Synthesis and Characterization of Soy-Based Polyurethane Foam with Utilization of Ethylene Glycol in Polyol

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Abstract

The use of vegetable oils on replacing petroleum has attracted attention of many researchers. The chemical structure of vegetable oils are different from petrochemicals, so the structure of soybean oil has to be chemically modified through its unsaturated fatty acid chain in triglyceride. A two step process was conducted for the preparation of soy-polyol in designated temperatures; 50 °C, 60 °C, and 70 °C. Ethylene glycol (EG) as co-reagent was taking part in soy-polyol synthesis, and the soy-polyol was used as a sole polyol for polyurethane synthesis. Referred to the previous study, the existence of EG in polyurethane synthesis can improved physical properties of polyurethane foam. The aim of this research is using soy-derived polyol for petro-polyol replacement aligned with drop-off of petro-derived reagent; EG. One step process was applied for the foam synthesis. The ingredients for foam synthesis; soy-polyol, Toluene diisocyanate (TDI): a mixture of 2.4 and 2.6 isomers in ratio of 80:20 (TDI T-80), surfactant, and distilled water. The synergize of stoichiometry ratio of co-reagent EG to soy-epoxide with best temperature, with the absence of EG in polyurethane formula can produce an ultimate property of polyurethane foam.

Abstrak

Sintesis dan Karakterisasi Busa Poliuretan Berbasis Kedelai Menggunakan Etilen Glikol dalam Poliol. Penggunaan minyak sayur sebagai pengganti minyak bumi menjadi perhatian banyak peneliti. Struktur kimia minyak sayur berbeda dari minyak bumi, untuk itu diperlukan modifikasi secara kimia rantai tak jenuh asam lemak rantai trigliserida dalam minyak kedelai. Proses dua tahap dilakukan untuk membuat poliol kedelai menggunakan suhu yang telah ditetapkan; 50 °C, 60 °C, dan 70 °C. Etilen Glikol (EG) sebagai co-reagen mengambil bagian dalam sintesis poliol kedelai, dan poliol kedelai menjadi poliol tunggal dalam sintesis poliuretan. Berdasarkan hasil penelitian terdahulu, ditemukan bahwa penggunaan EG pada sintesis poliol dapat memperbaiki sifat fisika busa poliuretan. Tujuan penelitian ini adalah menggunakan poliol kedelai menggantikan poliol minyak bumi dan sejalan dengan menghilangkan reagen yang terbuat dari minyak bumi; EG. Proses satu tahap dilakukan pada sintesis busa. Bahan yang digunakan untuk sintesis busa adalah poliol kedelai, Toluen diisosianat (TDI) adalah campuran isomer 2,4 dan 2,6 pada perbandingan 80:20 (TDI T-80), surfaktan, dan air suling. Sinergi perbandingan stoikiometri antara co-reagen EG dengan epoksida kedelai pada suhu terbaik, meski tanpa penambahan EG pada pembuatan poliuretan menghasilkan sifat akhir busa poliuretan.

Keywords: ethylene glycol, foams, polyol, soy polyurethane

1. Introduction

The global economy hasten the development of world polyurethane production and consumption [1-2]. Renewable resources have attracted the attention of many researchers because of their potential to replace petrochemical derivatives. New polymers must compete with petrochemicals in the area of economics and performance [3-6]. Soybeans are an inexpensive, readily available renewable resource that provide an excellent platform for polymeric materials.

Soybean oil is mainly composed of triglyceride molecules derived from unsaturated fatty acid such as linoleic acid (ca. 50%, two double bonds) and oleic acid (ca. 25%, one double bond) [7], oleic acid (22%), linoleic acid (55%), and linoleic acid (7%) [8], fielding an average number of 4.6 double bonds per molecule.

Although the double bonds as reactive sites, they needs to be functionalized for prepared polymers [9]. Though many vegetable oils are heterogeneous in composition and lack hydroxyl groups, the structure of triglyceride polyurethane based on vegetable oils is commonly water resistant and has excellent properties that permit a wide range of applications.

