Synthesis of Waste Cooking Oil-Based Polyol via One-Pot Epoxidation and Hydroxylation Reaction

Nurul Syazana Hasmaruddin, Syuhada binti Mohd Tahir

Abstract: ***This study was carried out to synthesize waste cooking oil (WCO)-based polyol for polyurethane via one-pot epoxidation and hydroxylation reaction. WCO was first pretreated prior to be used to synthesize WCO-based polyol. The effect of concentration of hydrogen peroxide (H_2O_2) as oxidant was observed using FTIR and GC-MS intruments and by determination of hydroxyl value (OHV) iodine value (IV). FTIR spectra of WCO-based polyol prepared using 35% hydrogen peroxide shows the formation of OH absorption peak as proof that the reaction successfully converted double bonds in WCO structure into OH. This supported by the increase in OHV from 5.030 (WCO) up to 229.32 mgKOH/g (WCO-based polyol using 35% H_2O_2). It was found that the OHV increased as the concentration of H_2O_2 used increased. GC-MS analysis of WCO-based polyol gave the molecular weight value of 597.3g/mol and functionality calculated is 2.44. This study showed that the chosen reaction is suitable for synthesis of WCO-based polyol and WCO exhibit promising potential as raw material for flexible polyurethane.***

Index Terms*: *Keywords: Waste Cooking Oil, Polyol, Polyurethane, Epoxidation and Hydroxylation.

I. INTRODUCTION

Polyurethane (PU) was first discovered by Professor Otto Bayer in 1973. Nowadays, PU is the sixth most used polymer in the world and 18 million tons of PU is produced annually (Simon et al., 2018). PU used in wide variety of applications depends on their physical forms. For example, PU foams are used as mattresses, automotive parts and buildings constructions, while the PU CASE (Coatings, Adhesives, Sealants, Elastomers) are used as parts in footwear and electronic devices. PU is a block copolymer containing urethane linkage group (-NHCO-O) produced from reaction of polyol and diisocyanate (Badri 2012; Pechar et al., 2006). Polyol, a chemical compound with multiple number of hydroxyl groups is conventionally derived from petroleum feed stocks. Massive production of PU requires a sustainable and environmentally friendly source for polyol (Purwanto et al., 2010).

Substantial amount of studies has been carried out to develop vegetable oil-based polyol as full or partial replacements for petroleum-derived polyol (Akintayo et al., 2013). Vegetable oil such as palm oil (Ismail et al., 2018), rubber seed oil (Hong et al., 2016), castor oil (Ahuja et al., 2016; Das et al., 2016), soybean oil (Liu et al., 2017; Ma et al., 2017; Pedro et al., 2017), cottonseed oil (Pawar et al., 2015) and many more had been used as raw material. Various reactions have been successfully developed to synthesize polyol from these vegetable oil namely transesterification (Arniza et al., 2014; Ibrahim at al., 2015), dihydroxylation (Sun et al., 2012), epoxidation and ring opening via hydroxylation (Siti Munira et al., 2013; Akintayo et al., 2013) or ozonolysis (De Souza et al., 2013). However, production of polyol using virgin vegetable oil requires high production cost and faces competition in food supply consumption.

The latest approach to synthesize polyol is by using waste cooking oil (WCO), an under-utilized and highly abundant raw material. During cooking or frying process, hydrolysis, oxidation, and polymerization reactions will occur. During hydrolysis reaction, water, a weak nucleophile, attacks the ester linkage of triacylglycerols and produces di- and monoacylglycerols, glycerol and free fatty acids (Choe and Min 2007; Chung et al., 2004). The presence of free fatty acid in WCO makes it suitable to be used as raw material for polyol since hydroxyl (OH) groups can be added at the unsaturated sites available on the free fatty acid chains via epoxidation and ring opening reaction.

In this study, WCO disposed by restaurant was collected as raw material and converted into polyol by one-pot epoxidation and hydroxylation reaction. The physicochemical and thermal properties of polyol obtained was analyzed.

