Fabrication of Seed Oil-Based Flexible Polyurethane and Identify Failures from the Processing Pathway

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Abstract

The preparation of polyurethane (PU) foam using green-based polyol from soybean oil as an alternative for petroleum-based polyurethane. The polyurethane was fabricated by using the prepolymer method following the two steps namely epoxidation and alcoholysis reaction. The FTIR, hydroxyl numbers were used to monitor the process of the synthesized polyol and determined the physicochemical properties. Choosing a suitable method for the processing of polyurethane foam soy-based became a major to the success of the production. Temperatures of operation, reactants, were not the only to be focuses dealing with organics the length of the reaction should also be considered. The research aimed to focus on the optimized fabrication of soy-polyol as intermediate to flexible foam polyurethane. Identify the use of the length of reaction to epoxidation reaction, and hydroxylation, and evaluates the correlation to the physical property of the foam product.

Keywords

Fabrication, flexible polyurethane foam, length of the reaction, foam physical property, soybean oil

1.Introduction

Polyurethane (PU) production from bio-based feedstock is being pursued to increase the renewable material fraction in foams. PU globally is consumed in the form of foams (Ionescu, 2016). Isocyanates and polyols are petroleum feedstocks as two major components in polyurethane (PU) production. The amount of isocyanate is greatly affected to the PU foams' performances (Javni, Zhang, & Petrović, 2003);(Pechar et al., 2006);(Guo, Javni, & Petrovic, 2000), include compressive strength. Altering the amount of isocyanate in the foam formula the mechanical property could be modified, where the excess of isocyanate results in more rigid PU foams because of a more complete conversion of OH groups in polyols.

2.Literature Review

The side reactions that occur during the polyurethane production may have intense effects on the final properties, the products were temperature-dependent equilibrium with reactants (Lee, 1985).

Isocyanate groups like TDI and TEA taking part in the growth of particles, where free isocyanates react with the hydroxyl functionality of polyol. The reaction was not closely controlled so it results in an undesirable property. The presence of secondary hydroxyl end groups in big amount in polyol medium unstabilized particle and emerge large size distribution. The idea of using seed oils in the formula provides an intrinsic hydroxyl functionality which suited to cost-competitive feedstocks (Firdaus, 2016).

The reactiveness of isocyanates relatively slow with hydroxyl at room temperature, this was reflected in the incompatibility of nonpolar to denser isocyanate and polar to less dense polyol of hydroxyl even though a surfactant and catalysts were applied.

The tertiary amine (R_3N) as catalyst drives reactions other than urethane formation (Tillet, Boutevin, & Ameduri, 2011);(Van Maris, Tamano, Yoshimura, & Gay, 2005), where the catalytic activity forming urethane bonds were

commonly known as gelling reaction tied in the rapid growth of molecular weight and increased viscoelasticity. The activity of isocyanates catalyzation and water resulted in a blow reaction to the formation of carbon dioxide as a result of blow reaction and forming a frothed morphologies (Sonnenschein, 2014);(Firdaus, 2011a).
The R_3N catalyst reacted with hydroxyl and isocyanates, the presence of water drives the blow reaction where it has higher efficiency than the gelling reaction. Referred to some research findings, there was a heat formation the value depends on the type of alcohol and isocyanate structure (Wang, Wang, He, Mao, & Sun, 2013).

At elevated temperature, the urethane bond can revert to isocyanate and hydroxyl functionality (Okrasa, Czech, Boiteux, Méchin, & Ulanski, 2008);(Mohammed & Sankar, 2011);(Yang, Zhu, Li, Xia, & Li, 2010), where the revert occurred as a function of the urethane structure stability (Firdaus, 2011b). The structure contributes to urethane thermal stability. The aliphatics are more thermally stable than aromatics, where delocalization of aromatics stabilizes the activated states of reversion results. It was found the urethanes synthesized from aromatic alcohols exhibit low thermal stability. Phenol somewhat often considered as aromatic alcohols where more acidic than aliphatic alcohols, has been widely used for protecting isocyanates to be available at elevated temperatures (>100 °C) (Kothandaraman, Nasar, & Lakshmi, 1994);(Wicks & Wicks, 1999).

