

Relationship of Reaction Temperature on Phosphate Oligomers Reactivity to Properties of Soy-Polyurethane

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Abstract—Polyurethane foam (PUF) were prepared by reacting polyols synthesized from soy-oil into mixture of 2,4-Toluene diisocyanate (TDI) with 4,4'-Methylene Diamine Isocyanate (MDI) with ratio of 70:30. The polyols obtained via esterification reaction were categorized into different temperature of reaction and by used of varied concentration of phosphoric acid catalyst. The purpose of catalysts is to shifting selectivity to a desired and value added of product. The effect of stoichiometric balance (molar ratio of epoxide/ethylene glycol) to the concentration of the catalyst on the final properties was evaluated.

Keywords—temperature, phosphate, soy polyurethane

I. INTRODUCTION

POLYURETHANE industrial foams manufacturing rely significantly on fossil fuels and its derivatives as major reactants for the production of polyols. These non-renewable resources are rapidly being exhausted. Vegetable oils such as soybean oil (SBO) are increasingly replacing petroleum-derived products owing to its environment-friendly, biodegradable, and noncorrosive properties^{[1]-[3]}.

The use of vegetable oils as a starting material offers numerous advantages: for example, low toxicity, inherent biodegradability, and high purity,^{[4],[5]} thus they are considered to be one of the most important classes of renewable resources for the production of biobased polymers.^[6]

Traditionally, plant oil-based polyols have been prepared starting from triglyceride molecules. These polyols have been successfully prepared using different methods; most common is the epoxidation of carbon-carbon double bonds and further oxirane ring-opening with alcohols or other nucleophiles.^{[8],[9]} Other methodologies involved the transesterification with multifunctional alcohols^{[10],[11]} and the combination of hydroformylation or ozonolysis.^{[12],[13]} Unfortunately, limited attention has been paid to the preparation of diols and polyols from fatty acids, which can be easily isolated from oils^{[14]-[15]}

Vegetable oil-based polyols produce PUs that have excellent chemical and physical properties, such as enhanced hydrolytic and thermal stability.^[16] Although SBO-based polyols have

shown promising results in the production of urethane-formulated products,^{[2],[17]} replacement of substantial portions of polyol and isocyanate with soybean oil-derived epoxides is economically significant.

Phosphoric acid ($\text{o-H}_3\text{PO}_4$) has been extensively used in the preparation of a series of soybean oil phosphate esters for rigid polyurethanes.^{[1],[3],[17]} Guo and coworkers^[1] reported that soy-polyols having tunable hydroxyl content and phosphate ester functionality are possible by controlling amount of polar solvent and phosphoric acid content added to the reactants. The phosphoric acid does not only catalyze ring-opening reaction of epoxide soybean oil (ESBO) but also chemically become part of the polyol product.^{[1],[3],[17]}

The main objective of this study was to functionalize soybean oil using chemical reaction routes to produce polyols, develop catalyst formulations, and made a link analysis the effect of temperature reaction to soy polyurethane properties.

This objective included verification of synthesis. Acid number, oxirane values,^[17] of the polyol were measured to evaluate the effect of $\text{o-H}_3\text{PO}_4$ 85% on ring-opening hydrolysis.

II. METHODOLOGY

A. Materials

Soybean oil of RBD (Refined, Bleached, Deodorized) was obtained from Variatama Jakarta with Iodine value 53,89 gram Iod/100 gr sample, viscosity 0.91 kg/cm^3 , acid value 0,024 mgr KOH/ sample, Hydrogen Peroxide from Brataco Chemika, Acetic Acid from Merck Germany, and Sulphuric Acid from Tedia Company, Inc. $\text{o-H}_3\text{PO}_4$ 85% aqueous, epoxidized soybean oil was reacted with 0.5% $\text{o-H}_3\text{PO}_4$ added drop wise in a beaker under vigorous mechanical stirring at room temperature. A homogeneous and highly viscous product is obtained after mixing for 5 minutes.

