



SYNTHESIS OF RIGID FOAM POLYURETHANE FROM RESIDUAL PALM OIL AND ALGAE OIL FOR INSULATED-FOAM PACKAGING CONTAINERS

By

JAVIER HERNANDO CHAVARRO GOMEZ

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

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DEDICATION

“The greatness of a man is not how much wealth he acquires but, in his integrity and his ability to affect those around him positively”

Bob Marley

Thankfully, life has rewarded me with so many positive influences and for this I feel the richest man in the world. To my parents Tulia Gomez and Hernando Chavarro who have been beside of me since my first cry and have taught me the integrity, effort and love means. To my lovely Sanitaz who have been my pillar, my strength and my greatest love in this pad. To my Sister Angela Chavarro, who showed me what dedication, passion for your work and excellency means and finally to my highly appreciated supervisor Dr. Rabitah Zakaria, whose encouraging words, dedication and patience guide me in my journey.

To all of you thank you heaps!

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The immense demand of plastics worldwide has created a huge pollution problem that appears not to have an end. However, new governmental policies and customer's preferences towards environmental friendly materials requires continued research on biodegradable plastic derived from biological resource. Therefore, in this study polyurethane (PU) derived from residual palm oil (RPO) and algae oil (AO) was explored. In the first part, rigid polyurethanes (RPU) from RPO, RPO mixed with 10 % AO and RPO with 10% jatropha oil (JO) were produced by one pot epoxidation and ring opening followed by polymerization with methylene diphenyl diisocyanate (MDI). Both JO and AO has similar iodine value, hence it will increase the hydroxyl number of the mixture and aid in the formation of a highly cross-linked PU. However, AO possess other unique properties such as the presence of polar lipid and a higher number of double bond in the fatty acid chain. The obtained epoxidized oils, polyols and polyurethanes were characterised and compared by different techniques such as TGA, DSC, DMA, FTIR and NMR. The results showed that PU with 10% AO presented significant improvement when compared to PU with 10 % JO or PU from RPO alone. Then, the epoxidation process was investigated using single factor analysis to improve the epoxidation conditions, the yield of production (i.e. >90%) and to reduce the degradation of epoxy rings. The optimised technique was used to produce rigid foam polyurethanes (RFPU) at different ratios of AO/RPO : 10/90, 20/80, 30/70, 40/60 and 50/50. Significant improvement of 49% was found in the hydroxyl number of the RPO(AO) polyol when the AO content was increased from 10 to 50%. Similarly, the homogeneous structure of the cell and the thermal stability of the final RFPU was increased in the samples with 50% AO. The foam rising characteristics of the RFPU containing 50% AO were found to be 6 times higher

than the sample containing only 10% AO. The thermal degradation profiles of the different samples from RPO/AO were found to be similar to RFPU with fire retardant and insulation properties whereby three stages of degradation were found. This suggests the inclusion of phosphate groups in the RFPU from RPO(AO). The compressive strength was found to be 0.34 MPa when 50% AO was combined with RPO while the biodegradability of the RFPU increase 60% between samples with 10 and 50% AO. Finally, the kinetics of the epoxidation process was studied using the modelling platform g-PROMS. Two approaches were investigated and their results were compared with experimental data. The two models analyzed named “two-phase model” and “pseudo homogeneous model” showed low fitting with the results obtained during experimental analysis. Hence, a new kinetic model was developed to include mass transfer resistance during epoxidation of the RPO/AO. The model was found to better correlate the data which indicates that when high viscosity oil such as algae oil is used, mass transfer restriction is dominant during the reaction. RFPU produced from renewable and environmental friendly RPO/AO showed that the material produced might fulfill the physical requirements for PU applications specifically when fire retardancy and thermal insulation is required while having the advantage of eventually being biodegraded.