II. EXPERIMENTAL

A. Materials

WCO used in this research were obtained from a restaurant situated in Kemaman, Terengganu, Malaysia. Formic acid were supplied by May & Baker Ltd (Dagenham, England), hydrogen peroxide from R&M Marketing (Essex, UK), hydrochloric acid from Fisher Scientific, petroleum ether and sodium chloride from QRec, sodium carbonate from Hamburg Chemical and sodium sulphate from PC Laboratory Reagent.

B. Pretreatment of Waste Cooking Oil

Pretreatment was carried out to remove suspended and dissolved contaminants

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present in WCO. WCO was filtered a few times and heated at 200 ºC for 2 hours.

C. Synthesis of Waste Cooking Oil Based Polyol via Epoxidation and Hydroxylation Reaction

Firstly, pretreated WCO (40 gram) and 5g of formic acid was added and stirred in a three-necked round bottom flask equipped with a filter funnel, magnetic stirrer and water condenser. Then, the flask was immersed in a cold water bath (10 ºC to 15 ºC) and 80 g hydrogen peroxide (25%, 30% and 35%) added drop wise into the reaction mixture while stirring. After complete addition of hydrogen peroxide, the temperature was raised to 50 ºC and allowed to continue for another 5 hours. Next, the mixture was cooled at room temperature and 50 ml of distilled water added followed by 5 ml of 11.6 M HCl. After that, temperature of the mixture increased gradually to 80ºC and continued for another 5 hours to allow hydroxylation reaction to occur by oxirane ring opening and hydroxyl group introduction. The final product obtained was extracted into petroleum ether and the ethereal layer was washed with aqueous sodium carbonate, followed by distilled water and sodium chloride solution. The ether layer was then dried over anhydrous sodium sulphate and ether was removed over rotary evaporator at 45ºC to obtain WCO-based polyol. The polyol was characterized using FTIR, TGA and GC-MS.

D. Characterizations

Fourier transformed infrared (FTIR) analysis the carried out to observe the formation of hydroxyl characteristic band to prove the reaction was successful. FTIR spectra were recorded using Spectrum 100, Perkin Elmer, in the range of 450-4000 cm^{-1} wavenumbers. Thermal properties of WCO-based polyol was analyzed by thermogravimetric analysis (TGA) instrument model Shimadzu TGA-90. About 5 mg sample was heated from room temperature to 600 ºC at heating rate 10 ºC/min. Gas chromatography-mass spectrometry (GC-MS) analysis was carried out to get the average molecular weight of polyol. The value will be used to calculate functionality of polyol, in this case is the average number of hydroxyl group per molecule of polyol. The analysis was carried out using HP 5975 Mass Spectrometer with HP Chem Station data system and gas chromatography HP 6890 with capillary GC column model. The temperature setting is 40 ºC for 4 minutes, followed by increase rate at 9 ºC per minute until 165 ºC and held still for 2 minutes. Hydroxyl value was determined using Lubrizol Test Procedure TP-AATM-02.

III. RESULTS AND DISCUSSION

The physical properties of WCO and WCO-based polyol were observed and compared. The consistency of liquid polyol was found to be more viscous than WCO and the colour changed from golden brown to cloudy white. Table I summarizes the physical properties observed.

Table I: Physical properties of waste cooking oil and waste cooking oil-based polyol

Physical properties	WCO	WCO-based polyol
State at 25ºC	Liquid	Liquid
Color	Golden brown	White cloudy
Odor	Foul	Odorless

FTIR spectra of WCO and WCO-based polyol were compared as shown in Fig. 1 below. The characteristic band for formation of WCO-based polyol is hydroxyl (OH) absorption peak around 3300 cm^{-1}. Only WCO-based polyol prepared using 35% hydrogen peroxide shows the presence of OH peak. This indicates that the process of hydroxylation of the waste cooking oil has successfully introduced OH groups on the double bonds in fatty acid structure of WCO.

