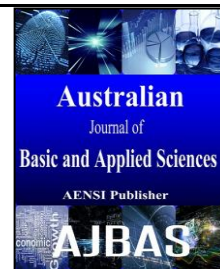




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### Epoxidation and Ring-Opening of Palm Oil to Produce High-Functionality Polyols

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#### ABSTRACT

Palm oil is a one of the most interesting renewable resources to prepare bio-polyol. With low unsaturated content, palm oil favors for making thermoplastic polyurethanes. In this work, we investigated the effect of reaction time on producing palm-based polyol through epoxidation and ring-opening reaction. By using water as nucleophilic agent, hydroxyl functionality increased resulted in improving properties of the corresponding polyurethane. In reaction time of 180 min, the epoxidation was achieved the highest conversion. In reaction time of 6 h, epoxy groups are completely disappeared, which indicated the formation of the bio-polyol. The polyurethane showed a glass transition temperature ( $T_g$ ) at 25 °C. The tensile strength was 6.05 MPa and elongation at break point was 62.05 %.

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#### INTRODUCTION

In recent years, renewable materials have attracted great interest due to the increasing cost of fossil fuels and environmental pollution concerns. Renewable resources such as vegetable fats, oils, cellulose, starch and sugars, are promising materials for synthesis of diverse biopolymers. The outstanding properties of vegetable oils, such as eco-friendly nature and cost-effectiveness, make them become potential alternatives for synthesizing biopolyols and their derivatives, Williams, C., K (2008) and Xia.,Y (2010).

There are widespread studies done to prepare vegetable oil-based polyols. In the effective route, the multifunctional compounds are obtained through ring-opening of epoxidized vegetable oils by using a variety of nucleophilic agents and in the presence of different catalysts. Owing to low reactivity of double bonds of triglyceride chains, most of unsaturated oils are converted to oxirane rings by epoxidation. By using *in situ* generation of performic or peracetic acid, the vegetable oils are well epoxidized, Kockritz., A (2008) and Petrovic, Z.,S (2002). Alcohol, amine, carboxylic acid, thiol and halogen halide are utilized to open the oxirane ring. The polyether polyols from soybean oil with primary and secondary hydroxyl group are obtained by employing alcohols, such as methanol, ethylene glycol and propanediol, Honghai., D (2009). In addition, the polyols with higher cross-linking are synthesized by using natural hydroxyl group of castor oil as a nucleophile agent in order to open the epoxy group on the backbone of soybean oil, Choqun., Z (2013).

However, the ring-opening process carried out with alcohol, amine or carboxylic acid results in transesterification as a major side reaction.

The functionality of polyol will increase double, comparing to functionality of vegetable oil, by using water in the presence of acid catalyst, Descroches., M (2012). The high functionality of polyols, increasing density of cross- linking, contributes better thermal and mechanical properties of the polyurethanes therefrom. There are many studies investigating the soybean oil-based polyol from ring-opening epoxy group using water, whereas only few researches on the ring-opening of epoxidized palm oil.

In order to gain a higher functionality polyol from palm oil, this study investigated the conditions to prepare the polyol and properties of the corresponding polyurethane. The reaction time in details was investigated with fixed mole ratio of reagents and temperature.

#### Experimentals:

##### Materials:

Palm oil, with iodine value 51, was bought from Sigma Aldrich. Formic acid (99 %), hydrogen peroxide (30% in the water), tetrafluoroboric acid (42% in the water) and anhydrous magnesium sulfate ( $MgSO_4$ ), chloroform, *N,N*- dimethylformamide (DMF) and ethyl acetate were purchased from Daejung Chemical (Korea), 4,4'- methylene diphenyl diisocyanate (98%) and dibutyltin dilaurate (95%) were obtained from Alfa- Aesar.

