# CHAPTER 21

# Synthesis of Used Frying Oil-Based Polyol for Rigid Polyurethane Foam

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**Abstract**

The Used Frying Oil (UFO) which was usually threw out and to be waste had potency to be used as the material of polyurethane. This study was carried out to determine the potential of UFO in preparation of rigid polyurethane (PU) foam. The raw UFO was first treated by filtration using food strainer and cheesecloth to remove the suspended particles and heated under the temperature of 105-110°C for 1 hour. Next, the filtered UFO was mixed with polyhydric compound to synthesize polyol via transesterification reaction. The UFO-based polyol was then combined with other chemicals at various ratios to form PU rigid foam. The UFO-based polyol showed the decrease in free fatty acid percentage (%FFA) from the filtered UFO, from 1.187% to 0.70% and increase in viscosity, from 60.5 mPa.s to 150.5 mPa.s. No alteration of functional group observed after filtration as proven by Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectrum of UFO-based polyol showed the formation of υ(OH) absorption peak at 3400 $cm^{-1}$. The formation of urethane linkage (NHCO) backbone in PU foam was confirmed using FTIR. The morphology of the surface was analyzed at magnification 20x and 50x. The properties of PU foam are highly dependent on the chemical composition. This study showed that UFO exhibit promising potential as raw material for PU formation.

## Introduction

Polyurethane (PU) is basically a polymer builds from the join of a chain of organic unit by urethane linkage (-NHCOO) as shown in Fig. 1 (Lee, 2014). In history, the classes of urethanes were originally discovered in 1937 by Otto Bayer and his co-worker, J. G. Farbenindustrie at Leverkusen, Germany (Sharmin and Zafar, 2012). During his research in 1938, Otto Bayer has prepared a number of linear polyurethanes from diisocyanates and polyols. Zhou et al. (2015) reported that the most promising commercial bio-polyols used for PU preparations are natural oil polyols such as soybean oil polyol, castor oil polyol and palm oil polyol. PU generally made up of petroleum-based polyols. During the formation of PU, an exothermic reaction occur when isocyanate are reacted with the polyol (Syuhada et al., 2015). Due to the depletion of petroleum sources, plant oil is used as a substitution. However, recent advancement of Used Frying Oil (UFO) is being synthesized in making UFO-based polyol. UFO usually cannot be consumed more than three times due to their high Free Fatty Acid percentage (%FFA) and high peroxide compound (Budi and Anggoro, 2012). UFO can be made as a starting material in making PU as it has similar organic structure to plant oil. It can be derivatized into polyol to produce UFO-based polyol (Syuhada et al., 2015). PU can be found in few type of foams such as rigid foams, semi-rigid foams, flexible open-cell foams and microcellular foams. In this study, a rigid PU foam is produced. Rigid PU foams have low thermal conductivity, good adhesion, good dimensional stability, and excellent mechanical strength even at low density. Hence, it has been widely used in industries. Furthermore, it is light in weight and multifarious (Chuayjuljit et al., 2007). Compared to other polymers such as polyethene and polypropene, polyurethane are made up into the final end product. They are widely produced as a large blocks of foam while other polymers are usually produced in a powder or granules form (CIEC Promoting Science, 2013). Today, PU have been widely used in many applications as core material for sandwich composite laminates due to their mechanical properties, light weight, versatility and insulation performance (Zhou et al., 2015). It began to develop and received an intensive attention among the researchers by the syntheses of many specialized forms, in surface coatings, adhesives, fibers and particularly plastic and rubbers in solid and cellular form.

