

Soy-Based Polyols from Oxirane Ring Opening by Alcoholysis Reaction

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ABSTRACT: A screening study was conducted to identify a catalyst that promotes epoxy ring opening of full epoxidized soybean oil (ESBO) avoiding side reactions at low concentration and temperature. Six catalysts different catalyst: formic acid, phosphoric acid, POLYCAT[®] 5, *p*-toluenesulfonic acid monohydrate, POLYCAT[®] SA-1, and DABCO[®] BL17 were evaluated in terms of acid number, oxirane oxygen content, and color analyses. *p*-Toluenesulfonic acid shows a particular behavior that promotes the reaction resulting in a maximum oxirane oxygen content reduction; low acid number and color index compare to the others catalyst. To create an alkoxy hydroxy ESBO molecule, ESBO was combined with methanol and ethylene glycol using 0.5% by wt of *p*-toluenesulfonic acid at 130, 150, and 170°C for different reaction times. Optimal

conditions for oxirane ring opening by alcoholysis reaction were determined varying temperatures and reaction times. FTIR spectrum confirmed the emergence of hydroxyl groups in the alkoxy hydroxy ESBO polyol sample. The polyol sample G was characterized in terms of its hydroxyl number and its potential of replacing up from 50–100% of the petroleum-based polyol in waterborne rigid polyurethane foam application. All polyurethanes foams were evaluated to determine their thermal conductivity, density, and compressive strength properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2552–2560, 2009

Key words: epoxidized soybean oil; polymerization; oxirane ring opening; alcoholysis; polyols

INTRODUCTION

Polyols plays an important role in the urethane industry and conventionally, a majority of them are derived from petroleum crude oil. The use of petrochemicals such as polyester or polyether polyols is disadvantageous in terms of energy, production, and transportation cost and the most importantly it is a nonrenewable resource. Consumer demand for “greener” products continues to grow in view of the environmental and sustainability aspects, new polyols have been prepared from vegetable oils. Soybean oil is more versatile, less costly, renewable, and environmental friendly component used to prepare vegetable-based polyols.

One of the important vegetable-derived polyols is epoxidized soybean oil (ESBO). ESBO can be synthesized by reacting hydrocarbon fatty acid glyceride from vegetable oil, such as soybean oils with peroxoacetic or peroxoformic acid in presence of solvent at mild temperatures.^{1–3} ESBO is used as plasticizers, lubricants, cross-linking agent, stabilizers, and pre-

polymers. Also they are used as intermediates for polyol production used in polyurethane and plastic resins after the oxirane ring is opened by hydroxylation or alcoholysis. Subsequently, modifications of ESBO, to improve the mechanical properties of the rigid polyurethane, can be achieved by adding extra hydroxyl functional groups to the polyols.^{4–7}

A variety of chemical modifications of ESBO are possible through epoxy moiety, and one of the most commonly used is the ring opening reaction with nucleophilic compound. Hydrolysis of epoxy rings in the presence of acids (phosphoric acid, sulfuric acid, formic acid, and acetic acid) was previously studied before.^{8–12} Different pathways for cycloaliphatic epoxides were also studied previously.^{13,14} Reaction of cyclohexene oxide with methanol and acetic acid gave four major products: two alcohol content compounds (cis and trans configuration) and two ether compounds (acetoxo and methoxy)¹⁵. Alcoholysis reactions using 2 ethylhexanol, 1-butanol, 1-decanol, and methanol were evaluated for lubricant formulations.^{16,17} Synthesis of alkoxyated of triacylglycerol from ESBO were developed using perchloric acid for epoxy ring opening.¹⁸

Several polyols derived from ESBO can be used to make aqueous polyurethane dispersions for flooring, hydrocarbon blends for coatings applications, elastomers, and polyurethane foam materials.^{19,20} Polyurethanes are formed by the reaction of polyisocyanate

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TABLE I
Description of Catalysts Used on the Screening Study

Catalyst	Description
POLYCAT [®] 5	Pentamethyldiethylenetriamine
DABCO [®] BL17	Acid-blocked version of 70% bis(dimethylaminoethyl) ether, 30% dipropylene glycol
Phosphoric acid	ACS reagent \geq 85%
Formic acid	ACS reagent \geq 88%
POLYCAT [®] SA-1	Heat-activated catalyst based on 1,8-diaza-bicyclo (5,4,0) undecene-7
<i>p</i> -Toluenesulfonic acid monohydrate	Fluka \geq 99% mixture of isomers

with a polyhydroxyl (polyol) compound. Rigid polyurethane foams can be used as polymeric concrete components, insulating materials, sealants, and others.²¹

Our research group is focused on the development on soy-based polyols production and polyurethane foam applications. In this study, ESBO was combined with ethylene glycol (EG) and methanol (ME) to produce a molecule that contains one epoxy moiety for every two alcohol moieties at low temperature using catalyst to promote the reaction. The purpose of this study were identifying a catalyst that promotes the epoxy ring opening reaction avoiding side reactions, kinetics study of the alcoholysis reaction or addition polymerization of ESBO, followed by polyol production of a preferred reaction condition to use in the water-blown rigid polyurethane foam formulation study.

