Manufacturing of Low Loading Application of Phosphoric Based Polyurethane from Edibles Epoxide Conversion

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Abstract

Polyurethane (PUR) is a type of polymer produced for a wide range of applications. Commonly polyurethane was made from synthetic materials. Due to the decreasing availability of petroleum and the risen global attention has made scientists made a breakthrough in using vegetable oil. The double bonds of essential fatty acids embedded in plants are advantages to be modified to attain an epoxidation reaction. Adding additives into the formula can improve the final properties of polyurethane, phosphate oligomer was used and prepared to be reacted to the active sites forming a network with intermediate's active site manufactured a phosphoric-based polyurethane foam to be required for use in low loading applications. This work aimed to investigate the epoxide conversion of the unsaturated bonds to attain a reactive chain and determined the relationship of the oxirane number and hydroxyl value to proceed as a polyurethane's intermediate. The temperature at 70^0C was the best according to cellular images but the density was best at 50^0C which was contrary to SEM images.

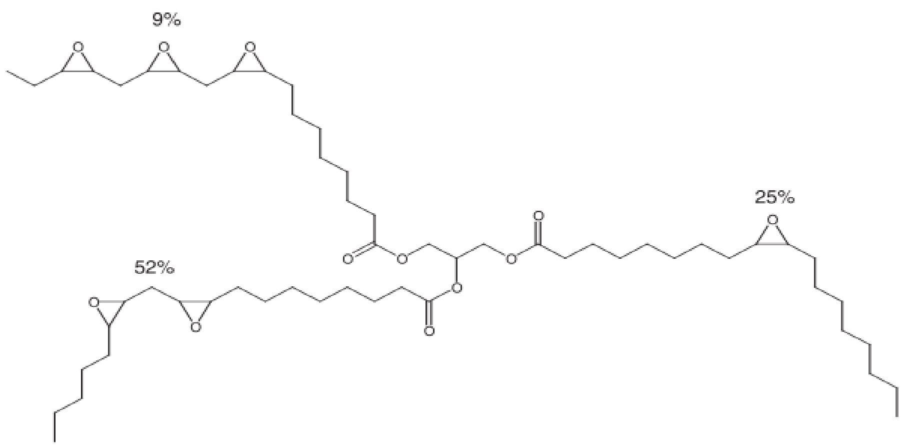
Keywords
Epoxide conversion, polyurethane intermediate, reactivity, plant fatty acid, vegetable oil

1.Introduction
Currently, the demand for polyurethane (PUR) materials is increasing, using petroleum-based may lead to initial consequences due to the low biodegradability (Firdaus, 2016). Commonly, the fabrication of polyurethane foams is using petro based as major reactants to be converted into polyols as intermediates of polyurethane. Today, there is growing global research on using edible resources and develop innovative industrial products. Most attention has been given to using vegetable oil-based polyol for environmental reasons (LI, LUO, & HU, 2015) like easily degraded, and non-corrosive (Ionescu, 2016);(Narine, Kong, Bouzidi, & Sporns, 2007), and building a more sustainable society. Soybean oil is one of kind, is abundant in supply is a cheap material for soy-based polyols production (Iwata, 2015). Soy-based polyols have shown promising results and economically significant in polyurethane production ranging from elastomers to flexible foams (Arquitectura et al., 2015); (Firdaus, 2014). The intermediate pathway to polyurethane produces soy-based epoxide to create soy-based polyols (Fan, Tekeei, Suppes, & Hsieh, 2012);(Kiatsimkul, Suppes, Hsieh, Lozada, & Tu, 2008). The synthetic routes according to several reports have used the OH- of hydroxyl to initiate reaction by interacted with triglyceride, one of them is epoxidation followed by oxirane opening (Zhang, Jeon, Malsam, Herrington, & Macosko, 2007). The formula to the polyurethane foam can be made as a mixture of polyol was synthesized from fossil to be blend with the polyol from soybean oil (Monteavaro et al., 2005); (John, Bhattacharya, & Turner, 2002).

