entanglement
M_n	Number average molecular weight
M_v	Viscosity average molecular weight
M_w	Weight average molecular weight
n	Flow index behavior
OH #	Hydroxyl number
OOC	Oxirane oxygen content
OO_{expt}	Experimental oxirane oxygen content
OO_{th}	Theoretical oxirane oxygen content
q	Heating rate
r	The hydroxyl to isocyanate ratio
R	Universal gas constant
RCO	Relative conversion to oxirane
SEM	Scanning Electron Microscope
Tan δ	Damping, ratio of E''/E'

TDI	Toluene diisocyanate, Tolylene diisocyanate
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
T_m	Temperature at maximum decomposition rate
WPE	Weight per epoxy equivalent
wt %	Weight percent
α	Extent of conversion
γ	Strain
δ	Phase angle/phase lag
η	Viscosity
η^*	Complex viscosity
λ	Relaxation time
ν	Poisson's ratio
σ	Stress
τ	Stress response
ω	Angular frequency
ε	Strain (extension)

CHAPTER 1

INTRODUCTION AND OVERVIEW

1.1. Introduction to Vegetable-based Polyurethane

Polyurethane represent a group of versatile polymer and wide range of technical applications. Generally polyurethanes are copolymers, composed of alternating soft and hard segments (some prefer to use flexible and rigid segments), which come from polyol and isocyanate groups. First polyurethane foam was discovered by Otto Bayer in year 1947 (Bayer, 1947). The discovery leads to various invention such as flexible, semi-rigid, rigid, elastomer, and adhesive polyurethane. In Malaysia, most of produced polyurethane is in the form of rigid and semi-rigid foam and flexible foam. Polyurethane is widely used in apparel, furniture, automotive, construction, packaging, medical and insulation area.

1.2. Problem Statement

Production of polyol from renewable resources has a strong root in the history of polyurethane industry (Desroches et al., 2012; Ionescu, 2005). Conventionally the polyurethane is produced industrially by reacting petrochemical-based polyol with isocyanates. Vegetable oil-based polyurethane is gaining popularity due to attractive and feasible routes of utilization as well as their environment and sustainability reasons. As the price of petroleum increased and stirring many concerns over its stability and sustainability, there is increasing demand to find viable alternative to produce plastics.

In recent years, much attentions have been paid for utilizing renewable materials such as vegetable oils and naturally fatty acid to substitute petroleum derived raw materials. Besides the continuous price increases, the consumption of petroleum release carbon dioxide gas which contributes to global warming. These problems could be partially alleviated by using renewable resources such as vegetable oils. Renewable resource such as vegetable oil is relatively inexpensive and make it an attractive candidates as polyol (Lligadas et al., 2010). Castor oil, which naturally have the hydroxyl group in the triglyceride, is directly used in to make polyurethane. As today, there are several reports on the progress of vegetable-based polyurethanes (Petrovic, 2008; Petrovic et al., 2008;2007;2005;2004; Zlatanic et al., 2004). In general, petroleum-based polyols have terminal hydroxyl groups which very reactive (Table 1.1). On the other hand, vegetable-based polyols have secondary hydroxyl groups and less reactive due to sterical hindrance. High content of hydroxyl groups contributes to higher viscosity (> 10,000 Pa.s) in petroleum-based polyol.

Table 1.1: Brief comparison between polyol produced from petrochemical and vegetable oil (Ionescu, 2005).

Type of Polyol	Petroleum-based	Vegetable-based
Reactivity	High reactivity	Low reactivity
Viscosity	High	Low
Environmental	Non-renewable	Renewable
Price	Depending on oil prices	Relatively stable

The study of vegetable-based polyurethane has received growing attentions and theoretical importance as it inherits heterogeneous structure due to variation in the structure of vegetable oils as shown in Table 1.2 below (Petrović, 2008). The fact that jatropha oil is non-edible and the price relatively unaffected by development in food industry make it an interesting candidate among vegetable oils for further commercialization in polyurethane manufacturing.

Table 1.2: Table of comparison of fatty acid in commonly used vegetable oil (Petrović, 2008).

	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Soybean	0.1	10.2	3.7	22.8	53.7	8.6
Cotton seed	0.7	20.1	2.6	19.2	55.2	0.6
Palm	1	42.8	4.5	40.5	10.1	0.2
Sunflower	0.2	4.8	5.7	20.6	66.2	0.8
Jatropha curcas	0.1	15.1	7.1	44.7	31.4	0.2

1.3. Objectives of the study

The fundamental objective of this study is to investigate feasible way to produce jatropha oil-based polyol, jatropha oil-based polyurethane and characterize them. The broad goal is to get deeper understanding on synthesizing polyurethane and analyze material responses, as well as linking jatropha oil and polyurethane industries. The specific objectives and concerns of this study are:

a. To functionalize and produce jatropha oil-based polyol via epoxidation and ring opened synthesis route. The epoxidized jatropha oil and jatropha oil-based polyol are monitored by a series of wet chemical analysis.

b. To prepare and produce jatropha oil-based polyurethane film by reacting the jatropha oil-based polyol and diisocyanates. The extend of reaction was monitored by changes in physico-mechanical and functional groups.

c. To study relationship between crosslink density and thermal/mechanical/frequency responses in jatropha oil-based polyurethane. The crosslink density are varied by regulating the ratio of hydroxyl to isocyanates as well as different diisocyanates (dipheylmethane-4,4'-diisocyanate, toluene-2,4-

diisocyanate). Both diisocyanates are the most produced isocyanate worldwide (Ionescu, 2005).

1.4. General overview of the thesis

This thesis present the investigation on transforming crude jatropha oil to polyol and use it in fabricating polyurethane. Chapter 1 addresses the concern in market trend towards vegetable-based polyurethane and an overview of research scopes.

Chapter 2 describes overview on jatropha curcas oil and the chemistry of polyurethane including isocyanate, main parameters for polyol such as hydroxyl number and functionality, a brief account of various method to produce polyol from vegetable oil, and a series of wet chemical analysis to characterize the epoxidized vegetable oil and the polyol. Later in the chapter is to review on different techniques in thermal, mechanical, and frequency analysis to characterize the polyurethane including a section on statistical analysis. Determination of crosslink density is presented as the swelling in solvent and molecular weight between crosslink or entanglement.

Chapter 3 outlines the laboratory works on synthesizing epoxidized and polyol from jatropha, the standard procedures to carry out the wet chemical analysis, and sample measurement procedures in the characterization instruments.

Chapter 4 elaborates the comprehensive study of the epoxidized and jatropha oil-based polyol including FTIR spectroscopy, oxirane number, hydroxyl number, viscosity, functionality, reactivity, and crosslink densities. Thermal analysis by DSC and temperature-varying DMA revealed the effect of crosslink density on the glass transition temperature. Meanwhile thermal analysis by TGA/DTG curves indicate the thermal stability and the associated kinetic of decomposition. Tensile stress-strain behavior correlate the glass transition Later in the section is the analysis on frequency response which introduce power law and effect of crosslink density on branching and molecular weight distribution.

Chapter 5 delivers the conclusion of the works and finding with some recommendations to enhance the processing jatropha oil-based polyurethane for future investigation.

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