Prior to their use in the preparation of polyurethane, soybean oil must be converted into polyols by means of chemical modification through epoxide soybean oil (ESO) reactive oxirane functionality by opening ring reactions to nucleophilic compounds [10-11].

The application of different alcohols as ring opening agents and chain extenders affects soft segment content in polyurethane foams [12], usually a short chain poly-hydroxy, which is defined as a low molecular hydrocarbon that produces a hard segment [13]. To increase the reactivity of soy epoxide, EG has been used as a co-reagent, in which role it has acted like a nucleophile during alcoholysis reaction. Several studies have reported success in the use of chain extension in the reaction, forming hard segments of polyurethane. Due to its nonselective reaction during the transformation to polyols, EG may cause the formation of greases and waxes [14].

There are many methods for tailoring the properties of polyurethane [15-17], such as by controlling the functionality of polyols (oligomers), introducing different substituents into the polyol structure, and varying the stoichiometry.

Polyols are the key components in polyurethane synthesis. Hydroxyl groups in polyol components are prepared to react with isocyanate to form urethane bonds. There are methods for the conversion of vegetable oils into polyols, each of which has advantages and disadvantages. The diversity in the degree of unsaturation allows the synthesis of polyols with variable hydroxyl numbers [18]. Polyols used to produce flexible foams should have low hydroxyl values (generally LOH < 100 mgr KOH/gr) and high molecular weight (Mn generally between 3000 gr/mol and 6000 gr/mol) for the best final products [19]. The content of the hydroxyl groups in polyols can be designed by choosing appropriate conditions for epoxidation reaction. The properties of polyol are summarize in Table 1.

Table 1. General Polyol Properties

Uses	Molecular Weight (Daltons)	Hydroxil Number (Mgr KOH/gr)
Flexible Polyols	2000-10000	18-56
Rigid Polyols	250-700	300-700
Variable Polyols	700-2000	0-280

In this work we have elaborated the molar ratios of epoxide/EG, with temperatures based on the previous findings. The goal is to identify the influence of ethylene glycol (EG) on the properties of polyurethane foams, the possibility of removing EG from the polyurethane formula, and the effect of EG to foam properties.

2. Methods

Materials selection. Food-grade soybean oil produced by Sione Darby Edible Products Ltd, Singapore, was purchased from a local grocery store. The oil had an iodine value of 53.89 gr Iod/100 gr sample, and viscosity at 27 °C was 443 cP.

The polyol was made by stoichiometry with epoxide/EG ratios of 1:01, 1:05, 1:07, and 1:09 (mol/mol) at three designation temperatures, 50 °C, 60 °C, and 70 °C. 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.

The optimized epoxidized soybeans obtained from previous work (oxirane number 5.1%) were used as the oil based for the synthesis procedure. The chemicals used in this research were acetic acid, sodium carbonate, sodium hydroxide, hydrogen peroxide (30%), sulfuric acid, EG, ethanol, acetic anhydride in pyridine, and o-phosphoric acid (85%).

Polyol Preparation. Soybean oil was treated with EG to form polyol, the intermediate product of the polyurethane synthesis. The roles of EG in polyurethane production at varied temperatures were a main part of the study.

The first step of the reaction was to convert the unsaturated fatty acids in the triglycerides to soy epoxide with peracetic acid (acetic acid and hydrogen peroxide), using sulfuric acid as a catalyst. The epoxide was made from the epoxidation of soybean oil using a $CH_3COOH:H_2O_2$ ratio of 1:01, 1:05, 1:07, and 1:09 (mol/mol) at 50 °C, 60 °C, and 70 °C. The hydroxylation of epoxide was done using an epoxide/EG concentration of 1:03, 1:05, 1:07, and 1:09, and o-phosphoric acid 85% at 1% (v/v).