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

SINTESIS POLIURETANA BUSA TEGAR DARIPADA SISA MINYAK SAWIT DAN MINYAK ALGA UNTUK BEKAS PEMBUNGKUSAN BUSA-BERTEBAT

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Permintaan yang tinggi terhadap plastik di seluruh dunia telah mewujudkan masalah pencemaran yang besar dan seperti tidak berakhir. Walau bagaimanapun, dasar baru kerajaan dan kecenderungan pengguna terhadap bahan mesra alam memerlukan penyelidikan berterusan dalam bidang plastik boleh urai yang diperolehi daripada sumber biologi. Oleh yang demikian, dalam kajian ini, poliuretana (PU) yang diperbuat daripada sisa minyak sawit (RPO) dan minyak alga (AO) telah diterokai. Di bahagian pertama, poliuretana tegar (RPU) dari RPO, campuran RPO dan 10% AO dan campuran RPO dan 10% minyak jatropha (JO) telah dihasilkan menggunakan "one-pot epoxidation" dan pembukaan bulatan diikuti oleh pempolimeran menggunakan methylene diphenyl diisocyanate (MDI). Kedua-dua JO dan AO mempunyai nilai iodine yang sama yang akan meningkatkan nombor hidroksi campuran minyak dan membantu dalam pembentukan PU yang berangkai silang. Walau bagaimanapun, AO memiliki ciri-ciri unik seperti mengandungi minyak polar dan bilangan ikatan berganda yang lebih tinggi di dalam rantai asid lemaknya. Minyak epoksi, polioliol, dan poliuretana yang diperolehi dicirikan dan dibandingkan dengan teknik yang berbeza seperti TGA, DSC, DMA, FTIR dan NMR. Keputusan menunjukkan bahawa PU dengan 10% AO menghasilkan peningkatan yang ketara apabila dibandingkan dengan PU dari 10% JO atau PU dari hanya RPO. Kemudian, proses epoksidasi dikaji dengan menggunakan analisa faktor tunggal untuk memperbaiki keadaan epoksidasi, hasil pengeluaran (iaitu > 90%) dan mengurangkan degradasi epoksi. Teknik yang optimum digunakan untuk menghasilkan poliuretana berbuisa tegar (RFPU) pada nisbah AO/RPO yang berbeza: 10/90, 20/80, 30/70, 40/60 dan 50/50. Peningkatan ketara sebanyak 49% telah didapati pada nombor hidroksi polioliol RPO (AO) apabila kandungan AO meningkat dari 10 hingga 50%. Begitu juga stuktur keseragaman sel dan kestabilan haba RFPU telah meningkat di dalam sampel yang mengandungi 50% AO. RFPU yang mengandungi 50% AO juga menunjukkan sifat berbuisa 6 kali lebih tinggi daripada sampel yang mengandungi hanya 10% AO. Profil kemusnahan haba daripada RPO/AO

didapati serupa dengan RFPU perencat api dan penebat di mana tiga peringkat penurunan telah ditemui. Ini menunjukkan RFPU dari RPO (AO) mengandungi kandungan kumpulan fosfat. Kekuatan mampatan adalah 0.34 MPa apabila 50% AO digabungkan dengan RPO manakala biodegradasi RFPU meningkat 60% antara sampel 10 dan 50% AO. Akhirnya, kinetik proses epoksidasi dikaji dengan menggunakan platform model g-PROMS. Dua pendekatan telah dikaji dan keputusannya dibandingkan dengan data eksperimen. Dua model yang dianalisa dinamakan “model dua-fasa” dan “model homogen pseudo” telah menunjukkan kelekapan yang rendah berbanding keputusan yang didapati dari analisis eksperimen. Oleh itu, model kinetik baru telah dibangunkan untuk memasukkan rintangan pemindahan jisim semasa epoksidasi RPO/AO. Model ini didapati lebih menepati data dan menunjukkan bahawa apabila minyak yang berkelikatan tinggi seperti minyak alga digunakan, rintangan pemindahan jisim adalah utama semasa tindak balas. RFPU yang dihasilkan daripada sumber yang boleh diperbaharui dan mesra alam seperti RPO/AO mempunyai potensi untuk menggantikan PU berasaskan petroleum terutamanya sebagai bahan perencat api atau bahan penebat haba disamping mempunyai kelebihan boleh diurai.

