CHEMICAL MODIFICATIONS TO PRODUCE SOY-BASED POLYOLS

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Doctor of Philosophy

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by

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The undersigned, appointed by the Dean of the Graduate School, have examined the dissertation entitled

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DISCLAIMER

This dissertation contains guidelines, procedure and protocols for performing reactions at severe temperature and pressure conditions. The author in no way implies that these procedures are described in complete detail or are safe to reproduce. When performing chemical synthesis or analyzing products, there is no substitute for good judgment and thorough background research on hazards and toxicities.

A list of possible hazards and hazardous environments when performing these experiments include, but are not limited to:

- High temperatures
- High pressures
- Chemical reactivity
- Chemical toxicity
- Chemical explotion
- Toxic vapors

The author assumes no responsibility for any incident that occurs when reproducing procedures similar to or the same as describe in this dissertation.

DISSERTATION FORMAT

This dissertation is written as a series of 8 chapters, where 6 chapters are technical papers that have been submitted for publication. Each paper has its own abstract, introduction, methods, materials, results and discussion as well as figures and tables.

Chapter 1 gives an overall introduction to polyol, polyurethane and soybean oil including their physical and chemical properties, market supply and uses.

Chapter 2 contains the first paper, which deals with the polymerization of soybean oil and acetol addition synthesis.

Chapter 3 contains the second paper, which deals with the polymerization of partially epoxidized soybean oil, soy-based synthesis and the flexible polyurethane foam application performance.

Chapter 4 contains the third paper, which deals with the soy-based polyols from oxirane-ring opening by alcoholysis reaction and the rigid polyurethane foam application performance.

Chapter 5 contains the fourth paper, which deals with the soy-based polyols from oxirane-ring opening by alcoholysis reaction (second part, concentration studies).

Chapter 6 contains the fifth paper, which deals with the one pot approach-epoxidation followed by alcoholysis reaction of soybean oil.

Chapter 7 contains the rigid and flexible water-blown polyurethane foam formulation and the foaming results for several soy-based polyol samples from each chapter depend on the application (flexible or rigid foam).

Chapter 8 contains the sixth paper which deals with the oil extraction from soybean seed using solvent, mechanical-press and enzyme routes.

Chapter 9 summarizes the results of the research and presents some suggestions for future investigations.

CHEMICAL MODIFICATIONS TO PRODUCE SOY-BASED POLYOLS

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ABSTRACT

Soy-based polyol used in polyurethane applications are sustainable and renewable materials which require less energy to produce and potentially lower production costs. They also have less environmental impact, expand the market for soybean farmers and help to reduce consumption of petrochemical-based materials. This project comprises several chemical routes to produce soy-based polyols for future use in polyurethane foam applications.

Soybean oil was polymerized by heat and catalyst to increase molecular weight, and viscosity for use as raw material for further reaction to form polyols in a batch reactor. Two different heat polymerization approaches were studied: non-catalyzed and catalyzed soybean oil using antraquinone as catalyst. A continuous flow reactor was designed to evaluate and compare with the batch reactor products.

One approach to imparting functionality was to react polymerized soybean oil. Synthesis consisted of three consecutive reactions: heat polymerization reaction of

soybean oil, alcohol addition reaction with acetol as alcohol and residual acid neutralization with epoxy soybean oil.

A second approach was based on the thermal polymerization reaction of partially epoxidized soybean oil and bodied partially epoxidized soybean oil with ethylene glycol. These products were tested in water-blown flexible foam polyurethane applications.

Polyols were also synthesized from oxirane ring opening of epoxidized soybean oil by alcoholysis reaction. Epoxidized soybean oil was combined with ethylene glycol and methanol to produce an alkoxy hydroxyl soy-based molecule at temperatures near 150 °C using p-toluenesulfonic acid to promote the reaction. In the first part of the study, different temperatures and reaction times were evaluated to optimize the reaction. In the second part of the study, different mole ratios of ethylene glycol and methanol were evaluated.

A single reactor (one pot) approach was developed to proceed from soybean oil to an epoxide intermediate and finally to an oligomeric polyol. Epoxidized soybean oil was synthesized by reacting soybean oil with peroxoformic acid at near-ambient temperatures followed by stripping of water and formic acid from the mixture and then alcoholysis. The final polyol product was evaluated in flexible and rigid water-blown polyurethane foam applications.

CHAPTER 1

INTRODUCTION

1.1. Introduction

Vegetable oils are lipid materials derived from plants. Physically, oils are liquid at room temperature; and chemically, oils are mostly comprised of triglycerides. Although many different parts of plants may yield oil, in commercial practice, oil is usually extracted from seeds such as corn oil, linseed oil, peanut oil, rapeseed oil, and soybean oil.

Vegetable oils are one of the most-established sources of renewable feedstock for the chemical industry with steady growth in demand. Environmental issues and sustainability are the primarily reasons to replace the petroleum based products with vegetable based products. The oleochemical industry is well-established and includes production of a range of chemicals based on fatty acids and triglycerides. In 2008, the US farmer's production record was 75 million of acres of soybean and the plans to expand to 76 millions of acres in 2009. Recently, the USDA raised the forecast of 2008/09 soybean exports by 25 million bushels to a record 1.21 billion. [1]

Soybean oil has an average molecular weight of 873 with other properties shown in Table 1. Typical polyol synthesis schemes result in moieties being attached to a triglyceride (avg. MW of ~873), diglyceride (avg. MW of 612), or monoglycerides (avg. MW of ~350). These molecular weights or the resulting polyols are low compared to "slabstock" polyols having molecular weight of 3,000 or greater, and this results in reduced flexibility in the final urethane and lower fractions of the B-side in the urethane

formulation. Possible methods to increase the molecular weight of a triglyceride (or triglyceride derivative) include:

1. Addition polymerization of oxides (like propylene oxide) to a glyceride-based polyol.

2. Oligomerization of fatty acids (or derivatives of fatty acids)

3. Oligomerization of triglycerides (or derivatives of triglycerides)

Each of these approaches is being studied or has been developed. The last two approaches have disadvantages associated with increased number and/or complexity of process steps. Oligomerization of the triglyceride is the least costly method to increase the molecular weight of the triglyceride to average values over 1500.

Table 1. Properties and composition of soybean oil

Properties	
Iodine no. (cg I_2/g)	130-140
Saponification no. (mg KOH/g)	189-195
Viscosity (cP) at 20°C	50-55
Density (g/cm^3) at 20°C	0.94-0.95
Fatty Acid Composition (wt-%)	
Palmitic acid	2.3-10.6
Stearic acid	2.4-6.0
Oleic acid	23.5-30.8
Linoleic acid	49.0-51.5
Linolenic acid	2.0-10.5

1.2. Polyurethanes

The term ‘polyurethane’ covers a wide range of materials produced by the reaction of polyfunctional isocyanates with polyols which are substances containing at

least two hydroxyl groups in the structure. The main chemical moiety resulting from this reaction is the urethane group (-NH-CO-O-) as illustrated on Figure 1.

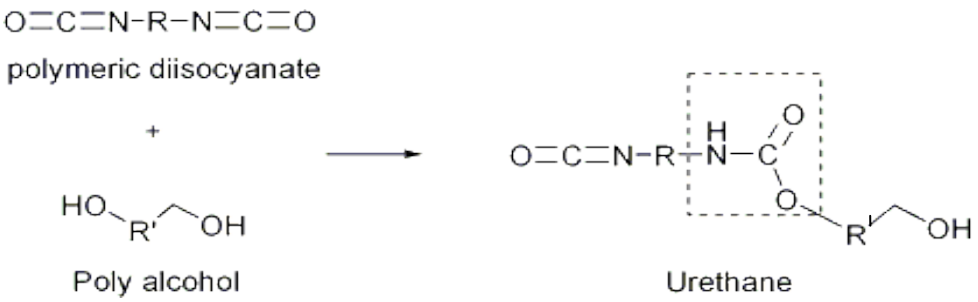


Figure 1. General polyurethane synthesis reaction

Other groups which may be formed in the synthesis reaction include: urea, amide, biuret, allophanate, ether and ester linkages; depending on reaction conditions and the particular catalysts used.

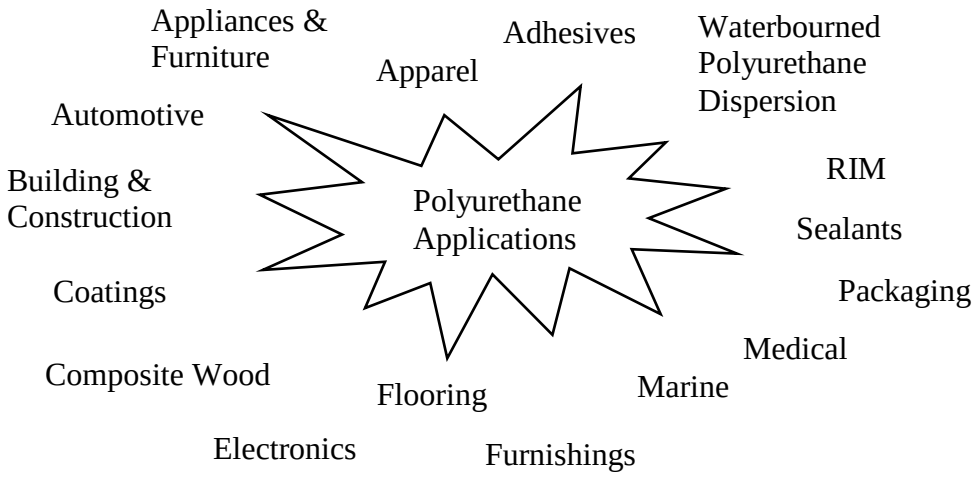


Figure 2. Polyurethane applications

Polyurethanes find application in many areas as illustrated on Figure 2. They can be used as impact modifiers for other plastics. Other applications include rollers or

wheels, exterior body parts, drive belts, and hydraulic seals. Polyurethanes can be used in film applications such as textile laminates for clothing and protective coatings for hospital beds, like paints and varnishes.

1.3. Polyols

Polyols used for the production of polyurethane foams are oligomers, containing at least two hydroxyl groups. They may be polyethers, polyesters, polyolefins or vegetable oil based polyols. Polyether and polyester polyols are the main compounds used in both rigid and flexible PU foams. The functionality and equivalent weight of the polyol can be controlled within wide limits and the materials are widely used for both rigid and flexible polyurethane foams.

1.3.1. Polyols Properties

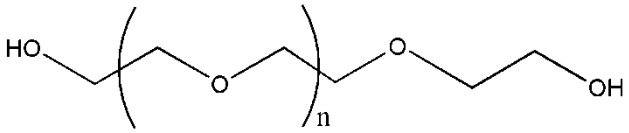
Important characteristics of polyols are their molecular backbone, molecular weight, hydroxyl number, acid number, functionality, and viscosity. The properties have significant effects on the characteristics of finished foams. The polyols contain saturated segments of fatty acid moieties that result in poor polyurethane properties causing dangling parts after the polymerization reaction. The typical polyol properties are shown in Table 2.

Table 2. Typical polyol properties

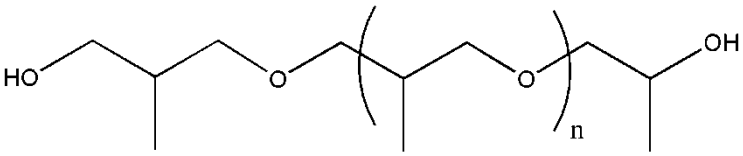
Uses	Molecular Weight (Daltons)	Hydroxyl number (mg KOH/g)
Flexible Polyols	2,000 to 10,000	18 to 56
Rigid Polyols	250 to 700	300 to 700
Variable Polyols (to add flexibility to base systems)	700 to 2,000	60 to 280

1.3.2. Petroleum-based Polyols

The petroleum-based polyols are the B-side material in the polyurethane synthesis reaction. They are higher molecular weight materials manufactured from an initiator and monomeric building blocks. Polyether polyols (90% of the polyols used industrially) are made by the reaction of epoxides (oxiranes) with an active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. Common polyether diols are polyethylene glycol, polypropylene glycol, and poly (tetra methylene ether) glycol.



Polyethyelene glycol (PEG)



Polypropylene glycol (PPG)

Figure 3. Petroleum-based polyols

1.3.3. Vegetable-based Polyols

Natural oil polyols, also known as NOPs or biopolyols, are polyols derived from vegetable oils by several different techniques. The primary use for these materials is in the production of polyurethanes.

There are a limited number of naturally occurring vegetable oils (triglycerides) which contain the unreacted hydroxyl groups that account for reactivity of these polyols. Castor oil is the only commercially-available natural oil polyol that is produced directly from a plant source.

Other vegetable oils such as soybean oil contain carbon-carbon double bonds but no hydroxyl groups (see Figure 4). There are several processes used to introduce hydroxyl groups into the carbon chain of the fatty acids; they usually involve oxidation of the carbon-carbon double bond like the epoxidation reaction.

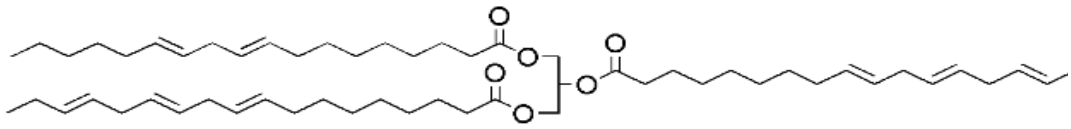


Figure 4. Soybean oil chemical structure

Many commercial soy-based polyols are usually derived from epoxidized soybean oil by hydrolysis of the epoxy group content in the molecule. Cargill Inc. has developed a manufacturing plant in Chicago, IL that produces soybean-based polyol, namely BiOH polyols. An interesting product from Cargill is “blown soybean oil” used in lubricants, coating and painting applications. A family series of X-0500 and X-0210 are the new polyol products in the plant used in polyurethane applications (furniture, carpet cushion, bedding and automotive products) [3]

Agrol® brand polyol products were developed by Bio-Based Technologies (LLC) in Lafayette, AR. Agrol® is a line of biobased polyols for commercial and industrial polyurethane applications for flexible (slabstock and molded) and rigid (insulation), coatings, adhesives, sealants and elastomers. The products have a broad range of

functionalities, viscosity, low acidity, up to 96% bio-content and can be manufactured from various natural oils.[4]

In 2007, Dow Chemical launched to market the natural oil-based polyol brand Renuva ™.[5] This technology helps create products with high levels of renewable content and reliable performance from soybean oil.

Urethane Soy Systems Company is producing two main groups of the soy-based polyols for PUs. One group is a two functional (R2 family) and the others are three functional (R3 family) polyols. The hydroxyl numbers are 50-60 and 160-180, respectively. The Urethane Soy Systems polyol products are commercialized under the trade name of Soyol®.[6]

Cognis Oleochemicals are providing several brand polyols to the market; some of their products are plant-based fatty alcohols. Sovermol® 1068 is made from soybean oil triglyceride. Emery® 610 is made from fatty acids distillate from soybean and other glycerin and fatty acid products from vegetable oils.[7]

1.4. Background Literature

There has been an increased interest in the use of renewable oleochemical oil polyols as a substitute for petroleum-based polyols, especially for use in the production of polyurethanes. A variety of processes have been employed to produce polyols. Blown vegetable oils are an example of a soy-based polyol. U.S. Patents 6,476,244 and 6,759,542 describe methods of synthesizing blown vegetable oils, which include use of air blown through the vegetable oils at elevated temperatures to promote partial oxidation.[8, 9] U.S. Patent 6,686,435 describes a method of making natural oil-based polyols consisting of reacting the epoxy moiety of an epoxidized natural oil with a

hydroxyl moiety of an alcohol in the presence of 10% to 30% water.[10] U.S. Patent 6,258,869 describes a process for production of polyols by reacting an agricultural feed stock with a multi-functional alcohol in the presence of a tin catalyst.[11]

Other examples of vegetable oil-based polyols include U.S. Patent No. 7,084,230; 6,433,121; 6,573,354 and European Patent WO2006012344.[12-15] Several processes has been suggested for converting an epoxidized vegetable oil into a polyol, some examples are U.S. Patent No. 5,266,714, 5,302,626 and 6,891,053.[16-18]

U.S. Patent Application 20080108782 relates to a method for making an fatty acid ester oil-based polyol comprising the step of admixing an epoxidized fatty acid ester oil with one or more alcohols, water, or a mixture, to form by hydroxylation an oil-based polyol, wherein no acid catalyst is added to the reaction mixture.[19] A solvent-free process for making polyol fatty acid polyester with a multi-functional hydroxyl compound in presence of alkali salt or base described in the U.S. Application 20040242910 and U.S. Patent No. 7,125,950.[20, 21]

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CHAPTER 2

SOYBEAN OIL POLYMERIZATION AND SOY-BASED POLYOLS

2.1. Abstract

In the absence of polymerization, soy-based polyols tend to have inadequate hydroxyl equivalent molecular weights for many critical urethane applications. In this paper, the polymerization (bodying) of soybean oil is presented as an effective method to increase the molecular weight of soy-based polyols. When bodying is combined with reaction steps for alcohol addition and acid reduction, soy-based polyols suitable for urethane applications can be synthesized. Two different heat-polymerization approaches, catalyzed and non-catalyzed bodied soybean oil (BSBO) were evaluated in continuous and batch processing. The catalyzed BSBO has lower iodine numbers and high viscosities than the non-catalyzed BSBO. This approach represents one of the least-costly means to increase the hydroxyl equivalent weights of soy-based polyols.

Keywords: soybean oil, bodied soybean oil, heat-polymerization, alcohol reaction, acetol

2.2. Introduction

The use of renewable materials contributes to global sustainability and the diminution of global warming gases. One of the more-inherently useful renewable materials is natural oils. Natural oils can be derived from both plant and animal sources and are available in all parts of the world. They are suitable chemical feedstock for a variety of commodity and specialty chemicals and plastics.

Polyurethanes (PURs) are usually made from petroleum based polyols and isocyanates and have widespread applications. Polyols are the key component in the polyurethane synthesis. Research on bio-based polyols has been increasing for decades with several soy-based alternatives gaining respectable market shares. Soy-based polyols are potentially low-cost materials and reduced impact on the environment. In addition, the introduction of natural oils into the polyurethane products can provide an opportunity for suppliers and customers to reduce their dependence on crude oil from petroleum.

Fats and oils are comprised primarily of triglyceride molecules. Soybean oil contains fatty acids that vary from 16 to 18 carbons in length, with 0 to 3 double bonds per fatty acid. Soybean oil contains 15% saturated fatty acid chains that are mostly palmitic (16:0) and stearic (18:0) fatty acid; 85% unsaturated fatty acid chains that are oleic (18:1), linoleic (18:2), and linolenic (18:3) fatty acid.[1] This fatty acid distribution leads to an average fatty acid functionality of 1.58 carbon-carbon π–bonds. The average functionality of the soybean oil triglyceride is three times this, or 4.74.

The iodine value is an ASTM method that characterizes unsaturation in triglycerides. Soybeans iodine value is typically between 120 and 143 (0 represents no un-saturation).[2] Soybean oil is a preferred feed stock for developing new industrial oil

products due to its prominence as the largest oilseed crop in the Americas and its unsaturated content that allows a variety of chemical modifications.

Heat polymerization of soybean oil is known to create triglyceride oligomers. Subsequent functionalization can then convert these oligomers to polyols. Powers reports different reactions that can be take place during the heat polymerization like isomerization, ring formation and diene conjugation.[3] Adams and Powers reported a statistical analysis and derived equations to predict the amount of fatty acid present according with the extent of the reaction.[4-6] The exten of reaction was calculated from iodine number and molecular weight, postulated that in the disappearance of a double bond two fatty acid chains are bonded together through a six member ring or intrapolymer.

Patents on bodying reactions were published early in the 1940's to 50's.[7] The US patent 2471577 describes bodying with heat and incorporating oil promoters designed to increase the rate of reaction at epoxy and alkenes groups.[8] US Patent 2,669,573 proposes adding catalysts to promote the bodying reaction.[9] The US Patent 2,317,915 presents a semi-continuous process for bodying of drying oil, involving the continuous feed stream of the oil into a pool of oil of appropriate size in a bodying kettle and simultaneously withdrawing corresponding amounts of the bodied oil.[10]

Soybean oil is relatively un-reactive in typical polymer formulations designed around petroleum-based monomers; soybean oil must be functionalized. The carbon-carbon double bonds in the soybean oil are reactive moieties that can be converted into hydroxyl groups. Several studies have been published on developing soy-based polyols from soybean oil. Different reactions such as epoxidation follow by epoxy-ring opening,

ozonolysis, hydroformylation, halogenations, esterification and transesterifications have being evaluated for polyurethane applications.[11-19]

The main objective of this work is based on the polymerization of soybean oil by two different reactor configurations: batch (closed) and continuous (flow) reactor. A solid catalyst has being evaluated in the bodying reaction at mild temperatures. The functionality of bodied soybean oil was improved by alcohol addition reaction and acid neutralization forming primary and secondary alcohols moieties in the final oligomer.

2.3. Experimental

2.3.1. Materials

Anthraquinone (AQ, 90%), hydroxyacetone (acetol, technical grade 90 vol % in water) and dicyclopentadiene (DCP, 95%) were purchased from Sigma-Aldrich (St. Louis, MO). Soybean oil RBD (0.1-0.2 wt % of water, iodine number 130) was purchased from a retail supplier. Epoxidized soybean oil (Vikoflex® 7170) was purchase from Atofina Chemicals (Philadelphia, PA). High purity grade nitrogen was obtained from Praxair (St. Louis, MO).

