



PREPARATION AND CHARACTERIZATION OF POLYOL USING WASTE COOKING OIL

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by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Material) (Hons).

The member of the supervisory committee is as follow:

.....

(DR. JEEFFERIE BIN ABD RAZAK)

ABSTRAK

Beberapa tahun kebelakangan ini, gabus Poliuretana (PU) terdiri daripada sumber-sumber yang tidak boleh diperbaharui seperti petrokimia yang boleh memberi impak negatif alam sekitar. Ke arah kelestarian alam sekitar, polyols berasaskan sumber asli boleh digunakan untuk menggantikan sumber hidrokarbon sedia ada yang tidak boleh diperbaharui. Selain itu, isu pelupusan sisa minyak masak terpakai menyumbang kepada masalah alam sekitar yang serius. Oleh kerana itu, kajian ini telah dijalankan untuk mencipta polyols berasaskan bahan semula jadi dengan memanipulasi sisa minyak masak. Tujuan kajian ini untuk mensintesis polyols bersumberkan Sisa Minyak Memasak (WCO) menggunakan idea penukaran sisa minyak masak menjadi polyols berdasarkan bahan hijau. Polyol yang telah disintesis berasaskan WCO disahkan melalui kehadiran hidroksil kumpulan (OH^-) dalam struktur molekul WCO. Sifat fizikal dan haba polyol berasaskan WCO dibandingkan polyol berasaskan CO dan sampel terkawal polyol komersial. Dalam kajian ini, proses transesterifikasi dan pengepoksidaan dilaksanakan untuk memperkenalkan kumpulan OH^- dalam struktur trigliserida. Selepas itu, pengeluaran polyol berasaskan WCO selanjutnya disahkan dengan menilai kehadiran OH^- menggunakan Fourier Transform Infrared (FTIR) spektroskopi. Pada akhir kajian, polyol berasaskan WCO telah disediakan dan diperincikan secara menyeluruh. Kehadiran kumpulan OH^- telah disahkan oleh kewujudan puncak kumpulan hidroksil (OH^-) dalam spektrum inframerah pada nombor gelombang daripada 3341cm^{-1} . Sifat-sifat fizikal polyol yang berasaskan WCO secara langsung memberi kesan kepada sifat haba. Sifat ketumpatan dan kelikatan polyol berasaskan WCO yang rendah menyebabkan peningkatan ciri-ciri penguraian haba. Ciri-ciri ini menjadi penyumbang negatif untuk sifat mudah terurai produk gabus poliuretana (PU) pada masa depan dan beberapa kajian untuk penambahbaikan diperlukan untuk memperbaiki batasan ini. Kesimpulannya, kajian ini penting kerana penggunaan sisa minyak masak dalam polyols bermanfaat demi menyelesaikan isu pelupusan minyak masak terpakai yang serius dan menyokong inisiatif dalam memelihara alam sekitar.

ABSTRACT

Over these recent years, Polyurethane (PU) foams are made up of non-renewable resources such as petrochemical which could negatively impact the environment. Towards sustainable environment, natural based resources polyols for PU synthesis could be utilized for replacing the existing non-renewable hydrocarbons resources. Moreover, waste disposal issue of frying or waste cooking oil were significantly contributed into serious environmental problems. Due to this situation, this research has been carried out to develop a natural based polyols by manipulating the waste cooking oil. The purpose of this study is to synthesize Waste Cooking Oil (WCO) based polyols with the idea of converting waste cooking oil into green based polyols. The WCO-based polyol synthesis is confirmed by the presence of hydroxyl (OH^-) group in the molecular structure of WCO. Physical and thermal properties of WCO-based polyol are compared with unused cooking oil (CO)-based polyol and controlled sample of commercial polyols. In this study, transesterification and epoxidation process were successfully implemented as to introduce OH^- group in triglyceride structure of WCO. After that, the production of WCO-based polyol is further confirmed by evaluating the presence of OH^- using Fourier Transform Infrared (FTIR) spectroscopy tool. At the end of this study, WCO-based polyol has been prepared and comprehensively characterized. The presence of OH^- group has been confirmed by the existence of identical peak of hydroxyl (OH^-) group in an infrared spectrum at a wavenumber of 3341cm^{-1} . In term of its physical properties, the WCO-based polyol would directly affect the thermal properties. Lower density and viscosity characteristics of WCO-based polyol had causes the increase of thermal decomposition behaviour. This behaviour negatively contributes for easy decomposition of future product of Polyurethane (PU) foam and some investigations for improvement are required to mend this limitation. To conclude, this research is significantly important since utilization of waste cooking oil in polyols may benefit to solve serious disposal issue of WCO while meaningfully could support the green initiative in preserving the environment.