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

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LIST OF ABBREVIATIONS AND NOMENCLATURES

List of abbreviations

RPO	Residual palm oil
AO	Algae oil
FFA	Free fatty acids
JO	Jatropha oil
ERPO	Epoxidized residual palm oil
CPO	Crude palm oil
HP	Hydrogen peroxide
AA	Acid acetic
PA	Peracetic acid
PV	Peroxide value
EU	Ethylene unsaturation
OO	Oxirane oxygen
OOC	Oxirane oxygen concentration
W	Water
[G]+[AG]	Glycol + acetyl glycol
RPO(AO)	Residual palm oil + 10% Algae oil
IER	Ionic exchange resin
PU	Polyurethane
RFPU	Rigid foam polyurethane

List of nomenclatures

Symbol	Unit	Description
a	m^2/m^3	Interface area
C_i	Mol/g	Concentration of the component i
C_t	Mol/g cat	Concentration of active site per unit mass of catalyst
i	Dimensionless	Component [HP], [AA], [PA], [EU], [OO], [W], [G+AG]
j	Dimensionless	Reaction coefficient
$K_{AA,G}$ and $K_{PA,G}$	L/mol and mol/L	Adsorption equilibrium constant for [AA] and [PA]
$K_{AA,J}$ and $K_{PA,J}$	Dimensionless	Partition coefficient for [AA] and [PA]
K_{AO}	Dimensionless	Partition coefficient for [AA] in the system oil-acetic acid-water
K_{AEO}	Dimensionless	Partition coefficient for [AA] in the system epoxy oil-acetic acid-water
$K_{L,AA}$	m/min	Mass transfer coefficient for acid acetic
$K_{L,PA}$	m/min	Mass transfer coefficient for peracetic acid
k_j	100g oil/s.mol	Kinetic rate constant of reaction j
k_{sr}	Dimensionless	Surface reaction rate constant for reaction
K_{j0}		Constant of reparametrized Arrhenius equation
$L-H-H-W$	Dimensionless	Langmuir-Hinshelwood-Hougen-Watson
N_i	Mol/L	Molar mass flow
r_j	Mol/min	Reaction rate of the reaction j
R	j/mol.K	Universal gas constant

t	Min	Reaction time
T	$^{\circ}\text{K}$	Temperature
V^{aq}	L	Volume aqueous phase
V^o	L	Volume oil phase
V	L	Volume
w_k	%	Catalyst to oil ratio



CHAPTER 1

INTRODUCTION

1.1 Introduction to polyurethanes

Polyurethanes (PU) are part of an extensive group of modified polymers with multiple applications. They can be stiff enough to be used in construction or soft enough to be used in cosmetics as sponge applicators. In these applications, the chemistry plays an important role and can be described as a combination of monomer molecules named “soft segments” linked together in great numbers by urethane groups which results in the formation of macro molecules. The urethane bonds are called “hard segments” due to their contribution to movement restriction in the final PU. Finally, the mixture of hard segments, soft segments with multiple degrees of crosslinking and the inclusion of plasticiser and/or additives affected the physical-mechanical, thermal and biological properties of the final PU (Mülhaupt, R., 2013).

PU can be petroleum or organic-based, however, the former is the main source because of the high mechanical properties that is obtained in the final product using macromolecules with high crosslinking (Thomson T., 2004). Dr Otto Bayer (1937) synthesised the first PU at IG Farbenindustrie (Germany) by reacting a short carbon chain polyester diol with diisocyanate and this opened a door to new novel macromolecular chemistry. This initiative provided a new way of synthesising polymers employing a reaction known as polyaddition reaction. Ethylene glycol, polypropylene glycol (Figure 1.1) and their combination are the most commonly used petroleum-based low molecular weight substances (i.e. pre-polymers) to “design” the properties of PU. Polyurethanes are obtained by the reaction of an oligomeric chain of low molecular weight pre-polymer with terminal hydroxyl groups (i.e. polyols) and a diisocyanate (or polyisocyanate) (Ionescu, 2005).