EXPERIMENTAL

Materials

ESBO (7.0% oxirane oxygen content, VIKOFLEX[®] 7170) was purchased from ATOFINA Chemicals Inc, Philadelphia, PA. EG (HPLC grade 99%), ME (HPLC grade 99%) were obtained from Fisher, Houston, TX. Formic acid (ACS reagent \geq 88%), phosphoric acid (ACS reagent \geq 85%), and *p*-toluenesulfonic acid monohydrate (Fluka \geq 99% mixture of isomers) were purchased from Sigma-Aldrich, St. Louis, MO. POLYCAT[®] 8, DABCO[®] DC5357, POLYCAT[®] 5, POLYCAT[®] SA-1, and DABCO[®] BL 17 were acquired for free from Air Products and Chemicals, Allentown, PA. VORANOL[®] 490 (petroleum-based polyether polyol) and PAPI[®] 27 (polymeric diphenylmethane diisocyanate, MDI) was purchased from Dow Chemical, Midland, MI.

Methods

Screening study

For the screening reaction study, a 100 mL three-necked round bottom flask was charged with 50 g of ESBO, 3.10 g of EG, and 0.25 g (0.5% wt) of catalyst.

Six different catalysts were evaluated formic acid, phosphoric acid, POLYCAT[®] 5, POLYCAT[®] SA-1, DABCO[®] BL17, and *p*-toluenesulfonic acid monohydrate in terms of the oxirane oxygen content, acid number, and color index. The reactions were run for 2 h at 150°C for each catalyst. Catalyst descriptions are illustrated in Table I.

Alcoholysis reaction

In the epoxy ring opening reaction, ESBO (200 g, 0.20 moles), EG (12.41 g, 0.20 moles), ME (4.80 g, 0.15 moles), and *p*-toluenesulfonic acid monohydrate (1.0 grams, 0.5% wt) were placed in a 250 mL Parr[®] reactor equipped with a thermocouple, stirrer, heating element, and Omega controller. Polyols properties were evaluated for different reaction times and temperatures, between 2 and 9 h at 130, 150, and 170°C, respectively.

Analytical methods

The final product was analyzed for acid number, iodine number, hydroxyl number, oxirane oxygen content, saponification value, color, and dynamic viscosity. The acid number (mg KOH/g sample) indicates the number of carboxylic acid functional group per gram of a dry sample, according to the AOCS official method (AOCS Te 1a-64 1997). The iodine value characterizes the concentration of carbon-carbon double bonds (unsaturation) according to ASTM D1959-97. The hydroxyl number (mg KOH/g sample) is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content per gram of sample according to AOCS official method (AOCS Tx 1a-66 1997), that only counts the primary alcohol functional groups in the molecule. The hydroxyl number (mg KOH/g sample) is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content per gram of sample according to ASTM E 222-00 that counts the epoxy functional group and the primary and secondary alcohol functional groups in the molecule (use only for foam formulation). The epoxy content percent of a dry sample is analyzed by AOCS method

Cd 9-57 (1997), oxirane oxygen in epoxidized materials. Saponification value represents the number of milligrams of potassium hydroxide required to saponify 1 g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. Gardner color scale was used to describe the color of the final polyol products according to ASTM D 1544-04. The dynamic viscosity of the samples was measured in centipoises (cP) at 22°C using a Model RS100 Rheometer made by Haake – Thermoelectron.

FTIR analysis

A FTIR Nicolet (Madison, WI) (model Magna 550 using Omnic 5.1 software) was used to follow the chemical structure of the polyols. The alcoholysis reaction was monitored as the change in the oxirane peaks at 825 and 845 cm^{-1} , and the appearance of the hydroxyl peaks between 3330 and 3500 cm^{-1} .

Extractability analysis

Polyurethane elastomer wafers were prepared by mixing 1 g of soy-based polyol with 0.5 g of isocyanate (PAPI[®] 27, MDI), dried at 110°C for 10 h. A gravimetric analysis was performed for a simple extraction analysis. The extraction comprised by soaking approximately 0.5 g of polyurethane plastic in 20 mL of hexane/hexanol (4 : 1 by volume) mixture. The weight difference before and after the extraction were evaluated and compared with the oil amount recollected. Samples were dried of solvent in an oven prior to weighing before and after extraction.