DEDICATION

Dedicated to
my beloved father, Shawal Bin Abdullah
my appreciated mother, Hayati Bt Md Isa
my lovely siblings,
my helpful housemates,
for giving me moral support, money, cooperation, encouragement and also understandings
Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

CO	-	Cooking oil
EPA	-	Environmental Protection Agency
FAME	-	Fatty Acid Methyl Esters
FTIR	-	Fourier Transform Infrared
FWCO	-	Filtered waste cooking oil
NaOH	-	Sodium hydroxide
OM	-	Optical Microscope
pH	-	Potential hydrogen
PU	-	Polyurethane
RWCO	-	Raw waste cooking oil
WCO	-	Waste Cooking Oil
TDI	-	Toluene diisocyanate
MDI	-	Diphenyl methane diisocyanate
pMDI	-	Polymeric methylene diphenyl diisocyanate

LIST OF SYMBOLS

°C	-	Degree celcius
%	-	Percentage
cm ⁻¹	-	Reciprocal centimeter
ρ	-	Rho (density)
dPas	-	Decipascalsecond
g	-	Gram
g/ml	-	Gram per millilitre
kg	-	Kilogram
kg/m ³	-	Kilogram per cubic meter
kPa	-	Kilo Pascal
MPa	-	Mega Pascal
GPa	-	Giga Pascal
M	-	Weight of dry container
N	-	Weight of container and polyol
OH ⁻	-	Hydroxyl group
V	-	Volume of container
wt %	-	Weight percentage

CHAPTER 1

INTRODUCTION

This chapter provides a concise background of study, problem statement, research objectives, scope of study, significance of study, report organization and overall summary of this chapter. From this chapter, the relevancy of conducting this research is justified. Other than that, the breadth and depth of investigation are also covered in the research scopes, while the real needs of conducting this study were clearly explained in the problem statement part.

1.1. Research Background

Traditionally, polymeric materials especially Polyurethane (PU) are made from petrochemical resources which are non-renewable (Garrison et al., 2016). According to Masa et al., (2013), about 80% of polymer is formed using petrochemical resources worldwide. The consumption of these non-renewable resources such as crude oil and fossil are not only impacted the environment, but also could deplete the priceless natural resource. The reduction of petroleum-based feedstock will be the main issue for polymer based industry in order to maintain the production of PU based product in the future (Ionescu, 2005). In other words, the petroleum based hydrocarbon resources will used up to the very limited of time.

The major purpose of this study is to manipulate the usage of waste resources in order to balance the ecosystem and at the same time to produce the bio-based polyol. There are many options of bio-based resources with high potential to replace the petrochemical resources such as vegetable oil, palm oil, castor oil and many others (Karak, 2012). For this research, waste cooking oil is chosen as bio-based polyol resources due to their superiority and accessibility

(Sharmin et al., 2012). This initiative could not only produce the potential bio-based polyol but may also reduce the disposal issue of waste cooking oil (WCO), which significantly would help to preserve the environment.

Recently, WCO are produced and discharged in huge amount and these could significantly contribute into serious environmental problems (Ibrahim et al., 2014). In year of 2013, a study is conducted for 352 households in order to investigate their awareness, attitudes and practices towards WCO recycling in Petaling District of Selangor State, Malaysia. Referring to this study, it has been reported that the average of WCO produced per household is about 2.34 kg/month (Ibrahim et al., 2014). Thus, this amount of waste could generate a massive disposal problem which later could lead into major pollution issues.