2.Literature Review
Currently, the manufacturing of polyurethane has been developed by using the source from edibles where the industry point of view seeing this become profitable because of the low operation cost and met the environmental (Pawlik &

Prociak, 2012). In PUR manufacturing vegetable oils can potentially replace polyols, where the hydroxyl groups are required to react with isocyanate. The polyols can be made by the existence of triglyceride in edibles. Many kinds of edibles can be used as feedstock for polyurethane, one of them is the oil of soyabean which can be modified to result into foams to have high stability to thermals which correspond to the properties of fossil polyurethane (Chian & Gan, 1998),(Hu et al., 2002). The production of polyurethane foam the flexible typed was the largest on using materials from edibles to be modified into intermediates product of polyurethane, where the product was more preferable. Phosphoric acid (o-H_3PO_4) has been widely used for preparing soy-derived phosphate ester for rigid polyurethane production (Firdaus, 2011) (Figure 1).

According to some researchers founding, the high hydroxyl value of polyol from soyabean was an advantage, with phosphate ester were performing on controlling the amount of polar solvent and also as a catalyst for ring-opening on epoxidation a triglyceride of soybean oil which chemically become part of polyol.



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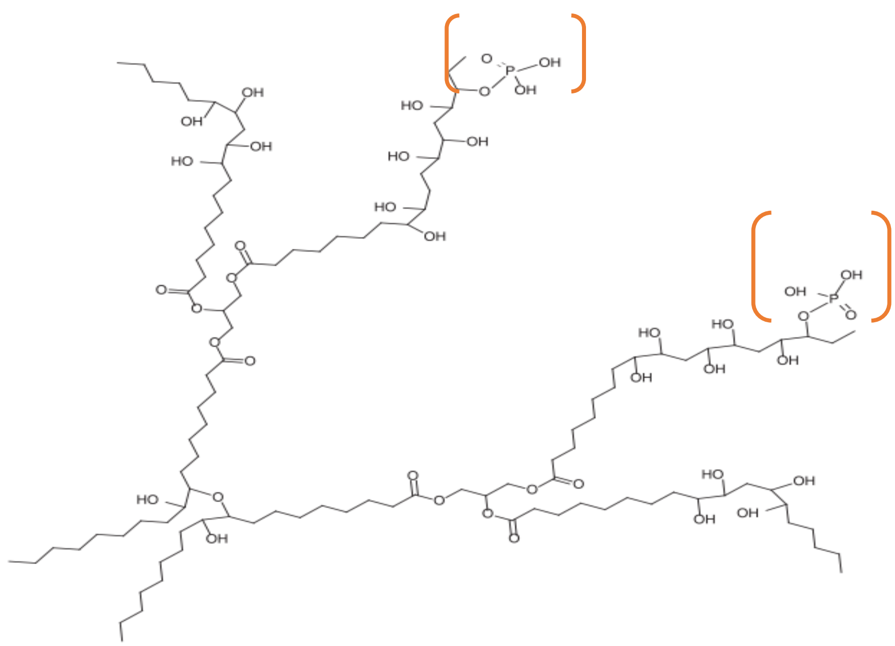

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Figure 1. a) Soy epoxide and b) Phosphate Ester Soy-based Polyol (Guo, Mannari, Patel, & Massingill, 2006)

In this work, we examined the production of soya epoxide from edible oil soyabean in the addition of phosphoric acid as the catalyst on hydrolysis reaction and part of the polyol product. The existence of phosphate ester has added value to soy-polyols and end-use applications.