Rigid polyurethane foam analysis

Foam procedure

The effect of replacing the B-side polyether polyol (VORANOL[®] 490) with 50–100% of alkoxy hydroxyl ESBO in the foam formulation on the properties of water-blown rigid polyurethane foam was studied. Few isocyanate indexes at 50, 75, and 100% of soy-based polyol replacement in the foam formulation, including a 100% of VORANOL[®] 490 as control for comparison purposes. The amount of isocyanate was based on the total hydroxyl number of the VORANOL[®] 490, polyol sample G, and distilled water used. The amount of the soy-based polyol used in the foam formulation was based on the hydroxyl number obtained by the ASTM E 222-00. The catalysts for rigid polyurethane foaming were POLYCAT[®] 5 and POLYCAT[®] 8. A surfactant, DABCO[®] DC5357, was used in rigid polyurethane foaming. Table II shows the foam formulation for

TABLE II
Formulations for Water-Blown Rigid Polyurethane Foam with Different Isocyanate Index

Ingredients	Parts by weight
B-side materials	
VORANOL [®] 490	100, 50, 25, 0
Alkoxy hydroxyl ESBO (Sample G)	0, 50, 75, 100
POLYCAT [®] 5	1.26
POLYCAT [®] 8	0.84
DABCO [®] DC 5357	2.5
Blowing agent (distilled water)	3.0
A-side materials	
PAPI [®] 27	Index ^a 110, 100, 90, 80

^a The quantity of isocyanate was based on an isocyanate index 110, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

water-blown rigid polyurethane foam for different isocyanate index.

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used. The petroleum polyol (VORANOL[®] 490), vegetable oil-based polyol, catalysts, surfactant, and blowing agent (B-side materials) were added by weighing into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s. PAPI[®] 27 (A-side material) was then added rapidly and stirring was continued for another 10–15 s at the same speed. The mixtures were poured immediately into a wooden mold (11.4 × 11.4 × 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C).

Foam properties measurement

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23°C) for 24 h, by a Fox 200 heat flow meter instrument (Laser Comp, Wakefield, MA), using ASTM procedure C 518-04. The dimension of the foam samples was 20 × 20 × 2.5 cm. Density of foam samples were measured according to ASTM procedure D 1622-03. Compressive strength of foams was determined by a TA.HDi Texture Analyzer (Texture Technologies, Scarsdale, NY) following ASTM procedure D 1621-04a. Both density and compressive strength were conducted after foams were stored for 7 days at room temperature and the dimension of the foam sample was 6.35 × 6.35 × 3.81 cm.

RESULTS AND DISCUSSION

Screening study to select a catalyst

To determine an appropriate catalyst for the epoxy ring opening by alcoholysis reaction, the impact on

TABLE III
Effects on Oxirane Oxygen Content, Acid Number, and Color Index of Screening Study Using Six Different Catalysts

Catalyst name	Concentration (wt%)	Temp/time (°C/h)	Acid no. (mg KOH/g)	Color index ^a	Oxirane (%)
Formic acid	0.5	150/2	1.41	1	6.40
Phosphoric acid	0.5	150/2	3.25	1	6.50
<i>p</i> -Toluenesulfonic acid monohydrate	0.5	150/2	0.70	1	5.95
POLYCAT® 5	0.5	150/2	0.70	5	6.74
DABCO® BL17	0.5	150/2	0.70	3	6.66
POLYCAT® SA-1	0.5	150/2	0.70	5	6.30

^a The Gardner color scale was used as a color index: 1 to 18 from light color to dark.

the oxirane content, color, and acid number were evaluated. Six different catalysts were used in ESBO and ethylene glycol reaction for 2 h, as shown in Table III. POLYCAT® SA-1, DABCO® BL17, and POLYCAT® 5 are catalyst currently used for final foam production. POLYCAT® SA-1 shows a considerable reduction on oxirane content of 6.30% and low acid number of 0.70. If POLYCAT® SA-1 compares in terms of color and oxirane content with *p*-toluenesulfonic acid monohydrate, the second product has the best color index and the maximal reduction between them. *p*-Toluenesulfonic acid monohydrate (*p*-TSAc) was preferred to use in the alcoholysis reactions due by the maximum yield of epoxy ring opening and no evidence of any side reaction occurs during the reaction.