B. Preparation of Soy based Polyol

The preliminary step on synthesizing polyol was made by mixing epoxide to alcohol; ethylene glycol in stoichiometric calculations. The mixed then reacted using catalyst $\text{o-H}_3\text{PO}_4$ with concentration of 0.5% (v/v).

The experiments were carried out in a 500 ml three necked round bottom flask which were equipped with a thermometer, mechanical stirrer. The whole apparatus was placed in a waterbath to maintain the temperature at range $75 \pm 0.5^\circ\text{C}$ which was measured inside the flask, and also inside the water bath. The obtained product was allowed to cool to room temperature.

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applied. Extractability of unreacted oil phase of the finely-cut samples was measured after 48 h of curing.

TABLE 1
PROPERTIES of SYNTHESIZED POLYOL

| Synthesized Epoxide (C) | Polyols | Epoxide/EG (mol/mol) | Oxirane (mgr KOH/gr) | Acid Number (mgr KOH/gr) | Water Content (%) |
|-------------------------|---------|----------------------|----------------------|--------------------------|-------------------|
| 50 | PO 1 | 1:01 | 4.7 | 2.9 | 0.022 |
| | PO 2 | 1:05 | 4.7 | 2.9 | 0.015 |
| | PO 3 | 1:07 | 4.7 | 2.2 | 0.048 |
| | PO 4 | 1:09 | 4.7 | 2.2 | 0.034 |
| 60 | PO 5 | 1:01 | 4.7 | 2.3 | 0.025 |
| | PO 6 | 1:05 | 4.7 | 2.2 | 0.029 |
| | PO 7 | 1:07 | 4.7 | 2.2 | 0.024 |
| | PO 8 | 1:09 | 4.7 | 2.2 | 0.048 |
| 70 | PO 9 | 1:01 | 4.7 | 2.2 | 0.027 |
| | PO 10 | 1:05 | 4.7 | 1.8 | 0.026 |
| | PO 11 | 1:07 | 4.7 | 1.8 | 0.033 |
| | PO 12 | 1:09 | 4.7 | 1.8 | 0.026 |

The amount of oligomers required in the synthesis were repeated with temperature differentiations. The batched charges are given in table 1. It was prepared as different polyols. The acid number of all polyols were found above value 1; which confirms the role of phosphoric acid in the esterification is not yet optimized.

C. Preparation of Flexible PU Foam

The foam formulation were polyols; a hydroxylation of soy epoxide to ethylene glycol (EG) using phosphoric acid; a homogeneous catalyst. The products respectively blend into petroleum polyol.

The foam were prepared by adding TDI (2,4):MDI (4,4') (70:30) to the polyol blend (soy polyol and petro polyol), which consisted of surfactant, and distilled water. The mixtures were vigorously mixed (stirring at 1000 rpm using high speed mixer for 1 min), then were poured into an open glass mold.

At the creamy stage (the mixture turning creamy), which was rose freely in an open mould. The foam then was removed from the mould and allowed to postcure for one day at room temperature before cut into the test specimens.

D. Polyurethane foam formation

Three types of foam has been prepared which are categorize into different temperature reactions. The route were using 0.5% o- H₃PO₄ for the catalysis reaction of epoxide which results a polyol; whereas the epoxide previously synthesized from temperature of 50,60, and 70°C. The preparation procedure of foam consisted into the following steps: (1) Mixing 25 polyol and 5 g TDI:MDI (70:30) in a 50-mL beaker on a hotplate equipped with stirrer (Moderate stirring at room temperature was employed to obtain uniform phase and consistency and also avoid bubbles formation); (2) Placing the samples in a 7cm x 11cm rectangular glass mold and degassed for 10 minutes at 45°C vacuum oven to get rid of CO₂, air trapped, or gases evolved during reaction; and 3) Postcuring samples for about 48 h at 45°C in an oven with no vacuum

III. RESULTS AND DISCUSSION

A. Characterization and Property Measurement of Soy Polyol

Polyols are made of molar ratio of epoxide to ethylene glycol of 1:1; 1:5; 1:7; 1:9 with constant phosphoric acid concentration 0.5% (v/v). The acid number were increased with increasing temperature reaction which are Polyol (50°C) > Polyol (60°C) > Polyol 70°C.

