

Synthesis of Palm Oil Based Polyol via Glycerolysis and Transamidation Reactions For Polyurethane Foam Production

Khairul Azhar Abdul Halim^{1,a}, Sabrina Soloi^{1,b*}, Rohah A. Majid^{1,c}

¹Polymer Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM),
Johor, Malaysia

^akazharhalim@gmail.com, ^bsabrinasoloi@yahoo.com, ^crohah@cheme.utm.my,

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Abstracts. Renewable sources like vegetable oil have been used to prepare many polymeric resins due to the awareness on environmental issue and depletion on petrochemical sources. In polyurethane (PU) production, petroleum-based polyols such as polypropylene glycol (PPG) have been replaced with plant-based polyols from canola oil, soybean oil and palm oil. However, these vegetable oils need to be chemically or physically modified in order to increase their functionalities especially hydroxyl groups. In this study, palm oil (PO) had been modified via two different reaction routes, namely, glycerolysis and transamidation. FTIR spectra of both routes confirmed that the hydroxyl groups (-OH) had been successfully introduced into the palm oil molecular structure. The modified PO was then be reacted with *p*-diphenylmethane diisocyanate (*p*-MDI) at 1:1 NCO:OH ratio in the presence of distilled water as blowing agent and silicone surfactant as foam stabilizer to produce palm oil based PU foam. Hardness test was conducted to study type of PU foam produced. Both foams exhibited nearly similar values at shore D 33.6 and 35.4 respectively, which these values fall within the range of rigid PU foam (shore D 30-59). The foams have potential to be used in many non-load bearing application such as insulator in building and refrigerator.

Introduction

The awareness of society on environmental issue and sustainability has invoked the effort to produce eco-friendly materials. In polyurethane (PU) foam production, petroleum-based-polyols such as polypropylene glycol (PPG) have been replaced with plant-based polyols such as canola oil [1], soybean oil [2] and palm oil [3]. In Malaysia, palm oil is abundant and an excellent renewable resource of polyol. However, the main functional group which is hydroxyl (OH) must be introduced onto the molecular structure of the oil prior reacted with isocyanate (NCO) to produce PU. Many methods have been discovered to transform triglycerides of vegetable oils into polyols such as glycerolysis [1], transamidation of diethanolamine [1] and epoxidation [4]. In this work, rigid PU foam was produced with palm oil-based polyol (PO-p) obtained from two synthesis routes, namely glycerolysis and transamidation reactions. Glycerolysis has been adopted from works of Tanaka [5] while transamidation route has been conducted according to Lee [1]. Later, PO-p was reacted with *p*-diphenylmethane diisocyanate (*p*-MDI) at 1:1 NCO:OH ratio in the presence of distilled water as blowing agent and silicone surfactant as foam stabilizer. Final properties of PU foam was investigated with Fourier Transform Infra-red (FTIR) and hardness test.

Experimental

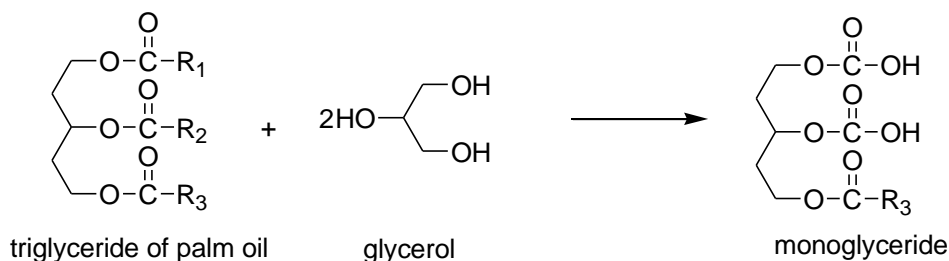
Materials: Refined Bleached Deodorized Palm Oil (RBDPO) was purchased from Delima Oil Products Sdn Bhd. Diethanolamine (DEA), Stannous Octoate catalyst, Triethylenediamine (TEDA) and *p*-methylene diphenyl diisocyanate (*p*-MDI) were obtained from Sigma Aldrich. Glycerol, sodium hydroxide (NaOH) and acid hydrochloric (HCl) were supplied by Fischer

Scientific. Silicon surfactant Tegostab B-8404 was obtained from Goldschmidt Chemical Corporation. All materials were used as received.