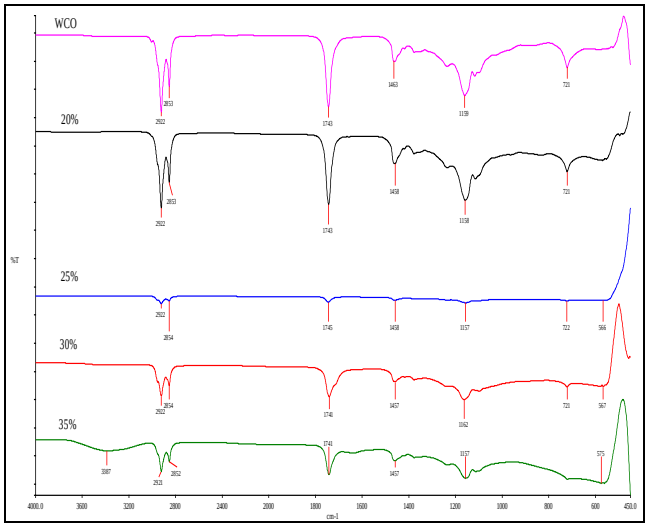

Fig. 1. FTIR spectra of waste cooking oil and waste cooking oil-based polyol

The formation of OH observed in FTIR is supported by hydroxyl value (OHV) results determined using Lubrizol Test Procedure TP-AATM-111A-02. Fig. 2 shows that the higher the concentration of hydrogen peroxide used, the higher the hydroxyl value in WCO-based polyol. WCO-based polyol prepared using 35% of hydrogen peroxide gave highest value of OHV at 229.32 mgKOH/g and thus was characterized further for determination of %FFA, acid value (AV), hydroxyl value (OHV), iodine value (IV) and thermal analysis. Table II summarizes all values for WCO-based polyol. IV represents the amount of double bond in the structure. Result shows IV reduced after conversion into polyol while the OHV increased. This again proves that the reaction chosen was successful.

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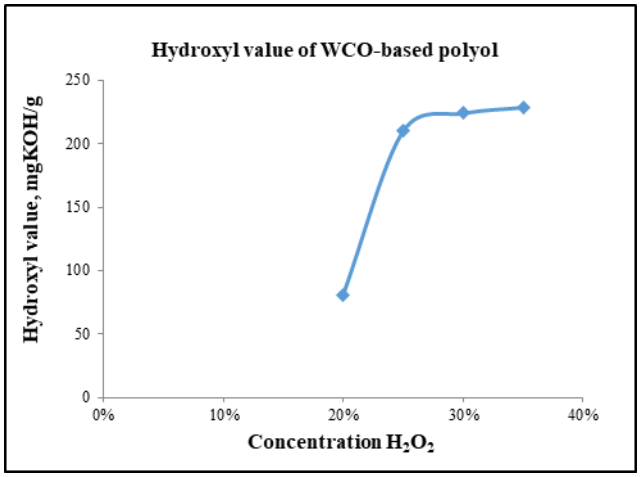

Fig. 2. Hydroxyl value of waste cooking oil-based polyol with different concentration of hydrogen peroxide, H_2O_2

Table II: Chemical properties of WCO and waste cooking oil-based polyol

Parameters	WCO	WCO-based polyol using 35% H_2O_2
%FFA	2.317	10.38
Acid value, (mgKOH/g)	4.6	20.7
Iodine value, (I_2/100g)	65.94	5.1
Hydroxyl value, (mgKOH/g)	5.030	229.32

Results for GC-MS analysis of 35% H_2O_2 polyol is shown in Fig. 3. GC-MS of the analyzed polyol gave average molecular weight of 597.3g/mol. The functionality of the WCO-based polyol calculated using this molecular weight and the determined hydroxyl value (OHV of 229.32 mgKOH/g) is 2.44 calculated. The formula is shown in the following Equation 1. The value of functionality obtained shows that the polyol produced is suitable for flexible PU application (Wood, 1990).