Foam Preparation. A one-step process was use to prepare 12 formulas of polyurethane foam. Isocyanate and polyol were combined to provide the end-product foam. The polyurethane was synthesized using 5 mL of TDI mixture of 2,4 and 2,6 isomers (TDI T-80) at a ratio of 80:20, soy polyol 8 mL, EG 4 mL, surfactant 2 mL, and distilled water 1 mL. The foam product was then compared to the compounds lacking EG. Compound R#1 was a blend of soy polyol and synthetic

polyol with no EG; R#2 was soy polyol with neither synthetic polyol nor EG; R#3 was synthetic polyol without EG. All of these were produced via polyurethane synthesis.

3. Results and Discussion

Epoxide as pre-polyol. The impact of the temperature and concentration of peracetic acid to acid is summarized in Figure 1. The acid numbers (mgr KOH/gr sample) indicate the number of carboxylic acid functional groups per gram sample. Epoxide as an intermediate product of polyol needed to be optimized before the procedure continues. At higher temperatures the final product became slightly darker, but the acid number decreased. The reaction profile was plotted separately.

The results at 70 °C for concentration 1:05, 1:07, and 1:09 (mol/mol) did not follow the theory that higher temperatures lead to increased acid numbers. The free acids promote an autocatalytic reaction. One possible explanation for this behavior is that the polymerization of the polyol at 50 °C and 60 °C was not complete. Monteavaro *et al.*, conducting research at 65 °C, found that the influence of reaction time on acid number was not linear. Their result after 60 min was 1.8 (mgr KOH/gr), after 100 min 2.2 (mgr KOH/gr), after 120 min 1.8 (mgr KOH/gr), and after 150 min 2.0 (mgr KOH/gr) [20].

The epoxy content was analyzed using AOCS methods, oxirane ring is epoxidised materials. At lower temperatures, epoxide is known to react with acid to reduce the acid number. During the oligomerization of soy-based epoxide, the oxirane numbers steadily increase. The reaction of each group to alcohol results in oligomers with oxirane numbers of 4.6-5.1%, as shown in Figure 2.

Figure 2 illustrates that at 50 °C the oxirane number is as high as 5.1% with acid number 1.8 (mgr KOH/gr). At 60 °C the lowest oxirane number was 4.6 (mgr KOH/gr) with acid number 2.2%.
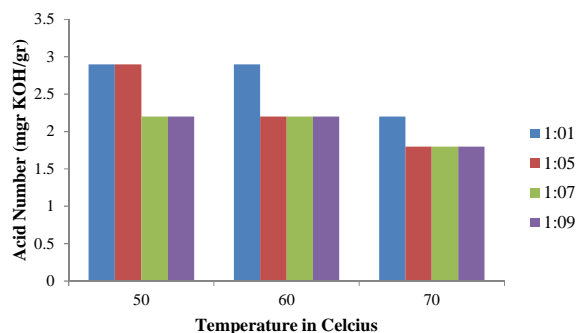
At higher temperatures, the oxirane number decreased during soybean heat polymerization. This can be attributed to the cleavage of the ester bond. Monteavaro *et al.* reported an oxirane number for soy epoxide of 4.9% and 2.7% [21].

The viscosity of polyol is a function of time and temperature, which was observed at 560.431 cP at 30 °C using an Ostwald viscometer.

Better cross-linking performance correlates to the hydroxyl number of soy polyols. This portion can initially be achieved when soy epoxide exists with the addition of EG, which can increase functional groups in polyols.

The concentration of epoxide/EG for polyol synthesis was 1:03, 1:05, 1:07, and 1:09 (mol/mol), as shown in Figure 3.

EG was added in the first step of epoxidation to control hydroxyl moieties, which can prevent the secondary reaction with hydroxyl groups, in the final product. In this research we found an epoxide/EG ratio of 1:07 resulted in the highest hydroxyl number.