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### *Synthesis of epoxidized palm oil with hydrogen peroxide and formic acid:*

The reaction system was set up by connecting 500 mL three neck flask and 100 mL dropping funnel with mechanical stirring. First, the palm oil and formic acid were successively added to flask and hydrogen peroxide was put into the funnel. Then, the flask was heated to  $40\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ , the hydrogen peroxide was dropped during 1 h under vigorous stirring. Though this step was carried out at low temperature, cooling methods should be prepared due to exothermic nature of the reaction. Temperature was increased to  $50\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  as dropping of the hydrogen peroxide finished. The crude product was purified with ethyl acetate, distilled water and  $\text{MgSO}_4$ . The final product was concentrated under high vacuum at  $60\text{ }^{\circ}\text{C}$ .

### *Synthesis of palm oil-based polyol:*

The method to synthesize the palm oil-based polyol is similar with the procedure described in the literature, Bo., L (2008). The epoxidized palm oil and distill water were heated to  $50\text{ }^{\circ}\text{C}$  in different systems. After that, water and catalyst were rapidly added to epoxy flask under vigorous mechanical stirring. After the catalyst was neutralized, unreactive agents were removed by extraction with chloroform and water. Then,  $\text{MgSO}_4$  was employed to dry sample. The final product was concentrated under high vacuum condition.

### *Synthesis of polyurethane:*

Polyol POP6 obtained after ring-opening within 6 h, with hydroxyl value = 223.9 mg KOH per g sample, (5g, 9.4 mmol) was dissolved in DMF at  $80\text{ }^{\circ}\text{C}$ . Then, 4,4'-methylene diphenyl diisocyanate (MDI) (1.2g, 9.87 mmol) was added and mixed under nitrogen within 1 h. The mole ratio of NCO/OH was 1.05. The product was cooled to ambient temperature, then dibutyltin dilaurate and 1,4-butadiol, as a chain extender, were added. Finally, the polyurethane was poured into the molds and put in the oven for 5 h at  $100\text{ }^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

### *Synthesis of epoxidized palm oil with hydrogen peroxide and formic acid:*

The effects of reaction time on conversion of double bonds to oxirane group were investigated by conducting four reactions at different time duration (120 min, 150 min, 180 min and 210 min). The rate of epoxidation increased at the high concentration of  $\text{H}_2\text{O}_2$  and formic acid. However, with high concentration of  $\text{H}_2\text{O}_2$ , the epoxy group was unstable. With high concentration of formic acid, epoxy degradation may become crucial. Considering the temperature of reaction, at high temperature, the conversion of epoxy group also increased. Consequently, the epoxidized palm oil was synthesized with different reaction time, with temperature of  $50\text{ }^{\circ}\text{C}$  and mole ratio of unsaturated, formic acid and hydrogen peroxide of 1: 5: 4, Derawi., D (2010). The properties of epoxidized product at different reaction time were listed Table 1.

**Table 1:** Reaction conditions of in situ epoxidation and product properties.

Sample name	Molar ratio			Temperature ( $^{\circ}\text{C}$ )	Reaction time (min)	Conversion <sup>a</sup> (%)	Yield <sup>b</sup> (%)
	Unsat.	$\text{HCOOH}$	$\text{H}_2\text{O}_2$				
E120	1	5	4	50	120	95.7	64.5
E150	1	5	4	50	150	91.2	55.33
E180	1	5	4	50	180	98.9	70.17
E210	1	5	4	50	210	92.6	49.8

<sup>a</sup>Conversion (%), conversion of double bonds to oxirane rings, calculated from  $^1\text{H-NMR}$  spectrum.

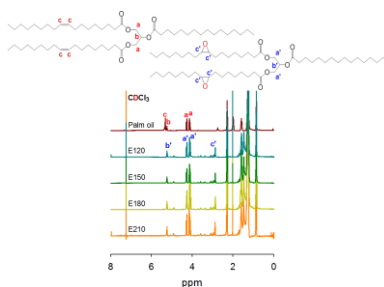
<sup>b</sup>Yield (%), yields of obtained epoxy group, calculated from  $^1\text{H-NMR}$  spectrum.