3.Method

a. Determination of Chemical structure
The characterization of PUR foams was using FTIR based on ASTME1252-98, to determine the chemical structures, examined group function of the polyol.
b. Acid Number
Measuring acid number was examined acid groups in a substance or a mixture of compounds. It is expressed as the mass (in mg) of potassium hydroxide needed to neutralize 1 g of a sample is referred to as ASTM D664
c. Hydroxyl Number and correction factor
these test methods measure the hydroxyl groups in polyester and polyether polyols containing primary and secondary hydroxyl groups. They also apply to many other hydroxyl-containing substances it referred to ASTM D4274 - 16
d. Density of PUR foam
The specimen of foam was prepared in the dimensions of 1 cm^3, to determine the density (ρ) as the ratio of mass to volume, it was calculated in the average value.
e. SEM Images
The Scanning electron microscope (SEM) was applied for solidified cured polyurethane foams. The open or closed cellular obtained depends on many factors; temperature, heating treatment, duration of the reaction, type reactant, with or without water, etc.

3.1 Experiment

Polyols are made using a formula using the epoxide-1,2 ethanediol in stoichiometric with the ratio of 1: 1; 1: 5; 1: 7; and 1: 9 (mol/mol). Then 85% o-H_3PO_4 (ortho hydrogen phosphate) was added; 0.5%, with three variation of temperatures : 50, 60, and 70^0C.

3.2.Composing of PU Foam

The step for composing the foam, by including the isocyanates as the blending of TDI (2,4) and MDI (4,4') with the ratio 70:30 (v/v) into polyol of soybean with derived phosphate ester which consisted of surfactant, and distilled water. Stirred at 1000 rpm for about 1 minute, then ready to be poured into the stainless mold to determine the effectiveness of o- H_3PO_4 content to the ultimate properties of PUR.

4. Result and Discussion

4.a Characterization of Polyol (P)

The o-H_3PO_4 performed as a tribasic catalyst dissociates with having three constants (tri, di, and mono), this has been affected to the increase of anions content and the nucleophile ability. Where in a journey it produces three kinds of esters with epoxides.

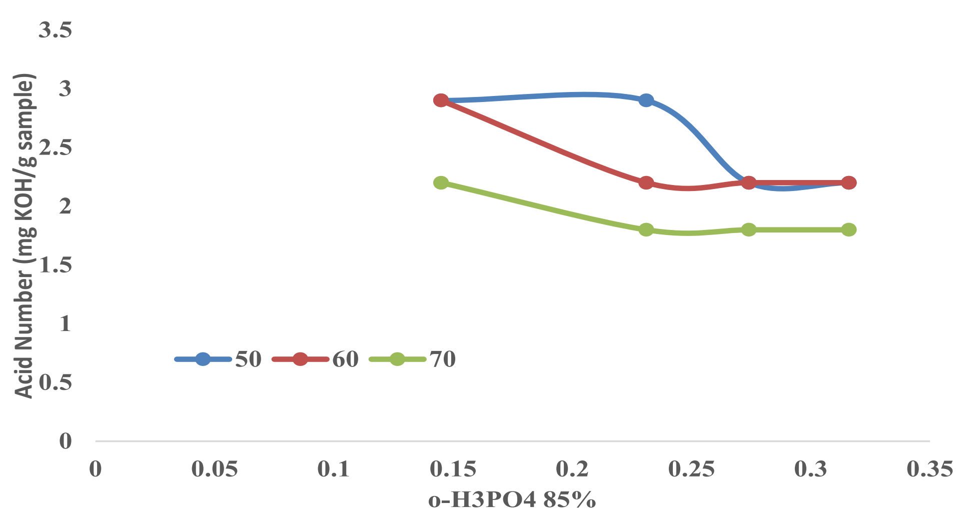

Figure 2. The effect of temperature and o-H_3PO_4 85%; 0.5% (v/v) to acid number to Acid number of PUR foam From epoxide -1,2 ethanediol (1:1; 1:5; 1:7; and 1:9) (mol/mol)

The phosphoric acid was applied in the polyols formula design with a ratio of epoxide to 1,2 ethanediol was 1:1; 1:5; 1:7; 1:9 (mol/mol). Several works of literature have quoted that the hydroxylation of epoxide occurred nucleophilic reaction which ready to attack the site activities of the oxiranes ring by H-O-H with the support of acid. The value was much significant (Figure 2).