2.3.2. Bodying reaction experimental setup

2.3.2.1. Batch reactor setup

Heat polymerization was carried out in a 2 L stainless steel closed reactor that includes an omega controller, heater, stirrer and 2 port valves (for sampling and volatiles removing). The reactor was purged constantly with nitrogen to remove the volatiles compounds and moisture, and heated to reach temperature up to 330^0C for reaction. Longer reaction times lead to products with lower iodine numbers and higher viscosities.

Unless otherwise specified, batch reactions were performed at a reaction time of 60 minutes.

The heat-catalyzed polymerization procedure was similar to the heat polymerization except for the addition of 2.5 wt % of (9, 10)-anthraquinone (AQ) catalyst. The reactor temperature were 260, 280 and 300°C. Reaction times were from 3 to 12 hrs depending on the reaction temperature, the desired viscosity, and the desired iodine number.

2.3.2.2. Continuous flow-reactor setup

The flow reactor system consisted of a stirred feed tank wrapped in heating tapes; a peristaltic pump drew the premixed feed from the feed tank, 25 ft of 0.75 OD copper tubing providing a reaction volume of 510 mL, a furnace for housing the reactor, a water/ice bath through which effluent flowed, and an open steel product tank. Typical conditions for the heat-polymerized reaction included a feed flow rate of 0.075 to 0.35 mL/sec and a reaction temperature of 350 and 370°C.

For heat-catalyzed polymerization, 2.5 wt % of the (9, 10)-anthraquinone (AQ) powder catalyst was added to the reaction mixture in the feed tank. Typical conditions included a feed flow rate of 0.09 mL/sec and reaction temperatures of 320 and 350°C.

2.3.3. Soy-based polyol reaction experimental setup

2.3.3.1. Alcohol addition

To created the BSBO:acetol-modified, BSBO, DCP, and acetol were placed in a 125 mL closed stainless steel vessel equipped with a thermocouple, stirrer, heating element, and omega controller. Two different alcohol (acetol) and DCP concentrations were evaluated at temperatures of 180, 200 and 220°C. After 20 hrs of reaction, the

samples were left at room temperature to cool, and subsequently washed several times with distilled water.

2.3.3.2. Acid reduction with ESBO

BSBO:acetol-modified products were combined with epoxy in an epoxy: acid molar ratio of 1:0.5. The acidity of the BSBO:acetol-modified was evaluated to identify the amount of epoxy to add. The mixture was reacted in an Erlenmeyer flask equipped with a magnetic stirring bar and under a nitrogen purge at 170°C. Reaction time was typically a few hours until the acid number of reaction mixture was less than 10 mg KOH/g.

2.3.4. Analytical methods

The final product was analyzed for acid number, iodine number, hydroxyl number, oxirane content, and dynamic viscosity. The acid number (mg KOH/g sample) indicates a 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 a measure of the hydroxyl groups in the polyester and polyether polyols according to ASTM D 4274-05. The epoxy content percent of a dry sample is analyzed by AOCS method Cd 9-57 (1997), oxirane oxygen content in epoxidized materials. The dynamic viscosity of the samples was measured in centipoises (cP) at 22°C using a Model RS100 Rheometer (Haake – Thermoelectron, Newington, NH).

Gel permeation chromatography (GPC), gas chromatography (GC-FID) and infrared spectroscopy (FT-IR) analytical analyses. GC-FID analysis of esters derived

from soybean oil and bodied soybean oil was performed to investigate the compositions of the fatty acid moieties in the oils. Ester tri-glycerides were esterifies with n-butanol and H_2SO_4 catalyst. To make butyl esters, a 4.5 mL vial contained 100 mg of sample was filled with HPLC grade n-butanol and 1 drop of H_2SO_4 (concentrated) was added. The reaction was allowed to take place at 70°C for 24 hours. The butyl ester products were analyzed by GC, HP 6890 GC (Wilmington, DE). The column was HP MXTWAX 70624, capillary 30.0 m x 280 m. x 0.25 m nominal and the detector was flame ionization (FID). The injection port temperature was 250°C. The temperature program was set from 160 to 220°C at 10°C/min and hold at 220°C for 12 min. Carrier gas was H_2 (40 mL/min). Make up gas was N_2 (35 mL/min). Air flow was 260 mL/min. The split ratio was 75:1.

GPC was used to investigate molecular weight (MW) distribution chromatograph. Dry sample (50 mg) was dissolved in 5.0 g of tetrahydrofuran (THF, Chromasol® from Sigma-Aldrich, St. Louis, MO) and 500 μL of the sample solution was transferred to a 1.0 mL vial. A standard curve, a plot of molecular weight (MW) against retention time, was generated from the GPC retention times of polyethylene glycols (MW= 3800, 1600, 1500, and 600), soybean oil, and linoleic acid.

The HPLC, Hewlett Packard series 1100 with degasser, quaternary pump and auto sampler was used. Data acquisition, program control, and analysis were set and done by the HP Chemstation software version 06.01 (Palo, Alto, CA, USA). The detector was a light scattering detection, Altech 500 ELSD (Deerfield, IL). Two Viscogel-columns, I-MBLMW-3078 from Viscotek (Houston, TX) were connected in series. The mobile phase was THF with a flow rate of 0.5 mL/min at a pressure of 16.2 psig. Drift tube

temperature for ELSD was 60°C. Compressed air was the nebulization gas with a flow rate of 3.0 L/min at a pressure of 7.5 psig. Sample injected volume was set at 25 μL and the needle injector was cleaned by THF after each sample injection. Analyzing time was 40 min per sample.

A FT-IR Nicolet (Madison, WI) model Magna 550 with Omnic 5.1 software was used to follow the chemical functional groups in the polyols. The polymerization (bodying) and alcohol addition (acetol) reactions were monitored as the disappearance of carbon- carbon π bonds peaks at 1680- 1600 cm^{-1}, and the appearance of the hydroxyl peaks at 3330 – 3500 cm^{-1}.

2.4. Results and discussion

2.4.1. Polymerization of soybean oil

Soybean oil averages 4.74 carbon-carbon π–bonds per molecule, and so, the Diels-Alder reaction can result in dimerization, trimerization, and higher degrees of oligomerization when the reaction is between fatty acid groups of different triglycerides. The prominent fatty acid groups participating in oligomerization is linoleic acid which has two double bonds separated by methylene carbon and linolenic acid has three double bonds similarly separated.

If the unsaturated acid is a non-conjugate acid, it is possible for heat to shift the structure to conjugated moiety. Conjugated moieties are more reactive. At heat bodying temperatures the double bonds migrate and conjugated dienes are formed. These conjugated dienes may then undergo the Diels-Alder reaction as illustrated by Figure 5.

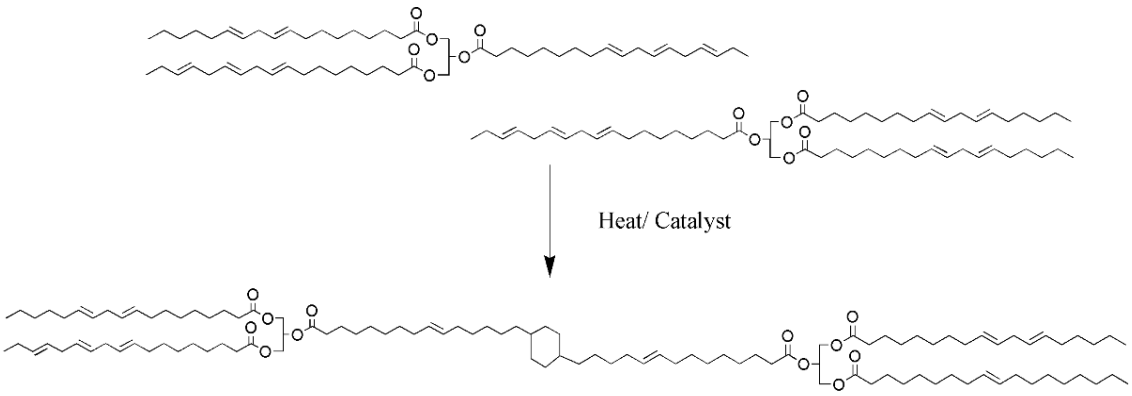


Figure 5. Possible polymerization reaction of soybean oil

Table 3summarizes heat-polymerization results for soybean oil in a batch reactor. A reduction in the iodine number characterizes the reduction in carbon-carbon π–bonds. The simultaneous increase in viscosity indicates that oligomerization is occurring.

Table 3. Final properties of heat polymerized soybean oil in 2L batch reactor

Sample	Temperature (C)	time (hrs)	Iodine No. (cg I_2/g)	Acid No. (mg KOH/g)	Viscosity (cP)
SBO no reaction	-	-	135	1.5	52
BSBO no catalyst	330	1	100	15	68
BSBO catalyzed with AQ	260	6	104	15	253
BSBO catalyzed with AQ	280	6	91	15	1158
BSBO catalyzed with AQ	300	6	70.5	15	2998

The catalyst plays an important role in the reaction by allowing the reaction to proceed at lower temperatures. The viscosity of the final product is a function of time and temperature. Depending on the temperature, the final product may have a light yellow to

dark brown color. Since a nitrogen purge is applied to keep oxygen from the system, the increase in acid number could be due for oil degradation as a result of high temperature applied.

Figure 6 provides the kinetic data for the batch reaction at 330°C. The viscosity increases with time, as the iodine number decreases. The rapid decrease in iodine number at the start of the reaction suggests that different reactions occur initially. During the heat process, linolenic was converted completely forming new fatty acids with similar stereochemistry as linoleic and oleic acid, as describe on GC analysis later.

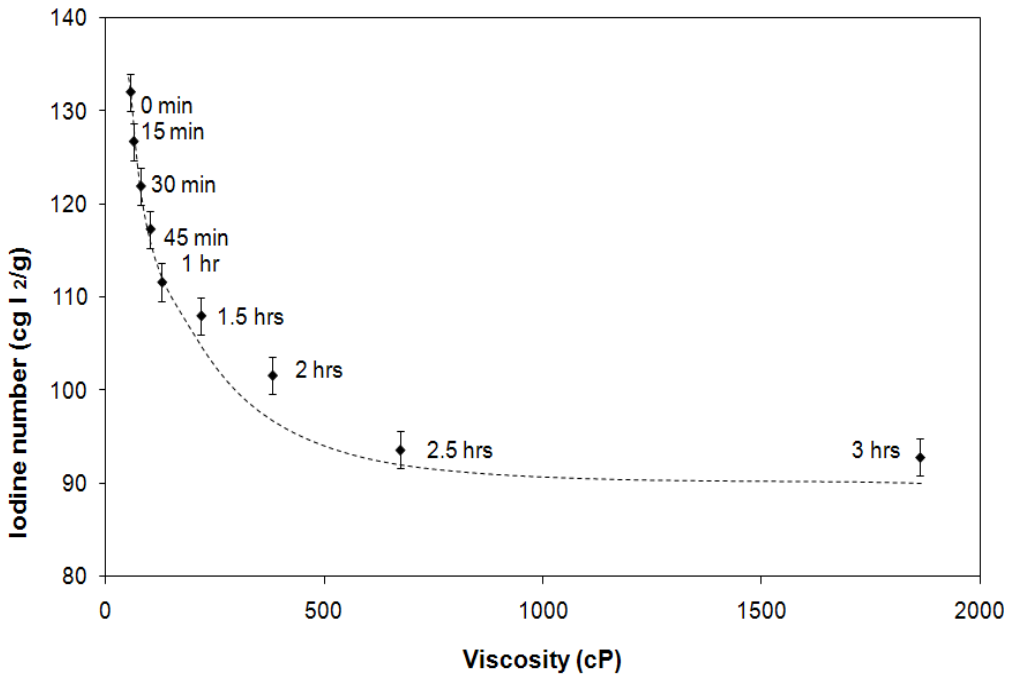


Figure 6. Kinetic study of heat polymerized soybean oil at 330°C

Figure 7 and Figure 8 summarize the impact of residence time on iodine number and acidity for the flow reactor at temperatures of 380, 390 and 410°C. At higher temperatures the final products become darker and the acid numbers increase.

Considerable reductions in iodine values were possible at short residence times at temperatures of 410 and 390°C.

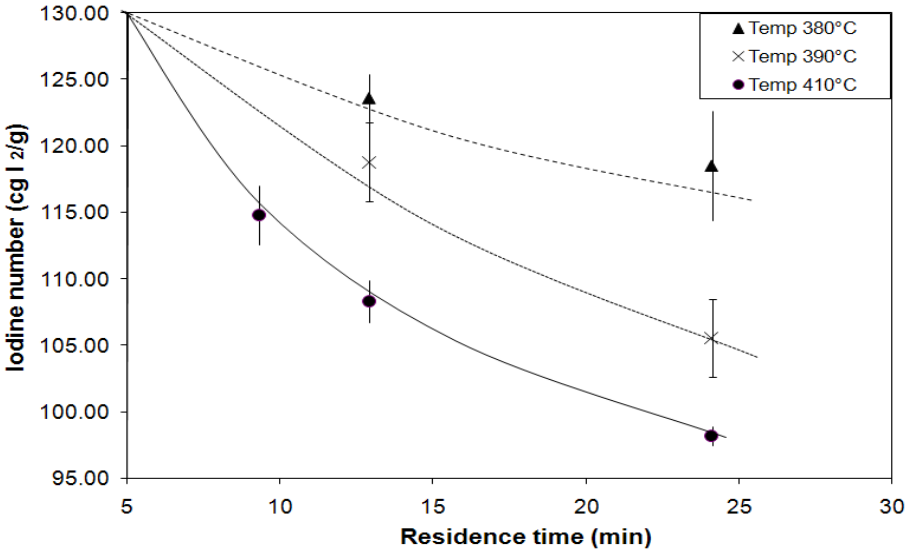


Figure 7. Iodine numbers as a function of residence time and temperature in the flow reactor

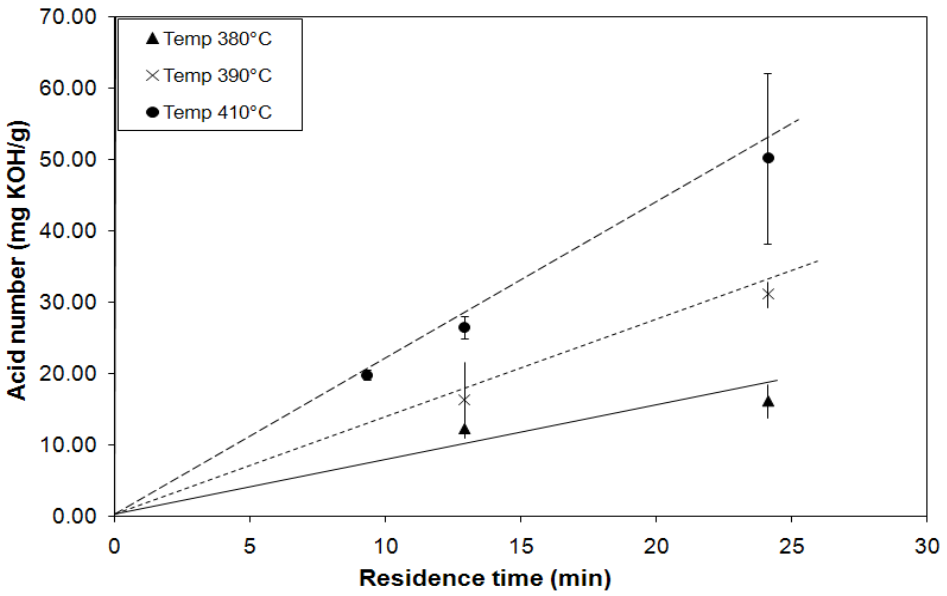


Figure 8. Acid numbers as a function of residence time and temperature in the flow reactor

The reaction profiles at lower temperatures are plotted separately (longer residence times) in Figure 9 and Figure 10. Superimposed are values for the batch reactions. Higher temperatures were used for the flow reactor due to the long times necessary to attain steady state and then to attain product.

The trends from 410 to 350 °C follow theory with increasing temperatures leading to higher reaction rates (faster reductions in iodine values). Interestingly, the batch reactor data at 330°C has conversion trends substantially similar to flow reactions at 350°C. This could be due to experimental temperature measurement deviation by assumption reaction temperature was tubing temperature ±10°C. However, the flow reactor performance is close enough to the batch reactor performance to allow batch reactor data to be used to identify the general operating conditions necessary for bodying in a flow reactor.

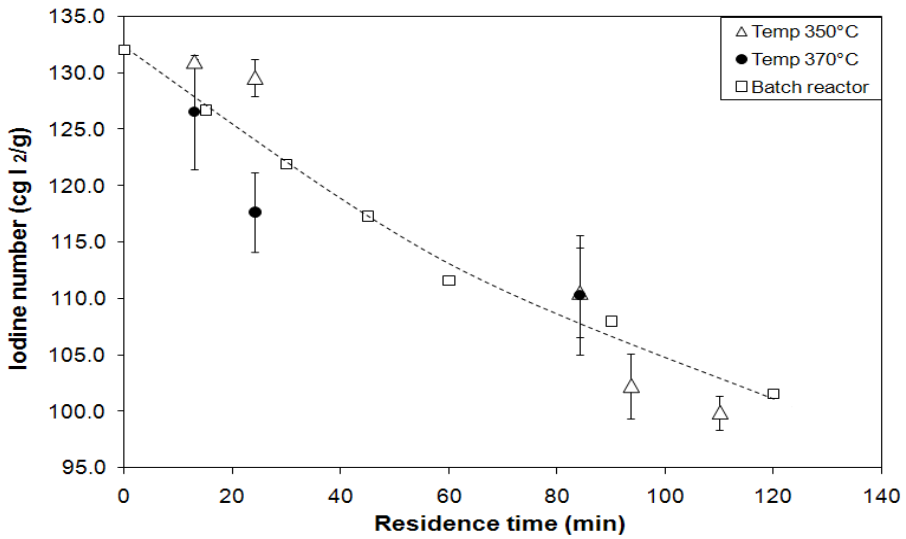


Figure 9. Iodine numbers as a function of residence time and temperature in the flow reactor at lower temperatures

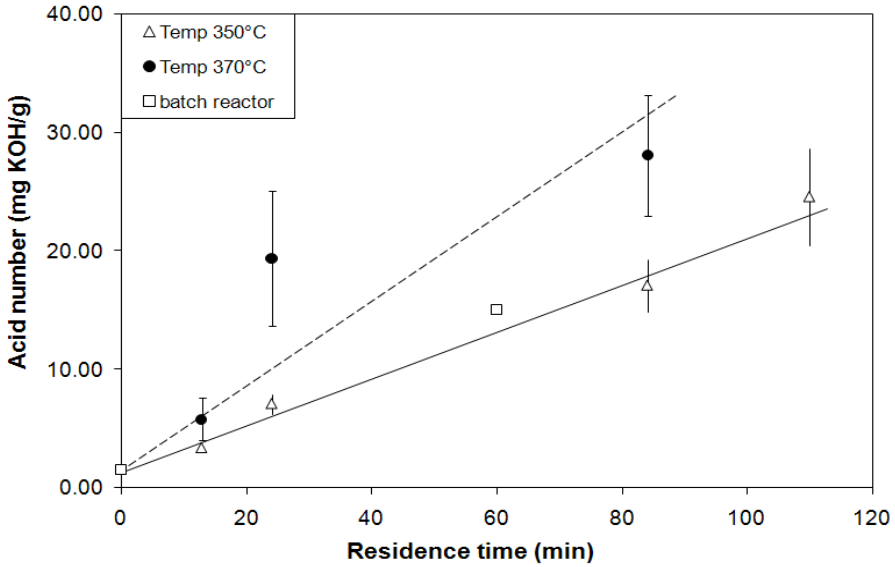


Figure 10. Acid numbers as a function of residence time and temperature in the flow reactor at lower temperatures

For both batch and flow reactor studies, the iodine values of the BSBO asymptotically approach an iodine value near 90 for reactions without catalysts. Erhan and Bagby present several heat-polymerization methods for soybean oil.[20] They used viscosity to estimate reaction rates. Follow his approach, the rate constant values were about 0.0019 to 0.005 min^{-1} for a batch reactor and 0.006 to 0.01 min^{-1} for continuous reactor, based on viscosity measures shown in Table 3 and Table 4. The behavior is that of a second order reaction mechanism (first order in conjugated diene moieties and first order in carbon-carbon π–bonds) where the reaction substantially ends as the conjugated dienes are consumed. The conversion profile for acid generation is different.

Within the experimental error of the data, the acid generation was proportional to the residence time, means that increase linearly as the reaction take place. Higher temperatures created acidity faster; however, the rate of acid generation relative to the rate of iodine number decrease was about the same during the initial phases of reaction. The acid generated in batch reaction was the same as the flow reactor of similar reaction times. Hence, the hypothesis in regard to free acids promoting an auto-catalytic mechanism for acid generation cannot be substantiated. A possible explanation for this behavior is the degradation of ester bonds during the polymerization reaction results by high temperatures.

Table 4 shows the final properties for the heat catalyzed BSBO in the flow reactor at two temperatures. Lower iodine numbers of 86 to 87 were readily attained using the catalyst while longer residence times and higher temperatures did not attain iodine values less than 95 for the non-catalytic reactions. It is possible that the catalyst allows for more reaction possibilities and greater degrees of polymerization.