In order to compete with petrochemical polyols, soy polyols should have the right functionality, molecular weight, and hydroxyl number [22].
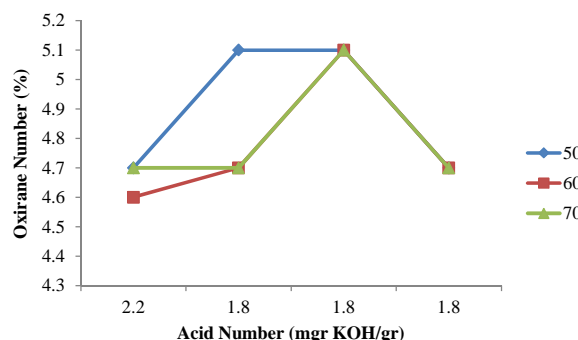
Figure 2. Oxirane Number as a Function of Temperature and Acid Number

Figure 1. Acid Numbers of Epoxide as a Function of Temperature and Concentration
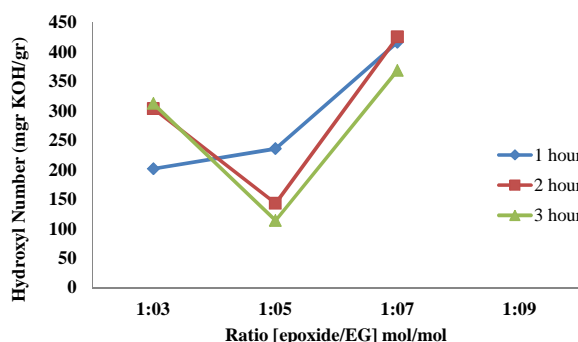
Figure 3. Influence of Epoxide/EG Ratio on Time of Reaction for Polyol Synthesis

In this work we have found a concentration of epoxide/EG of 1:05 (mol/mol) as the optimized condition for all reaction times. The concentration 1:09 (mol/mol) was found the gel formation. The hydroxyl observed for 1 hr, 2 hr, and 3 hr are 236.3 mgr KOH/gr, 143.4 mgr KOH/gr, and 224.2 mgr KOH/gr, respectively, with respective functionality of 2.5, 2.2, and 2.4, and respective molecular weights of 478.8, 782.5, and 500.5. These specifications are suited to rigid foam.This research has concluded that the best concentration for polyol synthesis is an epoxide:EG ratio of 1:05 (mol/mol) for the soy-based polyol.

Foam with a hydroxyl number below 100 mgr KOH/gr usually shrinks within a few days at room temperature [23], unlike foam from rapeseed oil, whose hydroxyl number is 255 mgr KOH/gr, sunflower oil (271 mgr KOH/gr), and linseed oil (320 mgr KOH/ gr) [24]. Guo *et. al* studied hydroxyl numbers using hydroformylation methods and found 230 mgr KOH/gr with the rhodium process and 67 mgr KOH/gr with the cobalt process.

Relative conversion to oxirane. A temperature of 50 °C was shown to produce the best conversion to oxirane, with a conversion of nearly 75% to ratio of epoxide/EG 1:05 (mol/mol) and 1:07 (mol/mol). Increasing the temperature to 70 °C decreased conversion to an average of 63%.

The percentage of relative conversion to oxirane was determined by using the following formula [25]:

$$RCO = (OO_{exp} / OO_{theo}) \times 100 \qquad (1)$$

OO_{exp} is oxirane content in epoxide, which was experimentally determined. OO_{theo} is theoretically determined from 100 gr oil using the following expression:

$$OO_{theo} = [(IV_0/2A_i)]/[100 + (IV_0/2A_i)A_o] \times A_o \times 100 \qquad (2)$$

A_i is the atomic weight of iodine and A_o is the atomic weight of oxygen, and IV_0 is the initial iodine value of oil.

