

Optimization The Process and Production of Polyurethane Foam from Soybean Oil

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Abstract

Polyurethane (PU) foams are widely used in the industry, because of the unique physical properties ranging from soft to rigid. The research on polymer using renewables sources urged to be developed, without exception to PU it was supported by enormous resources which possible to replace the decline reserved for petroleum. This work was done by processing 2,4-toluene and 2,6-toluene di Isocyanate isomers to be blended to soy-polyols forming foam formation as a balanced reaction between blowing and gelation. The best catalyst concentration can control the reaction and the synergistic to chain extender can achieve foam stability. It was found the best concentration was 1% (v/v) sulfuric acid at temperature 60°C. The method used in this research was a one-shot system. The goals were to determine the best process and production of PU. The chain extender used in this work was ethylene glycol, methanol, and butanol. The sulfuric acid was used for the catalysis and comparison purposes the butanol was catalyzed by bentonite. The morphology of the foam cellular, density, compressive strength was determined to support data.

Keywords

Hydroxy initiator, one-shot system method, polyurethane foam, polyol, soybean oil

1.Introduction

The use of renewable natural resources to replace petroleum for various applications is currently increasing. This was triggered by various considerations such as environment, availability, and lower prices [1]. The polymer industry, especially polyurethane (PU) producers, has taken various steps to maximize the use of natural reagents. Indonesia as one of the largest countries in the Asia Pacific (excluding Japan), statistically proven that it is a part of 17% of the world's Polyurethane users. Until now, most of the local polyurethane needs are still using products from abroad.

The preparation of polymers from renewable resources was economically significant to petroleum. The excellent numbers of edible oil can be utilized in reproducing valuable polymeric materials. The oils contain fatty acid, its unsaturated C=C can be chemically and characterized by the hydroxyl values. The soy-epoxide into soy-polyol is proceeding processing from soybean oil. The soy-polyol reacted to isocyanates to produce PU, elastomer, and coating [2-4]. Soybean is an expensive preferred raw material for developing industrial oil product applications due to the relatively unreactive in polymer formulations and readily available renewable resource that provides an excellent platform for polymeric materials. The fatty composition of the soybean oil in percentage by weight are (16:0) 17.75%; (18:0) 3.15%; (18:1) 23.2%; (18:2) 55.5% and (18:3) 6.31% [5]. This soy-oil can be functionalized by hydroxylation of the carbon-carbon double bonds, or functionalize the reactivity oxirane by opening ring reactions to nucleophilic compounds using peroxy acids or alcoholysis with triols like glycerol or triethanolamine to reach a hydroxyl value which was useful for PU foam production [6-9].

2. Literature Review

PU foam was the result of a reaction between isocyanates, polyols, and several other materials. The advantages possessed by flexible PU foam include the type of thermoplastic plastic, it is easily reshaped, and can be made according to market needs. The flexible nature of the process of the percentages of the soft segment was higher than the hard segment. This can be obtained when the ratio of polyol to isocyanate was greater than one (> 1) because polyol forms soft segments and isocyanates form hard segments. The flexibility of the foam can be made modified by adding a chain extender. The polyol with low hydroxy molecular weight can be added polyhydroxy to lengthen to achieve a specific property desired. The PU performed as filler or as matrix if the PU does not have mechanical properties as desired.

The chain extender with difunctional compounds (1,2 ethanediol or ethylene glycol) whereas compounds with higher functionality considered as cross-link agents. The chain extender is generally low molecular weight reactants that could produce hard segments resulted from an increased intermolecular bonding [10-11].

This research can be the basis for further research by maximizing local raw materials so that the products produced will be cheaper. The application of chain extender into soy-polyol was seldom studied to attain the best foam properties. The present work aimed to determine the best condition for processing from soy-oil until polyurethane. Determine the best catalyst concentration, chain extender, associated the microstructure to mechanical property.