Table 4. Temperature influence in the final properties of heat-catalyzed polymerization of soybean oil

Sample	Temperature (°C)	Residence time (min.)	Iodine No. (cg I_2 /g)	Acid No. (mg KOH/g)	Viscosity (cP)
F1	320	94	108	6.0	263.2
F2	320	94	104	7.0	263.2
F3	320	94	106	5.2	263.2
F4	350	94	87	13.4	671.0
F5	350	94	86	14.0	671.0

Figure 11 compares the ratio of acid generated to iodine value reduction as a function of reaction time for catalyzed and non-catalyzed flow reactors. The graph of these trends readily illustrates that the catalyzed reaction produces less acidity at the same degrees of polymerization. Lower temperature bodying, and especially lower-temperature catalyzed bodying, promote low acidity for a given degree of oligomerization.

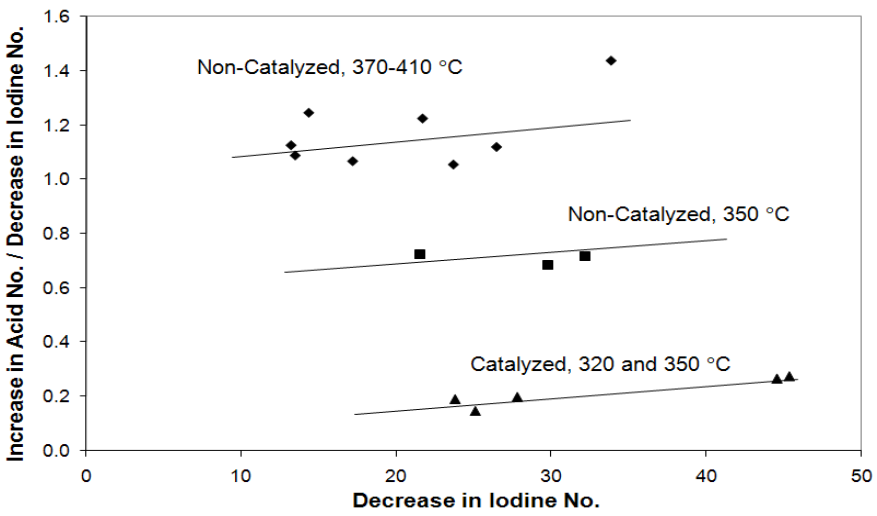


Figure 11. Acidity influence related with iodine number for polymerization reaction

catalyzed and non-catalyzed reaction in batch and flow reactor

2.4.2. Soy-based polyols

Hydroxyacetone (Acetol-alcohol) was added to both SBO and BSBO to attach hydroxyl functional groups to soy-based molecule. Figure 12 illustrates a possible allyl addition reaction mechanism for attaching an alcohol to the soybean oil (similar approach is established for BSBO).

As proposed in Figure 12, the unsaturated functionality in SBO and BSBO provide a location for addition reactions to attach hydroxyl to fatty acid chains of the triglycerides. An iodine number reduction accompanies the reaction as two carbon-carbon π–bonds react to form a single carbon-carbon π–bond.

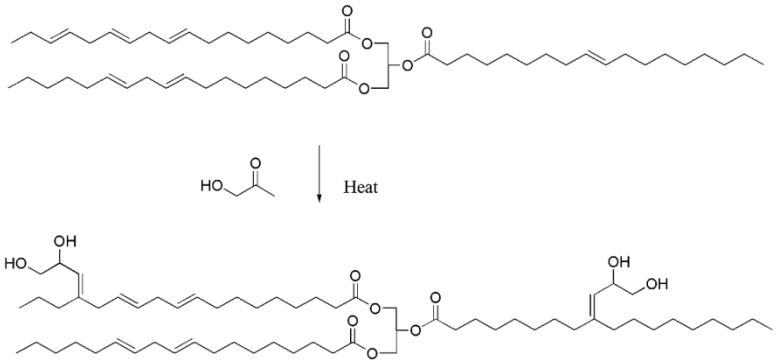


Figure 12. Possible reaction of alcohol addition (soybean oil and acetol reaction)

Table 5 summaries the reaction studies on addition of acetol to SBO and BSBO. Dicyclopentene (DCP), a cross linking monomer, was used at similar concentration to help in the addition reaction and increases viscosity in the final polyol. Acetol was added at 15% and 20% by weight. DCP was added at 14% and 20% by weight.

The results show a reduction in the iodine number which corroborated the alcohol addition to the carbon-carbon π-bond. The product was washed with water to remove

unreacted acetol after the reaction. The hydroxyl numbers represent the bound hydroxyl functionality attributed to acetol addition.

The increased concentrations of acetol did not lead to increased hydroxyl numbers. The addition reaction appeared to be limited. A few possible explanations for this behavior might be the reactivity of fatty acid present in the starting material such as: 1.) the amount of carbon-carbon π-bonds, and 2.) the stereochemistry.

However, the high reaction temperatures used lead to increases the acid number in the final polyol. This has been attributed to the cleavage of ester bonds as consequences of the water dissolves in the acetol. With acid numbers greater than 45, the products of Table 5 are considerably higher than preferred acid numbers of less than 2 or even less than 1. If the epoxidized soybean oil (ESBO) reacts with the products of Table 5 could be possible to reduce the acid number to less than 15.

Table 5. Properties for reactants and products in the alcohol addition reaction

No.	**Reactants**			**Reaction Conditions**		**Product Properties**				
	Oil	Acetol (%)	DCP (%)	Temp. (°C)	time (hrs)	Acid No.	Iodine No.	OH No.	% Red. Iodine	Viscosity (cP)
A	SBO	20	14	220	20	55	119	75	24	265
B	SBO	20	14	200	20	52	120	53	23	202
C	BSBO	15	14	220	20	48	106	63	26	665
D	BSBO	20	14	200	20	56	109	57	21	416
E	BSBO	20	20	210	20	45	118	58	22	514
F	BSBO	20	14	220	20	55	104	66	25	775
G	BSBO	20	14	200	20	52	111	42	20	554

H	BSBO	20	14	180	20	59	113	55	18	400
I	BSBO	20	14	200	20	54	92	68	29	1474
J	BSBO	20	20	180	20	57	118	56	13	450
K	BSBO	20	20	200	20	52	116	55	15	500
L	BSBO	15	14	200	20	57	89	56	64	591

Kiatsimkul et al. demonstrated the reaction mechanism cleavage of ESBO with a fatty acid product, similar mechanism was used for acid reduction of BSBO:acetol modified products with epoxidized soybean oil (ESBO).[21] In this reaction the epoxy groups react with the acid to form a hydroxyl group and ester linkage. An excess of epoxidized soybean oil was necessary, especially when residual acidity is not desirable in the final polyols.

Use of epoxidized soybean oil (ESBO) can lead to cross-linking or ramification compounds, increasing molecular weight of the polyol, and increasing viscosity. Other epoxy compounds like butylene oxide or propylene oxide will neutralize the acid without the cross-linking and no significant increase in viscosity. Table 6 provides reaction conditions and final polymer properties for the indicated reactions of ESBO with the products of Table 5.

Table 6. Final properties of reactants and products in the acid reduction reaction

No	Molar ratio(epoxy: acid)	Acid	Epoxy		Reaction Conditions			Product			
		mass	mole	mole	mass	Temp (°C)	time (hrs)	Acid No.	Epoxy (%)	OH no.	Viscosity (cP)
AE	1:0.5	40	0.04	0.08	18	160	7	10	0.98	126	1078
BE	1:0.5	40	0.04	0.07	18	160	7	12	0.85	108	889
CE	1:0.5	40	0.03	0.07	16	170	6	7	0.57	98	3075
DE	1:0.5	35	0.04	0.07	16	170	6	7	0.44	102	2807
EE	1:0.5	80	0.06	0.13	30	170	6	6	0.50	94	1026
FE	1:0.5	30	0.03	0.06	14	170	6	5	0.59	101	5570
GE	1:0.5	40	0.04	0.08	20	170	6	7	0.66	105	2096
HE	1:0.5	100	0.09	0.19	44	180	6	6	0.48	95	3606
IE	1:0.5	40	0.04	0.08	19	180	6	10	0.43	92	11212
JE	1:0.5	40	0.04	0.07	18	180	6	5	0.59	99	3243
KE	1:0.75	35	0.03	0.07	15	180	6	7	0.73	98	3642
LE	1:0.5	40	0.04	0.07	18	170	8	20	0.93	95	2270

2.4.3. GC-FID, GPC and FT-IR analytical results

The GC-chromatographs of fatty acid butyl esters of soybean oil and bodied soybean oil are presented in Figure 13. Soybean oil was not fully polymerized after 60 min of heat bodying process. Soybean oil has 85% unsaturated fatty acid chains: 22% oleic (18:1), 56% linoleic (18:2), and 7% linolenic (18:3) fatty acid. The linolenic acids (C18:3) were converted completely after 30 min of the heating process, but some of linoleic acid (C18:2) and oleic acid (C18:1) remained in the bodied soybean oil.

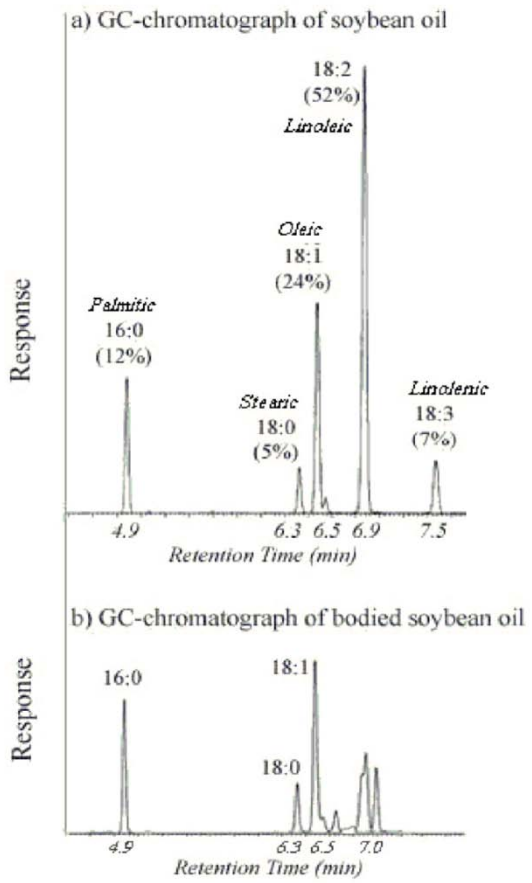


Figure 13. GC-MS chromatographs of acid moieties in soybean oil (a) and bodied soybean oil (b) at 330ºC for 1 hour

The reactivity of fatty acid depends on the amount and location of the carbon-carbon double bond or double allylic hydrogen present. The three carbon-carbon π-bond of linolenic acid has more activity to polymerize by oxidation or heat than linoleic (18:2) and oleic (18:1) acids as the conjugate fatty acid has more reactivity than a non-conjugated fatty acids.[22, 23] Erhan and Sheng also found the rapid reaction of linolenic acid moiety in the bodying reaction of soybean oil.[24]

The GC-chromatograph of bodied soybean oil revealed new fatty acid peaks next to the oleic acid and linoleic acid peaks. These new peaks could not be fully resolved by extending the heating time and decreasing the heating rate. These new peaks could be conjugates and isomers of linoleic acid and oleic acid.

GPC analyses of the BSBO catalyzed in the flow reactor, soy-based polyol products of BSBO with acetol at 15 and 20 % by wt. concentrations are show in Table 7. The BSBO-catalyzed GPC analysis confirms oligomers at a concentration of 57%, single-acid esters at 8%, and 35% monomer triglycerides. The oligomers present in BSBO-catalyzed consist of dimers (17.85 %), trimers (12.06 %) and tetra + (27.31 %).

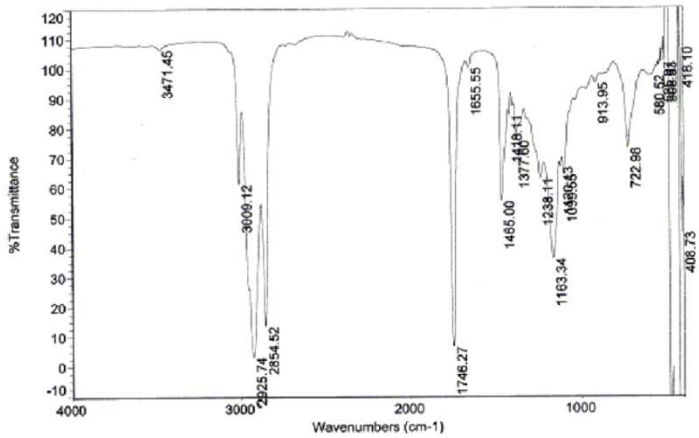
Comparing GPC analysis of two different BSBO:Acetol products, 15 and 20 % by wt, the sample prepared with a higher acetol loading had an increase in oligomer and decrease in free fatty acid concentrations. Most of the oligomers present in the acetol products are dimers (12 to 14 %) and trimers (43 to 55 %).

The GPC peaks calibrated at FA/FAME are likely fatty acid esters with acetol. The alcohol in acetol could readily undergo transesterification with the esters of the glycerides to yield single-acid esters.

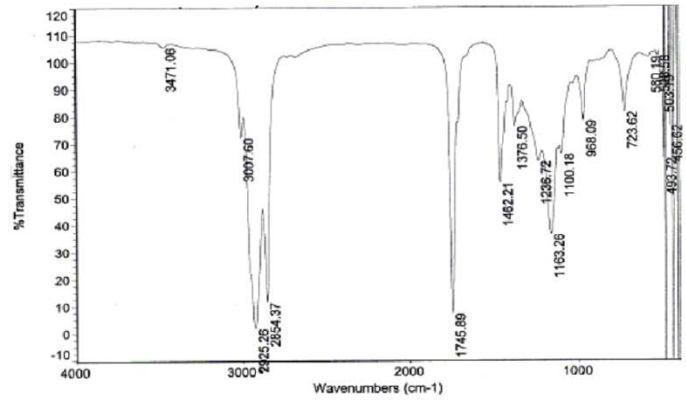
Table 7. GPC analysis and final properties for soybean oil, bodied soybean oil and two samples of bodied soybean oil with acetol (15 wt% and 20 wt%)

Properties	Samples			
	SBO	BSBO	BSBO:Acetol 15	BSBO:Acetol 20
Acid No.	0.5	13	17.3	5.2
Iodine No.	132	87	69.1	66.5
OH No.	15	23.84	95.37	105.27
Epoxy %	N/A	N/A	0.93	0.79
Viscosity (cP)	56.52	671.05	2270.15	2095.2
GPC analysis				
Monomer %	100	34.68	14.89	11.97
Oligomer %	0	57.23	57.36	67.72
FA/FAME %	0	8.09	27.75	20.31
Mn	292	948	599	776
MW	280-300	2422	1682	2054

FT-IR spectra of soybean oil, bodied soybean oil, and acetol-alcohol addition to soybean oil and bodied soybean oil were presented in Figure 14 and Figure 15. In comparison with the soybean oil spectra, the disappearance of carbon-carbon double bond at 1655 cm^{-1}, and the emergence of hydroxyl groups at 3470 cm^{-1} are obvious. These results confirm the mechanism for heat polymerization of soybean oil and the alcohol addition to add functionality in the final polyol.

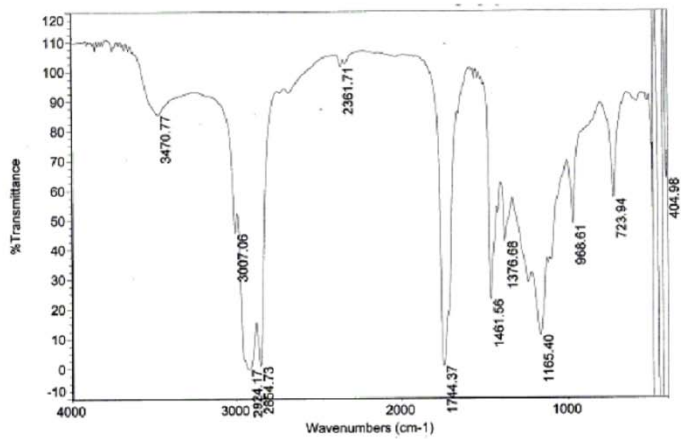


a.) FT-IR spectra of soybean oil

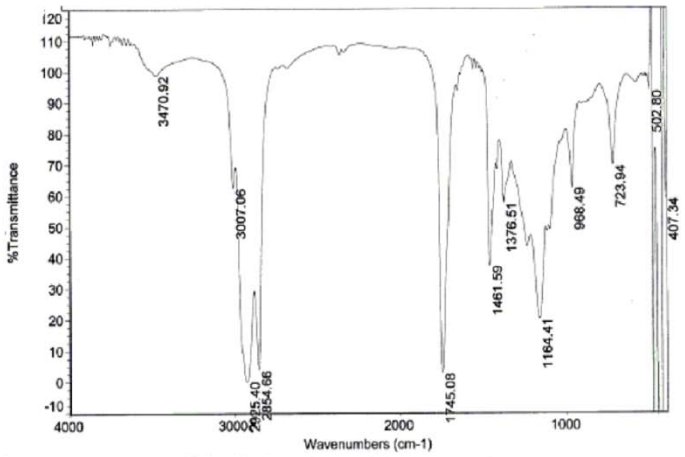


b.) FT-IR spectra of bodied soybean oil

Figure 14. FT-IR spectra for soybean oil (a) and bodied soybean oil (b)



a.) FT-IR spectra of soybean oil with acetol



b.) FT-IR spectra of bodied soybean oil with acetol

Figure 15. FT-IR spectra of alcohol addition of soybean oil with acetol (a) and bodied soybean oil with acetol (b)

2.5. Conclusion

Bodying of soybean oil was used to create a higher molecular weight feed stock for synthesizing polyols. Bodying increased the average molecular weight of SBO from its starting molecular weight of 948 to 1000-2400 for the bodied products.

Bodying in a flow reactor followed conversion trends as a function to temperature and residence time as projected in the batch reactor. Acidity increased steadily during the bodying process. Relative to the non-catalyzed reaction, the use of (9, 10)-anthraquinone as a catalyst led to decreased reaction times for the same increase in viscosity, led to lower iodine values, and to a decrease in acidity for a given decrease in iodine number (or increase in viscosity).

Acetol was able to undergo a reactive addition to both SBO and BSBO to provide alcohol functionality confirmed by FT-IR spectra. Polyols prepared using acetol exhibited marked increases in acid number due by the hydrolytic effect in the reaction. The average molecular weight for soy-based polyols made from the reaction of BSBO and acetol were about 1500 to 2100 depending on the iodine value of the starting material

2.6. Acknowlegment

We thank the United Soybean Board, Omnitech and CPBR for the financial support. We also thank Mr. Ali Teekei for his knowledge and collaboration in the polyol project.

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CHAPTER 3

SOY-BASED POLYOLS FOR POLYURETHANE APPLICATIONS

3.1. Abstract

Soy-based polyols were synthesized by oligomerizing partial epoxidized soybean oil. The oligomerization process appears to include Diels-Alder and epoxide chemistry mechanisms with the epoxidized soybean oil realizing more-rapid increases in viscosity than commercial soybean oil at similar oligomerization conditions. This oligomerization mechanism includes the consumption of epoxide moieties and creation of alcohol moieties.

Ethylene glycol was an effective co-reagent in the alcoholysis/oligomerization reaction of partially epoxidized soybean oil. A linear correlation between hydroxyl value and ethylene glycol concentration was observed at 250°C for 20 to 24 hrs of reaction. The increased reactivity of the products made with ethylene glycol (co-reagent) was attributed to the primary hydroxyl functionality made possible by the ethylene glycol.

Keywords: polyols, soybean oil, epoxidized soybean oil, alcohol addition, ethylene glycol reaction

3.2. Introduction

Vegetable oils are established sources of feedstock for the chemical industry. Glycerol from triglycerides has replaced petroleum-based glycerol production.[1] The oleochemical industry is well-established and includes production of a range of chemicals based on fatty acids.[2] The biodiesel industry, which converts vegetable oils to a diesel fuel substitute, is debatably the fastest growing industry in the U.S.[3]

In 2007 the bio-based industry reached an impacting milestone. The demands for commodity cereal crops exceed supply, and the rapid inflation of cereal commodity prices caused much of the biodiesel industry to cease production.[4] There is a basis for serious doubt to be placed on the sustainability of a renewable fuel industry that based on government subsidies. An indicator of this sustainability issue is the early 2008 price of soybean oil at 50-60 ¢/lb when the fuel made from this feedstock competes against petroleum based diesel at 30-35 ¢/lb.[5]

With petroleum-based polyol prices exceeding 100 ¢/lb, soy-based polyols may sustainable based on technologies having high atom economies and low production costs. The polyol industry can be broadly divided as polyols for rigid, flexible, and elastomer urethanes.

Typical soy-based polyol synthesis approaches result in moieties attached to a triglyceride (MW of ~873 g/mole), diglyceride (MW of ~612 g/mole), and monoglycerides (MW of ~350 g/mole). Those molecular weights are low compared to “slabstock” polyols with molecular weight of 3,000 or greater, and cause a reduction in flexibility of the final urethane product.[6] Improved soy-based polyols are needed for use in the flexible polyurethane foam market.