Alcoholysis reaction

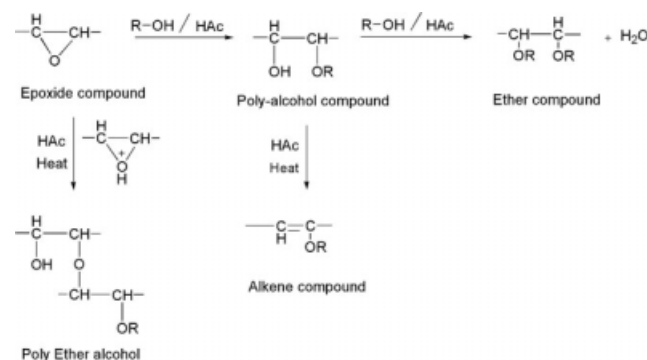
In the alcoholysis reaction or addition polymerization reaction, ESBO was combined with EG and ME using *p*-toluenesulfonic acid monohydrate (*p*TSAc) as catalyst to promote the oxirane ring opening and to form a high hydroxyl group molecule, as shown in Scheme 1. A general reaction mechanism for the acid-catalyzed ring opening hydrolysis of epoxy compound followed by glycol formation and alcohol dehydration producing ethers and alkenes are shown in Scheme 1. In the first pathway mechanism, the acid (HAc) reacts with the epoxide to produce a protonated epoxide and finally a glycol (polyalcohol compound) by nucleophilic substitution reaction. Two pathways are involved in dehydration of alcohol—alkene and ether formation. Ether formation occurs by an S_N2 mechanism with one alcohol moiety acting as nucleophile and a protonated alcohol moiety acting as the substrate. Higher temperature and an acid-catalyzed reaction are required to form an alkene from alcohol dehydration reaction. Oligomerization reaction between oxirane groups results in the formation of oligomeric ethers by protonation

of oxirane oxygen with acid catalyst, as illustrated in Scheme 1.

ME and EG act like nucleophiles during the acid-catalyzed epoxy ring opening reaction. In the presence of acids, alcohols acts as bases and accept protons from the acid forming a protonated alcohols. At this conditions, a S_N1 or S_N2 substitution reaction was possible depending on the class of alcohol present (primary or secondary alcohol). This modification proposes that for one oxirane ring present in the ESBO, two hydroxyl functional groups will generate in the molecule.

To follow the extent of the alcoholysis reaction, several properties were evaluated (a) oxirane oxygen content (Fig. 1), (b) iodine number (Fig. 2), (c) viscosity (Fig. 3), (d) oil extracted (Fig. 4), and (e) color index, acid, hydroxyl, and saponification numbers (Table IV). To see the impact on the oxirane ring opened by alcoholysis reaction, three temperatures (130, 150, and 170°C) at different reaction times were evaluated.

Figure 1 illustrates the oxirane oxygen content effect related with temperature and reaction time. As expected, at high temperature, 170°C, the oxirane oxygen content shows a great reduction compared with temperatures of 150 and 130°C. This abrupt reduction on oxirane oxygen content percent by high



Scheme 1 General mechanism for the alkoxy hydroxyl reaction (R-OH was an alcohol and HAc was an acid).

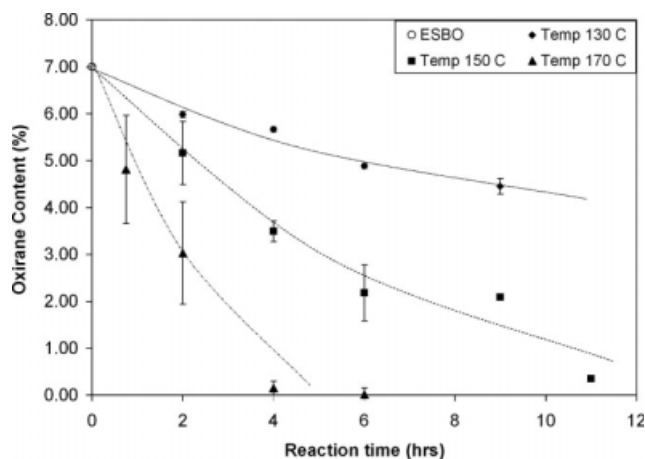


Figure 1 Effects on oxirane content of the alkoxy hydroxyl ESBO polyols related with temperature and reaction time (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 pTSA).

temperature (170°C) shows a high increment on acid number, iodine number, and color index (Fig. 2 and Table IV). In light of these changes, the experiments for 9 and 11 h were discontinued. As described in the mechanism, most of the oxirane ring groups are opened, and consequently a considerable amount was converted into alkene compound, polyether alcohol, polymerization, and some cleavage of ester bonds in the molecule.

At lower temperatures, 150 and 130°C, the reaction mechanism is more controllable. At 150°C, the oxirane oxygen content curves shows a smooth reduction (Fig. 2) during the reaction. Fairly low oxirane ring reduction was observed at 130°C for 9 h of reaction compared with 150°C for 9 h.

