SYNTHESIS AND CHARACTERIZATION OF ALKANOLAMIDE POLYOLS FOR RIGID POLYURETHANE FOAMS AS POTENTIAL THERMAL INSULATION MATERIALS

By

NORSUHAILI BINTI KAMAIRUDIN

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Chairman : Professor Luqman Chuah Abdullah, PhD
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Hydroxyl compounds currently used in the production of polyurethane foam (PUF) are petrochemical products. However, they are non-renewable resources and may cause environmental pollution, and maybe exhausted in the near future. Thus, the availability of methyl oleate (MO) derived from palm oil provides an excellent feedstock to produce bio-polyol for polyurethane applications. The main objective is to investigate rigid polyurethane foams (RPUFs) prepared from MO are potential for thermal insulating material. Firstly, MO underwent epoxidation reaction and produced epoxidized methyl oleate (EMO) with the oxirane oxygen content (OOC) of 5.10%. Then, EMO was further subjected to two types of epoxide ring-opening reaction, namely epoxide ring-opening reaction with glycerol and oligomerization reaction of EMO in solvent. For epoxide ring-opening reaction with glycerol, the reaction conditions were optimized in order to obtain the maximum hydroxyl value (OHV) of bio-polyol, denoted as MOG-polyol, giving the highest OHV of 306 mg KOH/g. For the oligomerization reaction of EMO in solvent, the highest OHV obtained was 166 mg KOH/g and denoted as OMOP-polyol. These two bio-polyols then undergo amidation reaction to increase OHV and produced alkanolamide polyols. The optimum reaction conditions for amidation reaction of MOG-polyol were 1:2 mole ratio of (MOG-polyol: DEA) with catalyst loading of 0.25% over 3hrs reaction at 120 °C, giving the highest OHV of alkanoamide polyol, denoted as MOAG-polyol of 313 mg KOH/g. The similar reaction conditions were used in order to synthesis alkanolamide polyol denoted as OMOAP-polyol from OMOP-polyol where the OHV obtained was 282 mg KOH/g. Both alkanolamide polyols were used as polyols for the production of RPUFs. RPUFs prepared from both of the alkanolamide polyols showed higher reactivity compared to the references foam which prepared from 100% of petroleum-based polyol due to its higher viscosity. RPUFs containing alkanolamide polyol also have higher apparent density (27.20-34.40 kg/m^3) and compressive strength (141-180 kPa) compared to the reference foams. Reference foam have largest cell size compared to the RPUFs that were modified with alkanolamide polyols. Thermal conductivity is closely correlated with closed cell content. Higher thermal conductivity was found in RPUFs due to lower closed cell content. However, the thermal conductivities of RPFUs are still within the range for thermal insulating materials (<0.1 W/mK). Thus, the RPUFs made from alkanolamide polyols are potential candidate to be used as thermal insulation for refrigerator or freezers.

Keywords: synthesis, alkanolamide polyol, thermal insulation, rigid polyurethane foams

SDG: GOAL 9: Industry Innovation and Infrastructure; GOAL 12: Responsible Consumption and Production

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN POLIOL ALKANOLAMIDE UNTUK BUSA POLIURETANA TEGAR SEBAGAI POTENSI BAHAN PENEBAT TERMAL

Oleh

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Sebatian hidroksil yang kini digunakan dalam penghasilan busa poliuretana (PUF) ialah produk petrokimia. Walau bagaimanapun, ia adalah sumber yang tidak boleh diperbaharui dan boleh menyebabkan pencemaran alam sekitar, dan mungkin habis dalam masa terdekat. Oleh itu, ketersediaan metil oleat (MO) yang diperoleh daripada minyak sawit menyediakan bahan suapan yang sangat baik untuk menghasilkan bio-poliol untuk aplikasi poliuretana. Objektif utama adalah untuk menyiasat busa poliuretana tegar (RPUFs) yang disediakan daripada MO berpotensi untuk dijadikan bahan penebat haba. Pertama, MO menjalani tindak balas epoksidasi dan menghasilkan metil oleat terepoksida (EMO) dengan kandungan oksigen oksirana (OOC) sebanyak 5.10%. Kemudian, EMO digunakan untuk dua jenis tindak balas pembukaan cincin epoksida, iaitu tindak balas pembukaan cincin epoksida dengan gliserol dan tindak balas oligomerisasi EMO dalam pelarut. Untuk tindak balas pembukaan cincin epoksida dengan gliserol, keadaan tindak balas telah dioptimumkan untuk mendapatkan nilai hidroksil (OHV) maksimum bio-poliol, dilambangkan sebagai MOG-poliol, memberikan OHV tertinggi sebanyak 306 mg KOH/g. Untuk