The bodying of soybean oil (BSBO), bodying of epoxidized soybean oil (BESBO), and bodying of partially epoxidized soybean oil (BPESBO) have been introduced as processing methods in two recent patent applications.[7, 8] This paper presents a more detailed discussion of partially epoxidized soybean oil (PESBO) oligomers and their performance in polyurethanes. This resulting polyols has higher molecular weight than those resulting from functionalization of soybean oil without oligomerization.

Polyols synthesized by oxirane ring opening of epoxidized soybean oil (ESBO) has been previously proposed.[9-12] Soy-based polyols have been synthesized by the catalytic ozonolysis process.[13, 14] Additional studies involving hydroformylation, esterification, and transesterification improved the synthesis process. However, the majority of the soy-based polyol synthesis methods cannot be easily converted to high molecular weight products (MW > 1500 g/mole) without the introduction of functional groups such as hydroxyl, epoxy or other groups.

Hydrolysis of ESBO shows a substantial degree of oligomerization due to oxirane-oxirane, and oxirane-hydroxyl reactions that occur.[15, 16] Different pathways for cycloaliphatic epoxides were studied previously.[17, 18] 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 (acetoxy and methoxy).[19, 20]

Kiatsimkul demonstrated that enzymes can be effectively used to remove saturated fatty acid moieties which results in glyceride molecules having primary-functional alcohols (saturated fatty acid are mostly positioned in the 1 and 3 positions of

glycerol in natural glycerides).[21, 22] Similar techniques may be useful to functionalized oligomers as discussed in this paper.

The present work proposes a few new soy-based polyols which are produced by oligomerization of triglycerides (or derivatives of triglycerides) and have high reactivity with isocyanate in elastomers and flexible polyurethane foam production. The emphasis is on enhanced bodying through reaction of epoxide moieties on triglycerides. The functionality of bodied oils was improved by alcohol addition reaction in the polyol production and their performance in the water-blown flexible polyurethane foam.

3.3. Experimental set up

3.3.1. Materials

Partially epoxidized soybean oil (PESBO) (2.11 % epoxy content) and epoxidized soybean oil (ESBO) (7.0 % epoxy content) were supplied from Arkema Co. (Prairie, MN.). Voranol® 4701 and PAPI® were obtained from Dow Chemical (Midland, MI). Voranol® 4701 is a petroleum-based polyether polyols with a hydroxyl number of 34 mg KOH/g and PAPI® 27 (a polymeric diphenylmethane diisocyanate: MDI) with 2.7 NCO functionality, has 340 average molecular weight and 31.4 % parts by weight of NCO content. Ethylene glycol (HPLC grade 99 wt.%) and (9-10) anthraquinone (97 wt.%) powder catalyst were purchased from Sigma-Aldrich (St. Louis, MO.). Soybean oil (SBO RBD) was acquired in a local store.

DABCO® 33-LV, DABCO® BL-17, stannous octoate, dibutyltin dilaurate were used as catalysts and DABCO® DC2585 was the surfactant for flexible polyurethane foaming. A cross-linker, diethanolamine, was used in flexible polyurethane foaming.

DABCO® 33-LV, DABCO® BL-17, DABCO® DC2585 were supplied from Air Products & Chemicals (Allentown, PA) for free. Stannous octoate, dibutyltin dilaurate and diethanolamine were purchased from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

3.3.2. Reaction Synthesis

3.3.2.1. Polymerization Reaction

Soybean oil (SBO) and partially epoxidized soybean oil (PESBO)were heated using a 2 L stainless steel closed Par® reactor to produce bodied soybean oil (BSBO) and bodied partially epoxidized soybean oil (BPESBO), respectively. The reactor was purged constantly with nitrogen to remove any volatiles compounds and set at 330°C and stirred at 200 rpm. Samples were collected on intervals of 30 minutes for 4 hours of reaction.

Catalyzed BPESBO was prepared by adding 2.50 wt. % of (9,10)-anthraquinone catalyst and PESBO in the Parr reactor, heated at 300°C and 200 rpm for 4 hours. In order to follow up the reaction kinetics two samples were collected for testing.

3.3.2.2. Alcohol Addition Reaction

BPESBO and ethylene glycol were placed in a 125 ml closed stainless steel vessel equipped with stirrer, heater, and temperature controller. Six different concentrations for ethylene glycol were evaluated at 250°C for 18 to 30 hours (epoxy content < 0.2%).

3.3.3. Analytical Methods

The final products were analyzed for acid number, iodine number, hydroxyl number, epoxy percent, color, and viscosity. The acid number (mg KOH/g sample) indicates the number of carboxylic acid functional group per gram of dry sample,

according to the AOCS official method (Te 1a-64, 1997). The iodine number gives the amount of un-saturation present in a dry sample, according to the ASTM D1959-97. The hydroxyl number (mg KOH/g sample) by the ASTM D 4274-05 measures the hydroxyl groups in the polyester and polyether polyols containing primary and secondary hydroxyl groups. The epoxy percent of a dry sample is analyzed by an official method, AOCS Cd 9-57 (1997), oxirane oxygen in epoxidized materials. The Gardner color scale was used to describe the color of the final products, ASTM D 1544-98. The dynamic viscosity of the sample measured in centipoises (cP) at 22°C was determined using a Model RS100 Rheometer Haake-Thermoelectron (Newington, NH).

3.3.4. Characterization Analyses

Gel permeation chromatography (GPC) was used to investigate molecular weight (MW) distribution. Dry sample (50 mg) was dissolved in 5.0 g of tetrahydrofuran (THF, Chromasol® from Sigma-Aldrich, St. Louis, MO.) and 500 μL of the sample solution was transferred to a 1.0 mL vial.

The HPLC, Hewlett Packard series 1100 with degasser, quaternary pump and auto sampler was used. Data acquisition, program control, and analysis were set and done by the HP Chemstation software version 06.01 (Palo Alto, CA.). The detector was a light scattering detector, Altech 500 ELSD (Deerfield, IL.). Two Viscogel-columns, I-MBLMW-3078 from Viscotek (Houston, TX.) were connected in series. The mobile phase was THF with a flow rate of 0.5 mL/min at a pressure of 16.2 psig. The drift tube temperature for ELSD was 60°C. Compressed air was the nebulization gas with a flow rate of 3.0 L/min at a pressure of 7.5 psig. The sample injected volume was set at 25 μL

and the needle injector was cleaned by THF after each sample injection. Analysis time was 40 minutes per sample.

A proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) analysis was used to follow the chemical structure of the polyols. All ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Varian Unity spectrometer at 300 MHz (Palo Alto, CA.).

3.3.5. Extractability Analysis

Polyurethane elastomer wafers were prepared by mixing 1.0 g of soy-based polyol with 0.5 g of isocyanate (PAPI® 27, MDI) for few seconds, and then dried at 110°C for 10 hrs. A gravimetric analysis was performed for a simple extraction analysis. The extraction comprised by soaking approximately 0.50 g of polyurethane elastomer 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 collected. Samples were dried of solvent in an oven prior to weighing before and after extraction.

3.4. Flexible polyurethane Foam Application

3.4.1. Foam Procedure

The effect of replacing the B-side polyether polyol (VORANOL® 4701) with 50% of soy-based polyol (modified BPESBO:EG) in the foam formulation on the properties of water-blown flexible polyurethane foam was studied. An isocyanate index of 80 was used for soy-based polyol replacement in the foam formulation, including 100 % of Voranol® 4701 as control for comparison purposes. The amount of isocyanate was based on the total hydroxyl number of the Voranol® 4701, soy-based polyol and distilled water used. Other factor in the foam formulation such as water content, catalysts and surfactant were

kept constant. Table 8 shows the foam formulation for water-blown flexible polyurethane foam.

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used. The petroleum polyol (Voranol® 4701), soy-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 seconds. The mixture was allowed to degas for 120 seconds. PAPI® 27 (MDI, A-side material) was then added rapidly and stirring was continued for another 10–15 seconds at the same speed. The mixtures were poured immediately into a wooden mold (11.4 x 11.4 x 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C).

Table 8. Formulations for water-blown flexible polyurethane foam

Ingredients	Parts by weight
B-side materials	
VORANOL® 4701	100, 50
Soy-based polyol	0, 50
DABCO® 33-LV	0.6
DABCO® BL-17	0.2
Stannous octoate	0.3
Dibutyltin dilaurate	0.3
Diethanolamine	2.2
DABCO® DC 2585	1.0
Blowing Agent (distilled water)	5.0
A-side materials	
PAPI® 27	Index[a] 80

a The quantity of isocyanate was based on an isocyanate index 80, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

3.4.2. Foam Properties

The density, 50% compression force deflection, 50% constant force deflection, and resilience (ball rebound test) of flexible polyurethane foams were measured according to ASTM procedure D 3574-05. Fifty percent compression force deflection was determined by a TA.HDI Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). For 50% constant force deflection or compression set, the initial foam thickness was measured first. The foam was then pressed to 50% of initial thickness and placed into a VersaTenn III Temperature-Humidity Chamber (Tenney Engineering Inc., Williamsport, PA) set at 70ºC and 6% RH for 22 h. The final thickness was measured after the foam was removed from the constant temperature-humidity chamber and placed in ambient environment (23°C and 50% RH) for 30 to 40 min. The compression set was calculated by the following equation:

$$C_t = \left(\frac{t_o - t_f}{t_o} \right) x100$$

where:

C_t = compression set expressed as a percentage of the original thickness, t_o = original thickness of test specimen, and t_f = final thickness of test specimen.

3.5. Results

3.5.1. Reaction Synthesis Results

In order to follow the extent of the polymerization reaction, several properties were measured: a.) iodine number (Figure 16), b.) viscosity (Figure 17), c.) oxirane oxygen percent (epoxy content) and acid number (Figure 18), and d.) hydroxyl number (Figure 19). Heat polymerization for commercial soybean oil and partially epoxidized soybean oil were compared in terms of iodine number for 4 hours of reaction at 330°C as shown in Figure 16.

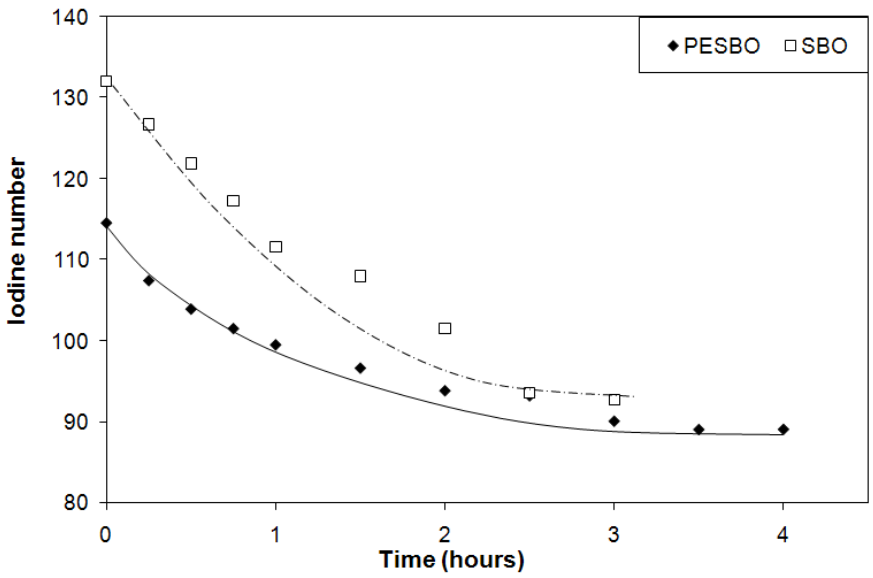

Figure 16. Effect on iodine number related with time for heat polymerization of PESBO and SBO at 330°C

Previous studies indicate a Diels-Alder reaction as the predominant mechanism during the oligomerization and result in a conjugated carbon-carbon π-bond reactant with a decrease in unsaturation. Meaning that three carbon-carbon π-bonds become two. The decrease in iodine number illustrated by Figure 16 suggests this olefin chemistry, perhaps the Diels-Alder reaction, also occurs during the oligomerization/bodying of PESBO.

Figure 17 shows the viscosity profiles for soybean oil (SBO) and partially epoxidized soybean oil (PESBO) oligomerization reactions. For 2.5 hours of reaction, the iodine number for soybean oil is similar that of PESBO; however, the viscosity increase for the PESBO is about six times that of the SBO. The sharp viscosity increase half the iodine number decrease indicates that there is an epoxide-based oligomerization reaction occurring as well as an olefin-based polymerization in the PESBO.

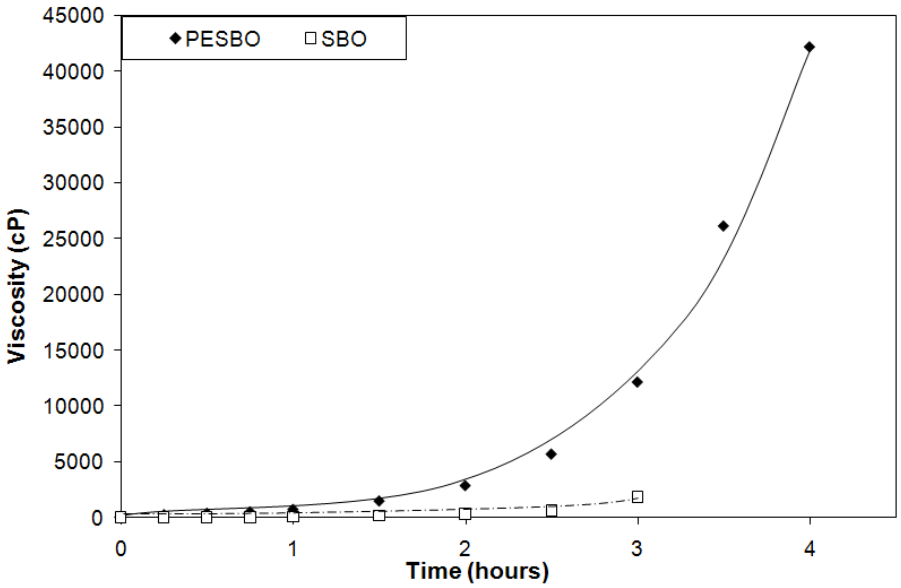

Figure 17. Viscosity effects related with time for heat polymerization of PESBO and SBO at 330°C

The oxirane oxygen content and acid number profiles are illustrated in Figure 18. The great reduction of oxirane oxygen content can be attributed to the polymerization reaction. Multiple reactions are likely in the bodying of PESBO, including: double bond migration, six-carbon ring formation, and oxygen addition. Also oligomerization reaction

between oxirane oxygen groups result in the formation of oligomeric ethers by protonation of oxirane oxygen at higher temperatures.

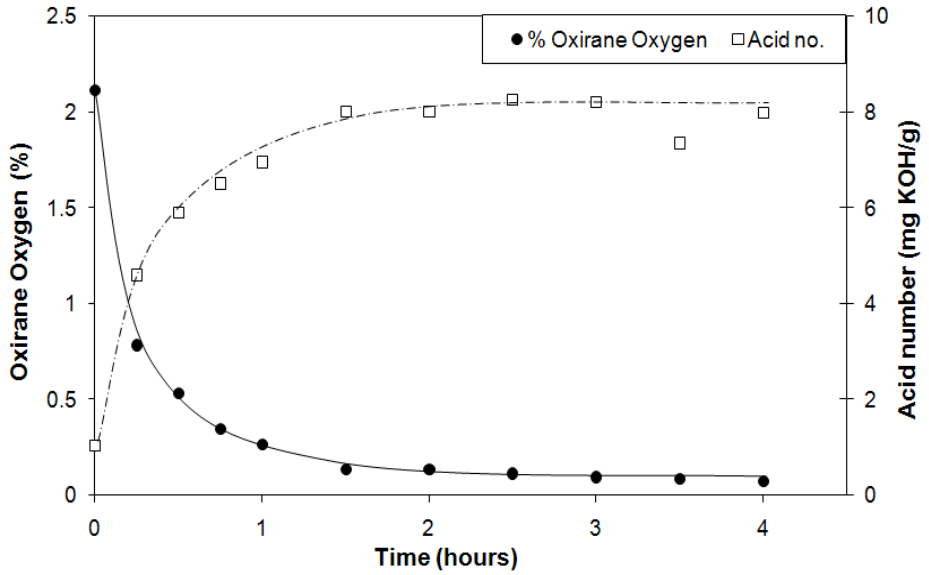

Figure 18. Acid number and oxirane oxygen content (%) related with time for heat polymerization of PESBO at 330°C

At higher temperatures, it was observed that acidity and hydroxyl numbers increase during soybean oil heat polymerization, and this is attributed to the cleavage of ester bonds. The acid and alcohol groups created by the cleavage of ester bonds provide a source for alcohols to initiate oxygen addition.

At lower temperatures epoxide functionality is known to react with acid to reduce the acid number. The increase in acid number for this system is likely due to the combination of: higher temperatures on the reaction of epoxy with acid, continuous ester bond cleavage which replenishes the acid concentration, and the low epoxy concentration after the first 30 minutes of reaction.

During the oligomerization of PESBO, the hydroxyl number steadily increases as shown Figure 19. If each epoxide group reacted to form an alcohol group the resulting oligomer would have a hydroxyl number of about 135 to 140 mg KOH/g (based on epoxy-ring opening hydrolysis reaction).

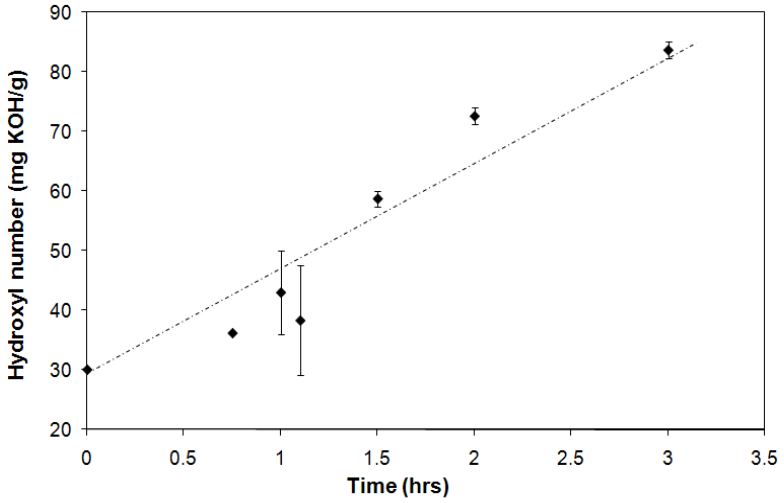

Figure 19. Hydroxyl number related with time for heat polymerization of PESBO at 330°C

The steady increase in hydroxyl number may attributed to continued breaking of ester bonds. When epoxide moieties react with ester or acids, each epoxide is converted to an alcohol moiety. When an alcohol formed from the reaction with an epoxide proceeds to react with another epoxide moiety, the alcohol is preserved but the one-to-one conversion of epoxide moieties to alcohol moieties is not preserved.

The impact of catalyst for polymerization reaction of PESBO was evaluated to reduce temperature and oil degradation by high temperature and reaction time. Table 9 shows the summarized results for polymerization of PESBO using 2.5 % by weight of 9,10-anthraquinone (AQ) catalyst concentration and heat polymerization of ESBO.

Increasing viscosity was observed for both polymerization reactions, BPESBO and BESBO respectively. The epoxy content decreased rapidly during the first hour. Since the epoxy content rapidly decreased, subsequent increases in viscosity are likely due to bodying of carbon-carbon π-bonds. The hydroxyl number for BPESBO increased rapidly during the epoxy-ring opening results in a significant change in acid number, iodine number and color. Also, at 300°C, the temperature may be higher than necessary in view of drastically reduction of epoxy content and color index.

A different mechanism is involved in the polymerization of ESBO: formation of oligomeric ethers by protonation of epoxy group at high temperatures. The polymerization or oligomerization of epoxy group content oil can lead to formation of high molecular weight polymers. High viscosity oligomers resulted in highly branches (high cross-linking) and high viscosities (indicative of high molecular weight), as shown in Table 9.

Table 9. Final properties for heat polymerization of ESBO and catalyzed polymerization of PESBO using 2.5 wt-% of AQ

Samples	Temp/time (°C/hrs)	Acid No. (mgKOH/g)	Iodine No. (mg I2/g)	Viscosity (cP)	Epoxy (%)	Hydroxyl No. (mgKOH/g)	Color Index
PESBO	25/0	1.1	114	73	2.11	32.0	1
BPESBO-2.5AQ	300/3	3.7	93	2173	0.05	49.0	3
BPESBO-2.5AQ	300/5	4.0	86	10182	0.03	69.8	5
ESBO	25/0	0.5	1	362	7.00	403.8	1
BESBO	300/1	-------	------	2799.9	3.40	137.8	5

Preliminary polymerization results of the BPESBO from Table 9 and Figure 19 revealed that the alcohol groups tended to react slower than the commercial polyol to which it was compared. The hypothesis attributed the slow reactivity to secondary alcohols and perhaps secondary alcohols that have significant stearic hindrance to reaction with isocyanates.

To increase the reactivity of the bodied PESBO, ethylene glycol was added as a co-reagent during the polymerization process. Ethylene glycol is relatively inexpensive and has a high hydroxyl number, 1807 mg KOH/g.