In this work, we have used the o-H_3PO_4 with a concentration of 0.5% which in previous work we have also done 1.0% and 1.5%. It was found that the increase of acid (%) has the trend to rising the acid number which caused to lowered esters. The 0.5% was used for producing the intermediates of PUR, by the approved 70^0C it has lowered the acid number were in sequence were 50 ^{0}C > 60 ^{0}C > 70 ^{0}C.

The functional groups of soy-based polyol were identified by using FTIR. The existence of the peak of FTIR absorbance was at a wavenumber of 1100 cm^{-1} and 1050 cm^{-1} indicates the presence of hydroxyl group in soy polyol (Figure 3).

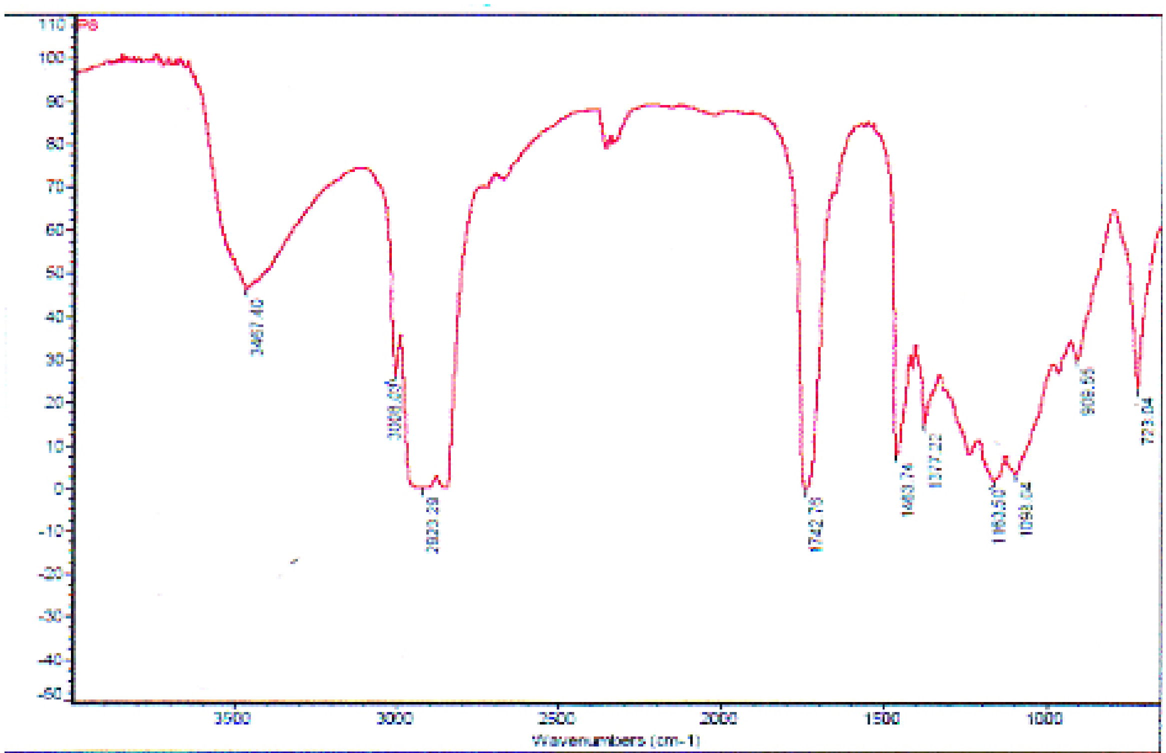

Figure 3. FTIR of Soy-polyol

The hydroxyl value of Polyol -1 (P1) was much higher among other polyols. The first P1, P2, and P3 were manufactured by 50^0C, and the next P4, P5, P6 in 60^0C, and lastly P7, P8, and P9 in 70^0C. For the proceed work we have limited the observation to three concentration which was 1:1; 1:5; and 1:7 to be focussing on the result (Figure 4).