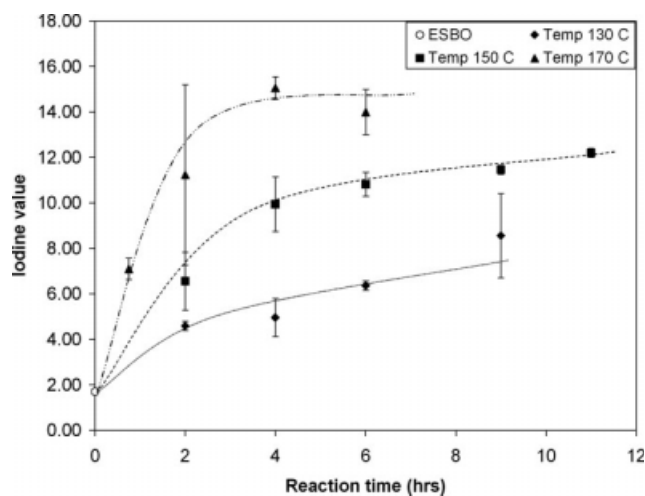


Figure 2 Effects on iodine value of the alkoxy hydroxyl ESBO polyols related to temperature and reaction time (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 pTSA).

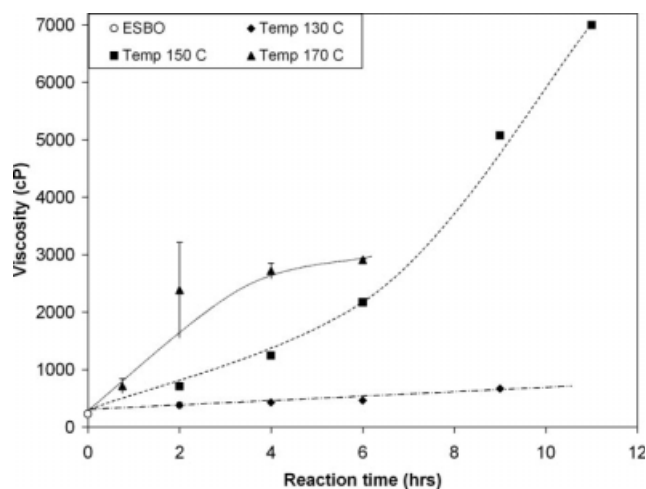


Figure 3 Viscosity effect of the alkoxy hydroxyl ESBO polyols related with temperature and reaction time (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 pTSA).

In Figure 2, asymptotical behavior tendency approach to 12 on iodine value for 150°C indicates a little increment in carbon-carbon double bond formations in the molecule. At lower temperature, 130°C, the π bonds formation is very low as long as the reaction goes up to 9 h. As it was shown in the mechanism, excessive heat was required to form an alkene compound.

A viscosity effect relates with temperature and reaction time as illustrated in Figure 3. A great increment in viscosity was observed at 150°C as a result of different mechanism of reactions involved, as mentioned before. A different effect on viscosity at 170°C was seen: an asymptotic behavior tendency approach to 3000 cP. This effect is explained by the

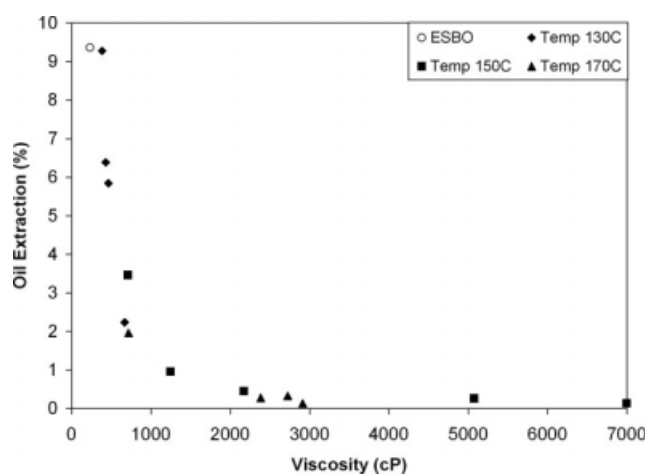


Figure 4 Viscosity effect relates with the oil extraction percent of the alkoxy hydroxyl ESBO polyols wafer-urethane elastomers (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 pTSA).

TABLE IV
Final Properties of the Alkoxy Hydroxyl ESBO Polyols

Sample	Temp/time (°C/h)	Acid value (mg KOH/g)	% Oxirane Oxygen	Saponification (mg KOH/g)	OH Exp. (mg KOH/g)	Color index ^a
ESBO	25/0	0.5	7.0	183.3	11.5	0.0
Control	25/0	0.7	7.0	177.7	166.0	1.0
A	130/2	0.7	6.0	168.7	157.4	1.0
B	130/4	0.7	5.7	168.3	159.0	1.0
C	130/6	0.7	4.9	170.0	162.6	1.0
D	130/9	0.7	4.5	172.4	157.6	1.0
E	150/2	0.7	5.2	177.5	156.2	2.0
F	150/4	0.7	3.5	171.7	158.4	2.0
G	150/6	0.7	2.2	170.2	154.0	3.0
H	150/9	0.7	2.1	176.0	150.0	3.0
I	150/11	0.7	0.4	174.6	129.6	3.0
J	170/0.75	0.8	4.8	167.4	159.4	1.0
K	170/2	1.0	3.0	167.7	153.8	3.0
L	170/4	16.5	0.2	162.4	109.6	5.0
M	170/6	17.7	0.0	164.4	101.4	6.0