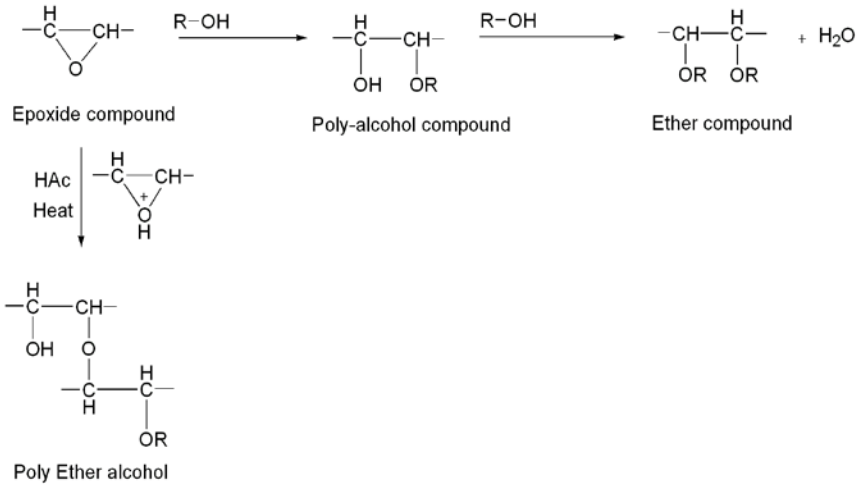

Figure 20. General mechanism for the epoxy-ring opening hydrolysis reaction (R-OH was an alcohol)

A general reaction mechanism for epoxy-ring opening hydrolysis of epoxy compounds with an alcohol compound followed by glycol formation and alcohol dehydration producing ethers are shown in Figure 20. Ether formation results when one alcohol moiety acts as nucleophile and a protonated alcohol moiety acts as the substrate. Oligomerization reaction occurs between epoxide compounds result in the formation of

oligomeric ethers by protonation of oxirane oxygen with heat, as illustrate in Figure 20. Ethylene glycol acts like nucleophile during the alcoholysis reaction. This modification proposes that for one oxirane oxygen present in the PESBO/BPESBO, two hydroxyl functional groups will be formed in the molecule.

Modified BPESBO:EG was evaluated using ethylene glycol (EG) concentrations of 1, 2, 2.5, 3.4, 5, and 10% with addition at 250°C. Results are shown in Table 10. The BPESBO was prepared by heating PESBO at 280°C for 3 hours with constant nitrogen purge.

Table 10. Conditions and product final properties for alcohol addition reaction to BPESBO

Simple description	Temp (°C)	Time (hrs.)	Acid No. (mgKOH/g)	Iodine No. (mg I2/g)	Oxirane (%)	Viscosity (cP)	Color Index
BPESBO	0	0	2.3	104	0.90	200	1
BPESBO with 1 wt% EG	250	1	8.2	104	0.80	213	1
BPESBO with 1 wt% EG	250	18	18.1	100	0.27	343	1
BPESBO with 2 wt% EG	250	20	5.0	96	0.21	486	2
BPESBO with 2.5 wt% EG	250	24	11.0	95	0.14	326	2
BPESBO with 3.4 wt% EG	250	24	2.6	94	0.56	355	3
BPESBO with 5.0 wt% EG	250	30	4.2	93	0.37	305	2
BPESBO with 10 wt% EG	250	24	4.2	97	0.13	354	2

The products of Table 10 are very different than the products without ethylene glycol present. The significant reduction in viscosity can be attributed to less carbon-carbon π–bond bodying at these lower temperatures; this is supported by the generally higher iodine numbers. The lower viscosities could also be attributed to pre-mature chain termination by the ethylene glycol.

Figure 21 illustrates trends in alcohol content. More ethylene glycol leads to moderately higher alcohol contents until more ethylene glycol is present than can react with the epoxy moieties. The samples has a surprisingly low final hydroxyl number at low concentrations of ethylene glycol, between 1 to 5 wt. %.

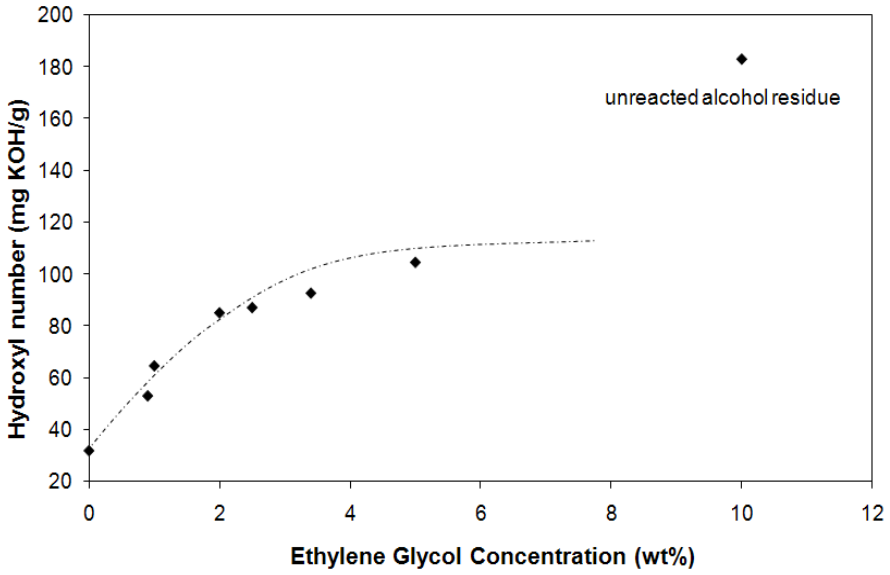

Figure 21. Hydroxyl number related with ethylene glycol concentration for BPESBO at 250°C

A favorable trend in the data of Table 10 is that at higher ethylene glycol contents, the acid numbers stabilize at 2.6-4.2 which is much lower than the previous data. The lower acid numbers are attributed to lower temperatures and that the alcohols (ethylene glycol) can react with acid groups to form ethers as illustrate in Figure 20.

3.5.2. Synthesis Characterization Results

Gel permeation chromatography (GPC) analysis for heat polymerization PESBO with viscosity of 1085 cP and viscosity of 1504 cP, and BPESBO with EG modified are summarized in Table 11.

The oligomers present for the BPESBO-1 and BPESBO-2 consisted mostly in dimers and trimers, with small amounts of tetra. The viscosity correlates well with the molecular weight. A high concentration of mono free fatty acid ester (FFA-ester) was found in samples of BPESBO with ethylene glycol. Evidently, the ethylene glycol undergoes substantial transesterification with the glycerides of the PESBO. This could be eliminated by using low temperature conditions in the alcohol addition reaction.

Table 11. Molecular weight distribution for heat polymerized PESBO and BPESBO with EG modified

Properties	Samples		
	BPESBO-1	BPESBO-2	BPESBO:EG 5 wt%
Acid No.	8.9	8.0	4.2
Iodine No.	97.8	86.0	93.0
OH No[a].	48.8	31.4	105.0
Oxirane Oxygen %	0.10	0.11	0.37
Viscosity (cP)	1085.0	1504.5	304.9
Color Index	2	3	2
	GPC analysis		
Monomer %	26.8	23.4	17.2
Oligomer %	61.1	74.0	37.3
Mono FFA Ester %	12.2	2.6	45.5
Mn	1029	1495	590
Mw	2483	7051	1038

[a] Hydroxyl number experimentally obtained by ASTM D 4274-2005.

Since many of the bodied PESBO products had viscosities in excess of 3,000 cP, it is projected that PESBO can be used to obtain highermolecular weights as well as viscosities greater than 3000 cP. The viscosity is an indirect method to evaluate the molecular weight in the final polyol. It appears that obtaining higher molecular weights with this approach is less of an issue than reducing the amount of mono FFA esters and triglyceride monomers.

Figure 22 shows the ^{1}H-NMR spectra of soybean oil (SBO) and heat polymerized soybean oil or bodied soybean oil (BSBO), respectively. The triglyceride of soybean oil has approximately 4.5 carbon-carbon double bonds per molecule according to the spectra, shown in Figure 22. The three side chains are composed of ~ 20-30% oleic acid (ester), ~ 50-80% linoleic acid (ester), ~5-10% linolenic acid (ester) and 15-25% of saturated fatty acids. The structure of bodied soybean oil is similar to that of the soybean oil, but with relatively low carbon-carbon double bonds (peak signals at 2.7-2.8 ppm bisallylic protons). Also, a reduction of olefinic protons was shown at 5.23-5.48 ppm indicating a low concentration in the BSBO molecule.

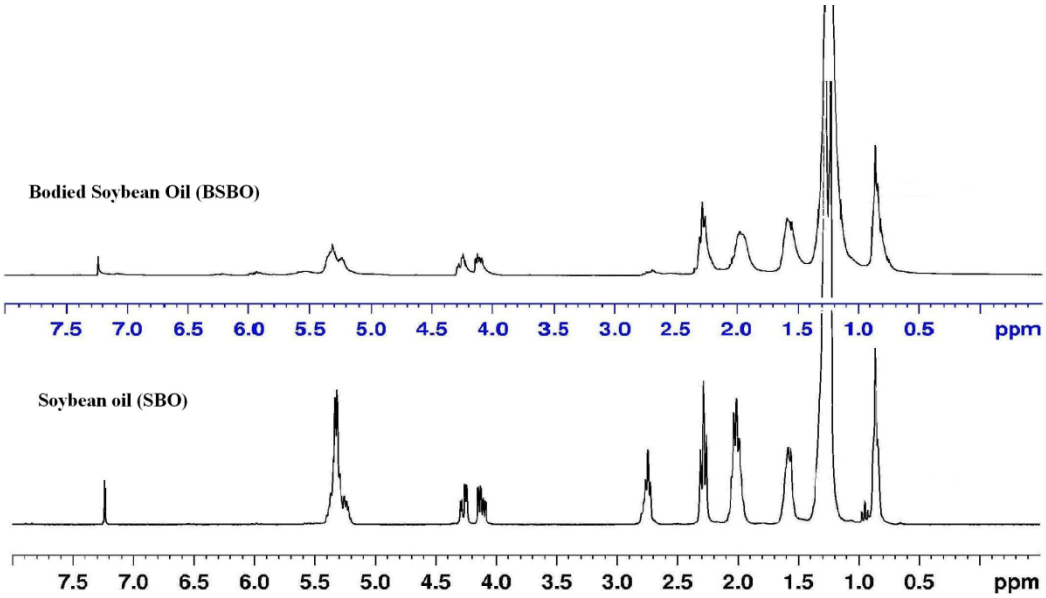

Figure 22. ^{1}H-NMR spectra of SBO and BSBO

Figure 23 shows the ^{1}H-NMR spectra of partially epoxidized soybean oil (PESBO) and bodied partially epoxidized with 5 wt% of ethylene glycol (BPESBO:EG modified). The structure of partially epoxidized soybean oil is similar to that of the soybean oil, but with relatively low carbon-carbon double bonds at 2.7-2.8 ppm and an

epoxide ring protons formation at 2.9-3.1 ppm. As shown in Figure 23, the olefinic protons at 5.23-5.48 ppm and the epoxide ring signal at 2.9-3.1 nearly disappear.

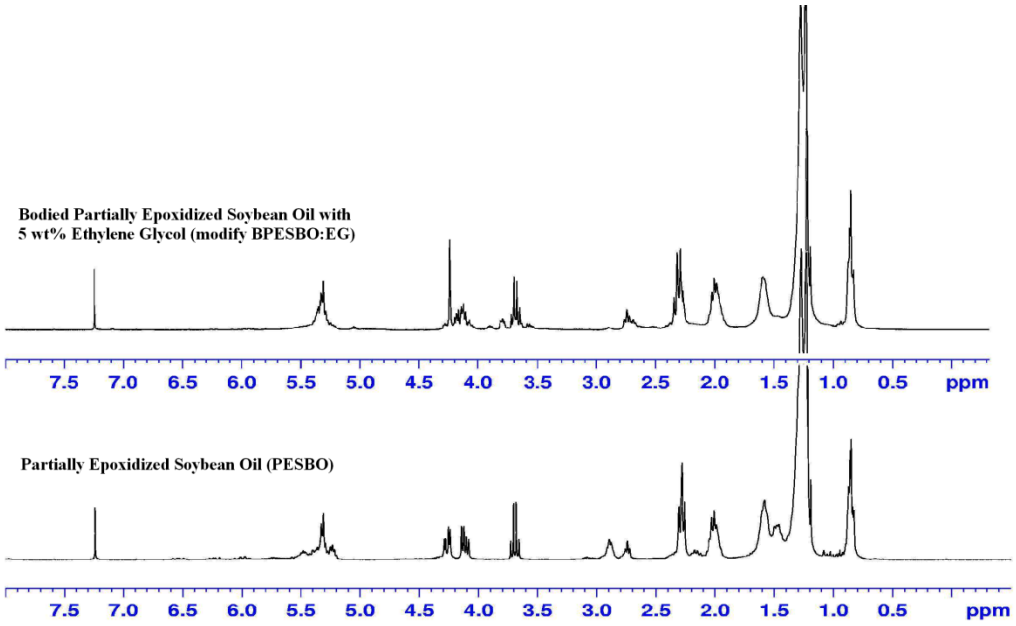

Figure 23. ^{1}H-NMR spectra of PESBO and modify BPESBO (5wt-% EG)

The presence of hydroxyl groups in the samples was confirmed by the appearance of a peak signal at 3.6-3.7 ppm indicating a multiplet signal for the $–CH_2$- or -CH in the hydroxyl groups formed, compared with the spectra of soybean oil, Figure 22 and Figure 23. Also, Figure 23 shows a reduction in the four methylene protons and methine proton from backbone structure (signal at 4.1-4.3 ppm). Lee and co-workers reported a comprehensive ^{1}H-NMR analysis for soybean oil and epoxidized soybean oil samples.[26]

3.5.3. Extractability Results

In theory, an increase in bodying would increase hydroxyl equivalent weights at the same hydroxyl number and this should decrease the extracted oil phase of the test

wafers. The low percent of oil extracted represents a high degree of cross-linking between isocyanate and polyol, which the polyol has more hydroxyl groups available to react with the isocyanate groups of MDI. Urethane wafer analyses were employed to the list of samples in Table 12 (Table 13 polyol properties) to determine any possible trend between oil extracted and polyol products.

Table 12. List of polyols for extractability analysis

Polyols	Product Synthesis
SBO	Soybean oil, commercial
ESBO	Epoxidized soybean oil, commercial
PESBO	Partially epoxidized soybean oil (25% epoxidized)
BPESBO-200cP	Heat treatment of PESBO at 280°C/3hrs
BPESBO-1000cP	Heat treatment of PESBO at 330°C/1hrs
BPESBO-2000cP	Heat treatment of PESBO at 330°C/2hrs
BPESBO-1 wt% EG	1% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs
BPESBO-2 wt% EG	2% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs
BPESBO-2.5 wt% EG	2.5% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs
BPESBO-3.4 wt% EG	3.4% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs
BPESBO-4.5 wt% EG	4.5% by weight Ethylene glycol in BPESBO and heat at 250C/20hrs
BPESBO-5 wt% EG	5% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs
BPESBO–10 wt% EG	10% by weight Ethylene glycol in BPESBO and heat at 250°C/20hrs

Figure 24 illustrates the trends between percent unreacted oil phase and heat polymerized products. As expected, higher degrees of oligomerization result in reduced unreacted oil phase. Bodied partially epoxidized soybean oil (with 7.0% unreacted oil phase) has shown considerable reactivity and cross linking with polymeric MDI,

compared to SBO, that does not set upon curing. BPESBO has a higher molecular weight than PESBO, so fewer reactive moieties yield reduced extractability.

Table 13. Properties of polyol used in the extractability analysis

Sample description	Acid No.	Iodine No.	OH[a] No.	Oxirane %	Viscosity cP	Color Index
SBO	5.0	132	10	0.00	57	1
ESBO	1.0	5	404	6.80	362	1
PESBO	1.0	114	32	2.11	73	1
BPESBO-200cP	2.3	104	32	0.90	200	1
BPESBO-1000cP	8.9	98	49	0.10	1085	2
BPESBO-2000cP	7.0	81	58	0.09	2318	2
BPESBO-1 wt% EG	18.1	100	65	0.27	343	1
BPESBO-2 wt% EG	5.0	96	85	0.21	486	1
BPESBO-2.5 wt% EG	11.0	95	87	0.14	326	2
BPESBO-3.4 wt% EG	2.6	94	93	0.56	355	2
BPESBO-4.5 wt% EG	4.2	97	100	0.50	295	3
BPESBO-5 wt% EG	4.2	93	105	0.37	305	2
BPESBO-10 wt% EG	4.2	97	183	0.13	354	2

[a] Hydroxyl number experimentally obtained by ASTM D 4274-2005.

Figure 24 illustrates the trends between percent unreacted oil phase and heat polymerized products. As expected, higher degrees of oligomerization result in reduced unreacted oil phase. Bodied partially epoxidized soybean oil (with 7.0% unreacted oil phase) has shown considerable reactivity and cross linking with polymeric MDI, compared to SBO, that does not set upon curing. BPESBO has a higher molecular weight than PESBO, so fewer reactive moieties yield reduced extractability.

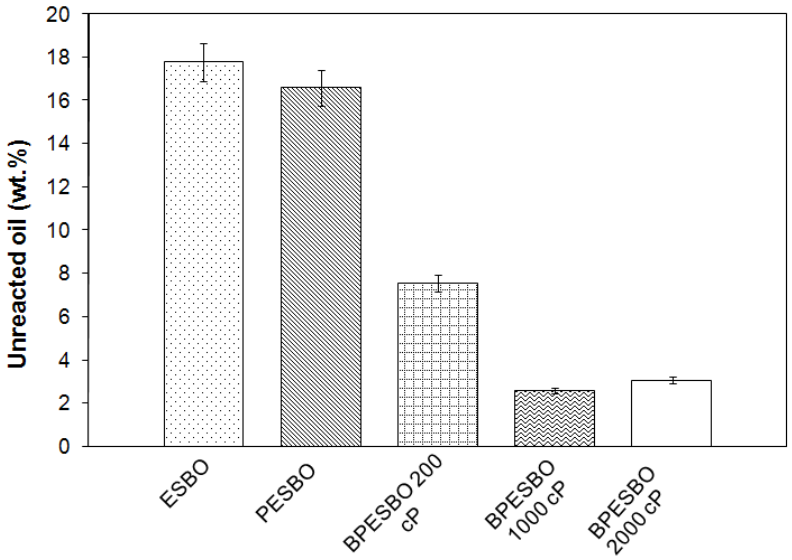

Figure 24. Effects on oil extracted wafer-urethane elastomer for ESBO and soy-based polyol samples

This illustrates that the primary goal of the bodying process is achieved—a larger molecular weight monomer was produced. The low percent of oil extracted represents a high degree of cross-linking between MDI and polyol since the polyol has more hydroxyl groups available to react with the isocyanate groups of MDI.

Figure 25 shows the effect on unreacted oil and the amount of ethylene glycol used in the alcohol addition reaction. Better cross-linking performance correlates with higher hydroxyl values of the soy-based polyols, which can be achieved initially bodying the partially epoxidized soybean oil and alcohol-addition of ethylene glycol to increase alcohol functional groups. Bodying PESBO reaction was initially employed to control hydroxyl moieties in the final product and avoid secondary reactions with hydroxyl groups.

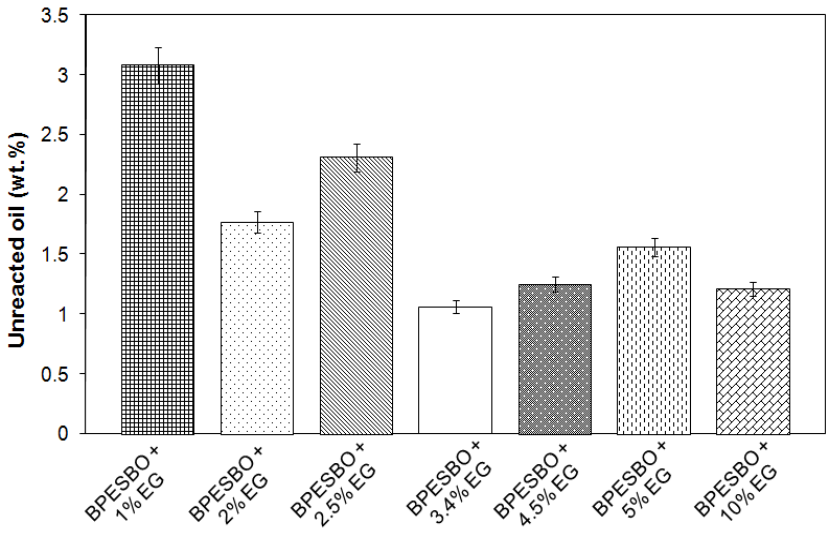

Figure 25. Effects on oil extracted wafer-urethane elastomer for soy-based polyol samples

A high amount of unreacted oil was expected for BPESBO with 2.5 wt% of ethylene glycol by high acid number. It's possible that the carboxylic acid present in the polyol reacts with the isocyanate forming an unstable compound. Also, the carboxylic acid is soluble in hexane solvent. The reaction between the isocyanate and the polyol was affected by the residual acidity of the sample.

3.5.4. PU Foam Results

The effect on replacing the B-side polyether polyol (Voranol® 4701) in the foam formulation was studied. The compression force deflection (CFD), constant deflection compression set (CDC), density, tear and resilience were determined. Table 14 shows the final foam properties for Voranol® 4701 compared with three BPESBO:EG modified samples at 50% replacement in the final foam formulation.