B. Chemical Structure of Soy Polyol

The chemical structures of the obtained PU foams were characterized by FTIR spectrophotometer (shimadzu) technique. It was employed to analyze the functional groups of soy based polyol (Figure 1a-b) shows the spectra of soy oil based polyol. The foam were measured according to ASTM E 1252-98; the presence of hydroxyl group in the soy oil- based polyol reflected by the absorbance peak at wave number of 1100 cm⁻¹ and 1050cm⁻¹.

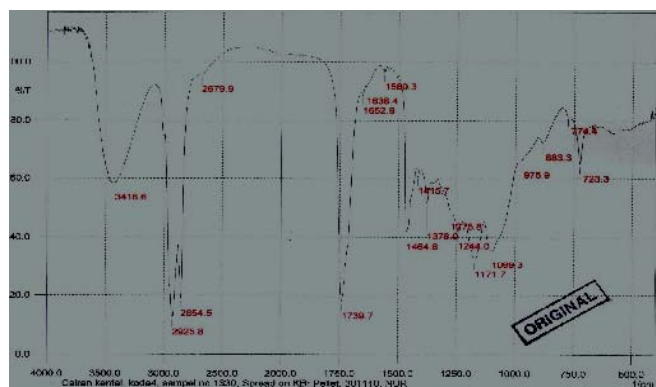


Fig.1 The FTIR spectrum of Soy Polyol

C. Polyurethane gel-times vs polyol reactivity

Gel times of polyurethane formation are a measure to the reactivity of polyols in the same isocyanate used. This work has conducted studies on gel times of polyurethane created from three type of temperature. The result of which are listed in fig.2. Which the temperature of 70°C is observed more reactive than 60 and 50°C.

TABLE II
CURING PROCESS OF POLYURETHANE

| | Cream Time (min) | | | Gel Time (min) | | |
|--------------|----------------------|-------|-------|----------------------|---------|---------|
| | Epoxide manufactured | | | Epoxide manufactured | | |
| epoxide*/alc | 50 | 60 | 70 | 50 | 60 | 70 |
| 0.042361111 | 23.45 | 36.96 | 37.11 | 4.17.42 | 3.16.95 | 3.26.52 |
| 0.045138889 | 19.61 | 20.12 | 21.15 | 2.44.39 | 2.03.42 | 2.20.97 |
| 0.046527778 | 22.57 | 22.33 | 21.46 | 2.32.65 | 2.44.34 | 2.56.30 |
| 0.047916667 | 20.78 | 21.51 | 22.5 | 2.50.43 | 2.66.41 | 2.60.23 |

The concentration ratio of epoxide to alcohols were 1:1; 1:3; 1:5; 1:7 and 1:9 (mol/mol) (table 3). The cream time occur in the reaction was differentiate to temperature reaction which were 50, 60, and 70°C. It seems the temperature used in the epoxide synthesis effected to the cream time of the polyurethane; epoxide 50 < 60 < 70 but in other way the gel time was randomly.