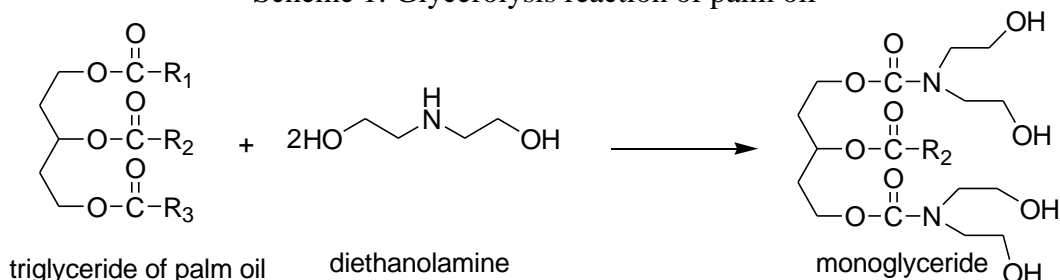
Preparation of Palm Oil Polyol (PO-p) via Glycerolysis: Approximately 20g of glycerol was placed in a 3-neck flask equipped with a condenser and a thermometer. Accurately weighed RBDPO was added into the flask together with 0.2g NaOH as catalyst. The ratio of glycerol to RBDPO was set at 1:5. The reaction mixture was allowed to react at 70°C for 2h with continuous stirring. Upon completion, the mixture was cooled down to room temperature. Later, 1.8 g of 10% HCl was added to neutralize the alkali catalyst. The reaction mixture was left overnight to allow the separation process. The top layer which was palm oil polyol (PO-p) was drawn off and filtered with filter paper. The obtained product was then analysed with Fourier transform infra-red spectroscopy (FTIR) in the range of 4000-360 cm^{-1} (a Perkin Elmer 180) with interferometer of 0.2 cm^{-1} for the functional group identification.

Preparation of Palm Oil Polyol (PO-p) via Transamidation: In a 3-neck flask submerged in a silicon bath equipped with a mechanical stirrer, thermometer and condenser, RBDPO was allowed to react with DEA at molar ratio of 1:3. The reaction was carried out at 110°C for 5h. The glycerol byproduct was not removed from the reaction mixture as it can act as a cross-linker in the polyurethane foam production. PO-p obtained was analysed for their functional group properties with by FTIR spectroscopy.

Preparation of Polyurethane Foam based on PO-p Polyol: The synthesized PO-p, stannous octoate catalyst, TEDA, silicone surfactant and distilled water as blowing agent were mixed in a 250 ml plastic container and were stirred vigorously at 100 rpm until the mixtures become creamy. Later, *p*-MDI was added and the mixture was stirred at the same speed until the mixture started to foamy. The mixture was then left to rise and was cured at room temperature (25 °C) for 7 days. The PU foam was analysed with FTIR and the foam hardness was measured with Shore D hardness tester (for hard rubber and plastic) according to ASTM D2240.



Scheme 1: Glycerolysis reaction of palm oil



Scheme 2: Transamidation reaction of palm oil

Result and Discussion

FTIR spectra of PO-p: The formation of broad absorption bands at 3473 cm^{-1} and 3392 cm^{-1} (in Figure 1) were assigned to hydroxyl (-OH) group of PO-p obtained from glycerolysis and transamidation, respectively. By comparing the spectra with pure RBDPO, the findings indicated that -OH groups had been successfully introduced into palm oil molecular structure, which is in agreement with other worker [5]. The increasing intensity of carbonyl groups (-C=O) that were detected at $1740\text{-}1744\text{ cm}^{-1}$ in spectra of PO-p via glycerolysis and PO-p via transamidation represent the formation of monoglyceride. This is thought due to conversion of triglyceride of palm oil into monoglyceride with addition of -OH groups. Meanwhile, the formation of amide group at 1602 cm^{-1} implied the completion of transamidation reaction of PO-p.