Table 14. Final water-blown flexible polyurethane foam properties for Voranol®4701 and three different soy-based polyols at 50% replacement

Foam	Sample description	Iso Index	Density (kg/m^3)	CFD (kPa)	CDC 50%	Tear (N/m)	Resilience (%)
1	Voranol® 4701	80	44.83	8.78	5.54	142.40	44.89
2	BPESBO with 3.4 wt% EG	80	36.25	8.81	44.11	146.71	27.56
3	BPESBO with 5.0 wt% EG	80	36.70	8.72	42.73	146.05	26.33
4	BPESBO with 10 wt% EG	80	37.16	11.4	48.53	144.33	24.00

The compression force deflection (CFD) test measures the force necessary to produce a 50 % compression over the entire top surface area of the foam specimen. A higher compression force deflection indicates the foam is firmer to do either a higher cross-linking density or a higher foam density or both. Similar 50% compression force deflection was observed for foams samples 1, 2 and 3. A small increase was observed for the foam sample 4 with a high hydroxyl number compared to the other samples.

This could be due to on foam density and cross-linking density. The cross-linking density increased (no data shown), because soy-based polyol had a higher hydroxyl number than Voranol® 4701. More isocyanate was used in the foam formulation, which increases the 50% compression force deflection.[27] The two effects might have cancelled each other; since there is no significant change compared with Voranol® 4701 as a control.

Constant deflection compression (CDC) test consists of deflecting the foam specimen to 50% initial thickness, exposing it to 70 ºC and 6% RH for 22 h and measuring the change in the thickness of the specimen after recovery at 23 °C and 50% RH for 30 to 40 min. A lower constant deflection compression set indicates the foam is more flexible and recovers its thickness better after deflection compression. As shown in the Table 14, all the foams made with 50% replacement of Voranol® 4701 with BPESBO:EG modified polyols has a nine times higher CDC compared with Voranol® 4701 as a control. It appears that the foams became less flexible and lost more of their initial thickness after deflection compression with 50% replacement of Voranol® 4701 in the foam formulation.[28]

The resilience of foams decreased steadily with the use of 50% replacement with BPESBO:EG modified polyols. The loss of resilience was most likely due to significant differences in the equivalent weight between Voranol® 4701 and BPESBO:EG modified polyol and their chemical structure. As a result, the foam containing soy-based polyols became stiffer and less resilient under the ball rebound testing conditions.

3.6. Conclusion

Soybean oil was partially epoxidized (about 25%) followed by bodying reaction to create higher molecular weight polyols. Bodying increased the average molecular weight of PESBO from its starting molecular weight of 950 to 2500-7050 for the bodied products. Low reactivity was identified as a problem with the bodied PESBO and was attributed to the prominence of secondary alcohols with stearic hindrance to reactions with isocyanates.

Alcohol addition to the oxirane was evaluated to improve number of hydroxyl functional groups. Polyurethane elastomer wafers analyses for BPESBO/EG products indicated a higher degree of cross-linking compared with ESBO and PESBO. Ethylene glycol and lower temperatures were effective in reducing acid numbers to 2.5-4.2 without further processing. Reducing the amount of mono free fatty acid esters (FFAE) formed from this process need to be studied.

3.7. Acknowledgments

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CHAPTER 4

SOY-BASED POLYOLS FROM OXIRANE-RING OPENING BY ALCOHOLYSIS REACTION I

4.1. 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 different catalysts: 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 promotes the reaction resulting in a maximum oxirane oxygen content reduction; low acid number and color index as 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 by varying temperatures and reaction times. FT-IR 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 for replacing up from 50 to 100% of the petroleum-based polyol in water-blown rigid polyurethane foam application. All polyurethanes foams were

evaluated to determine their thermal conductivity, density, and compressive strength properties.

4.2. Introduction

Polyols play an important role in the urethane industry and conventionally, a majority of them are derived from petroleum crude oil. The uses of petrochemicals such as polyester and polyether polyols are poor choices in terms of energy, production, and transportation costs; and the most importantly, petroluem is a non-renewable resource. Consumer demand for “greener” products continues to grow in view of the environment and sustainability; new polyols have been prepared from vegetable oils. Soybean oil is a more versatile, less costly, renewable, and environmental friendly component used to prepared vegetable-based polyols.

One of the important vegetable derived polyols is epoxidized soybean oil (ESBO). Epoxidized soybean oil can be synthesized by reacting hydrocarbon fatty acid glyceride from vegetable oil, such as soybean oils with peroxoacetic or peroxoformic acid in the presence of a solvent at mild temperatures.[1-3] ESBO is used as plasticizers, lubricants, a cross-linking agent, stabilizers, and pre-polymers. They are also 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, in order 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 a nucleophilic compound. Hydrolysis of epoxy rings in the presence of acids (phosphoric acid, sulfuric

acid, formic acid and acetic acid) were previously studied.[8-12] Different pathways for cycloaliphatic epoxides were also studied.[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 (acetoxy and methoxy).[15] Alcoholysis reactions using 2 ethyl hexanol, 1-butanol, 1-decanol and methanol were evaluated for lubricant formulations.[16, 17] Synthesis of alkoxylated 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 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 polyol production and polyurethane foam applications. In this study, epoxidized soybean oil (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 a catalyst to promote the reaction. The purposes for this study were identifying a catalyst that promotes the epoxy-ring opening reaction while avoiding side reactions. Select polyols were used in the water-blown rigid polyurethane foam formulation studies.

4.3. Experimental

4.3.1. Materials

Epoxidized soybean oil (7.0% oxirane oxygen content, VIKOFLEX® 7170) was purchased from ATOFINA Chemicals Inc (Philadelphia, PA). Ethylene glycol (HPLC grade 99 %), methanol (HPLC grade 99 %) were obtained from Fisher (Houston, TX). Formic acid (ACS reagent ≥ 88 %), phosphoric acid (ACS reagent ≥ 85 %) and *p*-toluenesulfonic acid monohydrate (Fluka ≥ 99 % mixture of isomers) was 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 diphenyl methane diisocyanate, MDI) was purchased from Dow Chemical (Midland, MI).

4.3.2. Methods

4.3.2.1. Screening study

For the screening reaction study, a 100 mL three-necked round bottom flask was charged with 50 grams of ESBO, 3.10 grams of ethylene glycol and 0.25 grams (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 hours at 150°C for each catalyst. Catalyst descriptions are illustrated in Table 15.

Table 15. Description of catalyst used on screening study

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

4.3.2.2. Alcoholysis reaction

In the epoxy-ring opening reaction, epoxidized soybean oil (200 grams, 0.20 moles), ethylene glycol (12.41 grams, 0.20 moles), methanol (4.80 grams, 0.15 moles) and *p*-toluenesulfonic acid monohydrate (1.0 grams, 0.5 wt.%) were placed in a 250 mL Par® reactor equipped with a thermocouple, stirrer, heating element, and Omega controller. Polyols properties were evaluated for different reaction times and temperatures, between 2 to 9 hours at 130, 150 and 170 °C, respectively.

4.3.3. 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), which 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 (used 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 1g 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 Haake – Thermoelectron (Newington, NH).

4.3.4. FT-IR Analysis

A FT-IR 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}.

4.3.5. Extractability analysis

Polyurethane elastomer wafers were prepared by mixing 1 gram of soy-based polyol with 0.5 grams of isocyanate (PAPI® 27, MDI), dried at 110°C for 10 hrs. A gravimetric analysis was performance for a simple extraction analysis. The extraction comprised by soaking approximately 0.5 grams 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 collected. Samples were dried of solvent in an oven prior to weighing before and after extraction.

4.3.6. Rigid polyurethane foam analysis

4.3.6.1. Foam procedure

The effect of replacing the B-side polyether polyol (VORANOL® 490) with 50 to 100% of alkoxy hydroxyl ESBO in the foam formulation on the properties of water-blown rigid polyurethane foam was studied. The isocyanate indexes at 50, 75 and 100 % of soy-based polyol replacement in the foam formulation were measured, 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 16 show the foam formulation for 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 seconds. The mixture was allowed to degas for 120 seconds. PAPI® 27 (A-side material) was then added rapidly and stirring was continued for another 10–15 seconds at the same

speed. The mixtures were poured immediately into a wooden mold (11.4 x 11.4 x 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C).

4.3.6.2. Foam properties measurements

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23°C) for 24 hr, by a Fox 200 heat flow meter (Laser Comp, Wakefiled, MA), using ASTM procedure C 518-04. The dimension of the foam samples was 20 x 20 x 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 x 6.35 x 3.81 cm.

Table 16. Formulation for water-blown rigid polyurethane foam with different isocyanate index

Ingredients	Parts by weight
B-side materials	
VORANOL® 490	100, 50, 25, 0
Alkoxyl 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.

4.4. Results

4.4.1. Screening study to select a catalyst

To determine an appropriate catalyst for the epoxy ring opening by alcoholysis reaction, the impact on the oxirane content, color and acid number were evaluated. Six different catalysts were used in ESBO and ethylene glycol reaction for 2 hours, as shown in Table 17. POLYCAT® SA-1, DABCO® BL17 and POLYCAT® 5 are catalysts 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 maximum reduction between them. *p*-Toluenesulfonic acid monohydrate (*p*-TSAc) was preferred in the

alcoholysis reactions due by the maximum yield of epoxy ring opening and no evidence of any side reaction occurs during the reaction.

Table 17. Effect on oxirane oxygen content, acid number and color index for screening study using six different catalysts

Catalyst Name	Concentration (wt. %)	Temp/time (°C/hrs)	Acid No. (mgKOH/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
p-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.

4.4.2. Alcoholysis reaction

In the alcoholysis reaction or addition polymerization reaction, ESBO was combined with ethylene glycol (EG) and methanol (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 Figure 26. 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 Figure 26.

In the first mechanism, the acid (HAc) reacts with the epoxide to produce a protonated epoxide and finally a glycol (poly-alcohol 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. An oligomerization reaction between oxirane groups results in the formation of oligomeric ethers by protonation of oxirane oxygen with acid catalyst, as illustrate in Figure 26.

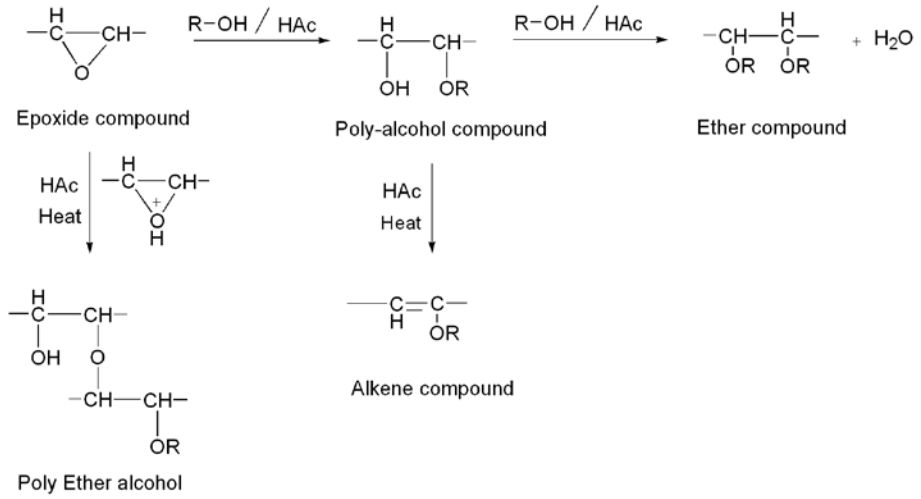

Figure 26. General mechanism for the alkoxy hydroxyl reaction (R-OH was an alcohol and Hac was an acid)

Methanol (ME) and ethylene glycol (EG) acts 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. Under these 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 be generated in the molecule.

In order to follow the extent of the alcoholysis reaction, several properties were evaluated: a.) oxirane oxygen content (Figure 27), b.) iodine number (Figure 28), c.) viscosity (Figure 29), d.) oil extracted (Figure 30), and e.) color index, acid, hydroxyl,

and saponification numbers (Table 18). To see the impact on the oxirane-ring opened by alcoholysis reaction, three temperatures (130°C, 150°C and 170°C) at different reaction times were evaluated.

Figure 27 shows the oxirane oxygen content effect as a function of temperature and reaction time. As expected, at high temperature, 170°C, the oxirane oxygen content shows a sharp reduction compared to temperatures of 150°C and 130°C. This abrupt reduction of oxirane oxygen content percent at high temperature (170°C) shows a high increase in acid number, iodine number and color index (Figure 28 and Table 18). In light of these changes, the experiments for nine and eleven hours were discontinued. As described by the mechanism, most of the oxirane-ring groups were opened, and consequently a considerable amount was converted to alkene compound, poly-ether alcohol, polymerization, and some cleavage of ester bonds in the molecule.

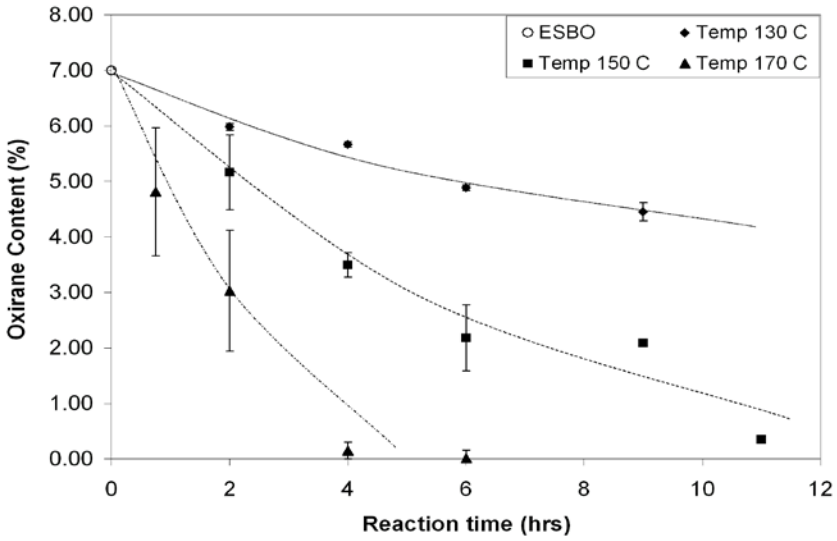

Figure 27. Effects on oxirane content of the alkoxy hydroxyl ESBO polyols related with temperature and reaction time

At lower temperatures, 150°C and 130°C, the reaction mechanism is more controllable. At 150°C the oxirane oxygen content curves shows a smooth reduction (Figure 28) as the reaction occurs. Fairly low oxirane-ring reduction was observed at 130°C after nine hours of reaction compared with 150°C for nine hours.

In Figure 28, the asymptotic approach to an iodine number of 12 at 150°C indicates a little change in carbon-carbon double bond formations in the molecule. At the lower temperature, 130°C, the π bonds formation is low as the reaction proceeds to nine hours. As described in the mechanism, higher temperature is required to form an alkene compound.

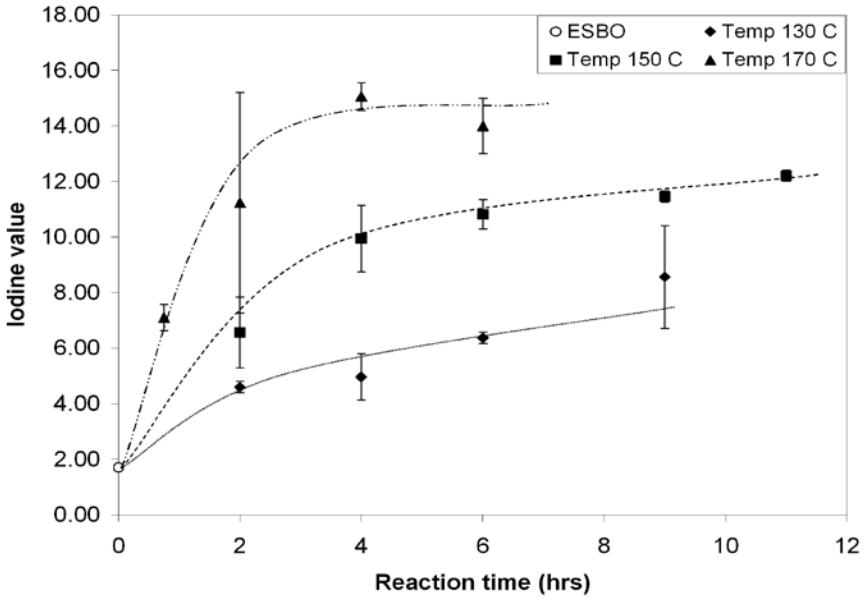

Figure 28. Effects on iodine value of the alkoxy hydroxyl ESBO polyols related to temperature and reaction time

The viscosity changes with temperature and reaction time as illustrated in Figure 29. A large increase in viscosity was observed at 150°C as a result of oligomerization

reaction and ether formation mechanism involved, as mentioned before. A different viscosity effect occurs at 170°C: an asymptotic approach to 3000 cP. This effect is explained by the complete reduction of oxirane oxygen content followed by a high degree of oligomerization (poly ether alcohol compound and ether compound) and alkene formation. As expected, there is no significant increase in viscosity at 130°C. This indicates that the poly alcohol reaction mechanism occurs instead of the poly ether alcohol mechanism.

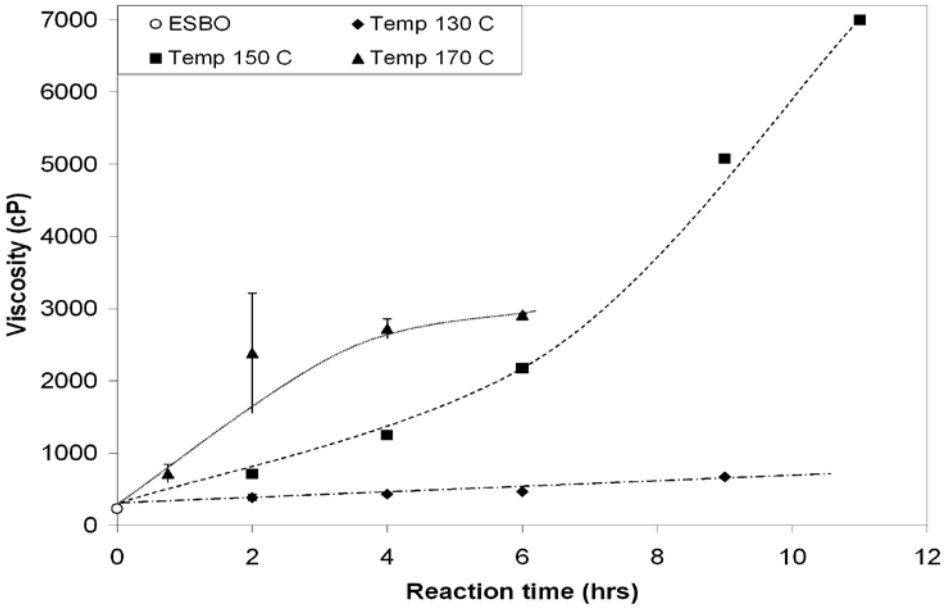

Figure 29. Viscosity effect of the alkoxy hydroxyl ESBO polyols related with temperature and reaction time

Table 18 shows the final properties of the alkoxy hydroxyl ESBO polyols at different temperatures and reaction times. 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. The color for this set of samples

drastically changes from 1 to 6 in the Gardner scale, and the saponification number shows that a small reduction indicates high molecular weight fatty acids present. The polyol sample I show a considerable decrease in hydroxyl number from 166 to 129.6 mg KOH/ g of dry sample respectively, by ether formation.

Table 18. Final properties of the alkoxy hydroxyl ESBO polyols: color index, acid, saponification and hydroxyl numbers

No.[a]	Temp/time (°C/hrs)	Acid value (mgKOH/g)	Oxirane Oxygen (%)	Saponification (mgKOH/g)	OH Exp. (mgKOH/g)	Color Index[b]
ESBO	25/0	0.5	7.0	183.3	11.5	0
Control	25/0	0.7	7.0	177.7	166.0	1
A	130/2	0.7	6.0	168.7	157.4	1
B	130/4	0.7	5.7	168.3	159.0	1
C	130/6	0.7	4.9	170.0	162.6	1
D	130/9	0.7	4.5	172.4	157.6	1
E	150/2	0.7	5.2	177.5	156.2	2
F	150/4	0.7	3.5	171.7	158.4	2
G	150/6	0.7	2.2	170.2	154.0	3
H	150/9	0.7	2.1	176.0	150.0	3
I	150/11	0.7	0.4	174.6	129.6	3
J	170/0.75	0.8	4.8	167.4	159.4	1
K	170/2	1.0	3.0	167.7	153.8	3
L	170/4	16.5	0.2	162.4	109.6	5
M	170/6	17.7	0.0	164.4	101.4	6

[a]Polyol recipe: 200 g ESBO, 12.41 g EG, 4.80 g ME and 1.0 g pTSA. [b]The Gardner color scale was used as a color index: 1 to 18 from light color to dark.

4.4.3. Extractability Results

Figure 30 shows the increase in viscosity of each polyol sample as a function of oil extraction. 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. Higher cross-linking between the reagents produces low extractable oil.