^a The Gardner color scale was used as a color index: 1 to 18 from light color to dark. Color index, acid, saponification, and hydroxyl numbers (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 g pTSA).

full reduction of oxirane oxygen content followed by a high degree of oligomerization (polyether alcohol compound and ether compound) and alkene formation. As expected, low temperatures (130°C) do not show any significant increments in viscosity. This clearly indicates that the polyalcohol reaction mechanism occurs instead of the polyether alcohol mechanism.

Table IV shows the final properties of the alkoxy hydroxyl ESBO polyols at different temperature and reaction time. At higher temperature, 170°C, the acid number increases dramatically from 0.8 to about 18 mg KOH/g of dry sample, and the hydroxyl number decreases by ether and alkene formation. Also, the color for this set of samples drastically changes from 1 to 6 in the Gardner scale, and the saponification number shows that a little reduction can be indicative of high molecular weight fatty acids present. Any significant changes were observed at 130 and 150°C in terms of color index, saponification, hydroxyl, and acid numbers. The polyol sample I shows a considerable decrease in hydroxyl number from 157 to 129.6 mg KOH/g of dry sample, respectively by ether formation.

Figure 4 illustrated the influence on oil extraction percent relates with the final viscosity of the alkoxy hydroxyl-ESBO samples. The amount of oil extracted decreases as the viscosity for each sample increase as a results of cross-linking between the hydroxyl groups and the ether formation with the isocyanate groups in the wafer-urethane elastomer.

In theory, the low percent of oil extracted represents a high degree of cross-linking between diphenylmethane diisocyanate (MDI) and polyol means that the polyol has more hydroxyl groups available to react with the isocyanate groups of diphenylme-

thane diisocyanate (MDI). Figure 5 shows the correlation between oil extracted (unreacted polyol) and the alcoholysis soy-based polyol products. As expected, low oil extracted at 170°C results in oligomerization (polyether alcohol), high amount of carbon-carbon double bond formation, and cleavage of ester bond by high acid number. A linear behavior tendency for oil extracted at 130°C indicates a controlling degree of oligomerization, polyalcohol formation, and low quantity of π bonds.

FTIR spectroscopy

FTIR spectra of the ESBO (unreacted ESBO) and the prepared alkoxy hydroxyl-ESBO (Sample G) were

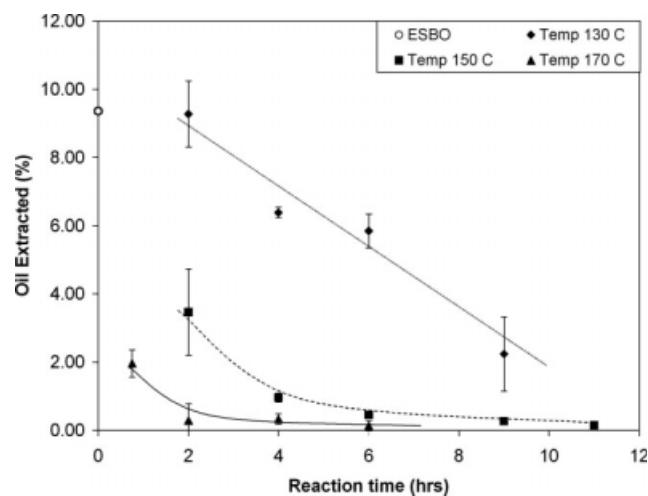


Figure 5 Effects on oil-extracted wafer-urethane elastomer of alkoxy hydroxyl ESBO polyols related with temperature and reaction time (polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME, and 1.0 pTSA).

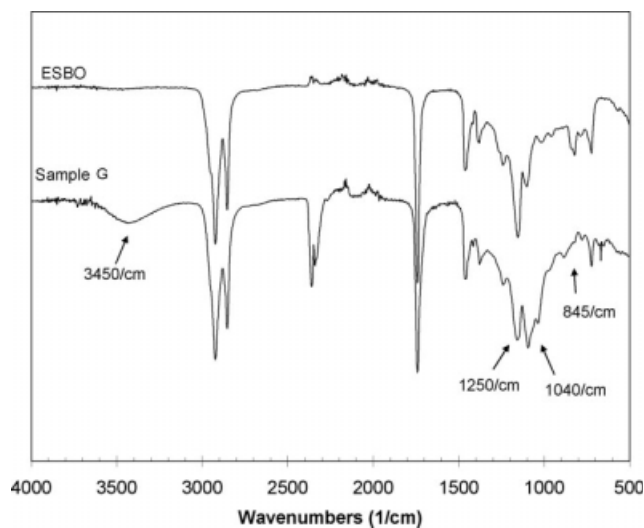


Figure 6 FTIR spectra of epoxidized soybean oil (ESBO) and alkoxy-hydroxyl ESBO (Sample G).

presented in Figure 6. In comparison with the spectrum of the unreacted ESBO, the disappearance of epoxy groups at 825, 845 cm^{-1} , and the emergence of hydroxyl groups at 3450 cm^{-1} are obvious. The final polyol product (sample G) shows a characteristic signal at 1050 cm^{-1} indicating the presence of ester groups.