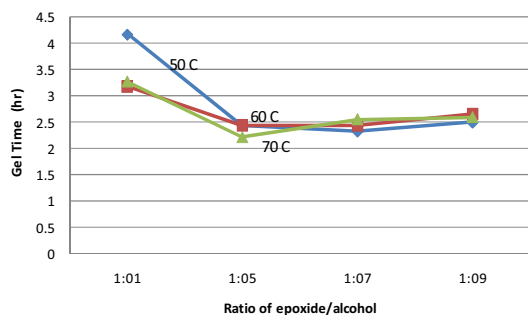


Fig 2 Polyurethane Gel Times

The obtained PU foams were characterized by using density measurement, the foams were cut into specimens with dimension of 1cmx1cm x1 cm. The specimens were accurately weighed to determine their densities using the equation, density = mass/ volume. The density for each foam was ascertained using average value. Many factors and conditions can influence the foaming process of flexible cellular polyurethanes. The density of PU can be seen on table 3.

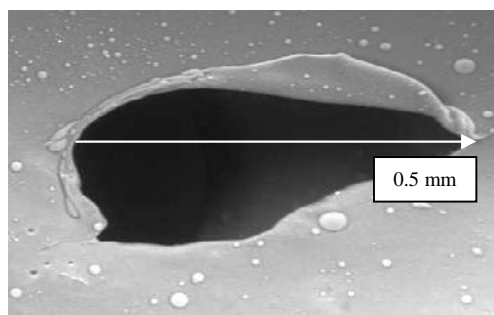
TABLE III
THE DENSITY of POLYURETHANE FOAM

| Temp. C | Product Polyol | | | Polyurethane | | Designation Urethane | Density (gr/cm3) | Density (pcf) |
|---------|-------------------|-------------|------------------|-----------------|-------|----------------------|------------------|---------------|
| | Molar R: Epoxide/ | Acid Number | Petro Polyol(ml) | Soy polyol (ml) | | | | |
| 50 | 1:01 | 2.9 | 20 | 5 | PU 1 | 0.3257 | 20.32368 | |
| 50 | 1:05 | 2.9 | 20 | 5 | PU 2 | 0.2792 | 17.42208 | |
| 50 | 1:07 | 2.2 | 20 | 5 | PU 3 | 0.2446 | 15.26304 | |
| 50 | 1:09 | 2.2 | 20 | 5 | PU 4 | undefined | undefined | |
| 60 | 1:01 | 2.9 | 20 | 5 | PU 5 | 0.3015 | 18.8136 | |
| 60 | 1:05 | 2.2 | 20 | 5 | PU 6 | 0.2724 | 16.99776 | |
| 60 | 1:07 | 2.2 | 20 | 5 | PU 7 | 0.2154 | 13.44096 | |
| 60 | 1:09 | 2.2 | 20 | 5 | PU 8 | 0.239 | 14.9136 | |
| 70 | 1:01 | 2.2 | 20 | 5 | PU 9 | 0.2036 | 12.725 | |
| 70 | 1:05 | 1.8 | 20 | 5 | PU 10 | 0.2055 | 12.8232 | |
| 70 | 1:07 | 1.8 | 20 | 5 | PU 11 | 0.2146 | 13.39104 | |
| 70 | 1:09 | 1.8 | 20 | 5 | PU 12 | 0.2542 | 15.86208 | |

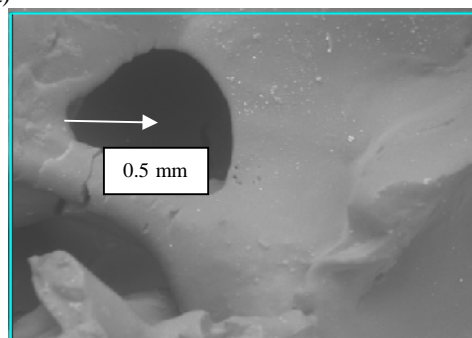
D. Cell Morphology

SEM micrograph was used to take images of cured solid polyurethane foams polyurethane, the differentiate of temperature effected to the morphology of PU foam. Figures 3-4 shows the scanning images of selected samples. Morphology of foam samples with formulation of polyurethane depicted the cell nucleation tends to occur unhomogeneous. The foam cell were irregular with mainly in large cells. The dominant cell nucleation mechanism in temperature reaction 70°C is assumed to be more homogeneous nucleation. Than 50 and 60°C. Which seems voids at temperature of 70°C is smaller than formed at