tindak balas oligomerisasi EMO dalam pelarut, OHV tertinggi yang diperolehi ialah 166 mg KOH/g dan dilambangkan sebagai OMOP-poliol. Kedua-dua bio-poliol ini kemudiannya menjalani tindak balas amidasi untuk meningkatkan OHV dan menghasilkan poliol alkanolamide. Keadaan tindak balas optimum untuk tindak balas amidasi MOG-poliol ialah nisbah mol 1:2 (MOG-poliol: DEA) dengan pemuatan mangkin sebanyak 0.25% dalam tindak balas 3 jam pada suhu 120 °C, memberikan OHV tertinggi, iaitu sebanyak 313 mg KOH/g dan poliol alkanoamide dilambangkan sebagai MOAG -poliol. Keadaan tindak balas yang sama digunakan untuk mensintesis poliol alkanolamide yang dilambangkan sebagai OMOAP-poliol daripada OMOP-poliol di mana OHV yang diperolehi ialah 282 mg KOH/g. Kedua-dua poliol alkanolamide digunakan sebagai poliol untuk penghasilan RPUF. RPUF yang disediakan daripada kedua-dua poliol alkanolamide menunjukkan kereaktifan yang lebih tinggi berbanding dengan buih rujukan yang disediakan daripada 100% poliol berasaskan petroleum kerana kelikatannya yang lebih tinggi. RPUF yang mengandungi poliol alkanolamide juga mempunyai ketumpatan ketara yang lebih tinggi (27.20-34.40 kg/m3) dan kekuatan mampatan (141-180 kPa) berbanding dengan buih rujukan. Buih rujukan mempunyai saiz sel terbesar berbanding RPUF yang diubah suai dengan poliol alkanolamide. Kekonduksian terma berkait rapat dengan kandungan sel tertutup. Kekonduksian terma yang lebih tinggi didapati dalam RPUF kerana kandungan sel tertutup yang lebih rendah. Walau bagaimanapun, kekonduksian terma RPFU masih dalam julat untuk bahan penebat haba (<0.1 W/mK). Oleh itu, RPUF yang diperbuat daripada poliol alkanolamide adalah calon yang berpotensi untuk digunakan sebagai penebat haba untuk peti sejuk atau penyejuk beku.

Kata Kunci: Sintesis, poliol alkanolamide, bahan penebat haba, busa poliuretena tegar

SDG: MATLAMAT 9: Industri Inovasi dan Infrastruktur; MATLAMAT 12: Tanggungjawab Penggunaan dan Pengeluaran

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AOCS	American Oil Chemists' Society
AV	Acid value
CCRD	Central composite rotatable design
$CDCl_3$	Deuterated chloroform
Da	Dalton
DEA	Diethanolamine
DTG	Derivative thermogravimetry
EMO	Epoxidized methyl oleate
FAME	Fatty Acid Methyl Ester
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HDMI	Hexamethylene diisocyanate
IPDI	Isophorone diisocyanate
IV	Iodine value
KI	Potassium iodide
MDI	Diphenylmethane diisocyanate
MO	Methyl oleate
MW	Molecular weight
NCO	Isocyanate group
NMR	Nuclear magnetic resonance
OH	Hydroxyl group
OHV	Hydroxyl value
OOC	Oxirane oxygen content
PDI	Polydispersity Index

PRESS	Prediction Error of Sum Squares
PU	Polyurethane
PUFs	Polyurethane foams
RPUFs	Rigid polyurethane foams
RSE	Residual Standard Error
RSM	Response surface methodology
SEM	Scanning electron microscopy
SV	Saponification value
TDI	Toluene diisocyanate
TPUs	Thermoplastic polyurethanes
TGA	Thermogravimetric analysis
wt	weight
2D	Two dimensional
3D	Three dimensional

CHAPTER 1

INTRODUCTION

1.1 General Background of Study

Polyurethane (PU) is a versatile polymer which has been employed in a wide range of applications such as coatings, adhesives, foams, elastomers, and others. With a proper selection of reactant, PU products ranges from high performance of elastomers to tough and rigid plastics can be easily fabricated (Lu & Larock, 2008). Polyurethane foams (PUFs) are among the most important class of specialty PU. It can be divided into two major classes which are flexible and rigid polyurethane foams (Lee *et al.*, 2007). Foams are also divided into categories depending on their pore morphology (open or closed) (Prociak *et al.*, 2019). The rigid polyurethane foams (RPUFs) have been attracting more and more interest over the recent years becausee of excellent thermal insulating properties, low apparent density, and good resistance to various weather (Kurańska & Prociak, 2016; Tan *et al.*, 2011). RPUFs have been primarily used as thermal insulation materials due to their beneficial properties in applications such as construction industry, domestic appliances and refrigerators, transportation of liquified natural gas and insulation of cryogenic space (Dutta, 2018). In principle, the required physical properties of appliances RPUFs include low foam density, high dimensional stability and low thermal conductivity. The preparation of RPUFs can be performed using petroleum-based polyol as well as with the biobased polyol (Ionescu *et al.*, 2012). They are usually formed via the reaction of isocyanates and polyols having lower molecular weight which are usually smaller than 1000 Da and hydroxyl value (OHV) of 250 – 400 mg KOH/g (Gama *et al.*, 2018).