The considerable drop in the relative conversion to 68.6% reflects an excess of EG; that amount of catalyst is not necessary for the reactions. Factors such as high temperature and time of reaction had a minor impact on yield. The molar ratio of epoxide/EG 1:07 or higher may have caused a slow conversion rate because of excessive dilution of the epoxide. Increasing the ratio will also rearrange the product and result in the production of ketones. This implies incomplete epoxide conversion.

Rios has reported that at a constant temperature after 6 hr the conversion was 59% and after 24 hr the conversion
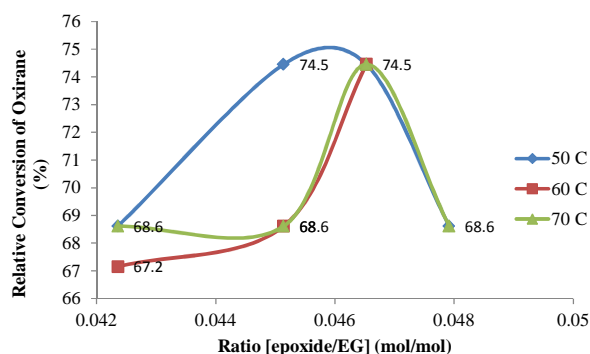
Figure 4. **Effect of the Ratio of Epoxide/EG to Relative Conversion**

was 89% [26]. The lower conversion of polyol leads to poor mechanical strength in the corresponding polyurethane [27]. In an attempt to increase the conversion to the desired level, the molar ratio of epoxide/EG was 1:05 (mol/mol) at 50 °C. This slower conversion has yielded more stable oxirane rings than those at higher temperatures. Temperatures above 50 °C are detrimental to oxirane rings, which can form glycol, an unwanted by-product. This condition is not acceptable because exothermia when hydrogen peroxide is added during epoxide synthesis leads to explosions.

Foam characteristics. The foams rose freely. After they had risen, each of the polyurethane foams were placed in open air for proper curing.

The polyurethane foam was tested for elasticity, firmness, and constant deflection or compression (CDC). It was also tested using ball rebound for impact resilience (IR), a measure of elasticity, bounce, or springiness, expressed as % of return or % resilience.

Foam density. Density was measured as per ASTM 1622-03, mass/volume, which can expressed in pounds per cubic foot (pcf) or in gram per cubic centimeter. All concentrations at a temperature of 50 °C have higher density than they do at 60 °C and 70 °C; for the concentration 1:09 (mol/mol), the density was less at all temperatures.

Flexible polyurethane foam is available in a broad range of densities. All of the products were in a tolerable range, from as low as 1.2 pcf to as high as 2.5 pcf. Density of reference is 0.9 to 2.5 pcf [27]. The density usually varied with the hydroxyl number of each polyol mixture.

Density is the main factor in determining properties. Increasing a foam's density will increase that foam's mechanical strength. This property is related to the foam's firmness, which is its ability to re-form to its original height. Resilience is extremely important for

flexible foam, which is affected by its cell morphology, specifically by soft segments and hard segments.

In certain well-defined circumstances, density can directly affect durability. The major durability issue is in the load-bearing characteristics and softening. The resilience of density 2.3 pcf, which was tested for at 50 °C, cannot be seen in Figure 5. Neglecting it is justified because the foam rose imperfectly; the elasticity was 0%.

The density obtained from conditions at 60 °C and 70 °C had the resilience values of 14% and 7%, respectively. This is related to the production process. The foam's resilience seems to be significantly affected at a temperature of 70 °C, with $R^2 = 0.89$ at 70 °C; for temperatures of 50 °C and 60 °C, $R^2 = 0.445$ and $R^2 = 0.188$, respectively.

The resilience of the foams in the investigation were in the range of 6–18%, whereas R#1, R#2, and R#3 are 2%, 12%, and 13% respectively. The resilience of the reference foam was 12% and 13% [26]; Pawlick found 8% and 11% [28].