$$\text{Functionality} = Mw \times OHV / 56100 \quad (1)$$

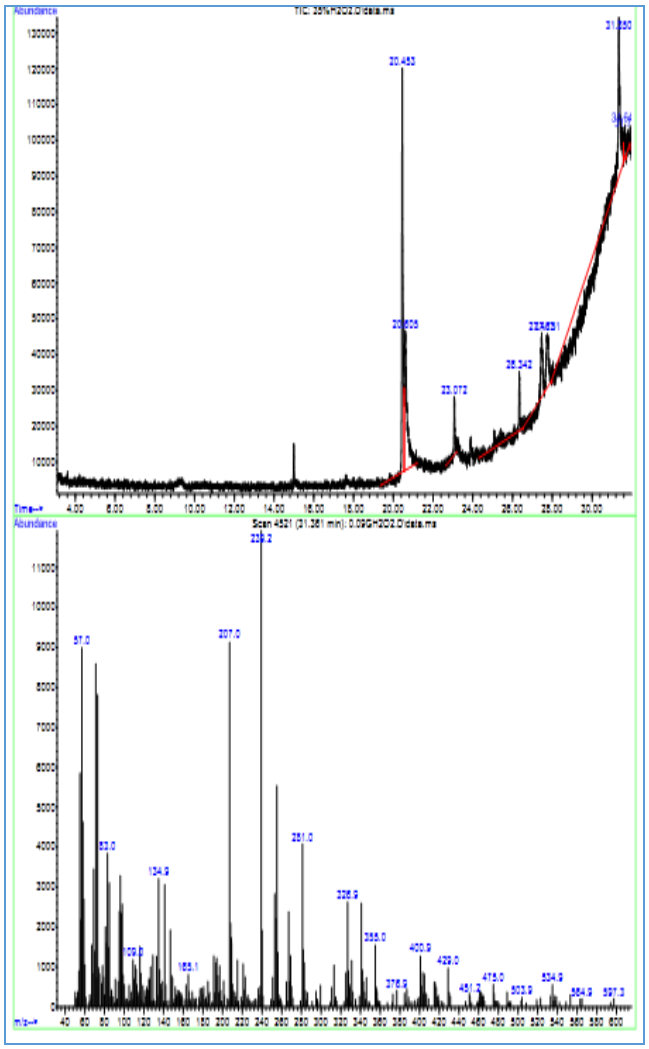

Fig. 3. GC-MS analysis of WCO-based polyol

IV. CONCLUSION

Epoxidation and hydroxylation process was proven to be successful to produce polyol from the WCO in order to introduce OH groups in the structure. The presence of OH groups in the WCO-based polyol structure has been observed by FTIR spectrometer and the intensity the OH peak increased as the concentration of oxidant, H_2O_2 used increased. Highest hydroxyl value obtained from this experiment is 229.32 mgKOH/g for 35 % H_2O_2. Then, functionality calculated for this WCO-based polyol is 2.44. It has been verified that the use of WCO as the raw material meets the requirement production of PU with high content of hydroxyl value and the functionality obtained shows that WCO has great potential in replacing petroleum and vegetable oils as starting raw material for flexible PU foam.

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REFERENCES

[1] Badri, K.H., (2012). Biobased polyurethane from palm kernel oil-based polyol, 448-470.

[2] Pechar T.W, Sohn S, Wilkes G.L, Ghosh S., Frazier C.E, (2006). Characterization and comparison of polyurethane networks prepared using soybean-based polyol with varying hydroxyl content and their bleds with petroleum-based polyol.

[3] Purwanto, E., (2010). The synthesis of polyol from rice bran oil (RBO) through epoxidation and hydroxylation reactions.

[4] Akintayo, C.O., Akintayo, E.T., Thomas, Z. and Babalola B.M., (2013). Newly developed epoxy-Polyol and epoxy- polyurethane from renewable resources.

[5] Aloysius Yuli W and Lie Hwa, (2013). Synthesis of polyol from edible oil waste with ozonolysis technology.

[6] Ferraro L.G, Alvarenga F.B.S, Gelfuso M.V and Thomazini D., (2014). Investigation to obtain polyols from residual frying oil.

[7] Simon, D., Borreguero, A. M., de Lucas, A. and Rodriguez, J. F. (2018). Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability. *Waste Management*.