3. Methodology

3.1. Material

Soybean oil was purchased from the grocery in Jakarta with specifications with Iodine value 53,89 gram Iod/100 gr sample. Other edibles oil such as linseed, and canola were meant to be used as a comparative study. Hydrogen peroxide from Brataco Chemika, acetic acid from Merck Germany, and sulfuric acid, reagent ethylene glycol, methanol, and butanol from Harum Sari Jakarta. For the catalyst, we have used homogeneous and heterogeneous which are sulfuric acid and bentonite catalyst. Another reagent also used was glacial acetic acid, pyridine, KOH, anhydrous acetic acid, acetic acid, distilled water, PP indicators, and methylene blue.

3.2 Experimental Work

The epoxide was prepared by in situ peracetic method using peroxide reagent, glacial acetic acid, and an acid catalyst. In the epoxidation process, a three-neck flask was required, equipped with a stirrer, thermometer, spin bar, measuring cup, volumetric pipette, Erlenmeyer, and beaker. Other equipment that also supports magnetic stirrer, pycnometer, titration device, digital scale, oven, water bath, Buchner funnel. The epoxide compound will then undergo a hydroxylation reaction to form polyols.

The polyol was synthesized in a 500 ml triple neck flask equipped with a reflux condenser. The three samples of 15 ml of epoxide were prepared to be added with four chain extenders; ethylene glycol, methanol, and butanol using a homogeneous acid catalyst namely as butanol (1), one sample of epoxide were prepared to be added with butanol by using heterogeneous catalyst bentonite namely as butanol (2), as for comparison. The temperature was kept constant at 60°C following the boiling temperature of the reagents. Neutralization was carried out. Filtered. The PU was synthesized by using 5 mL of TDI isomers 2,4 and 2,6 isomers at a ratio of 80:20, soy polyol 8 mL.

The product characterization was carried out; iodine number, oxirane number, hydroxyl number, functional groups using FTIR, and NMR. The product optimization of epoxides and polyols was justified to the cellular structure which confirmed the mechanical properties of PU. Following the production, there was the characterization of the polyol that can assist in forecasting the type of PU products :

- a. Hydroxyl number (mgr KOH/gr) was the number in milligrams of KOH which equivalent to the number of OH groups in 1 gram of sample. The standard test method uses ASTM D4274. Polyol is the raw material of PU as commonly measured by the hydroxyl number. The equivalent hydroxyl weight can be calculated based on the following equation:

$$\text{Hydroxyl of polyol (gr)} = \frac{56.1 \times 100}{\text{hydroxyl value}} \quad (1)$$

- b. Oxirane number was the percent of oxygen absorbed by an unsaturated raw material during epoxidation; a measure of the amount of epoxidized double bond in a material.

4. Result and Discussion

Catalyst optimization for epoxidation reaction

The purpose of determining the optimized sulfur catalyst concentration was to run the epoxidation inefficient time with a good result, this was done before starting the major work. The catalyst was applied in several edibles oil; soybean, linseed, and canola before were selected to be used for the proceeding work. The concentration of the sulfuric acid catalyst were 1%, 2%, 3%, 4%, and 5% (v/v). Samples were made in Duplo. From the work done it was found the catalyst 1% (v/v) of soybean oil with temperature 60°C was the best, was used for the proceed epoxidation processing reaction will be used for the proceed reaction because the oxirane number was the highest it was 7.3 mg KOH/g while increasing the catalyst concentration it tends to lower the oxirane number [12].

The existing high oxirane number of linseed using bentonite catalyst was significant to using a sulfuric acid catalyst. This can be signified the type of catalyst effect on the effectiveness of the epoxidation reaction. In general, the application of sulfuric catalysts does not significantly affect to the oxirane number of the edibles. It should be noted the epoxidation processing reaction (edible oil to epoxide), the high oxirane number was considered the best, but in the polyol processing reaction (epoxide to polyol), the product with high hydroxyl value was expected or otherwise low oxirane number [13].