As shown in Figure 1, all the double bonds at  $\delta$  5.27- 5.41 ppm converted to epoxy group at  $\delta$  3.0-3.1 ppm. When reaction duration was extended, the intensity of epoxy peaks increased gradually. From calculation, after reaction time of 180 min, the epoxy content was a maximum percentage of 70,17%. In addition, the percentage of conversion of double bonds to epoxy also attained a maximum value 98.9%.

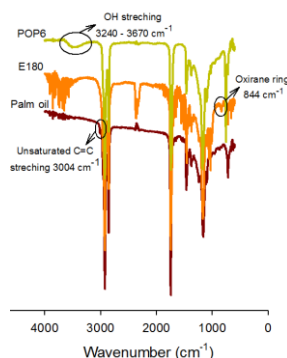
Moreover, Figure 2 confirmed again the presence of oxirane in the structure of epoxidized palm oil through the appearance of epoxy peak at  $844\text{ cm}^{-1}$  and disappearance of unsaturated  $\text{C}=\text{C}$  stretching band at  $3004\text{ cm}^{-1}$ . Following the results from FT- IR and  $^1\text{H-NMR}$  spectra, the optimized reaction time was 180 min with condition at  $50\text{ }^{\circ}\text{C}$  and mole ratio 1: 5: 4 of unsaturated: formic acid:  $\text{H}_2\text{O}_2$ .

### *Synthesis of palm oil-based polyol:*

To optimize the reaction time, the ring-opening reaction was also carried out at six different duration, 1 h, 2 h, 3 h, 4 h, 5 h and 6 h at  $50\text{ }^{\circ}\text{C}$  in the presence of water and tetrafluoroboric acid catalyst. Amount of reagents employed was summarized in Table 2. With low concentration of nucleophile agent, the reaction favored oligomerization, than ring-opening reaction. Therefore, the mole ratio of oxirane ring and water was used at 1: 11. Firstly, functionality of polyol increased from 2.38 to 3.61, then it declined to 3.58. At the first time, ring-opening dominated over oligomerization, whereas oligomerization dominated with extent of reaction time. With longer reaction time, the gained hydroxyl group was more than remained epoxy group; thus, the oligomerization became prominent.



**Fig. 1:**  $^1\text{H-NMR}$  spectra of epoxidization of palm oil with different reaction time.



**Fig. 2:** FT- IR spectra of palm oil, epoxidized palm oil E180 and polyol POP6.

The oxirane cleavage completely accomplished after 6 h as mole ratio of oxirane, water and tetrafluoroboric acid was 1: 11: 1 % wt. As reaction time was expanded, the intensity of epoxy signal at  $\delta$  3.0- 3.1 ppm in Figure 3 was reduced and totally vanished at reaction time of 6 h. At the same time, the new peaks occurred at  $\delta$  3.6 ppm and  $\delta$  3.4 ppm, corresponded to the proton of  $-\text{CH-OH}$  and  $-\text{OH}$ . In

addition, signal intensity of the peaks gradually increased as extending reaction time. Comparing with FT-IR result in Figure 1, the epoxy peak at  $844\text{ cm}^{-1}$  disappeared and new band stretching at  $3240\text{-}3670\text{ cm}^{-1}$  of hydroxyl group was formed. It was asserted that the required reaction time to open all oxirane rings was 6 h.

**Table 2** Reaction conditions of ring-opening epoxidized palm oil.

Sample name	Molar ratio Epoxy/ $\text{H}_2\text{O}$	Catalyst (% wt)	Temperature ( $^{\circ}\text{C}$ )	Time (h)	OH value <sup>a</sup> (mg KOH/ g)	Functionality
POP1	1 11	1	50	1	148.7	2.38
POP2	1 11	1	50	2	159.3	2.55
POP3	1 11	1	50	3	162.5	2.60
POP4	1 11	1	50	4	198.6	3.18
POP5	1 11	1	50	5	225.4	3.61
POP6	1 11	1	50	6	223.9	3.58

<sup>a</sup>OH value (mg KOH/g), determined by titration method following to ASTM E 1899- 97 standard.