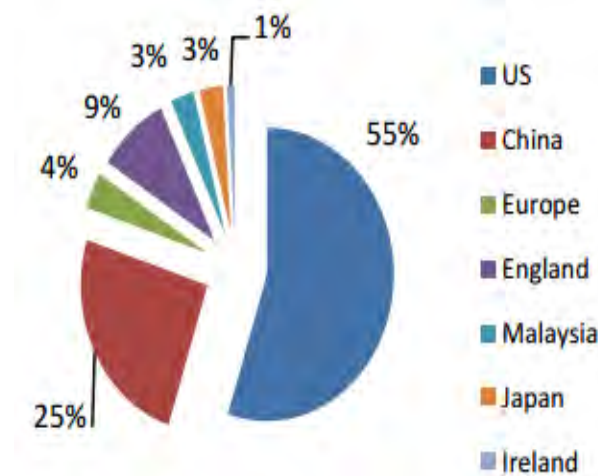


Figure 1.1: Total production of WCO by the countries (EPA, 2016)

Besides, United State Environmental Protection Agency (EPA) had revealed the total production of WCO by the countries as depicted in Figure 1.1. It is demonstrated that the United States had produced about 55% of WCO per year, which represented for 10 million tons of WCO. Meanwhile, Ireland is the lowest producer of WCO which indicates only 1% for about 153,000 tons per year. All in all, based on the statistic; Malaysia had produced only 3% of waste cooking oil that is about 459,000 tons per year (Wan et al., 2015).

The number from local contribution is considered huge to cause serious disposal issues. This phenomenon may contribute to environmental impact such as blocking drainage system that would lead into the required fixing and repairing. Due to this alarming situation, WCO is going to be manipulated in this research with the novel idea of converting WCO into green based diol or polyol.

In this research, WCO that is obtained from 'keropok lekor' will be filtered to eliminate as maximum number of contaminants and particles. Later, the particle WCO will be characterized using Fourier Transform Infrared (FTIR) Spectroscopy to evaluate the presence of organic functional groups as well as chemical substances. By having the understanding from WCO results, the WCO will be converted into polyol through the transesterification route. After confirming the occurrence of polyols from WCO is verified using FTIR. Lastly, this study provides the elements of sustainability through converting the waste into wealth and provides the platform towards resolving never ending story of WCO disposal issues.

1.2. Problem Statement

The growing interest in environmental issues had increased the need for developing new candidate of advanced materials that are more environmental friendly. Recently, demand of polyol resources increase dramatically. Most of existing PU foams is produced by utilizing the petrochemical resources such as crude oil and natural gases. This practice has been performed at around the globe.

However, the hydrocarbon based resources are inadequate and will be used up to their certain limits of time (Ionescu 2005). This kind of resources is not sustainable and might not able to fulfill the needs of future generation. Compared to renewable resources, petrochemical based hydrocarbon contains more toxicity and utilize high amount of energy, thus resulting massive effects of greenhouse pollution. This condition would harm the environment, health as well as affecting the economy at a long run.

Theoretically, 'Polyol' is defined as oligomeric backbones that must contain two or more hydroxyl group (Sonnenschein et al., 2011). Since waste cooking oil (WCO) is obtained from the vegetable source, there are no presence of hydroxyl group were detected (Fan, 2011). Hence, other alternative of structural modification should be applied in order to introduce hydroxyl group at the structure of WCO. This can be actualized by performing the transesterification process.

Eventhough transesterification process may introduce hydroxyl group into the structural unit of WCO, there are some other challenges should also be concerned. Maisonneuve et al., (2016) had claimed that the major issue that always appears in the transesterification process are heterogeneity of monomer, which caused by the presence of double bond in triglyceride structure. Therefore, synthesizing natural based polyol may minimize the properties of PU foams either structurally or mechanically.

Another concern related with Polyurethane based foams are on their limitation toward heat exposure. This thermoset based PU is not able to withstand at higher temperature. Since PU foam is a thermoset polymer, it has contains certain degree of thermoplasticity and able to fall off at an elevated temperature (Hepburn, 1992). Besides, PU foam is flammable polymer (Ionescu, 2005a). These heat sensitivity problems of PU materials are required to be investigated further, in order to make sure that this material could be able to perform well with extra-ordinary resistance at higher temperature environment. This can be strategized at the earliest stage of polyol synthesis, whereby heat sensitivity of PU could be tackled from the transesterification process through monomeric heterogeneity minimization efforts.

In this research, the potential of WCO as green source of polyol was investigated and evaluated. The selection of WCO is based on the economical and environmental factor reasons while appreciating the nature of carbon based molecules that originated from WCO.