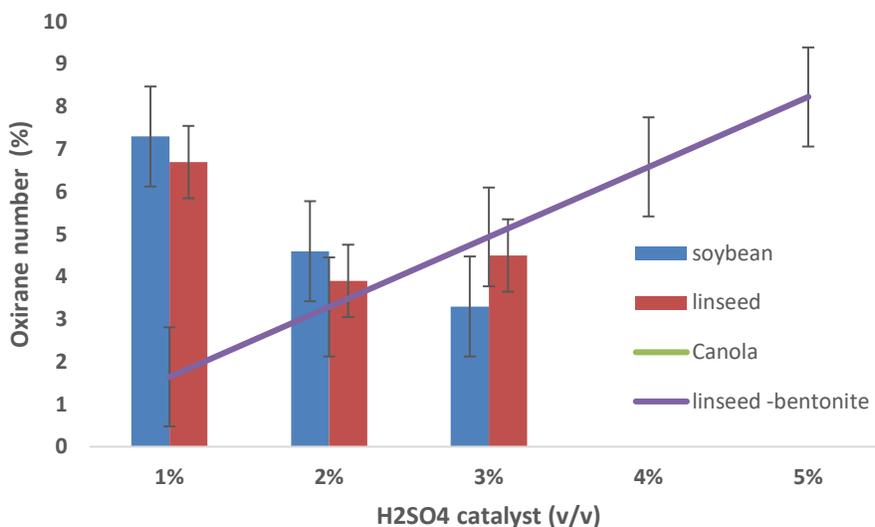


Figure 1. Optimization of catalyst for epoxidation of edibles Oil

The polyol production

a. Using ethylene glycol

The reaction converting epoxide into polyol was applied by using three kinds of chain extender; methanol, ethylene glycol, and butanol into an epoxide. The ratio concentration epoxide was prepared in the concentration 1:1; 1:3; 1:4; 1:6; 1:7; 1:9; and 1:10 (mol/mol).

Production of polyol using different chain extenders will result in a different response of oxirane number. In this stage it the best concentration of the ethylene glycol was the lowest oxirane number of the polyol. It was found the ratio epoxide/ ethylene glycol 1:4 (mol/mol) was the lowest oxirane number which was 0.079 % in three hours reaction, this indicated at this point the highest hydroxyl number. Besides, three hours reaction also the highest existing oxirane number which indicates the lowest hydroxyl number. It can be seen in (Figure 2).

b. Using methanol

Optimization of the polyol manufacturing process using methanol chain extender. It was performed variations of time and concentration ratio of epoxide to the reagent. The measured parameter was the number of oxiranes. It results obtained at a concentration of 1: 6 (mol/mol) was the same if the reaction was done in two hours and three hours as can be seen in the following (Figure 3).