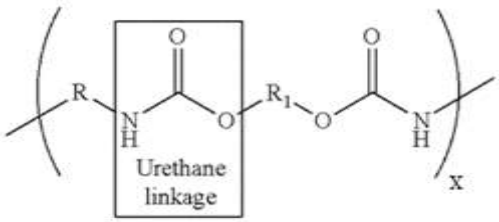


Fig. 1 Urethane linkage

## Methodology

*UFO treatment process*

Source of UFO was collected from several restaurants in Kuala Pilah area. The oil collected is originated from palm oil. Before UFO undergo filtration, the oil was first analyze using Fourier Transform Infrared (FTIR) spectroscopy to identify the functional groups exist. It was then undergo filtration process under normal sieve using food strainer and cheesecloth to remove the unwanted suspended particles. Then, it is stirred and heat for 1 hour at 105 – 110 °C before being analyzed again using FTIR spectroscopy to identify the loss of any functional groups. The analysis was continued with Free Fatty Acid Percentage (% FFA), Acid Value and Viscosity.

*Synthesis of UFO-based polyol by transesterification reaction*

Diethanolamine (DEA), Monoethylene Glycol (MEG) and Potassium Acetate (PA) was mixed in the ratio of 270:21:9 by mass to prepare polyhydric compound. The compound was then stored in a glass bottle and physically shaked until homogeneous. In a 4 neck round bottom flask, the filtered UFO was mixed with polyhydric compound to prepare polyol. The mixture was heated in the reactor until 185 °C for 8 hours (Badri, 2012). The mixture was constantly flushed with nitrogen gas and connected with vacuum pump. The polyols obtained was then undergo FTIR analysis, % FFA, Acid Value and Viscosity.

*Synthesis of Polyurethane (PU)*

PU is synthesized by the mixing of UFO-based polyols with other chemicals at various chemical compositions as stated in **Table 1** below. The chemicals were mixed together in the reaction container by using magnetic stirrer until foaming occur. The morphology was confirmed under magnification of 20x and 50x and the difference in functional groups was identified by FTIR analysis.

Table 1
Chemical compositions for preparation of rigid PU foam

| **Chemicals** | **Composition** | | |
|---|---|---|---|
| | **1** | **2** | **3** |
| **Glycerol** | 60 | 50 | 40 |
| **Water** | 54 | 54 | 54 |
| **UFO-based polyol** | 90 | 90 | 90 |
| **DEA** | 40 | 40 | 40 |
| **MDI** | 23g | 22g | 21g |

## Results and Discussion

Properties of treated UFO and UFO-based polyol

After several usage, raw UFO contains high free fatty acid compared to other plant oils. Treatment of UFO results in decreasing of %FFA which will helps to increase the processability of polyol produced because transesterification process could not occur if the free fatty acids amount were above 3 %. The %FFA continued decreasing in UFO-based polyols . Since %FFA and acid value are closely related, the decreasing of %FFA will also decrease the acid value of UFO-based polyol from the treated UFO. However, the viscosity of UFO-based polyol showed and increasement from the treated UFO due to the mixture of UFO with polyhydric compound during transesterification process. The properties of the treated UFO and UFO-based polyol is tabulated in Table 2 below.

Table 2
Properties of treated UFO and UFO-based polyol

| **Properties** | **Treated UFO** | **UFO-based polyol** |
|---|---|---|
| **%FFA** | 1.187 % | 0.70 % |
| **Acid Value** | 1.850 mg NaOH/g | 1.096 mg NaOH/g |
| **Viscosity** | 60.5 mPa.s | 150.5mPa.s |

FTIR spectroscopy analysis

FTIR spectroscopy analysis were carried out in four stages starting with the untreated UFO, treated UFO, polyol UFO and PU UFO to confirm the disappearance and appearance of functional groups. Fig. 2 shows the FTIR spectra conducted.