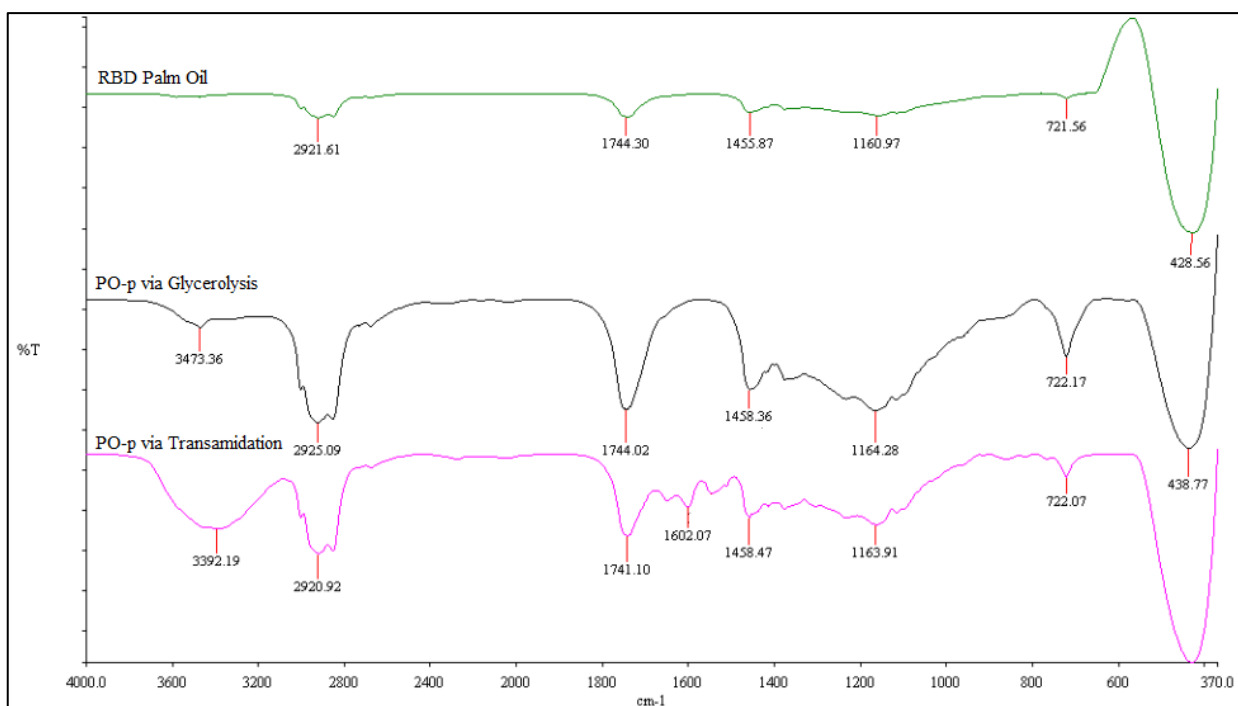


Figure 1: FTIR spectra of RBDPO, PO-p via glycerolysis and PO-p via transamidation

Characteristic of Polyurethane based PO-p Foam: PU foams obtained from both polyols have the characteristic of urethane linkage band at 1513 cm^{-1} for transamidation and 1511 cm^{-1} for glycerolysis, as shown in Figure 3. These peaks are associated -NH bending band which confirms the formation of polyurethane linkage in the foam. The weak signal detected at 2277 cm^{-1} , implying the presence of small amount of unreacted NCO in the sample. This is probably due to -NCO group has been hindered to reach the -OH group of PO-p due to long and branch structure of PO-p.