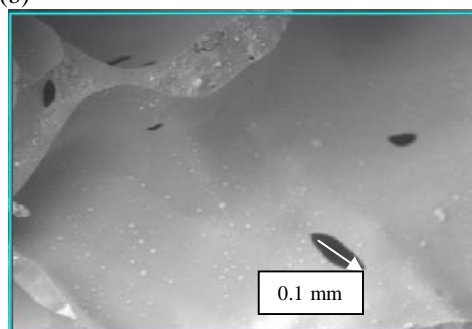
temperature of 50°C. Although the manufacture of polyols made in the same temperature is 75°C.



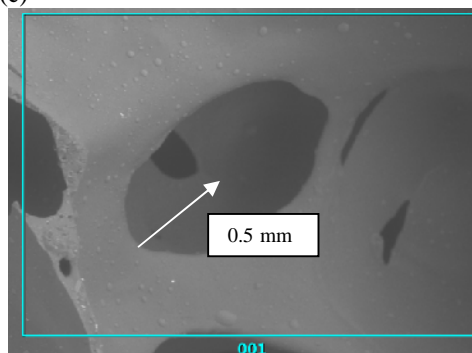
(a)



(b)



(c)

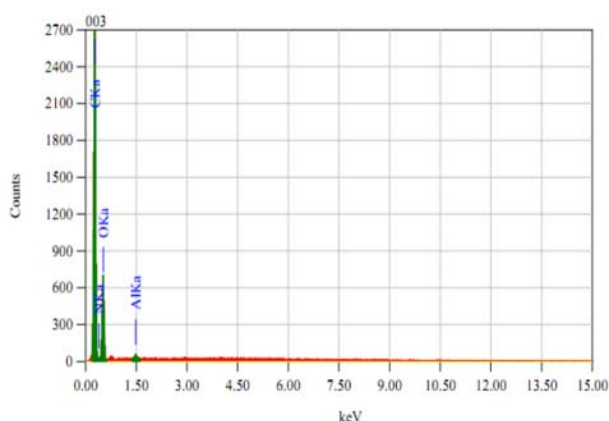


(d)

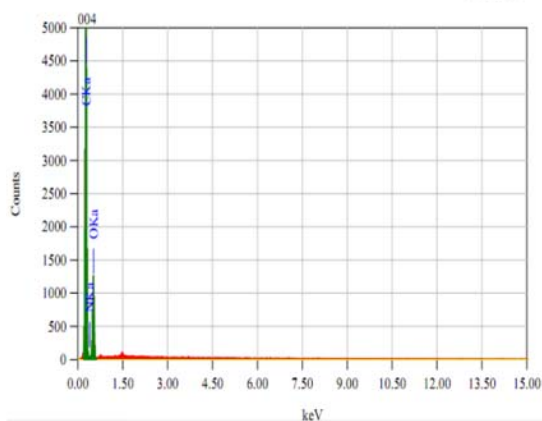
Fig. 3 High magnification SEM images of PU with temperature differentiations of (a) PU 12 at 70°C (b) PU 4 at 50°C (c) PU 9 at 70°C and (d) PU 1 at 50°C

The temperature reaction during formation of epoxide can effected to the properties of polyurethane. In general the mass of Carbon and Nitrogen of polyurethane foams are increasing by temperature of 70°C either initiated by