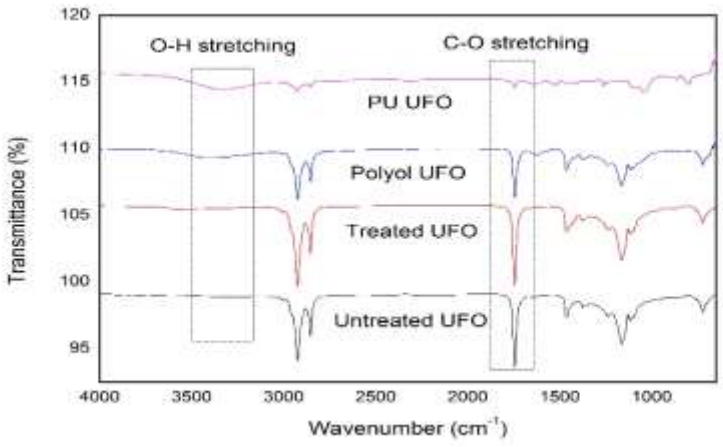


Fig. 2: FTIR spectra

Table 3
Comparison of functional group from FTIR spectra

| Functional Group | Wavenumber ($cm^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Untreated UFO | Treated UFO | Polyol UFO | PU UFO | Comparison (Appear/Absence) |
| **O-H** | - | - | 3400 | 3325 | Appear |
| **C=O** | 1744 | 1746 | 1746 | 1746 | Remain |
| **C-N** | - | - | - | 1515 | Appear |
| **N-H** | - | - | - | 3720 | Appear |
| **C-O** | 1161 | 1163 | 1163 | 1260 | Remain |

Fig. 2 shows the appearance of hydroxyl absorption peak in polyol UFO and PU UFO at around 3500 cm-1 and obvious remains of urethane carbonyl at around 1746 cm-1. However, the intensity of the C=O stretching decreasing in towards the formation of PU UFO. There are also the appearance of C-N at 1515 cm-1, υ (N-H) at 3720 cm-1 and the consistency of C-O at around 1161 cm-1 to 1260 cm-1 as being shown in Table 3.

Morphology Analysis

The morphology of the rigid PU UFO foam was analyzed at 20x and 50x magnification by using Dino-Lite Digital Microscope. Fig. 3 shows the structure obtained at 20x magnification and Fig. 4 shows the structure obtained at 50x magnification.


(a)


(b)

Fig. 3 PU UFO at 20x magnification

(a)


(b)

Fig. 4 PU UFO at 50x magnification

## Conclusion

The treatment of UFO successfully lower the %FFA of the oil without modifying the organic structure of the UFO itself. UFO-based polyol was successfully synthesized by transesterification process and it was confirmed by the appearance of υ(OH) absorption peak at 3400 cm-1. Rigid PU foam was successfully synthesized in this study. Hence, the abundance UFO can be utilized as the raw materials in PU making.

## References

Badri, K. H. (2012). Biobased polyurethane from palm kernel oil-based polyol (pp 447-470). Intech.

Budi, F., & Anggoro, D.D. (2012). The optimization of diphenyl methane diisocyanate polymerization process with the used frying oil polyalcohol to foam polyurethane using RSM: Proceeding of International Conference on Chemical and Material Engineering.

Chuayjuljit, S., Sangpakdee, T., & Saravari, O. (2007). Processing and properties of palm oil-based polyurethane foam: Journals of Metals, Materials and Minerals, 17(1), 17-23.

CIEC Promoting Science (2013). Polyurethanes. The Essential Chemical Industry. Retrieved March 18, 2013 from http://essentialchemistry.org/

Sharmin, E., & Zafar, F. (2012). Polyurethane: an introduction. Intech. Retrieved from http://cdn.intechopen.com/pdfs-wm/38589.pdf

Lee, A. (2014). Synthesis of polyurethane from one hundred percent sustainable naturl materials through non-isocyanate reaction. Smartech Gatech. Retrieved from https://smartech.gatech.edu/bitstream/handle/1853/5308/LEE-THESIS-2014.pdf

Syuhada, T., Wan Norfirdaus, W.S., Nur Syahamatun, N.H., Nor Fatihah, E., & Nurul Aina, I. (2015). Synthesis of waste cooking oil-based polyol using sugarcane bagasse activated carbon and transesterification reaction for rigid polyurethane foam: Material Science Forum, 846, 690-696.

Zhou, X., Mohini, M.S. & Oksman, K. (2015). Semi-rigid biopolyurethane foams based on palm-oil polyol and reinforced with cellulose nanocrystals. Composites:Part A.