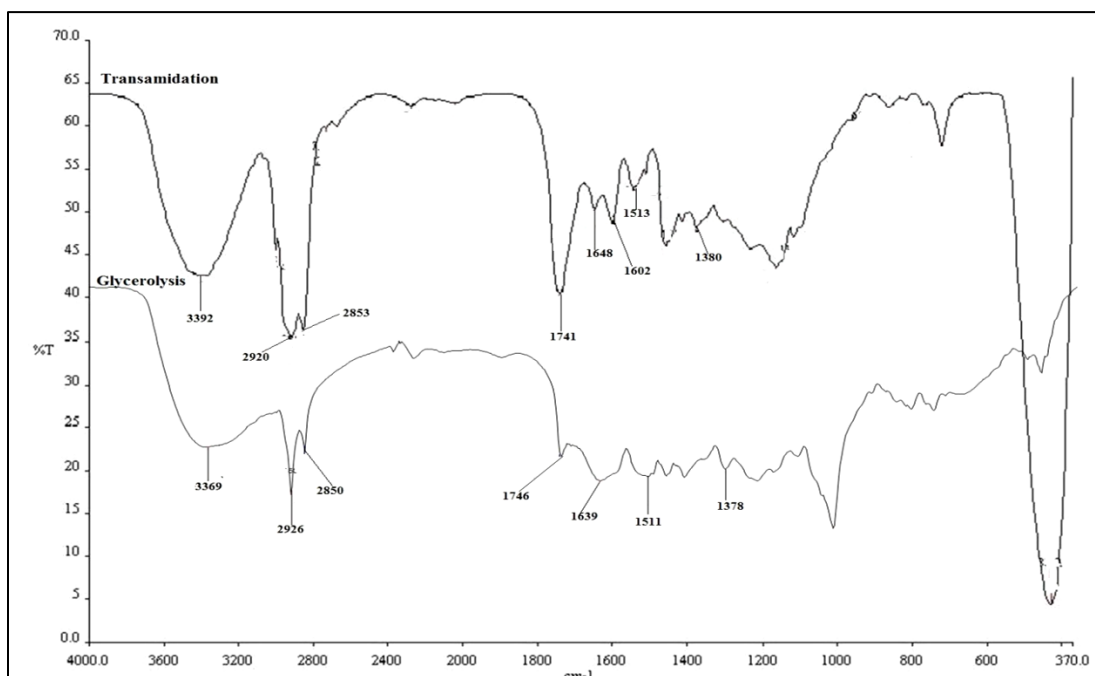


Figure 2: FTIR spectra of polyurethane foam obtained from both route

Meanwhile, the hardness test for PU foams were conducted for both routes, triplicate sample has been done in this measurement. In this study, hardness test was performed using shore D-hardness tester according to ASTM D2240. It was found that the hardness of two routes have nearly similar values which were shore D 33.6 and 35.4 respectively. These indicates that the produced foams are rigid type (Shore D 30-59) [6]. According to previous study, palm oil polyol gives flexible foam due to the presence of soft segment from monoglyceride chain of the palm oil [5]. However, in this study, rigid foams were obtained because MDI was used as isocyanate system. Theoretically, hard segment of the isocyanate group controls the hardness of the system. When MDI used, the foam obtained are harder and stiffer compared to other isocyanate type such as toluene diisocyanate (TDI) [7]. Both foams have a potential to be used in non-load bearing applications such as insulator in building or refrigerator.

Conclusion: In this study, it was proven that palm oil based polyol can be used as an alternative source to replace the petroleum based polyol in PU foam production. Both polyols produced via glycerolysis and transamidation pathways gave comparable hardness of PU foam. Further study is in progress to investigate the effects of both routes on the thermal, compressive strength and morphology of foam.

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