The formation of urethane in the absence of a change in stoichiometry upon cooling exceedingly unaffected to the change of overall molecular weight (Koberstein, Gancarz, & Clarke, 1986). As the nucleophilicity increased it influenced the reactivity of an active hydrogen compound. It is well understood steric factor affected the reactivity of the isocyanate structure in NCO, where the electrophilic attack increased the negative charge density of the isocyanate oxygen which increased reactivity (Figure 1).

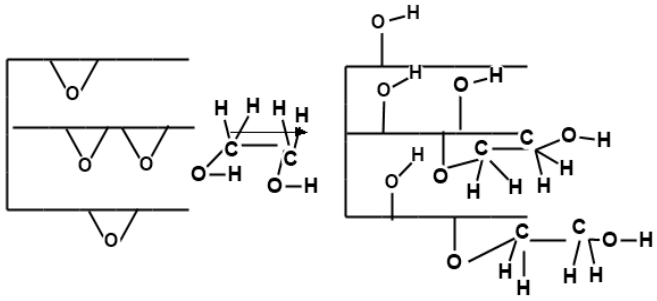

Figure 1. Scheme of Polyol using 1,2 ethanediol

Based on the reference above, it was stated the success of the polyurethane production was generally affected by temperature, the reaction endurance during the process was abiding. The research aimed to focus on the optimized fabrication of soy-polyol as intermediate to flexible foam polyurethane. Identify the use of the length of reaction to epoxidation reaction, and hydroxylation, and evaluates the correlation to the physical property of the foam product.

3.Methods

The soybean oil was purchased from the local store commonly known as cooking oil. It was produced by Sione Darby Singapore. The epoxide and polyol were synthesized in stoichiometry calculation. The epoxidation reaction was done by using peracetic (acetic acid and peroxide acid) to modify the unsaturated C=C triglycerides of soybean oil. The ratio of CH_3COOH/ H_2O_2 was done 1:4; 1:5.4; 1:6, 1.6.1; 1:6.4; 1:6.9; and 1:7.1 (mol/mol) with temperature 60°C using hot plate. The oxirane number was determined. The next step was preparing for a hydroxylation reaction of soy epoxide. It was done by using soy epoxide and 1,2 and ethanediol with the ratio of 1:3, 1:5; and 1:10 (%, v/v). The oxirane number and hydroxyl value were determined. The experiments were carried out in a 500 mL three-necked, round-bottomed flask equipped with a thermometer and a mechanical stirrer. The whole apparatus was placed in a water bath to maintain a temperature of 110°C ± 5°C (Arniza et al., 2015).

3.1 Characterization of the product

- The acid number was used for quality control to ensure uniformity, it was also used as a correction factor for the true hydroxyl number. The reagents used were ethanol, toluene dry, and Phenolphthalein. The titrant concentration

used was KOH = 0.1 mol/L dissolved in alcohol either ethanol or methanol with a concentration of 50% (v/v), then have it neutralized previous the addition of 0.3 mL phenolphthalein/100 mL and KOH.

$$Ac_N = \frac{C_F\,[KOH]V_T M_{W\,KOH}}{S} \quad (1)$$

Where

Ac_N : acid number (mg KOH/ g)
V_T : titrant (mL) for first endpoint
C_F : correction factor
$M_{W\,KOH}$: 56.11 (g/mol)
S : sample (g)

- The hydroxyl value directly correlates to the number of polyols it was an important characterization according to ASTM E1899. The hydroxyl value was given in mg KOH per g sample to know the degree of esterification of the sample. 60 mL deionized water is added to approximately 180 mg Potassium hydrogen phthalate (KHP). The mixture was then stirred for about one minute to let the KHP dissolved, titrated until it reached the first equivalence point using Tetrabutylammonium hydroxide (TBAOH) as [TBAOH] = 0.1 mol/L. An appropriate amount of was weighed dissolved in 10 mL acetonitrile, the mixture solution stirred with the rate 8 for 30 seconds, 10.0 mL Toluene-4-sulfonyl-isocyanate (TSI) were added and covered, stirred with the rate 4. Then 0.5 mL deionized water was added, closed again, and stirred with a rate of 4 for another 60 seconds. The solution 40 mL acetonitrile was added and then titrated until outreached the second endpoint with [TBAOH] = 0.1 mol/L.

$$Ms = \frac{40}{OHV_{expected}} \quad (2)$$

Where

Ms : sample size in g
OHV : expected hydroxyl value

- FTIR measurements were aimed to characterized organic compounds both qualitative and quantitative. There were two characteristic absorptions of the oxirane ring in the range between 4000 cm^{-1} and 400 cm^{-1}. The first one, at 915 cm^{-1}, was attributed to the C-O deformation of the oxirane group.