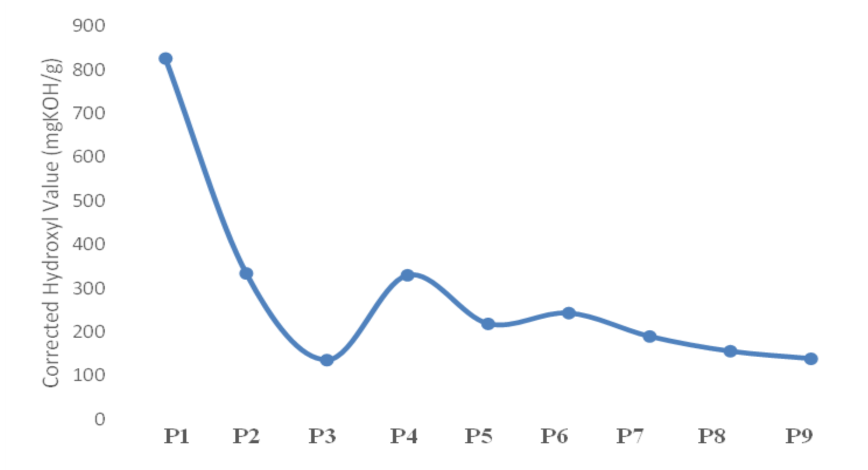

Figure 4. The hydroxyl value of Polyol (P) with a correction factor
The true hydroxyl value was the subtraction of hydroxyl value by a correction factor

The cream and gel time (minute) was the process to achieve the foam to expand in sustain. Where the gelling comes after the creaming process. The gel time in the production of polyurethane can be used to measure the reactivity of polyols into isocyanates. The temperature of 70^{0}C was observed more reactive than 60^{0}C and 50^{0}C (Table 1).

Table 1. The creaming and Gelling time during the PUR processing

Polyurethane	Cream time			Gel time	
	50	60	70	50	60	70
PU1,PU2,PU3	23.45	36.96	37.11	4.17	3.16	3.26
PU4,PU5,PU6	19.61	20.12	21.15	2.44	2.03	2.2
PU7,PU8,PU9	22.57	22.33	21.46	2.32	2.44	2.56

The density of PUR was measured, it was found the density of (PUR1) was higher among other polyurethanes. This assumes the 50 ^{0}C was the best reaction temperature. Since the foam was designed for flexibles the density obtained was not met into the wide of applications, in fact only for low loading application (Figure 5).

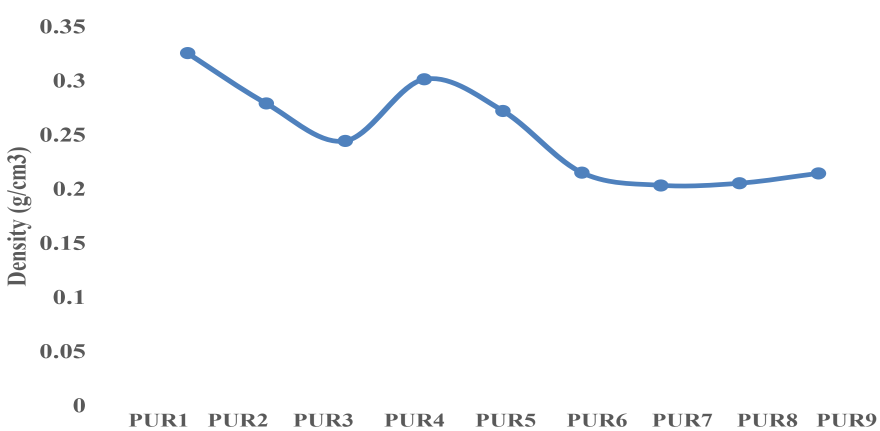

Figure 5. The density of polyurethane (PUR) foam

4.b Characterization PUR Foam

The cellular of polyurethane foam was determined into nine types of polyurethane, it was PUR1, PUR2, PUR3, PUR4, PUR5, PUR6, PUR7, PUR8, and PUR9 (Figure 6).