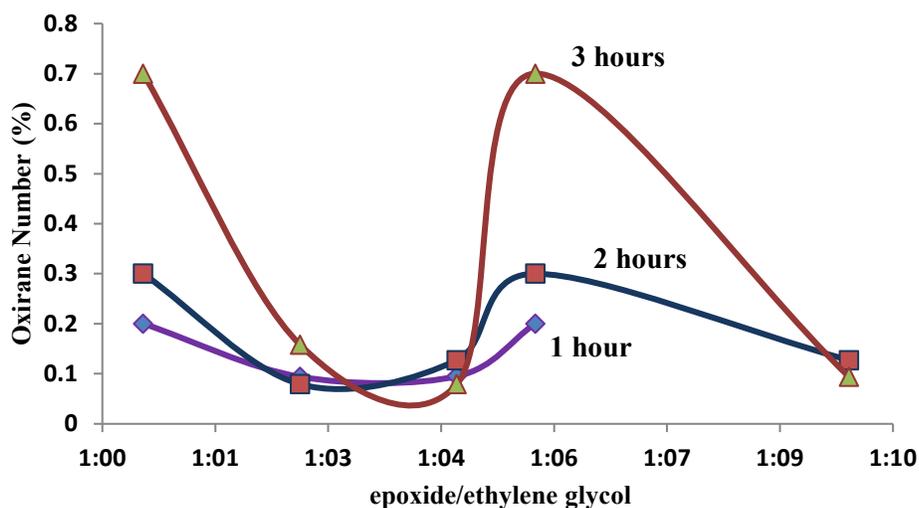


Figure 2. The optimized of Polyol using Ethylene Glycol

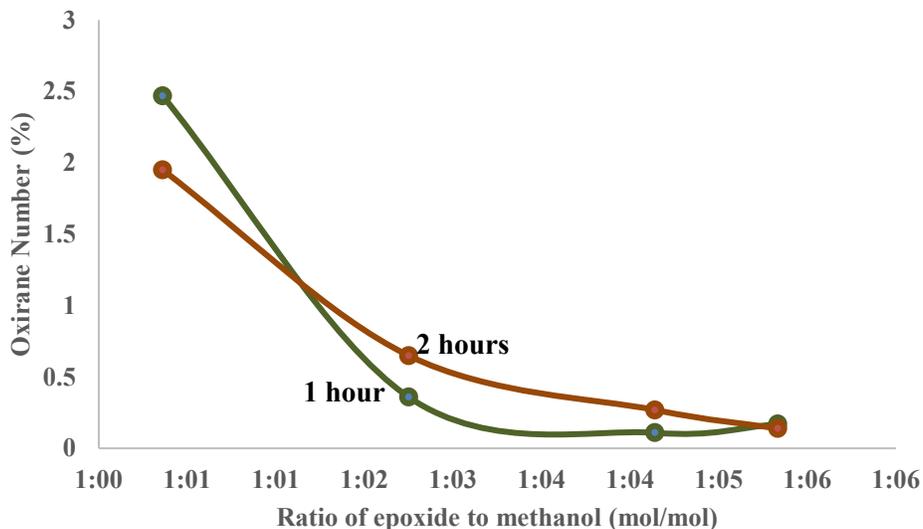


Figure 3. The optimized of Polyol using Methanol

c. Using Butanol

The polyol product was manufacture using butanol as a chain extender. At this stage was tried to using sulfuric acid namely as a homogeneous catalyst and compared the product to butanol using another catalyst; bentonite namely as a heterogeneous catalyst. The parameter measured for the comparison was the oxirane number. It can be seen that the polyol product using an acid catalyst produces the smallest oxirane number at a concentration ratio of 1: 3 (mol/mol) for a two-hour reaction, namely 0.09 mgr KOH/g (Figure 4). While using bentonite it showed the polyol 1:4 (mol/mol) for a two-hour reaction (Figure 5).