4. Result and Discussion

Production of soy epoxide, it was found that the ratio of CH_3COOH / H_2O_2 1: 6.4 (mol/mol) was the best, as evidenced by the highest oxirane number was 6.8, exceeding the previous average value of oxirane in the range 4.5-5.6 mg KOH/g (Figure 2).

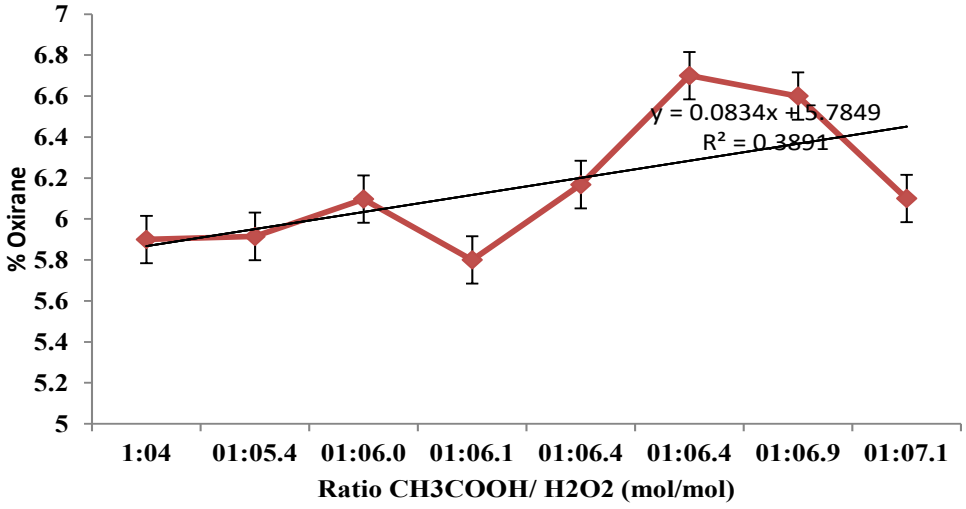

Figure 2. The optimized of Soy-epoxide with the length of reaction 90 minutes

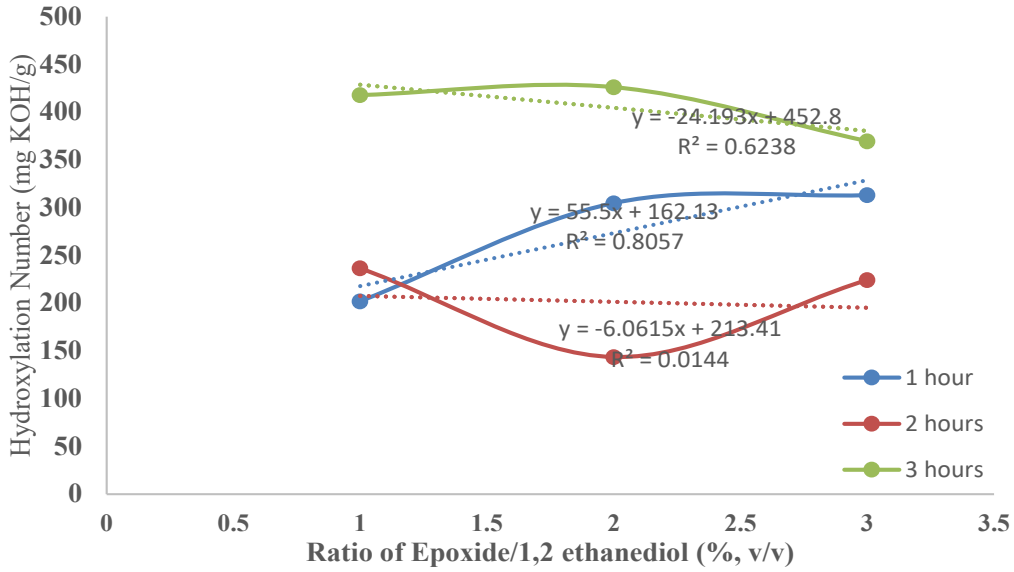

Figure 3. The optimized of soy-polyol

The duration of the reaction will lead to better results (Firdaus, 2014). For the manufacture of polyols, it can be seen that the reaction time of three hours was the best, where the hydroxyl numbers were the highest compared to one and two hours (Figure 3).