As shown in Figure 4, comparing the GPC curve of epoxidized palm oil with palm oil, the peak at the left side indicated that the oxirane cleavage and oligomerization happened among epoxy groups in epoxidation process. Owing to the absence of hydrolysis, there were two peaks in the curve of polyol, oligomerization and main product peak. The left peak corresponded to oligomerization of the obtained secondary hydroxyl groups reacted with remain oxirane rings. The peaks of main product slightly moved to shorter elution time, it illustrating that the polyol increased the molecular weight.

### Synthesis of polyurethane:

#### FT- IR analysis:

Owning to high cross- linking, polyurethane cannot dissolve in any solvents. Therefore, the formation of polyurethane was confirmed by FT-IR spectrum. The spectra of polyurethane, polyol POP6 and MDI were illustrated in Figure 5. The band at  $3340\text{-}3670\text{ cm}^{-1}$  and  $2280\text{ cm}^{-1}$  were assigned to hydroxyl group of polyol POP6 and  $-\text{NCO}$  group of MDI, they completely disappeared in polyurethane spectrum. In addition, a new band at  $3300\text{ cm}^{-1}$  was attributed to  $-\text{N-H}$  stretching of urethane group. Two peaks of amide and urethane were also observed at  $1620\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ . It suggested that MDI totally reacted with polyol and polyurethane was produced.

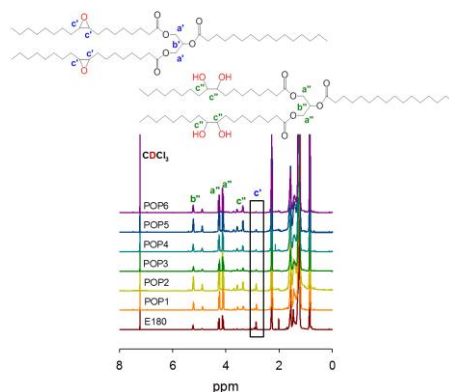


Fig. 3:  $^1\text{H-NMR}$  spectra of ring-opening epoxidized palm oil with different reaction time.

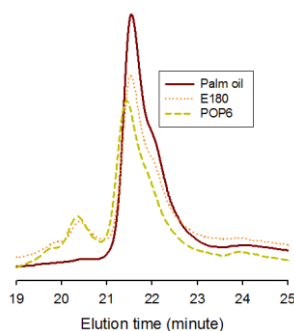


Fig. 4: GPC curves of epoxidized palm oil and palm oil-based polyol.

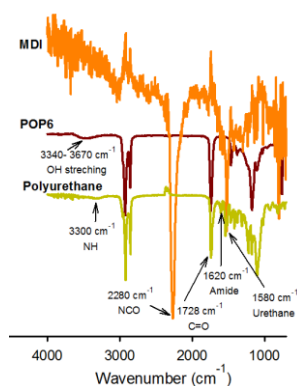


Fig. 5: FT- IR spectra of MDI, polyol POP6 and Polyurethane.

#### Thermal properties:

The polyurethane film was checked thermal properties through DSC and TGA analysis. Following the DSC thermogram in the Figure 6a, the  $T_g$  was determined at 25 °C. In addition, the thermal stability of polyurethane was observed through TGA curve in Figure 6b. One stage of thermal degradation was ranged from 158 °C to 560 °C. The phenyl group in the polyurethane led to raising thermal property as well as sample remained 5 % weight at 800 °C.