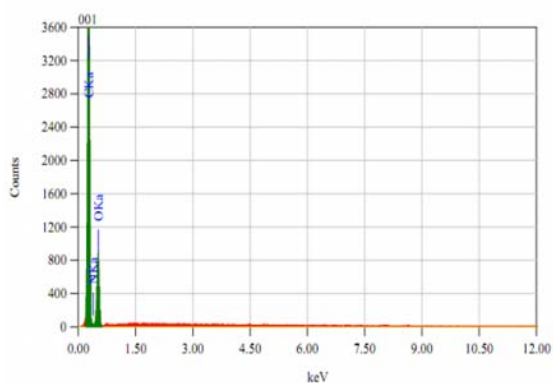
temperature 50 and 60^o. At concentration of 1:7 and 1:9 there was mass of atom K which are detected from XRD. This remain to be a question of which tends to decline with the rising temperature up to 70^oC. the percentage of C, N tends to increase with increasing of temperature, but the percentage of K tends to decline, with the increase concentration to 1:7 and 1:9 temperature rise which occur otherwise decline in percentage of N and K.



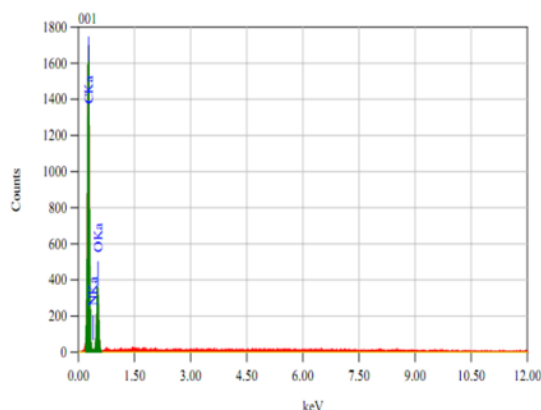
(a) PU 12 at 70^oC



(b) PU 4 at 50^oC



(c) PU 9 at 70^oC



(d) PU 1 at 50^oC

Fig 4. EDX spectra of PU with temperature differentiations

In table 4 tried to summarizes the relationship between temperature and the atomic compositions of PU.

TABLE IV
 THE EFFECT OF TEMPERATURE on MASS and ATOMIC COMPOSITION OF PUR

| Temp. (oC) | Ratio Epoxide/ alcohol (mol/mol) | | | | | | | | | |
|------------|----------------------------------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
| | 1:01 | | 70 | | 1:05 | | 60 | | 1:07 | |
| | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% |
| C | 41.17 | 46.71 | 41.47 | 46.86 | 40.56 | 45.97 | 43.47 | 48.65 | 42.51 | 47.94 |
| N | 26.21 | 25.5 | 28.93 | 28.03 | 28.51 | 27.71 | 32.27 | 30.97 | 28.95 | 27.99 |
| K | 32.62 | 27.79 | 29.6 | 25.11 | 30.93 | 26.32 | 24.26 | 20.38 | 28.3 | 23.96 |
| Al | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.24 | 0.12 |

| Temp. (oC) | Ratio Epoxide/ alcohol (mol/mol) | | | | | | | | | |
|------------|----------------------------------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
| | 1:07 | | 60 | | 1:09 | | 50 | | 70 | |
| | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% | Mass % | Atom% |
| C | 40.79 | 46.45 | 40.83 | 46.27 | 41.2 | 46.71 | 40.91 | 46.52 | 40.43 | 45.96 |
| N | 25.3 | 24.7 | 27.97 | 27.19 | 27.08 | 26.33 | 26.35 | 25.7 | 26.83 | 26.16 |
| K | 33.47 | 28.62 | 31.2 | 26.55 | 31.59 | 26.89 | 32.23 | 27.52 | 32.56 | 27.79 |
| Al | 0.44 | 0.22 | 0 | 0 | 0.14 | 0.07 | 1.486 | 0.26 | 0.18 | 0.09 |

IV. CONCLUSIONS

Polyurethane were prepared from three type categorizations of soy polyol; which are temperature reaction differentiations; 50, 60, and 70^oC. It was found the temperature much effected to the void formations. The increasing temperature will result smaller gas trapped in the bulk whereas gives smaller cellular formation. The sequential temperature of fine cellular are 70>60>50^oC. The density as one of the parameter of product firmness was best at 50^oC, on contrary to SEM images.

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