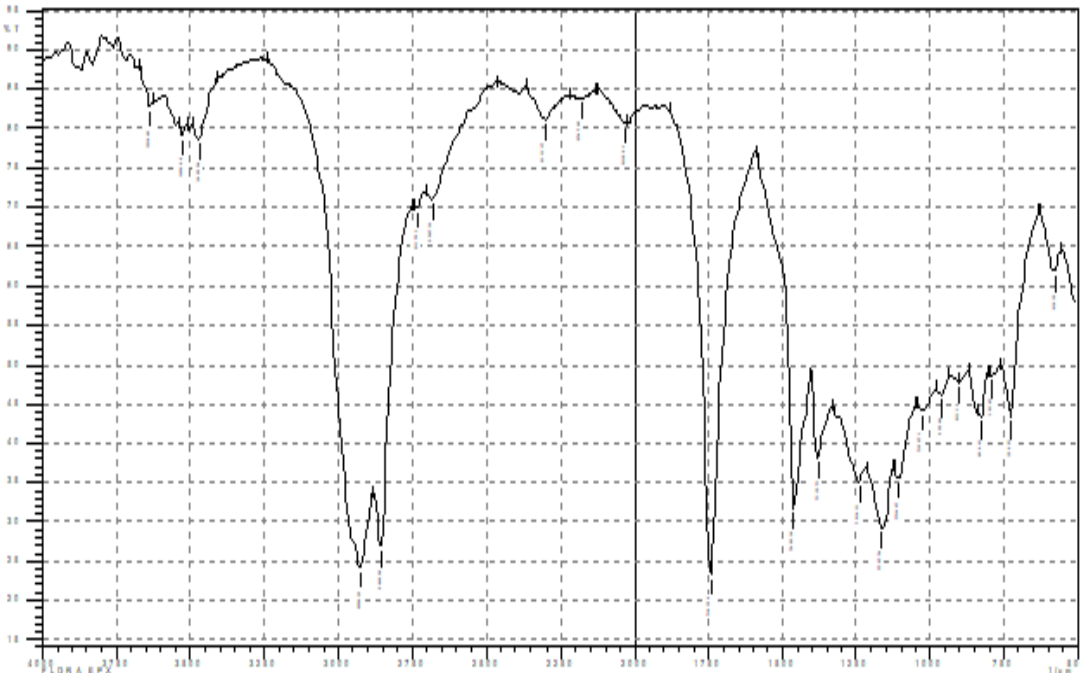

Figure 4. FTIR images of Soy epoxide

Indeed it was proven by the R^2 value. The FTIR spectrum of soybean epoxides was shown by the loss of epoxy groups at 825 cm^{-1}, 845 cm^{-1} and the appearance of hydroxyl groups at 3450 cm^{-1} was clear from soy-based polyols showing a characteristic signal at 1050 cm^{-1} indicating the presence of ester groups (Firdaus, 2011b).