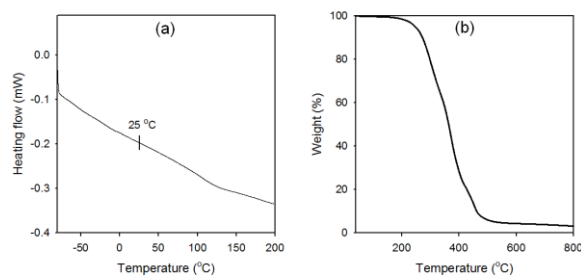
#### Mechanical properties:

The Figure 7 depicted the stress- strain behavior of polyurethane film. The tensile strength of polyurethane was 6.05 MPa, corresponding to

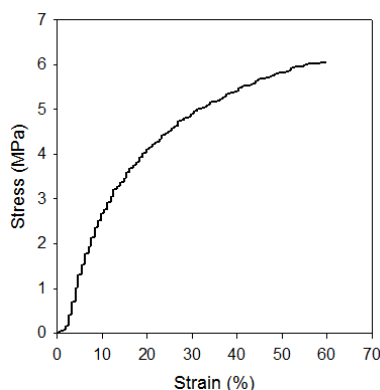
elongation of 62.05 %. The average functionality of polyol was around 3.58, which resulted in quite high cross- linking as well as slight high tensile strength. Moreover, the length of cross-linking was short due to structure of polyol, which created low elongation at break point.

#### Conclusion:

In this study, the conditions were optimized step by step for preparing polyol from palm oil. The reaction time of 180 min and 6 h were required to carry out the epoxidation and ring-opening reaction. The polyol (POP6,  $f= 3.58$ ) and polyurethane had quite good thermal and mechanical properties. Furthermore, this polyol can be modified to produce the polyurethane with desired properties.



**Fig. 6:** Thermal analysis of polyurethane film based on POP6: (a) DSC and (b) TGA thermograms.



**Fig. 7:** Stress- strain curve of polyurethane film based on POP6.

#### ACKNOWLEDGMENTS

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#### REFERENCES

Bo., L. Liting, Yang, Honghai, Dai, Aihua, Yi, 2008. Kinetic Studies on Oxirane Cleavage of Epoxidized Soybean Oil by Methanol and Characterization of Polyols. *J Am Oil Chem Soc*, 85: 113- 117.

Chaoqun, Z., X. Ying, C. Ruqi, H. Seungmoo., A.J. Patrick and R.K. Michael, 2013. Soy-castor oil based polyols prepared using a solvent- free and catalyst- free method and polyurethanes therefrom. *Green Chem*, 15: 1477- 1484.

Derawi, D. and S. Jumat, 2010. Optimization on Epoxidation of Palm Olein by using Performic Acid. *E J Chem*, 7(4): 1440-1448.

Desroches, M. M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin, 2012. From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. *Polym. Rev.*, 52: 38- 79.

Honghai, D., Y. Liting, L. Bo, W. Chenshuang and S. Guang, 2009. Synthesis and Characterization of the Different Soy- Based Polyols by Ring Opening of Epoxidized Soybean Oil with Methanol, 1,2-Ethanediol and 1,2- Propanediol. *J Am Oil Chem Soc*, 86: 261- 267.

Kockritz, A. and A. Martin, 2008. Oxidation of unsaturated fatty acid derivatives and vegetable oils. *Eur J Lipid Sci Technol*, 110: 812- 824.

Petrovic, Z., S.A. Zlatanovic, C.C. Lava and F.S. Sinadinovic, 2002. Epoxidation of soybean oil in toluene with peroxy acetic and peroxy formic acids- kinetics and side reactions. *Eur J Lipid Sci Technol*, 104: 293- 299.

Williams, C.K. and M.A. Hillmyer, 2008. Polymers from renewable resources: a perspective for a special issue of polymer reviews. *Polym. Rev.*, 48: 1- 10.

Xia, Y. and R.C. Larock, 2010. Vegetable oil-based polymeric materials: synthesis, properties and applications. *Green Chem*, 12(11): 1893-1909.