Basically, PU backbone structures consists of a soft segment from polyol and hard segment from isocyanates. Polyols are compounds containing multiple hydroxyl functional groups. As one of the major feedstocks for polyurethane (PU) production, most polyols used today in the PU industry are petroleum derived. Concerns about depletion and price increases of the world's petroleum resources, have led to increased research and industrial interests in developing bio-polyols from renewable resources as alternatives to conventional petroleum-based polyols (Luo *et al.*, 2013). In addition, a replacement of petrochemical components by low-cost natural oils allows a reduction of the carbon footprint. Thus, for the economic and environmental reasons, the use of vegetable oils in polyol synthesis has been investigated by many researchers.

Bio-polyols can be obtained from different types of vegetable oils. The chemical structure of oils allows two types of modification in their molecular structures: modifications in ester bonds and/or in alkene groups (Prociak *et al.*, 2018). A well-known method based on epoxidation of alkene groups can produce polyol with different chemical structures through epoxide ring opening with reagent containing OH group likes methanol, diethylene glycol and ethanol. This method is very often used given its industrial applicability and low cost. Self-oligomerization is one type of ring-opening at epoxide group but the different is, it will produce bio-polyol with lower hydroxyl value (Soi *et al.*, 2017). Thus, it needs to be functionalized at the ester group to increase the OHV. The functionalization at the ester bond known as amidation reaction. This reaction produced bio-polyol named as alkanolamide. Alkanolamide can be made using a variety of reactants. Alkanolamide is produced from the reaction between the reactant is that one reactant is a fatty acid, methyl ester or triglyceride and the other is an alkanolamine, most commonly diethanolamine. The commonly used raw material is methyl ester. Methyl ester will become a serious consideration if it is used because methyl ester produces abundant foam (Sari *et al*., 2017). In addition, alkanolamide is physically and chemically stable nitrogen containing compounds. It has a broad spectrum of uses due to their diversity of unique properties, economy and ease of preparation. Alkanolamides can be used as anti-slip and anti-block additives for polyethlene films, water repellents for textiles, coating for paper, mold release agent, lubricant additives, printing ink additives, defoaming agents and flow improvers (Salleh *et al*., 2001).

Recently, the successful synthesis of RPUFs from vegetable oils-based polyol derived from palm oil, rapeseed oil, castor oil and mustard oil has been reported (Arniza *et al.*, 2015; Borowicz *et al.*, 2020; Lee *et al.*, 2021; Prociak *et al.*, 2018). However, to the best of the author's knowledge, no research has been reported on the production of RPUFs from palm oil derivatives namely, methyl oleate (MO). Therefore, in this research, functionalization of MO was made and utilized to produce RPUFs and they were characterized and evaluated as the potential for thermal insulating materials.

1.2 Problem Statement

In the modern chemical society, most of the organic chemicals likes polymers are produced using non-renewable resources such as coal and fossil fuels. In order to obtain chemicals from these resources, a substantial amount of carbon dioxide is released into the open environment during processing, which has contributed to the acceleration of global warming. In addition, the refinery and fractionation process of petrochemical produced more harmful derivatives such as phenol, toluene, xylene and others which is harmful to human health and environment. On the other hand, the limited supply and non-renewable nature of fossil feedstock that resulted in a price increase for chemicals derived from petroleum (Singh *et al.*, 2019).

Polyurethanes (Pus) are one of the most promising polymers in the polymer family, with a worldwide production of 18 million tonnes in 2016, and it is anticipated that the global polyurethane market would reach a value of $149.91 billion by 2023 (Leszczynska *et al.*, 2021). As one of the major feedstocks for Pus production, most polyols used today in the Pus industry are petroleum derived. Polyols are compounds containing multiple hydroxyl functional groups. Owing to the aforementioned factors, modern industries have prompted concerned researchers to propose renewable biobased polyol as the alternatives. The starting material to produce polyols can be derived from renewable vegetable oil. In fact, vegetable oil represents one of the most abundant and economically competitive biological feedstocks available today. Its use as the starting material for the production of polyols has attracted interest because of its positive attributes, including the inherent biodegradability and the low toxicity (Abril-Milan *et al.*, 2018).