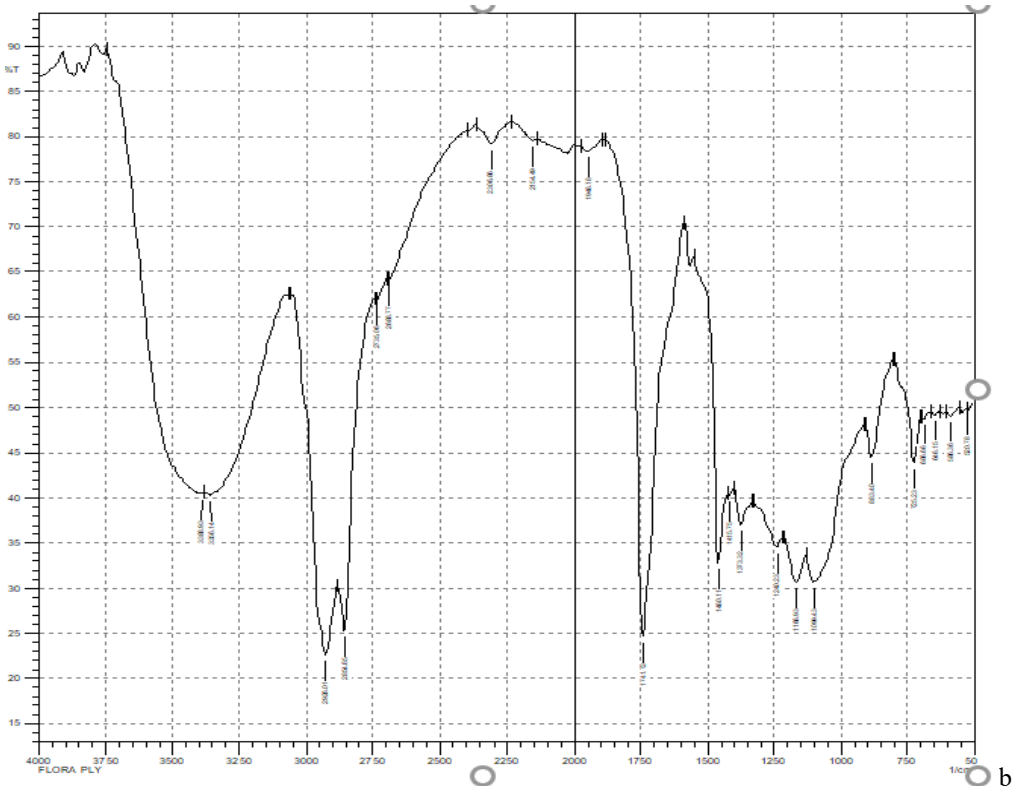

Figure 5. FTIR images of Soy -Polyol

In making polyurethane using the prepolymer method. The mixture of peracetic acid reagent (CH_3COOH with H_2O) was intended to oxidize the unsaturated C = C bond in soybean oil triglyceride, namely the ratio of CH_3COOH and H_2O_2: 1 / 5.962; 1 / 6.219; 1 / 7.25; 1 / 7.255; and 1: 7.8 (mol/mol). The temperature applied was 55 ^{0}C, and 60^{0}C, the length of the reaction was 90; 120; 150; and 180 minutes (Figure 4) and (Figure 5).