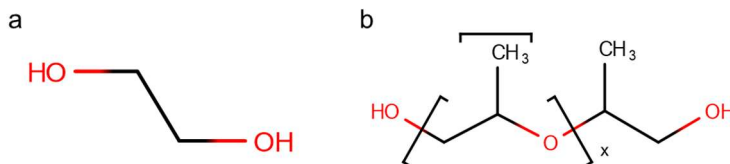


Figure 1.1 : (a) Ethylene glycol. (b) Polypropylene glycol

The term ‘polyol’ is often utilised in relation to PU fabrication, for all polyhydroxylic intermediates used. In organic chemistry, the pre-polyol is used for low molecular weight organic substances, distinctly recognised as molecular entities, possessing more than two hydroxyl groups, such as: glycerol, propylene

glycol, and so on. However, the name 'polyol' refers to the package of multiple molecular species not necessary from one unique source and can possess high molecular weight distribution. This, among other structural factors affects the final properties and application of the PU.

For example, in the formation of rigid PU, high rigidity can be achieved when more urethanes linkages are introduced as primary hard segments during the polymerization. These rigid materials are commonly used as hard resins for multiple application such as coating, flooring, casting, etc (Azam et al., 2001). Also, PU foams can be modified by developing individual degree of crosslinking and molecular weights which make this PUs one of the most important molecule because of the wide range of applications ranging from soft and flexible to hard and rigid. Rigid foam PU (RFPU) can be further classified in three major groups rigid, semi-rigids and flexible. These high number of products comply with the requirements of many industries such as furniture, bedding, electronics, automotive parts, etc.

Unfortunately, the long-time usage and the increasing demand of these materials in the lifestyle of the modern world have started to charge the toll to the environment. Petroleum-based plastics are non-biodegradable, non-renewable and difficult to recycle (e.g. 93% of the US production end up in landfill or incinerated) (Hottle et al., 2013). These disposal techniques release hazardous pollutants into the atmosphere, water and soil which increase the carbon footprint and have direct impact in the destruction of the planet and climate change. In addition, government policies such as the *weekly No plastic campaign day*, *No plastic bag day* in Malaysia (Zen and Omar, 2013) and customers' preference toward environmental friendly materials have increased the demand of novel bio-based polymers that can be bio-degradable and renewable.

1.2 Polyurethanes from vegetable oils

In the past few years, several researchers have refocused their attention to the development of biopolymers from vegetable oils (VO) due to straightforward processing, biodegradability and renewability of the raw material. For example, drying oils such as linseed oil (Zlatanic et al., 2004) showed great performance to produce biopolymers especially for paint coating applications due to effortless epoxidation. Semi-dry oils such as soybean (Caillol et al., 2012) and sunflower (Desroches et al., 2012) were shown to produce bio polymers with similar characteristics to petroleum-based rigid PU. Non-drying oils such as cottonseed oil (Dinda et al., 2008), castor oil (Benes et al., 2012) and palm olein (Badri et al., 2012) have been used for the development of foams and elastomers by different polymerisation methods with the inclusion of additives from different resource.

Therefore, the purpose of this study was to synthesis RFPU from a combination of RPO and AO at different ratios (AO/RPO) and to investigate the physical,

mechanical and thermal characteristics of the final material for possible uses in different fields such as food packaging, insulating, reinforcing, etc. The final RPFPU can provide an environmental friendly, relatively low cost and simple process to produce RFPFU from non-edible, renewable, unused and biodegradable feedstock.

1.3 Problem Statement

In recent years, the usage of vegetable oils (VO) as a source for the production of bio polyurethanes (bio-PU) has attracted the attention of many researchers' due to the simplicity of the polymerisation process especially for highly unsaturated oils (i.e. drying oils). Generally, the polymerisation process for the synthesis of polyurethanes can be summarised in three steps. First step, it is named epoxidation and can be achieved by taking advantage of the autoxidative characteristics of the multiple double bonds (e.g. Ethylenic bond) with air and other relatively low-cost organic oxidants. Second step consist in the conversion of epoxidized oils into hydroxylated oils named polyols by ring opening of the epoxy bond using alcohol at moderate high temperature. Finally, the last step consists in the reaction of the hydroxylated oils with isocyanates to increase the molecular size and stability of the polyurethane by creating a urethane bridges between the hydroxyl groups.