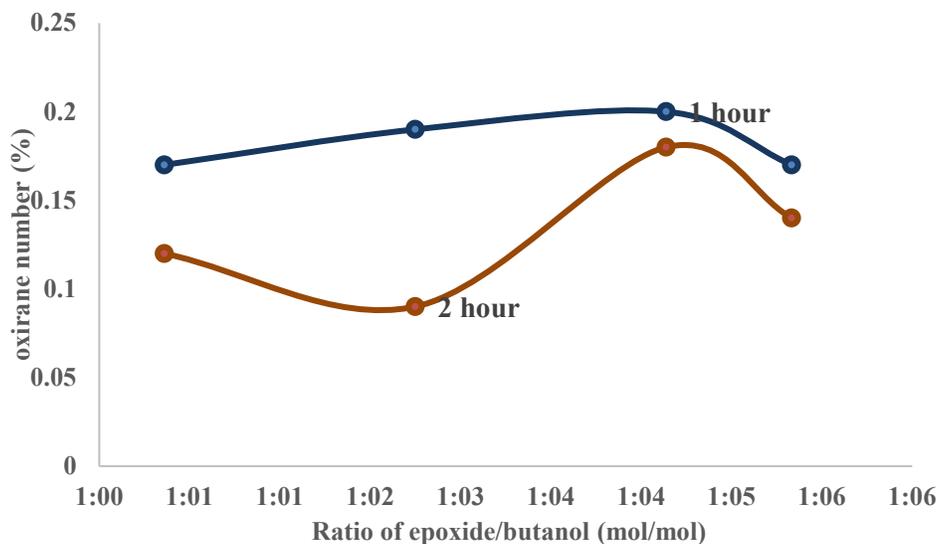


Figure 4. The optimized of Polyol using Butanol catalyst H_2SO_4

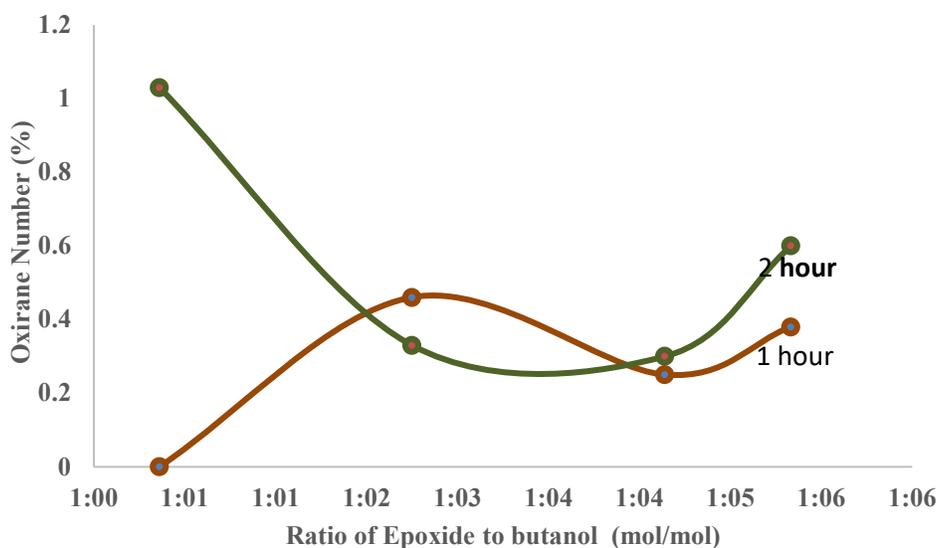


Figure 5. The optimized of polyol using chain extender Butanol with Bentonite catalyst

The low oxirane number of polyol manufactured using ethylene glycol, methanol, butanol using sulfuric acid, and butanol using bentonite. It was found the highest hydroxyl number or as indicated as the lowest oxirane number was obtained by butanol using bentonite catalyst, followed by butanol using sulfuric acid catalyst, then methanol and ethylene glycol.

Production of Polyurethane

Polyurethane was a tailor-made polymer [14-15]. The higher the hydroxyl number of the polyol means the high possibility to result in the rigid polyurethane. It was assumed the flexibility of polyurethane made from ethylene glycol was higher than methanol, butanol using sulfuric acid, and butanol using bentonite as was depicted in Figure 6. The viscosity of the polyol was also tested, polyol from ethylene glycol was 18.864 cps, methanol was 231.828 cps, and butanol using sulfuric acid was 569.431 cps.

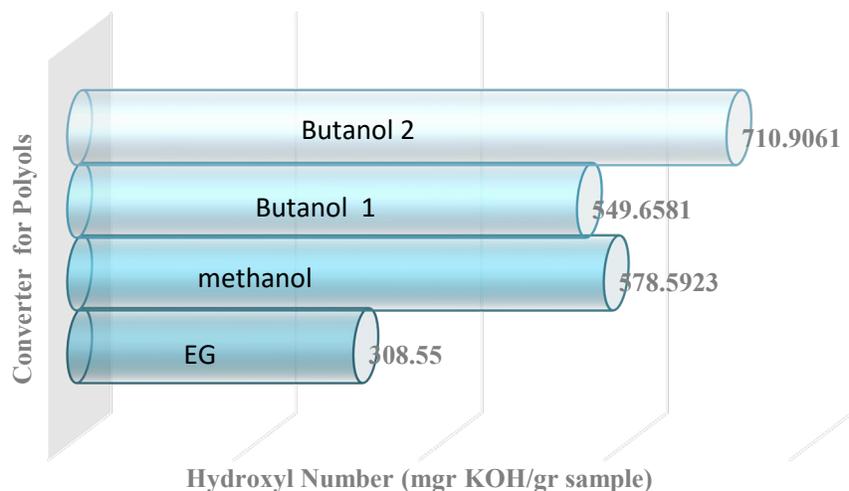


Figure 6. The optimized Hydroxyl number of several polyols
Butanol 1: using sulfuric catalyst; butanol 2: using bentonite catalyst