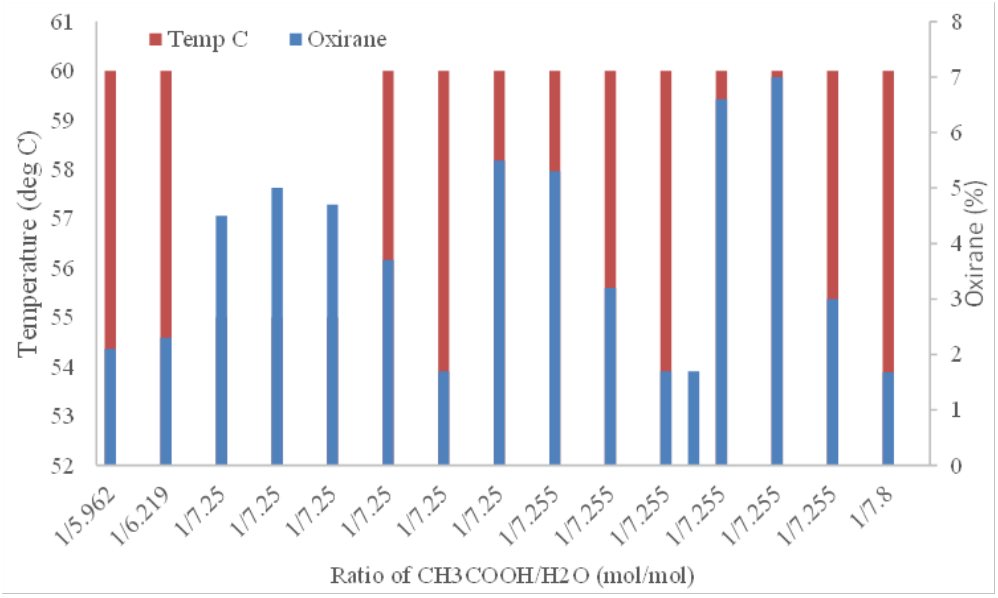

Figure 6. The Effect of temperature and ratio of peracetic to the oxirane number

Each formula was made in Duplo form. At a ratio of 1/7.25 (mol/mol), the reaction time of 150 minutes and with an operating temperature of 60 ^{0}C has resulted in an oxirane number of 5.5%. If applied the same ratio and reduce the reaction time to 120 minutes, the oxirane number obtained was also low were 1.7%. If the temperature was lowered to 55 ^{0}C with the reaction time was 150 minutes, the resulting oxirane number slightly improved to 4.7% if the time above was shortened to 90 minutes, the oxirane number increased if the time reaction was increased to 120 minutes (Figure 6).

From the above results, it can be concluded the epoxidation was considered to affect the oxirane number, in other words, the completion of the reaction depended on the length of the reaction which has to modify the unsaturated C=C. This was adjusted to the composition of the C = C double bond present in the soybean oil triglycerides. The temperature and the reactants were not the only points to be considered, but the length of the reaction also become major to the success of the process. The increased peracetic ratio to 1/7.8 with the operating temperature at 60 ^{0}C where the time was also extended to 180 minutes, this does not make the oxirane number increased. The best provisional conclusion was 150 minutes and an operating temperature of 60^{0}C with a ratio of peracetic was 1/7.25. But the resulting acid number was 8.9 which was still quite high. Likewise, at 1/7.25 with the temperature was 60^{0}C and the reaction time was 150 minutes the acid number was 7.8, the same thing also happened to the ratio of 1/7.8 at 60 ^{0}C and the reaction time was 180 minutes acid number was 8.9. These high acid numbers can be done by neutralization using distilled water until the acid number range (AN) was obtained $0 \leq AN \leq 1$. Based on laboratory work the twice neutralization was sufficient in reducing the acid number to within the threshold. Overall, the percentage of water in the epoxide was quite small in the range of 0.0004 to 0.46 (%) (Figure 7).

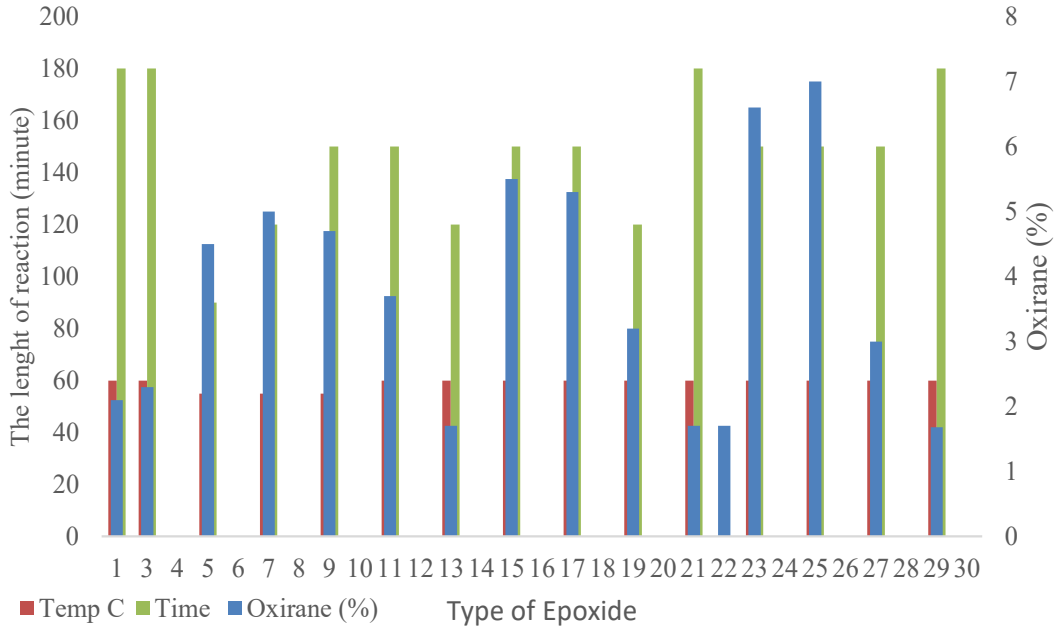

Figure 7. The Effect of Length of the reaction and Type of Epoxide to Oxirane Number