Constant deflection compression test. The CDC test consists of foam deflection to 50% of its initial thickness; changes are measured after recovery. A lower CDC set indicates the foam is more flexible and recovers its thickness better.

In our investigation the rebound of a ball was observed as the effect of the polyol content in the polyurethane. This directly related to the reaction condition that was undertaken during the process.
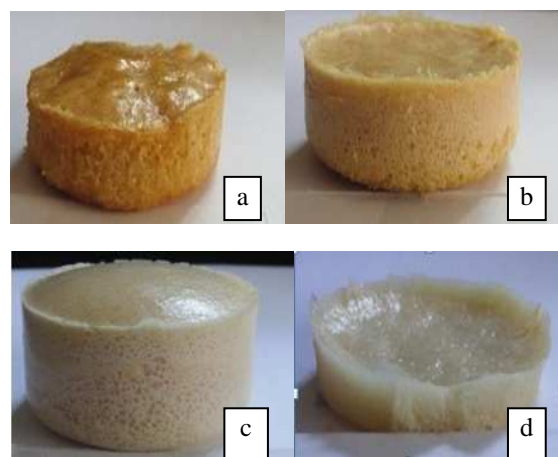
Polyurethane (PU) formula without EG. Based on the performance of polyurethane foam derived using EG, which has previously been proven suitable for flexible foam, testing PU made without EG seems to be unnecessary. The performance of foams made with EG is much different from foams made without EG. Compared to the mixed blend of soy and synthetic
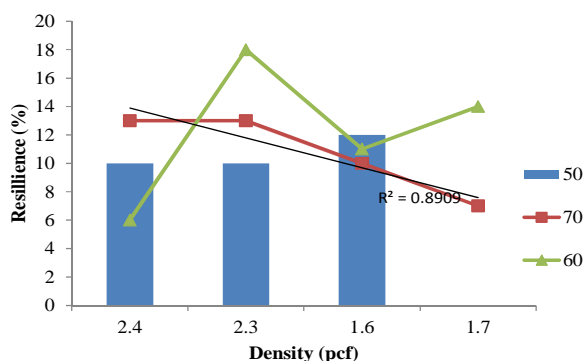
Figure 5. Influence of Temperature on Foam Density and Resilience
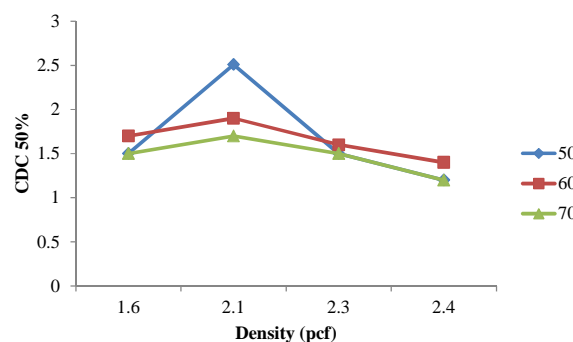
Figure 6. Influence of Temperature, and Foam Density, on CDC 50%

Figure 5. (a) Soy-based PU with EG, (b) R#1 (Blend of Soy-Synthetic-based PU without EG), (c) R#2 (Soy-based PU without EG), (d) R#3 Synthetic based PU

formula, which has resulted in more voids, this is much affected by the foaming process.

Synthetic-based polyurethane foams seem not to be appropriate for the intended use because they rise imperfectly and tend to be stickier.

4. Conclusions

In all observed cases of epoxide hydroxylation, the temperature contributes to the ultimate properties of the polyurethane foam products produced. EG has not yet performed its role desirably in polyurethane synthesis, even though generally the hydroxyl number and physical properties of flexible polyurethane are in the acceptable range. It can be concluded that EG does not need to be included in the formula.

Attempts to replace petrochemicals with soybean polyol are in progress, with exclusion of EG from the polyurethane formula becoming attractive from an economic point of view.

Acknowledgements

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