Various types of vegetable oil, such as palm oil, soybean oil, and sunflower oil, have been studied. However, the majority of polyol obtained through chemical modification of vegetable oil almost solid or semi-solid at room temperature which is a major drawback for the production rigid polyurethane foams (Polaczek *et al.*, 2021). The manufactures of RPUFs requires polyol need to be in liquid form because it can be easily blended with isocyanates. Additionally, most of the bio-polyols prepared from vegetable oils have hydroxyl values lower than 250 mg KOH/g and molecular weight higher than 1000 Da (Arniza *et al.*, 2015; Kuranska *et al.*, 2020; Tan *et al.*, 2011). These bio-based polyols were found not suitable for making RPFU but rather more suitable for making semi-rigid PU and flexible PU foams. Generally, polyols for making RPUFs should have molecular weight between 500 – 1000 Da and hydroxyl value in the range of 250 – 400 mg KOH/g. Polyols with these properties are desirable for making RPUFs with optimal strength, rigidity and stability and suitable for thermal insulation material.

Conventional thermal insulation materials have a lot of limitation as compared to RPUFs insulation. RPUFs insulation eliminates thermal bridging, provides air sealing, and minimizes moisture build up, which are encountered in conventional insulation materials such as polystyrene, mineral wool, glass wool or hemp. All of these feature's help minimize heating and cooling costs, creating a cozy and cost-effective working environment. Insulation requires space and just how much depends on the insulating performance of the material used. Conventional insulating materials will consume too much spaces. RPUFs insulate better than most other conventional insulating materials. That makes thinner solutions possible and creates more living space. RPUFs panels can be cut to any size using simple tools. Even more design flexibility can be achieved by foaming the insulation material (Petcu *et al.*, 2023).

On the other hand, most of the vegetable oils are classified as first generation of bio-based raw materials. This means that the synthesis of polyols based on edible oils is competing with the production of food. Therefore, one of the main non-food applications of vegetable oils is biodiesel and for this application, vegetable oil is converted to fatty acid methyl ester (FAME). Methyl oleate (MO) is one type of fatty acid methyl esters (FAME), derived from the transesterification of fats or vegetable oils. Due to the abundant availability of palm oil in Malaysia, this situation drives Malaysia towards the development of biodiesel technology and production. The biodiesel production capacity in Malaysia is about 10.2 million ton (Tuan Ismail *et al.*, 2018). However, Malaysia Biodiesel Industry faced some challenges due to the insignificant public support and escalating nontariff barrier, which indirectly influence the demand on the palm oil biodiesel (Lim & Teong, 2010). Diversification of methyl oleate (MO) into other chemical products would assist to decrease the excess supply and capacity of the biodiesel industry. Thus, functionalization of methyl oleate (fatty acid methyl ester) by introducing hydroxyl functional group may develop new useful bio-based products such as bio-polyol, which has been one of the most promising developments in the oleochemical industry. It worth to mention that, the lower molecular weight of MO which is only 312 Da, is suitable to use as starting material and functionalized through series of reaction in order to maximize the hydroxyl value without molecular weight exceed than 1000 Da as targeting for making RPUFs for insulating material.

Due to the environmental concern and sustainability, RPUFs based vegetable oil is preferred. Although there are many studies on vegetable oil to produce RPUFs have been reported, most of them have a higher molecular weight (>1000) and lower hydroxyl value less than 250 mg KOH/g and are not suitable to be used as insulation materials. Therefore, current study focuses on using polyol with lower molecular weight to obtain better insulation properties.

1.3 Objectives of the Study

The aim objective in this study is to investigate the potential of rigid polyurethane foams (RPUFs) derived from palm oil derivatives for thermal insulating materials. To achieve this objective, specific objectives have been identified:

1. To synthesis the alkanolamide polyol from epoxide ring-opening reaction with glycerol and followed by amidation reaction.
2. To synthesis the alkanolamide polyol from self-oligomerization reaction and followed by amidation reaction.
3. To evaluate the physical, mechanical and thermal properties of RPUFs made from both alkanolamide polyols as potential for thermal insulating materials.

1.4 General Overview of the Thesis

The thesis is organized in five chapters and structured as indicated hereafter. The first chapter provides the background of the research with a brief introduction to rigid polyurethane foams and bio-polyols, followed by problem statements and the objectives of the present study.

The second chapter reviews the literature related to preparation of polyurethane, the modification of vegetable oil to polyol as well as a review about rigid polyurethane foam from the previous study. The third chapter presents the materials, multistage preparation and various characterization process of the synthesized bio-polyol and rigid polyurethane foams.

Chapter four covers the experimental results and discussion of all the experimental works. This chapter is divided into four parts; i) production of alkanolamide polyol from epoxide ring opening reaction with glycerol and followed by amidation reaction ii) production of alkanolamide polyol from self-oligomerization and followed by amidation reaction, and iii) characterization and evaluation of rigid polyurethanes foams as potential for rigid polyurethane foams. The conclusion and recommendations for future works are summarized in chapter five.

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