The polyols from renewable-based oil were significantly different from polyols derived from petroleum, the hydroxyl of vegetable oil for example was located at the center of the polyol chain. Compared to most polyols derived from petroleum, it has primary hydroxyl and secondary hydroxyl with only one covalent bond was lost from the petroleum chain, while in vegetable oil there was the possibility of 5-8 covalent bonds was lost, this was expressed as a disadvantage for natural polyols concerning the gelling reaction (Figure 8).

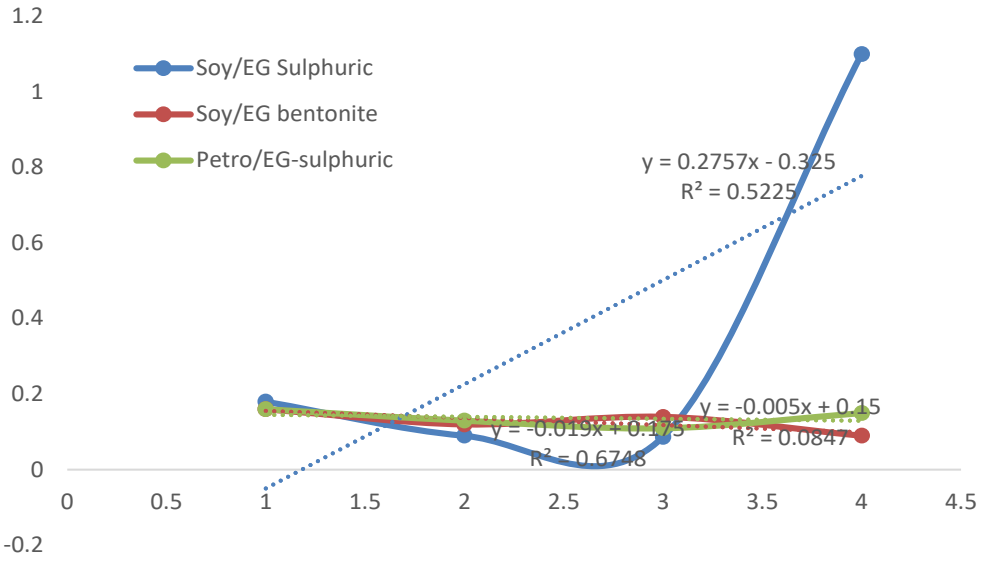

Figure 8. Comparing the Density to Petro based Polyol

The main ingredients for manufacturing the polyurethane foam are isocyanates, polyols, equipped with a catalyst. Water was important enough for the foam to expand properly. Several other additives such as chain extender, crosslinker, plasticizer, etc can be added if the resulting product has certain desired properties (Firdaus, 2011a). There are several conditions contributes to the failure of the foaming process. Such as water became major co-reagant for the foam to expand where it found the best range was 2.22 to 2.78% for foam to rise in maximum. One other thing should be concerned was the concentration of surfactant, it was fairly in the concentration 3% from the whole formula of polyurethane, where the polyol from the previous as intermediates should also have a good hydroxyl value from the reaction product which takes into account the reaction process duration (Figure 9).

Figure 9. The Failure of Polyurethane Foam in the absence of expanding reagent

Conclusion

The success of polyurethane production was determined apart from the materials used and the formula used, it determined by the processing include the length of the reaction. The chemical structure of polyols synthesized from renewable materials has a significant difference from polyols from petroleum materials. This of course will give an ultimate differentiation of mechanical properties. The tactic that can be done was to modify the unsaturated chain of

the triglyceride chain by observing the reaction time. From the results, it was found that this will affect the oxirane number and hydroxyl value as an intermediate to a polyurethane product. The formation of polyurethane was influenced by a perfectly swelling process, the absence of water causes the foam to fail to expand because it does not form CO_2.

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