1.3. Objectives

In ensuring the success of this study, there will be three (3) main objectives as the following stated:

- (i) To synthesize natural-based polyol using Waste Cooking Oil (WCO).
- (ii) To analyze the presence of hydroxyl (OH^-) group in WCO based polyol.
- (iii) To compare the physical and thermal properties of WCO based polyol, cooking oil (CO) based polyol and control polyol.

1.4. Scope of Study

- (i) Prepare natural based polyol using WCO resourcing from ‘keropok lekor’ frying oil. It is chosen in order to avoid variation of contaminants. Since there are many hawkers of ‘keropok lekor’ in the neighbourhood; the raw WCO is easily supplied.
- (ii) Analyse the presence of hydroxyl group in WCO based polyol using Fourier Transform Infrared (FTIR) spectroscopy method.
- (iii) Comparison of physical and thermal properties of WCO based polyol, CO based polyol and control polyol. For physical properties, density and viscosity are measured while pyrolysis is conducted to test the thermal properties of WCO-based polyol.

1.5. Significant of study

Waste cooking oil (WCO) is utilized in this research because of its ability to replace the petrochemical resources. WCO contains required molecular structure and could be modified in order to produce natural-based resources. This research is significant because of its own advantages. Utilization of WCO in this research is one of the best ways to decrease huge amount of WCO disposal in Malaysia which resulting to reduce the usage of non-renewable resources.

1.6. Organization of study

In overall, this research are majorly consists of five chapters which are introduction, literature review, methodology, result and discussion as well as conclusion and recommendation. For initial chapter which is introduction, it briefly provides an overview of background study of this research, problem statement regarding this study, objectives and scope involved as well as significance or importance of this research to industry.

Next, Chapter Two had emphasized on literature review on previous related research on this topic. This chapter involved fundamental procedure to generate polyol for application of Polyurethane (PU) foam. Concerning on this project, natural based polyol which is a one types of polyol is generated using waste resources in order to reduce the consumption of petrochemical resources. The procedure of producing existing polyol is implemented and innovated into the creation of natural based polyol.

Later, Chapter Three which is Methodology had covered the method involved in order to produce WCO based polyol. The methodological flow is explained in detail starting with the filtration of WCO, synthesizing WCO based polyol via transesterification process and analyzing the presence of OH^- group using FTIR spectroscopy. All of the result and finding are explained and analyzed in Chapter Four which is Result and Discussion. Finally, Chapter Five contains the overall conclusion of findings result and new ideas recommended and suggested in order to improve the research in the future.

1.7. Summary

For this chapter, it can be concluded that, there is a need to convert WCO waste into wealth by inventing the proper method to produce natural based polyols by using WCO as for application of PU foam. The need for this study had been explained in previous subtopic of background of the study. The problem statement of this research is fully justified. There are three main objectives stated for this research whereby, it is expected that WCO could be transformed into natural based polyol for easy reaction with isocyanate, in order to produce product based on PU foam in the future application.

CHAPTER 2

LITERATURE REVIEW

This second chapter highlights the fundamental of Polyurethane (PU) and their categorization. The industrial applications of PU are distinguished between classification of different PU type, chemistry and technology as well as the forming process. Furthermore, this chapter summarized the implementation of bio-based resources in order to reduce the consumption of petro-chemical resources.

2.1. History of Polyurethane (PU)

According to Kricheldorf et al. (2005), Polyurethane (PU) polymer was discovered in 1930 when Otto Bayer proposed to use diol and di or poly isocyanate to prepare macromolecules. Moreover, Nina et al. (1998), also stated that Otto Bayer and his co-workers at the laboratories of I.G. Farbenindustrie, Leverkusen, Germany had introduced an interest in PU to the worldwide in the year of 1937. This work had resulted to the finding of PU that was carried out to synthesize novel materials which were not covered by the polyamide patents of Nylon materials. This discovery was performed by Carothers at E.I du Pont de Nemours & Co (Szycher, 2013).

Then, Bayer achieved to create material by reacting diamines and aliphatic diisocyanates. Thus, an infusible and strong hydrophilic material was produced which is known as polyurea. Next, PU material with better properties that could be used in fibrous application was formed by putting an extra effort in synthesizing aliphatic diisocyanate and glyols. After around 65 years later, PU has becoming as one of the most popular, versatile and dynamic groups of