[8] Tuan Noor Maznee et al., (2018). Oligomeric Composition of Palm Olein-Based Polyols: The Effect of Nucleophiles, *European Journal of Lipid Science and Technology*, **120**(4).

[9] Jian Hong, Xiao-Qin Yang, Xianmei Wan, Zhifeng Zheng and Zoran S Petrović, High value polyurethane resins from rubber seed oil, *Polymer International*, **66**, 1, (126-132), (2016).

[10] Dheeraj Ahuja and Anupama Kaushik, Castor oil-based polyurethane nanocomposites reinforced with organically modified clay, Journal of Elastomers & Plastics, 10.1177/0095244316653263, **49**, 4, (315-331), (2016).

[11] Sukanya Pradhan, Priyanka Pandey, Smita Mohanty and Sanjay K. Nayak, Synthesis and characterization of waterborne epoxy derived from epoxidized soybean oil and bioderived C-36 dicarboxylic acid, Journal of Coatings Technology and Research, **14**, 4, (915)

[12] Haijing Liu, Cong Li and Xiuzhi Susan Sun, Soy-oil-based waterborne polyurethane improved wet strength of soy protein adhesives on wood, International Journal of Adhesion and Adhesives, 10.1016/j.ijadhadh.2016.09.006, **73**, (66-74), (2017).

[13] Huan Ma, Xiaoqin Yang, Yuanbo Huang, Zhifeng Zheng and Ryan M. Richards, Phosphotungstic Acid Based Mesoporous Silica Catalysts for the Preparation of Soybean Oil-Based Polyols, Catalysis Letters, 10.1007/s10562-016-1965-5, **147**, 3, (716-726), (2017).

[14] Pedro A. Ourique, Israel Krindges, Cesar Aguzzoli, Carlos A. Figueroa, Javier Amalvy, Cesar H. Wanke and Otávio Bianchi, Synthesis, properties, and applications of hybrid polyurethane–urea obtained from air-oxidized soybean oil, Progress in Organic Coatings,10.1016/j.porgcoat.2017.04.002, **108**, (15-24), (2017).

[15] Sonalee Das, Priyanka Pandey, Smita Mohanty and Sanjay kumar Nayak, Effect of nanosilica on the physicochemical, morphological and curing characteristics of transesterified castor oil based polyurethane coatings, *Progress in Organic Coatings*, 10.1016/j.porgcoat.2016.04.012, 97, (233-243), (2016).

[16] Manisha S. Pawar, Aparna S. Kadam, Pratiksha C. Singh, Vipul V. Kusumkar and Omprakash S. Yemul, Rigid polyurethane foams from cottonseed oil using bio-based chain extenders: a renewable approach, *Iranian Polymer Journal*, 10.1007/s13726-015-0401-9, 25, 1, (59-68), (2015).

[17] Choe, E. and Min, D.B. (2017). Chemistry of Deep-Fat Frying Oils. *Journal of food science*. 72 (5), R77-R86.

[18] Chung J, Lee J, Choe E. (2004). Oxidative stability of soybean and sesame oil mixture during frying of flour dough. *J Food Sci*. **69**:574–8.

[19] Arniza, M.Z., Hoonh, S.S., Idris, Z., Yeong, S.K., Hassan, A.H., Din, A.K., and Choo, Y.M., (2015). Synthesis of transesterified palm olein-based polyol and rigid polyurethanes from this polyol. *Journal of the Americal Oil Chemistrys Society*. 243-255.

[20] Ibrahim, S., Ahmad, A. and Mohamed, N., (2015). Characterization of Novel Castor Oil-Based Polyurethane Polymer Electrolytes. *Polymers, 7*(4), 747-759.

[21] Siti Munira, Y., Mohd, A. F.and Rahmah, M., (2013). Synthesis and Characterization of Palm Oil Based Polyol". *Advanced Materials Research*. 275-280.

[22] De Souza, V.H.R., Silva, S.A., Ramos, L.P., (2012). Synthesis and Characterization of Polyols Derived from Corn Oil by Epoxidation and Ozonolysis**.** *Journal of the American Oil Chemists' Society*. 1723–1731.

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