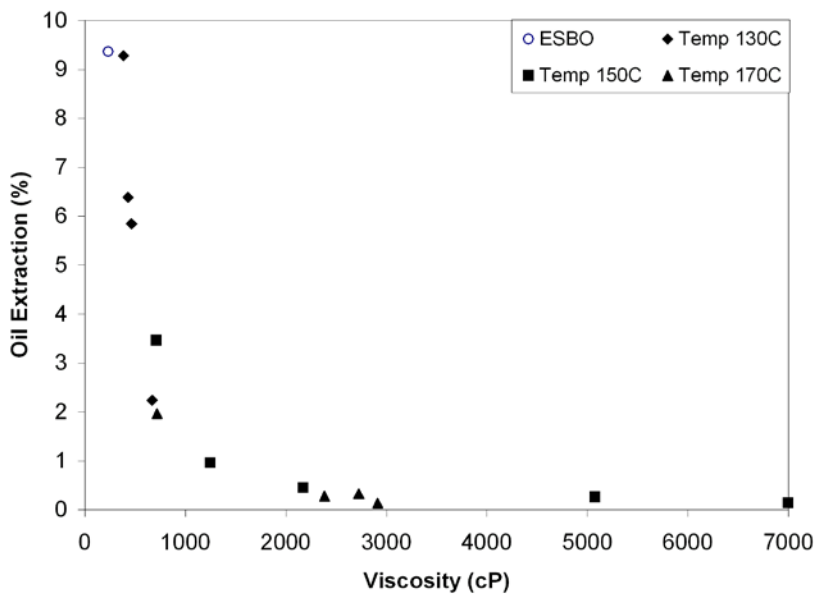

Figure 30. Viscosity effects relates with the oil extraction percent of the alkoxy hydroxyl ESBO polyol wafer-urethane elastomers

The low percent of oil extracted represents a high degree of cross-linking between diphenylmethane diisocyanate (MDI) and polyol this indicates that the polyol has more hydroxyl groups available to react with the isocyanate groups of diphenylmethane diisocyanate (MDI). Figure 31 shows the trend between oil extracted (unreacted polyol) and the alcoholysis soy-based polyol products. As expected, low oil extracted at 170°C results in oligomerization (poly-ether alcohol), high amount of carbon-carbon double

bond formation, and cleavage of ester bond by high acid number. A linear behavior for oil extracted at 130°C indicates a controlled degree of oligomerization, poly-alcohol formation and low quantity of π bonds.

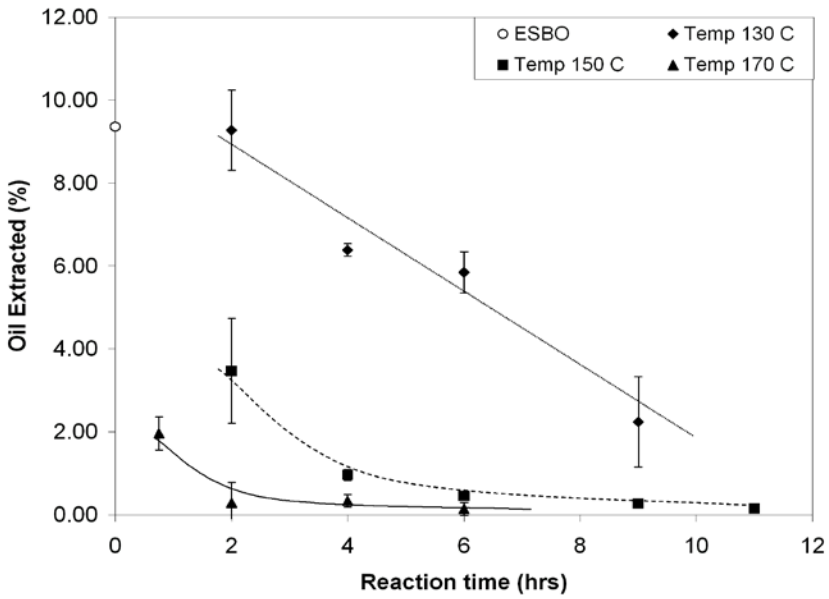

Figure 31. Effects on oil extracted wafer-urethane elastomer of alkoxy hydroxyl ESBO polyols related with temperature and reaction time

4.4.4. FT-IR spectroscopy results

FT-IR spectra of the epoxidized soybean oil (unreacted ESBO) and the prepared alkoxy hydroxyl-ESBO (Sample G) are presented in Figure 32. 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 mechanisms in Figure 26 were confirmed by the FT-IR spectra of sample G in Figure 32. The poly-alcohol compound formation was confirmed by peak signal at

3450 cm^{-1}. The ether compound and poly-ether alcohol compound formation were confirmed by peak signals from 1250 to 1040 cm^{-1}.

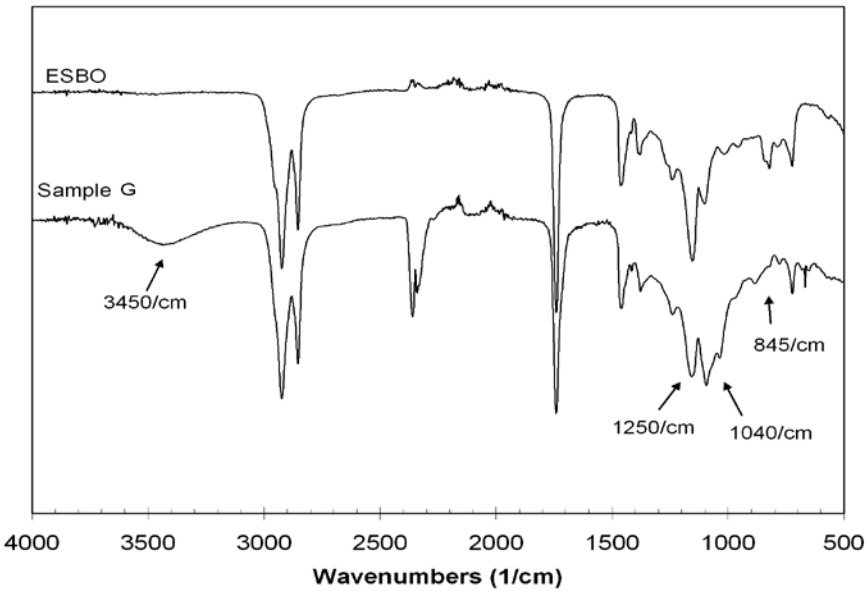

Figure 32. FT-IR spectra of epoxidized soybean oil (ESBO) and alkoxy hydroxyl ESBO (sample G)

4.4.5. Polyurethane foam results

The alkoxy hydroxyl ESBO polyol, sample G (properties shown in Table 18, 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 for water-blown polyurethane foam. VORANOL® 490 is a polyether polyol with 4.3 alcohol functionality, 460 average molecular weight and 490 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 were affected by the OH number of each polyol mixture. The hydroxyl number of each polyol mixture was calculated as follows:

$$OH_m = (OH_{Voranol\,490} \cdot A) + (OH_{soy-polyol} \cdot B)$$

Where OH_m is the hydroxyl of the mixture, $OH_{voranol490}$ is 484.4 mg KOH/g, $OH_{soy\text{-}polyol}$ is 278 mg KOH/g, A is the mass percent of VORANOL® 490 and B is the mass percent of polyol sample G.

Figure 33 shows the relationship between density of foams and the hydroxyl number of the polyol mixture. As shows the results, the high foam density was related to the higher isocyanate index or high amount of isocyanate present to react with the polyol mixture. The foam density is determinated 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 with a low OH_m usually shrank within a few days of storage at room temperature. This effect reduced the dimensions of foam resulting in higher density foams.

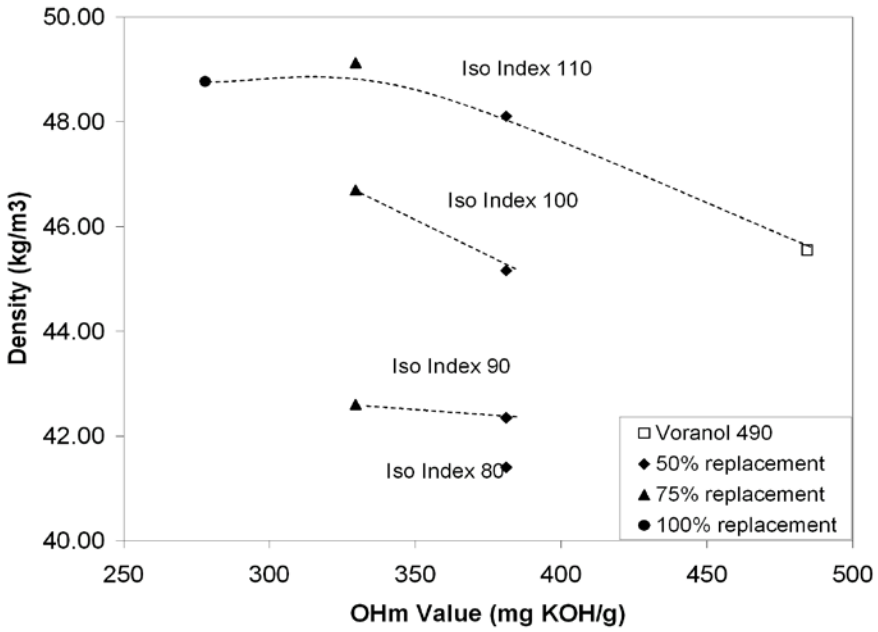

Figure 33. Density of foam for Voranol®490 and three different percent of replacement (50, 75 and 100%) versus hydroxyl number of polyol mixture

Table 19 show the effect on thermal conductivity for each foam sample at three different replacement percentages compared with VORANOL®490, as a petroleum-based control. The hydroxyl number did not significantly affect the thermal conductivity of the foams; most foam made from polyol sample G had results similar to foams made with 100% VORANOL®490. The thermal conductivity of foams is determined by the thermal conductivity of gas trapped in the foam cells, the thermal conductivity of foam cell membrane material, convection in the cell gas, cell size, the cell orientation, the closed cell content, the foam density, and thermal radiation. While the hydroxyl number of polyol mixtures (OH_m) influences the cross linking density of foams, the convection of gas is governed by the open cell content.

Table 19. Thermal conductivity of foams for Voranol® 490 and three different percent of replacement (50, 75 and 100%) with hydroxyl number 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 34 illustrate the effect of compressive strength with 0, 50, 75 and 100% of replacement of VORANOL®490 in the foam formulation versus hydroxyl number of each polyol mixture. This shows that compression strength of foams decreased with decreasing OH_m number of polyols. At lower OH_m number of polyols will consume less isocyanate yielding foams with lower cross linking density. This was probably caused by: 1) the slight reduction in isocyanate content when increasing alkoxyl hydroxyl-ESBO lowering the foam cross-linking density and 2) a weaker three-dimensional foam network with increased 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) .

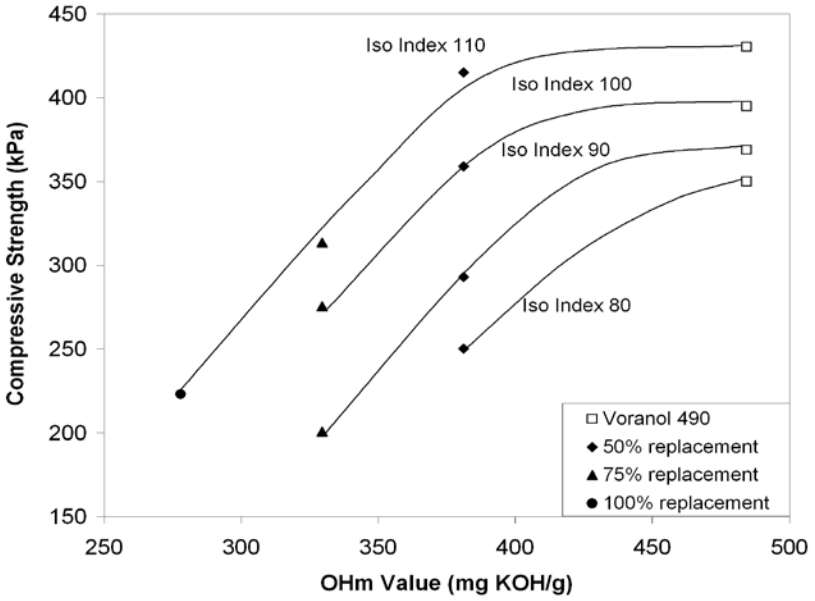

Figure 34. Compressive strength of foams for Voranol®490 (control) and three different percent of replacement (50, 75 and 100%) at four isocyanate index (110, 100, 90 and 80) versus hydroxyl number of polyol mixture

It is interesting that the foam made of 50% of polyol sample G and 50% of VORANOL®490 with 100 and 110 of isocyanate index had a better density, compressive strength and thermal conductivity properties than foams made with 100% of VORANOL®490. As shown in the Figure 34, the compressive strength decreases as the isocyanate index and the hydroxyl number of the polyol mixture decreases.

4.5. 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. *p*-Toluenesulfonic acid

monohydrate (pTSA) shows a high catalytic reactivity that promotes the ring-opening reaction yield a maximum oxirane oxygen content reduction compared to catalysts 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 and the average hydroxyl equivalent weights in the final polyol.

Higher temperatures (≥ 170°C) yields low oxirane oxygen content and hydroxyl numbers, but high acidity and color index. Low temperatures (≤ 130°C) result in low reduction of oxirane oxygen content because the reaction rate is slow. Optimal conditions for the reaction were found at 150°C between 4 to 11 hours 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 lower 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 FT-IR 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 FT-IR spectra showed agreement with the results previously obtained for oxirane oxygen content and hydroxyl value by the chemical analysis via titration.

4.6. Acknowlegments

We would like to thank the United Soybean Board, Omnitech, Missouri Soybean Merchandising Council and the Consortium for Plant Biotechnology Research for the financial support.

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CHAPTER 5

SOY-BASED POLYOLS FROM OXIRANE-RING OPENING BY ALCOHOLYSIS REACTION II: CONCENTRATION STUDIES

5.1. Abstract

Vegetable oils are promising candidate feedstocks as substitutes for petroleum oils in polyurethane production. To create a hydroxylated soy-polyol, epoxidized soybean oil was oligomerized with methanol and ethylene glycol using 0.5 wt. % *p*-toluenesulfonic acid catalyst at 150°C. Several different concentrations of the reagents were studied to evaluate the impact on the final properties of the polyols. Oxirane oxygen content percentages, viscosities, color indices, hydroxyl numbers and acid numbers of the products were followed. The reaction products were confirmed by FT-IR analysis and extractability analysis. To a first approximation, the alcohol added to the reaction mixture is conserved in the reaction and greatly improves the final polyol properties. At molar ratios of 4:6:3 (soybean oil:ethylene glycol:methanol) good combinations of viscosity and hydroxyl number were obtained for use in rigid and flexible foam applications.

Keywords: epoxidized soybean oil, polymerization, oxirane-ring opening, alcoholysis, polyols

5.2. Introduction

Renewable raw materials will play an important role in the development of sustainable green chemistry. The majority of the polyols used in the urethane industry are derived from petroleum crude oil. The use of petrochemicals such as polyester or polyether polyols competes with energy production and transportation fuels. These products come from a non-renewable resource. Oils and fats of vegetable and animal origin share the greatest proportion of the current consumption of renewable raw materials in chemical industry. Soybean oil is more versatile, least costly, renewable, and an environmental friendly component used to prepare vegetable-based polyols.

Most of the work on polymeric materials derived from natural oils involves functionalized oils. Soybean oil consists primarily of triglyceride with long chains of saturated and unsaturated fatty acids. The presence of the double bonds makes this oil suitable for chemical modifications. Polymerization of soybean oil has been evaluated to improve the molecular weight and viscosity of soybean oil for functionalization reactions. Polymerized soybean oil was used as a starting material for polyol production by enzyme hydrolysis, glycerolysis (transesterification) and acetol addition (alcohol addition).[1-5]

The preparation of polyols from oils has been the subject of many studies, but limited attention has been given to the effect of different alcohols of low molecular weight like its use as the epoxy-ring opening reagent with epoxidized soybean oil (ESBO). ESBO can be synthesized by reacting the hydrocarbon fatty acid glycerides from vegetable oil, such as soybean oils with peroxoacetic or peroxoformic acid in the presence of a solvent at mild temperatures. [6-8] Subsequently, modifications of ESBO,

in order to improve the mechanical properties of the rigid polyurethane, can be achieved by adding extra hydroxyl functional groups to the polyols. [9-13]

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 a nucleophilic compound. Hydrolysis of epoxy rings in the presence of acids (phosphoric acid, sulfuric acid, formic acid and acetic acid) was previously studied before. [14-18] Alcoholysis reactions using 2-ethyl hexanol, 1-butanol, 1-decanol and methanol were evaluated for lubricant formulations. [19, 20] Synthesis of alkoxylated triacylglycerol from ESBO were developed using perchloric acid for epoxy ring opening. [21]

Our research group is focused on the development on soy-based polyols production and polyurethane foam applications. In our recent study, a screening study was conducted to identify a catalyst to promote epoxy ring opening of ESBO. Optimal conditions of temperature and reaction time were determined for the alcoholysis reaction of epoxidized soybean oil (4:4:3 fixed molar ratio ESBO:EG:ME). [22]

In this study, epoxidized soybean oil (ESBO) was combined with ethylene glycol (EG) and methanol (ME) to produce a hydroxylated soy-polyol from ESBO using p-toluenesulfonic acid as catalyst to promote the ring-opening reaction. The impact of the relevant process variables on the alcoholysis reaction of epoxidized soybean oil was studied in detail. The molar concentration of the reactants and the reaction time swere considered in this study to obtain optimal conditions to produce a soy-based polyol with high molecular weight, high hydroxyl number and low acid number that can be used in a polyurethane formulation.

5.3. Experimental Setup

5.3.1. Materials

Epoxidized soybean oil (7.0% oxirane oxygen content, VIKOFLEX® 7170) was purchased from ATOFINA Chemicals Inc (Philadelphia, PA). Ethylene glycol (HPLC grade 99 %), methanol (HPLC grade 99 %) were obtained from Fisher (Houston, TX). Tetrafluoroacetic acid (reagent grade ≥ 98%-wt., tFAA), tetrafluoroboric acid (48%-wt. in water, tFBH), *p*-Toluenesulfonic acid monohydrate (Fluka ≥ 99 % mixture of isomers) was purchased from Sigma-Aldrich (St. Louis, MO). PAPI® 27 (polymeric diphenylmethane diisocyanate, MDI) was purchased from Dow Chemical (Midland, MI).

5.3.2. Alcoholysis Reaction

In the epoxy-ring opening reaction, epoxidized soybean oil, ethylene glycol, methanol and *p*-toluenesulfonic acid monohydrate were placed in a 250-mL Parr® reactor equipped with a thermocouple, stirrer, heating element, and Omega controller. Polyol properties were evaluated for different concentrations of ethylene glycol (2, 4, 6 and 8 molar ratio based on 4 mole of ESBO) and methanol (3, 6 and 9 molar ratio based on 4 mole of ESBO) at 150ºC between 2 to 7 hours of reaction.

5.3.3. Analytical Methods

The final product was analyzed for acid number, iodine number, hydroxyl number, oxirane oxygen content, 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 milli-grams of potassium hydroxide equivalent to the hydroxyl content per gram of sample according to AOCS official method (AOCS Tx 1a-66 1997), which only counts the primary alcohol functional groups in the molecule. The epoxy content percent of a dry sample is analyzed by AOCS method Cd 9-57 (1997), oxirane oxygen in epoxidized materials. 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 (Haake – Thermo electron, Newington, NH).

5.3.4. Characterization Analysis

A Fourier Transform Infrared spectroscopy was used to follow the chemical structure of the polyols. The FT-IR spectra were recorded on model Magna 550 using Omnic 5.1 software (Madison, WI).

5.3.5. Extractability Analysis

Polyurethane elastomer wafers were prepared by mixing 1 gram of soy-based polyol with 0.5 grams of isocyanate (PAPI® 27, MDI), dried at 110°C for 10 hrs. A gravimetric analysis was performed for a simple extraction analysis. The extraction method involved soaking approximately 0.5 grams of polyurethane plastic in 20 mL of hexane/hexanol (4:1 by volume) mixture for 3 minutes. The weight difference before and after the extraction were evaluated and compared with the amount of oil recovered. Samples were dried of solvent in an oven prior to weighing before and after extraction.

5.3.6. Catalyst-Alcoholysis Study

In the catalyst-methanolysis or alcoholysis study, epoxidized soybean oil, methanol and catalyst were placed in a 250 mL three necklace flask with a condenser and thermometer over a hot plate. Tetrafluoroacetic acid (tFAA), tetrafluoroboric acid (tFBH) and *p*-toluenesulfonic acid monohydrate (pTSA) catalysts were evaluated on the alcoholysis reaction at 150°C for 4 hours. Additional samples using ethylene glycol in the formulation were made for comparison purpose.

Epoxy-ring opening reaction using methanol at 70°C, Petrovic Patent Application was tested for several samples between 4 to 10 hours of reaction. The same catalyst describe above were used on the epoxy-ring opening reaction. The following properties such as acid number, oxirane oxygen content, hydroxyl number and viscosity were tested.

5.4. Results

5.4.1. Synthesis Results

In the alcoholysis reaction, ESBO was combined with ethylene glycol (EG) and methanol (ME) using *p*-toluenesulfonic acid monohydrate (*p*TSA) as catalyst to promote the oxirane-ring opening. 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 Figure 35.