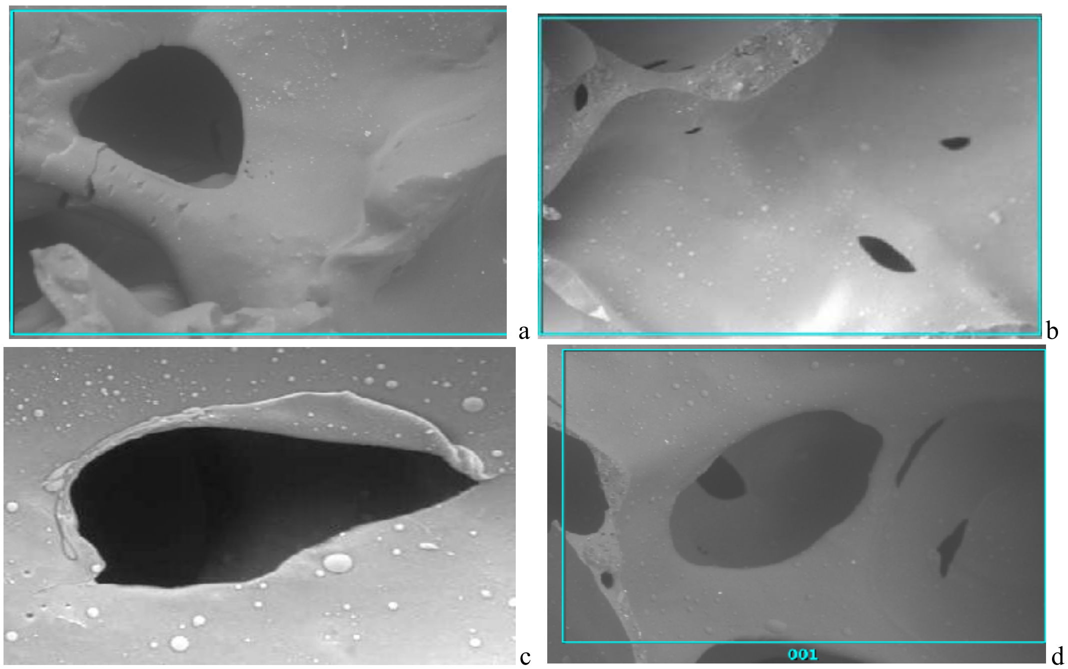

Figure 6. The cellular images of PUR
a) PUR 4 at 50^0C b) PUR 9 at 70^0C c) PUR 2 at 70^0C d) PUR 1 at 50^0C

The intermediate product of polyurethane production, include temperature and certain solvent contributed to the foaming process. The open cell may occur open or closed cell. If the amount of open-cell was higher than closed-cell it can state the foam obtained categorized as flexible it embedded to the properties where can be applied only for low loading material.

Conclusion

Polyurethane foam was prepared from soybean oil using o-H_3PO_4 in the polyol formula. It was found the incorporation of H_3PO_4 much contributed to the ultimate polyurethane foam. With the synergize between reactant and temperatures applied, it can be concluded the best density was obtained at temperature 50^0C. Nevertheless, temperature 70^0C was the best according to cellular images where the temperature has lowered to the formation of the small cavity. The increased heat potentially trapped CO_2 in a small amount and gives smaller cellular formation. The fine cellular obtained in sequential temperature $70^0C > 60^0C > 50^0C$. The product firmness indicated through density was best at 50^0C which were on contrary to cellular images.

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Biography

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