The pathway mechanisms showed in Scheme 1 were confirmed by the FTIR spectra of sample G, illustrated in Figure 6. The polyalcohol compound formation was confirmed by peak signal at 3450 cm^{-1} . The ether compound and polyether alcohol compound formation were confirmed by peak signals from 1250 to 1040 cm^{-1} .

Polyurethane foam study

The alkoxy hydroxyl ESBO polyol, sample G (properties shown in Table IV, hydroxyl number of 278 mg KOH/g according to the ASTM E 222-00 and 154.0 mg KOH/g according to the AOCS Tx 1a-66 1997), was used in the replacement effect study of water-blown polyurethane foam. VORANOL[®] 490 is a polyether polyol with 4.3 of alcohol functionality, 460 of average molecular weight and 490 of hydroxyl number, used as control in this study.

The foams were made 0, 50, 75, and 100% of replacement, polyol sample G, and VORANOL[®] 490 as the B-side components and 3% water was added as blowing agent. The amount of the soy-based polyol used in the foam formulation was based on the hydroxyl number obtained by the ASTM E 222-00, previously reported. The compressive strength, density, and thermal conductivity usually were affected by the OH number of each polyol mixture. The hydroxyl number of each polyol mixture was calculated as follows:

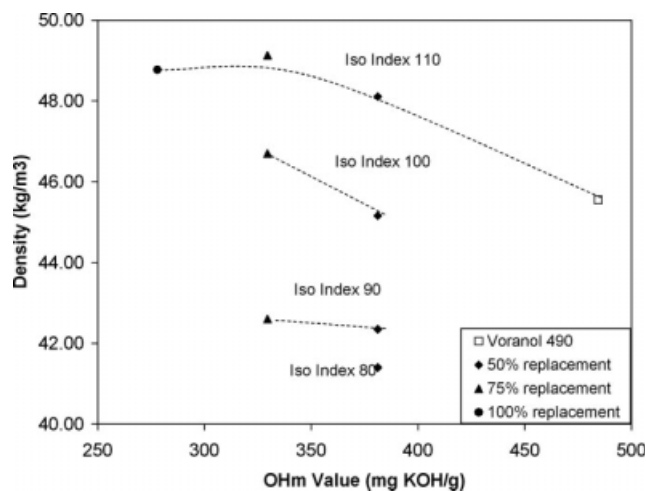


Figure 7 Density of foam for VORANOL 490 and three different percent of replacement (50, 75, and 100%) versus hydroxyl number of polyol mixture.

$$\text{OH}_m = (\text{OH}_{\text{Voranol490}} \cdot A) + (\text{OH}_{\text{soy-polyol}} \cdot B)$$

where OH_m is the hydroxyl of the mixture, $\text{OH}_{\text{Voranol490}}$ is 484.4 mg KOH/g, $\text{OH}_{\text{soy-polyol}}$ is 278 mg KOH/g, A is the mass percent of VORANOL[®] 490, and B is the mass percent of polyol sample G.

Figure 7 shows the relationship between density of foams and the hydroxyl number of polyol mixture. As the results show, high foam density was related with a higher isocyanate index or high amount of isocyanate present to react with the polyol mixture. The foam density is dictated by the weight and volume of the plastics making up the foam matrix and the gases trapped in the foam cells. Most of the foams made from vegetable-based polyol having a lower OH_m usually shrank within a

TABLE V
Thermal Conductivity of Foams for Voranol[®] 490 and Three Different Percent of Replacement (50, 75, and 100%) with Hydroxyl of Polyol Mixture

No.	% Replacement	Iso index ^a	Hydroxyl number mixture (mg KOH/g)	Thermal conductivity (W/mK)
0	0 (100%V490)	110	484.4	0.02692
1	50	110	381.2	0.02601
2	50	100	381.2	0.02571
3	50	90	381.2	0.02558
4	50	80	381.2	0.02614
5	75	110	329.6	0.02662
6	75	100	329.6	0.02620
7	75	90	329.6	0.02600
8	100	110	278.0	0.04327

^a The quantity of isocyanate was based on an isocyanate index 110, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