Unfortunately, the complexity of this polymerization process increases dramatically when non-dry oils such as palm oil is used as resource. The low amount of ethylenic groups presented in the palm oil and derivatives reduces significantly the reactivity of the oils due to low functional groups suitable for the reaction with isocyanates to form urethane bonds requiring the addition of petro-additives as described by Maznee et al. (2001). Inclusion of additives or chemical modification by different polymerisation technique might be investigated to overcome this issue specially for highly degraded oils such as residual palm oil. The inclusion of additives can be considered as a simple and low-cost solution to produce bio-polyurethanes because polymerisation can be carried out by the same straight forward process of epoxidation and ring opening which reduces the need for expensive catalyst, limit the steps in the process and other risks associated to chemical structure modification.

Therefore, the additive plays an important role and several characteristics must be considered to ensure a simple, renewable, easy and low-cost process which can produce a good biodegradable polyurethane suitable for multiple applications. For instance, the selected material must be from a renewable source that minimize environmental impact and demand. Second, the additive should increase the amount of ethylenic groups when blended with the residual palm oil to enhance the mechanical properties of the polyurethane. Third, the additive should have low demand and high availability to maintain the economic viability of the residual palm oil. Fourth, the additive should be biodegradable to maintain the biodegradable characteristics of the final polymers produced by low unsaturated vegetable oils. Finally, the additive used must provide polar

molecules that might promote the biodegradability of the bio-polymer while providing wet resistant for application such as food packaging.

Algae oil from *Chlorella sp* might satisfy the characteristics and requirements to improve the molecular structure of the palm based rigid foam polyurethanes while complying with renewability, demand and biodegradability.

1.4 Hypothesis

1. AO and JO can be suitable sources of high unsaturated oils that when combined with RPO might improve significantly the characteristics of the epoxidized RPO. However, improved characteristics can be presented using AO due to higher crosslinking and the inclusion of phosphate groups.
2. The epoxidation process for RPO(AO) might be optimized to increase the crosslinking in the bio-PU and to obtain high yield of conversion.
3. The combination of RPO and AO might allow the formation of rigid foam polyurethanes.
4. The chemical characteristics of the bio-PU produced from RPO and AO might provide outstanding mechanical and thermodynamic properties that can be compared with existing rigid foams produced from petroleum basis.
5. The nature of the AO might allow degradation of the bio-PU by composting.

1.5 Research aim and objectives

1. To synthesise, characterise and compare the polyol and rigid polyurethane from residual palm oil upon the inclusion of algae oil and jatropha oil as additives to the process.
2. To investigate the suitable parameters to produce polyurethane from residual palm oil biomass with algae oil as additive.
3. To evaluate the physical, thermal, biodegradable and biological properties of palm-algae based polyurethane foam.
4. To develop the kinetic model of the palm-algae oil polyol production.

1.6 Scope of work

The aim of this thesis is to provide an understanding of the polymerisation process to form rigid foam polyurethane using residual palm oil (RPO) and algae oil (AO). The disadvantages of petroleum-based polymers and benefits of renewable sources are highlighted throughout the manuscript. The characteristics of the rigid polyurethane from RPO and AO were compared with a polyurethane produced from RPO and JO under identical conditions. The characterisation of the materials produced was conducted using TGA, DMA, FTIR, H-NMR, DSC, DMA among others chemical analysis and the benefits the high unsaturation as well as phospholipids compounds presented in the AO were highlighted. Then, the optimal conditions for the epoxidation of RPO(AO) were investigated using single factor analysis. The result of the optimisation was used to produce rigid foam polyurethanes (RFPU) from different ratios of RPO/AO and the analysis of the obtained foam by different techniques such as DMA, FTIR, DSC and TGA was conducted. Finally, biodegradability analysis and toxicity analysis were performed.