The compressive strength of polyurethane of polyol with the load 10% (kN) from ethylene glycol was 17 (kN), methanol 18 (kN), and butanol 18 (kN), for this result each of the product does not significantly affect to the differences of the mechanical property as tabulated in Table 1. Referred to the specification of polymer in general the minimum compressive strength was 449.5 KN/m² where the maximum could reach as high as 6106 kN/m². In this case, this product should not be stand-alone bu using only edible oil-based even though some of the reagents are synthetics but it did not apply to specification, except if it would be applied to the nonassessable environment. The assumption to this result the previous design of the research should add an additive from petroleum-based or may be directed to using fiber filler to obtain a more strong material polyurethane composite.

Table 1. The Property of polyurethane

Type of Polyurethane ^a	Compressive strenght	
	at 10% (MPa)	Max Load 10% (kN)
PU1 (Ethylene Glycol)	3,06x10 ⁻³	17
PU2 (Methanol)	3,4x10 ⁻³	18
PU3 (Butanol)	3,3x10 ⁻³	18

The nature of polyurethane foam was a function of the cellular structure. In more detail, the cell structure was influenced by several factors, such as size, shape, and place. The cell diameter and average volume are often used to characterize the cell size [16]. The images of polyurethane from methanol, butanol, and ethylene glycol seems very much different. Visibly the bubble forming on the surface of the foam also through the inner of the foam. Physically the foam performance respectively is not significantly different, and there were risen smoothly. The microstructure of ethylene glycol-based polyurethane foam was seemed a little different from the butanol and methanol but this could not be analyzed as the big differences because the physical properties do not approve to be different.

There are several cell shapes, such as the shape of the pentagonal dodecahedron which has twelve sides sometimes four to six sides. According to research, polyurethane foam has good physical properties if it was built by the geometric shape of fourteen sided cells. Besides, polyurethane foam also depends on the degree of cell opening, is the hole in the flexible foam polyurethane structure surrounded by a polymer membrane or polymer frame after the blowing process is complete. The membrane holes are formed in the cell structure, causing air to be able to enter [17-19]. If the cell inserts into the membrane, the polyurethane will be relatively rigid, causing less air to enter the cell. This image was the confirmation of the hydroxyl value of the polyol obtained previously (Figure 7).

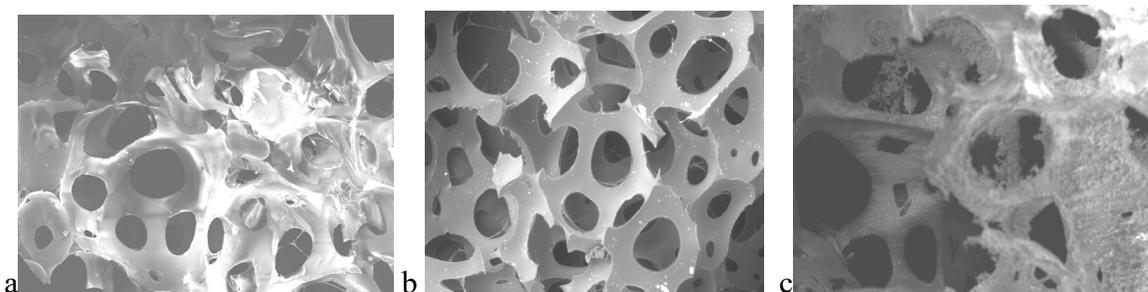


Figure 7. The cellular morphology of Polyurethane from Polyol synthesized from
a)Methanol b)Butanol and c) Ethylene Glycol

Conclusion

Polyurethane is a tailor-made polymer. The property of the product from soft to rigid can be managed by choosing the type of catalyst because the homogeneous catalyst will result in different properties compared to heterogeneous catalyst even though using the same epoxide and ratio. Another thing that should be considered is the chain extender, which performs a major role in resulting in the property of the product besides the time of the processing.

Acknowledgments

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