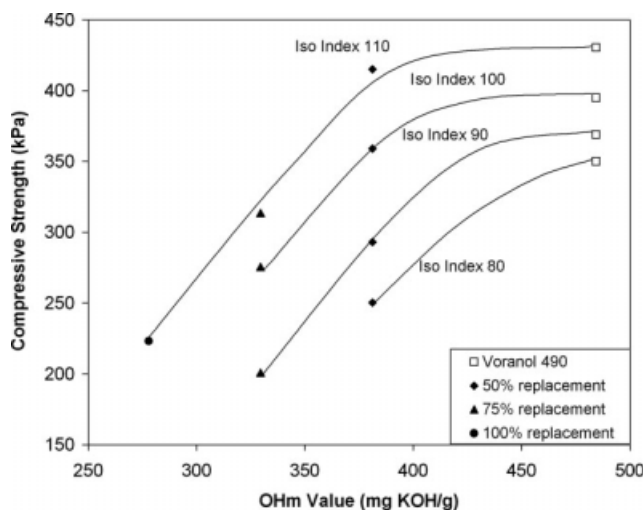


Figure 8 Compressive strength of foams for VORANOL 490 (control) and three different percent of replacement (50, 75, and 100%) at four isocyanate index (110, 100, 90, and 80) versus hydroxyl number of polyol mixture.

few days of storage at room temperature. This effect reduced the dimensions of foam resulting in higher density foams.

Table V shows the effect on thermal conductivity for each foam sample at three different percent of replacement compared with VORANOL[®] 490, as a control from petroleum based. As shown, the hydroxyl number did not significantly affect the thermal conductivity of foams; most foam made by polyol sample G had similar results as foams made with 100% VORANOL[®] 490. The thermal conductivity of foams is contributed by the thermal conductivity of gas trapped in the foam cells, thermal conductivity of foam cell membrane material, convection of cell gas, cell size, cell orientation, closed cell content, foam density, and thermal radiation. Although the hydroxyl number of polyol mixtures (OH_m) influences the cross-linking density of foams, the convection of gas is mainly governed by the open cell content.

Figure 8 illustrates the effect of compressive strength at 0, 50, 75, and 100% of replacement of VORANOL[®] 490 in the foam formulation versus hydroxyl number of each polyol mixture. It is evident that compression strength of foams decreased with decreasing OH_m number of polyols. At lower OH_m , number of polyols will consume less isocyanate causing foams to have a lower cross-linking density of foams. This was most likely caused by (1) the slight reduction in isocyanate content when increasing alkoxy hydroxyl-ESBO lowered the foam cross-linking density and (2) a weaker three-dimensional foam network when increasing alkoxy hydroxyl-ESBO content due to a lower reaction rate of alkoxy hydroxyl-ESBO (containing primary and

secondary reactive functional groups) with isocyanate than VORANOL[®] 490 (containing primary hydroxyl groups).⁴

It is interesting to note that the foam made of 50% of polyol sample G and 50% of VORANOL[®] 490 with 100 and 110 of isocyanate index had an encouraging and better density, compressive strength, and thermal conductivity properties than foams made with 100% of VORANOL[®] 490. As shown in Figure 8, the compressive strength decreases as the isocyanate index the hydroxyl number of the polyol mixture decreases.

CONCLUSION

The oxirane ring opening by alcoholysis reaction of ESBO is a slow reaction which requires an acid catalyst to improve the rate of reaction. pTSA shows a high catalytic reactivity that promotes the ring opening reaction yield a maximum oxirane oxygen content reduction compare to the others catalyst used in this study. Ample and good degrees of freedom were observed to control the average number of alcohols per molecule, the oxirane oxygen content percent, and the average hydroxyl equivalent weights in the final polyol.

Higher temperatures, $\geq 170^\circ\text{C}$, yield low oxirane oxygen content and hydroxyl numbers, but high acidity and color index. Low temperatures, $\leq 130^\circ\text{C}$, result in low reduction of oxirane oxygen content because the reaction rate is very low. Optimal conditions for the reaction were found at 150°C between 4 and 11 h depending on the viscosity and oxirane oxygen content desired. A considerable amount of cross-linking between polyol and isocyanate was observed for most of the final polyols.

A 100% of replacement in the water-blown rigid polyurethane foam can be made using the soy-based polyol, sample G, obtaining an interesting results. A low thermal conductivity was observed by most of soy-based PU foams compared to the petroleum-based foams.

An alkoxy hydroxyl ESBO reaction was confirmed by the FTIR spectra of the final product (sample G). The changes of epoxy groups in the spectrum of fingerprint region and the emergence of the hydroxyl groups in the FTIR spectra showed good agreement with the results previously obtained for oxirane oxygen content and hydroxyl value by the chemical analysis via titration.

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