Finally, two kinetic models available in the literature for the epoxidation of vegetable oils were investigated using gPROMs modelling software and the results are presented. Mass restriction during epoxidation process is fundamental for this process and was included in a new proposed model due to the high viscosity of the AO. The novelty of the new RFPU from RPO and AO, the high efficient and environmental friendly polymerisation process from unexplored renewable source are presented which can highly reduce pollution to the environment.

1.7 Aims

The aim of this research is to obtain a rigid foam polyurethane from recovered palm oil. The produced material was investigated and the physical and mechanical characteristics of a novel rigid foam polyurethane from recovered palm oil and algae oil were improved in order to provide a possible material for commercial usage. Finally, the kinetic conditions required for the optimisation of the rigid foam polyurethane were investigated.

1.8 Novelty of the research

1. Non explored residual palm oil was used for the production of rigid foam polyurethanes.
2. AO was included as additive to improve the characteristics of the final rigid foam polyurethane.

3. Optimal conditions for the production of epoxidized AO with RPO were found with high yield of conversion.
4. A new kinetic model was proposed with the inclusion of mass transfer restriction for the epoxidation of RPO with AO due to the high viscosity of the materials used.

1.9 Organisation of the Thesis

The aim of this thesis is to provide an understanding on the oleo-chemistry, process optimisation, synthesis and kinetics involved in the production of rigid foam bio-polyurethane from new novel source such as residual palm oil which was mixed with algae oil to be used for multiple application and specially in food packaging because of the resulting characteristics. Chapter one describes briefly the importance of vegetable oil chemistry during the polymerisation and the limitation of using residual palm oil as main source. Moreover, this chapter presented the overall view of the potential contribution of residual palm oil to the polyurethane market. This introductory chapter also identified the statement of the problem and identified the research objectives.

Chapter Two provides the Literature Review which describes the specific details regarding the amount of polymers produced for food packaging applications. The disadvantages of the petroleum-based polymers and the complication during recycling and processing are explained. Further, explanations of the chemistry and multiple reactions pathways from petroleum and vegetable oils polymerisation are presented. Specific attention is given to the route of epoxidation when compared to non-oxidable reactions. Finally, the kinetics developed for the epoxidation process of vegetable oils is explained and compared.

Chapter Three presents the Methodology followed during the experimental work. Different processes used for the recovery of the materials, their storage and handling are explained. Materials, equipment and analytical procedures such as IV value, oxirane oxygen content, hydroxyl value, peroxide value and acid acetic concentration used for the understanding of the reaction are also explained. Moreover, analytical equipment used to understand and validate the chemistry of the reactions and the physical characteristics of the final polyurethanes is provided. Finally, other assays conducted to determine the environmental friendly nature and characteristics are described and explained.

In Chapter Four the results from the vegetable oil characterisation and the different conditions used for the development of epoxidised oils from VO and AO are presented. First, epoxidation from CPO, residual palm oil, jatropha oil, algae oil and mixtures at different concentrations are presented and compared. The validation of the epoxidation, hydroxylation and polymerisation process

conducted by different analytical methods are presented showing the advantages of AO compared to other similar source of functional groups such as Jatropha oil. Then, the epoxidation process of residual palm oil and AO was optimised based on temperature of reaction, concentration of reactants, catalyst and oxidative donor. Also, the physical characterisation of the rigid foam polyurethanes that prepared after optimization and with different concentration of AO are described by thermo gravimetric analysis, differential scanning calorimeter, dynamic mechanical analyser, thermal conductivity, compression strength, flexural strength, toxicity and biodegradability are presented and compared. Finally, two kinetic models commonly used for the epoxidation of dry vegetable oils are evaluated for the epoxidation of residual palm oil and algae oil which is important to correct and safe design chemical reactor and process as well as to improve the industrial application of the investigated polyurethane.

Finally, the conclusion of the work is presented in Chapter Five. The results of the comparison between the objectives planned and the results are analysed. Also, in this chapter the benefits of the new material developed, and the highlights of its characteristics are provided with special emphasis in the potential market applications for the novel rigid polyurethane produced.

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