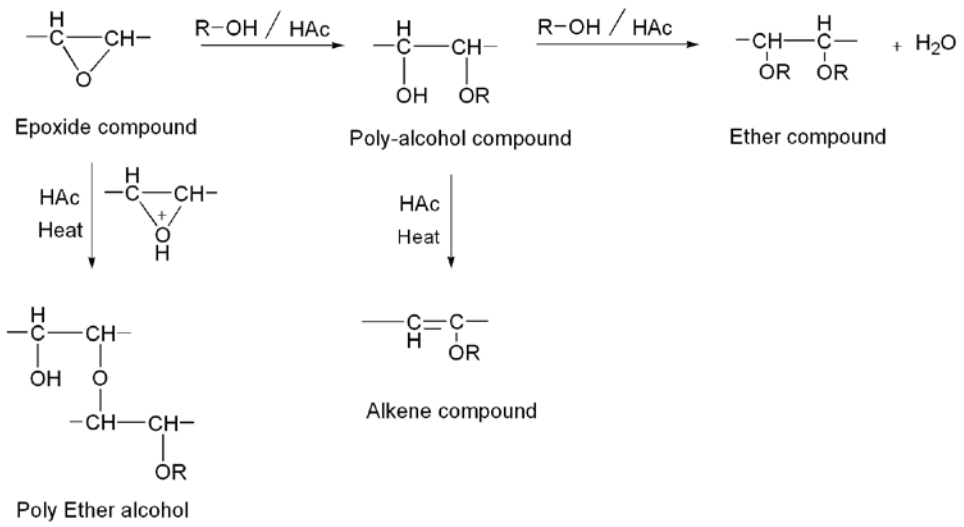

Figure 35. General mechanism for the ESBO alcoholysis reaction

In order to follow the extent of the alcoholysis reaction, several properties were evaluated: acid number, oxirane oxygen content, iodine number, hydroxyl number and color index. The samples are organized by series holding methanol constant in each group (ESBO:EG:ME molar ratios).

Table 20 summarizes the hydroxylated polyol series 4:2:3, 4:4:3, 4:6:3 and 4:8:3 at 2, 4 and 6 hours of reaction (series A). Table 21 summarizes the hydroxylated polyol series 4:2:6, 4:4:6, 4:6:6 and 4:8:6 at 2, 4 and 6 hours of reaction (series B). Table 22 summarizes the hydroxylated polyol series 4:2:9, 4:4:9, 4:6:9 and 4:8:9 at 2, 4 and 6 hours of reaction (series C).

Table 20. Final properties for hydroxylated soy-based polyols series 4:2:3, 4:4:3, 4:6:3 and 4:8:3 at 2, 4 and 6 hours of reaction. (ESBO:EG:ME molar ratios)

No.	*Molar ratio*	*Rxn. Conditions*		*Experimental Properties of Polyols*					
	ESBO:EG:ME	Temp (°C)	Time (hrs)	Acid no. (mg KOH/g)	Oxirane Oxygen(%)	Hydroxyl no. (mg KOH/g)	Iodine no (cg I_2/g)	Viscosity (cP)	Color Index[a]
1A	4:2:3	150	2	0.7	5.19	106	6.5	517	2
2A	4:2:3	150	4	0.7	4.69	105	6.9	791	2
3A	4:2:3	150	6	0.7	3.89	129	9.5	1102	2
A	4:4:3	150	2	0.7	5.20	156	6.5	711	2
5A	4:4:3	150	4	0.7	3.50	158	9.4	1248	2
6A	4:4:3	150	6	0.7	1.45	183	14.0	4970	2
7A	4:6:3	150	2	0.7	4.10	186	7.2	935	2
8A	4:6:3	150	4	0.7	2.78	234	11.4	1709	3
9A	4:6:3	150	6	0.7	0.34	247	13.2	13240	3
10A	4:8:3	150	2	0.7	4.61	216	6.6	740	2
11A	4:8:3	150	4	0.7	2.10	293	10.3	2152	3
12A	4:8:3	150	6	1.7	0.22	206	16.9	11835	3

[a]The Gardner color scale was used as a color index: 1 to 18 from light color to dark. ESBO has a color index of 1.

Table 21. Final properties for hydroxylated soy-based polyols series 4:2:6, 4:4:6, 4:6:6 and 4:8:6 at 2, 4 and 6 hours of reaction. (ESBO:EG:ME molar ratios)

	Molar ratio	*Rxn. Conditions*		*Experimental Properties of Polyols*					
No.	ESBO:EG:ME	Temp (°C)	Time (hrs)	Acid no. (mg KOH/g)	Oxirane Oxygen (%)	Hydroxyl no. (mg KOH/g)	Iodine no (cg I_2/g)	Viscosity (cP)	Color Index[a]
1B	4:2:6	150	2	0.7	4.83	140	6.6	475	2
2B	4:2:6	150	4	0.7	2.99	182	12.1	996	2
3B	4:2:6	150	6	0.7	1.87	186	12.9	1496	3
B	4:4:6	150	2	0.7	4.24	166	11.2	765	2
5B	4:4:6	150	4	0.7	3.25	176	15.6	1109	2
6B	4:4:6	150	6	0.7	1.29	199	17.7	2612	3
7B	4:6:6	150	2	0.7	3.59	217	13.3	898	
8B	4:6:6	150	4	0.7	1.43	263	12.9	2280	3
9B	4:6:6	150	6	11.2	0.08	188	16.9	2801	5
10B	4:8:6	150	2	0.7	4.14	219	12.1	702	3
11B	4:8:6	150	4	0.7	0.97	297	12.5	3301	3
12B	4:8:6	150	6	9.9	0.06	238	23.8	1341	6

[a]The Gardner color scale was used as a color index: 1 to 18 from light color to dark. ESBO has a color index of 1.

Table 22. Final properties for hydroxylated soy-based polyols series 4:2:9, 4:4:9, 4:6:9 and 4:8:9 at 2, 4 and 6 hours of reaction. (ESBO:EG:ME molar ratios)

	Molar ratio	*Rxn. Conditions*		*Experimental Properties of Polyols*					
No.	ESBO:EG:ME	Temp (°C)	Time (hrs)	Acid no. (mg KOH/g)	Oxirane Oxygen (%)	Hydroxyl no. (mg KOH/g)	Iodine no (cg I_2/g)	Viscosity (cP)	Color Index[a]
1C	4:2:9	150	2	0.7	4.45	169	7.3	359	2
2C	4:2:9	150	4	0.7	2.73	206	12.3	495	2
3C	4:2:9	150	6	0.7	1.85	206	13.4	663	3
4C	4:4:9	150	2	0.7	3.17	219	12.1	801	2
5C	4:4:9	150	4	0.7	1.84	236	12.2	877	3
6C	4:4:9	150	6	6.5	0.02	197	11.4	1026	6
7C	4:6:9	150	2	0.7	2.10	288	10.3	887	2
8C	4:6:9	150	4	0.7	1.60	285	12.6	1103	2
9C	4:6:9	150	6	8.0	0.14	219	12.5	615	6
10C	4:8:9	150	2	0.7	1.74	282	12.9	1015	3
11C	4:8:9	150	4	14.2	0.08	234	18.5	586	5
12C	4:8:9	150	6	13.9	0.02	201	22.1	499	6

[a]The Gardner color scale was used as a color index: 1 to 18 from light color to dark. ESBO has a color index of 1.

The fast reduction on oxirane oxygen content using high molar ratios of ethylene glycol and methanol (4:6:9, 4:8:6 and 4:8:9) resulted in a high increase in acid number, iodine number and color index.

(Table 20, Table 21 and Table 22). In light of these changes, the experiments for 9 hours were discontinued. As described in the mechanism, most of the oxirane-ring groups are opened, and consequently a considerable amount was converted into an alkene compound or poly-ether alcohol or brought about polymerization and some cleavage of ester bonds in the molecule.

Little oxirane-ring reduction was observed at very low molar ratios of ESBO:EG:ME, 4:2:3 polyol sample. A complete epoxy-ring opening occurred after 5 to 6 hours of reaction time for polyol samples: 4:8:6, 4:6:9, 4:6:6 and 4:4:9. Previous studies indicate that high concentration of methanol in an acid-catalyzed process helps in the oxirane-ring opening reaction. [23]

Figure 36 and Figure 37 illustrated the viscosity effects with different molar concentration of ethylene glycol and fixed molar concentration of methanol at 4 and 6 hours of reaction, respectively. A significant increase in viscosity was observed for polyol samples 4:6:3 and 4:8:3, indicating a good combination of ethylene glycol and methanol, shown in Figure 36 and Figure 37.

(Table 20) The low concentration of methanol associated with the *p*-toluenesulfonic acid promotes the oxirane-ring opening reaction. The ethylene glycol acts as a copolymer in the oligomerization reaction resulting in a high-viscosity polyol indicating an increase on molecular weight of the final polyol.

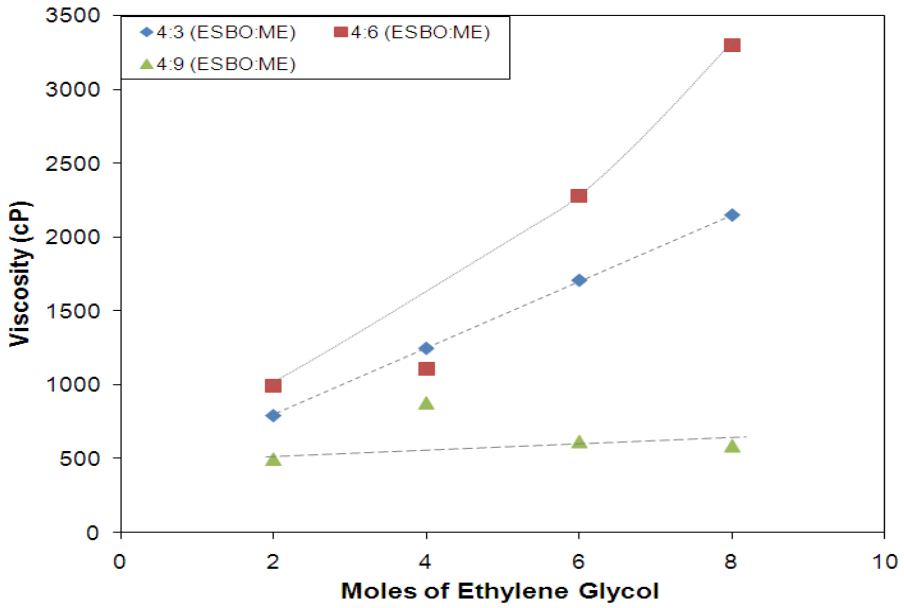

Figure 36. Effect on molar concentration of ethylene glycol at fixed molar concentration of methanol relates with viscosity of the final polyol samples for 4 hours of reaction

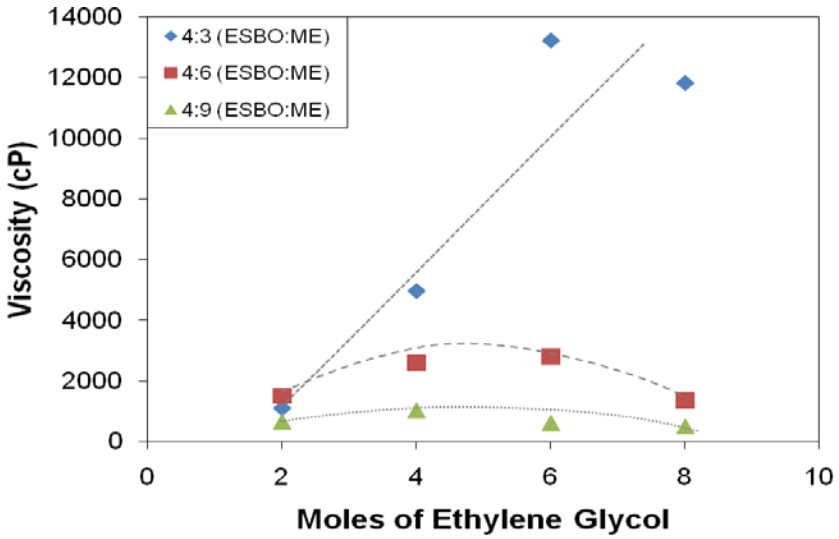

Figure 37. Effect on molar concentration of ethylene glycol at fixed molar concentration of methanol relates with viscosity of the final polyol samples at 6 hours of reaction

Figure 36 and Figure 37 illustrated the viscosity effects with different molar concentration of methanol and fixed molar concentration of ethylene glycol at 4 and 6 hours of reaction, respectively. The polyol sample 4:8:6 had a different effect on viscosity that gave a maximum viscosity at 4 hours of reaction and then gradually decreased to 2000 cP as shown in Figure 36 and Figure 39. The maximum viscosity was obtained by the complete epoxy-ring opening obtained at approximately 4 to 5 hours of reaction. The decrease in viscosity can be explained as the chain termination effect by methanol reagent (ether formation).

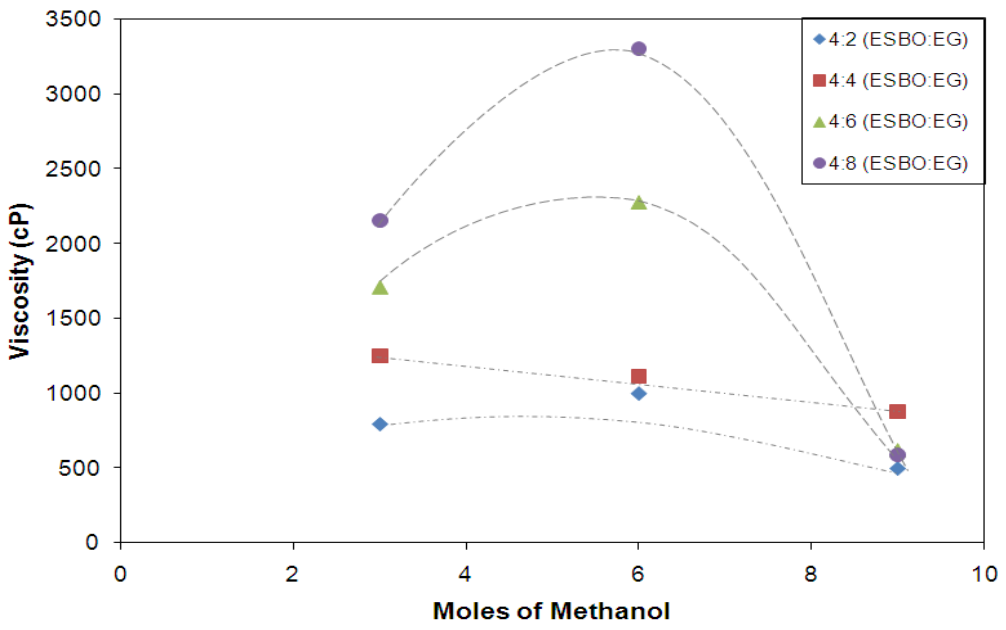

Figure 38. Effect on molar concentration of methanol at fixed molar concentration of ethylene glycol relates with viscosity of the final polyol samples for 4 hours of reaction

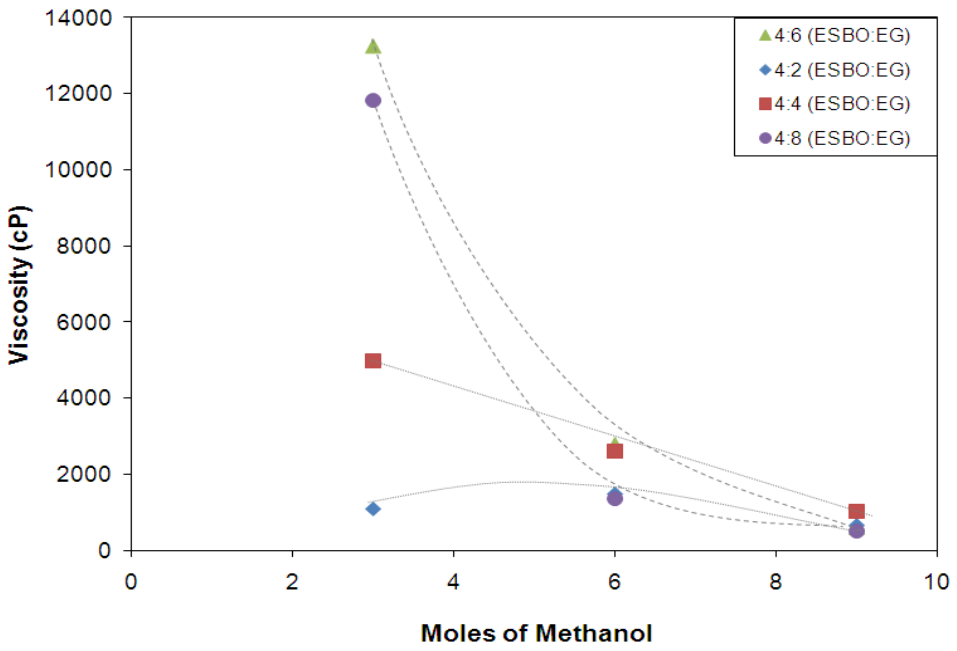

Figure 39. Effect on molar concentration of methanol at fixed molar concentration of ethylene glycol relates with viscosity of the final polyol samples for 6 hours of reaction

A slow increase in viscosity was observed for polyol samples 4:4:3, 4:4:6 and 4:6:6 which approaches to 2000- 4000 cP at 6-7 hour of reaction. This effect depends on the amounts of the reactants, the amount of epoxy-rings opened and the carbon-carbon double bonds formed in the molecule. As expected, low concentrations of ethylene glycol (4:2:3, 4:2:6 and 4:2:9 polyol samples) did not show significant increments in viscosity. This indicates that the poly-alcohol reaction mechanism occurred instead of the poly-ether alcohol mechanism, as shown in Figure 35. The data series shows a conservation of hydroxyl groups in each polyol combination series.

Table 20, Table 21 and Table 22). As indicated by the mechanism, some of the hydroxyl groups formed by the opened epoxide group react with alcohol groups, while some alcohols are left or remain intact in the molecule. Most of the polyol samples exhibit “equilibrium” between the alcohols and the ethers groups formed in the molecule, as shown in Figure 35.

Higher molar ratios of ethylene glycol and methanol (4:6:9, 4:8:6 and 4:8:9) show a high increase in acid number and lower reduction of hydroxyl number after 3 to 5 hours of reaction. These samples also showed high color index indicating degradation in the final sample, shown in Table 21and Table 22. Most of the polyol combination series do not show any significant acid number change.

Figure 40 illustrates the influence of extractable content with the final viscosity of the hydroxylated ESBO samples. The amount of oil extracted decreases as the viscosity for each sample increases as a result of cross-linking between the hydroxyl groups or ether formed with the isocyanate groups in the PU elastomeric wafers. The low percentage of oil extracted represents a high degree of cross-linking between diphenylmethane diisocyanate (MDI) and polyol. This indicates that the polyol has more hydroxyl groups available to react with the isocyanate groups of diphenylmethane diisocyanate (MDI). As expected, most of the samples show a very low amount of oil extracted as a consequence of the high hydroxyl content obtained by the alcoholysis reaction.

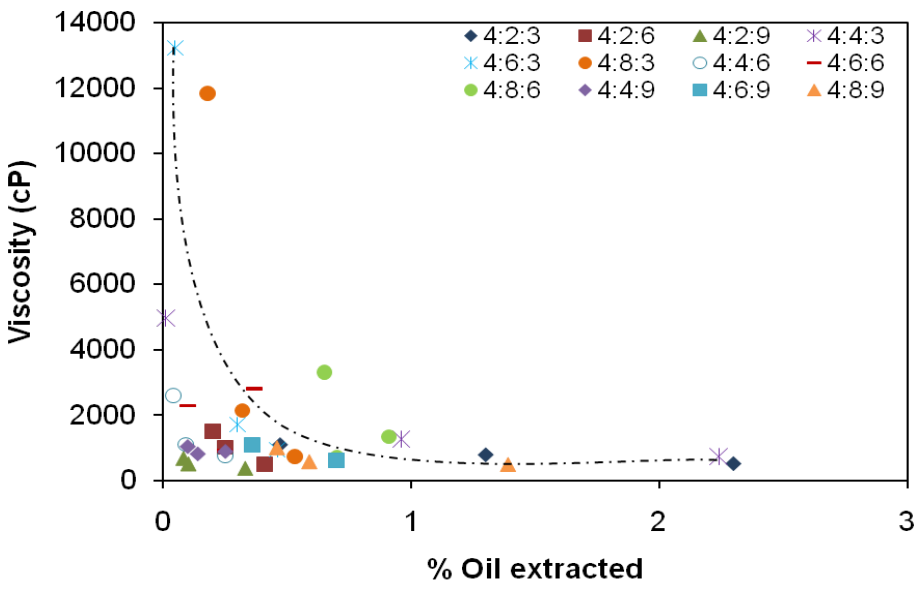

Figure 40. Effect on viscosity relates with the oil extraction percent of the soy-based polyol wafer urethane elastomers

5.4.2. Characterization Results

The FT-IR spectra of epoxidized soybean oil (ESBO) and three molar concentrations of ethylene glycol (4:2:3, 4:4:3 and 4:8:3) is presented in Figure 41. The FT-IR spectra of epoxidized soybean oil (ESBO) and three molar concentrations of methanol (4:4:3, 4:4:6 and 4:4:9) is illustrated in Figure 42. These samples in comparison with FT-IR spectra of ESBO show the obvious disappearance of epoxy groups at 823 cm^{-1} and the emergence of hydroxyl groups at 3420 cm^{-1}. The final polyols show a characteristic signal at 1090-1030 cm^{-1} indicating the presence of ester groups (stretching of C-O bond).

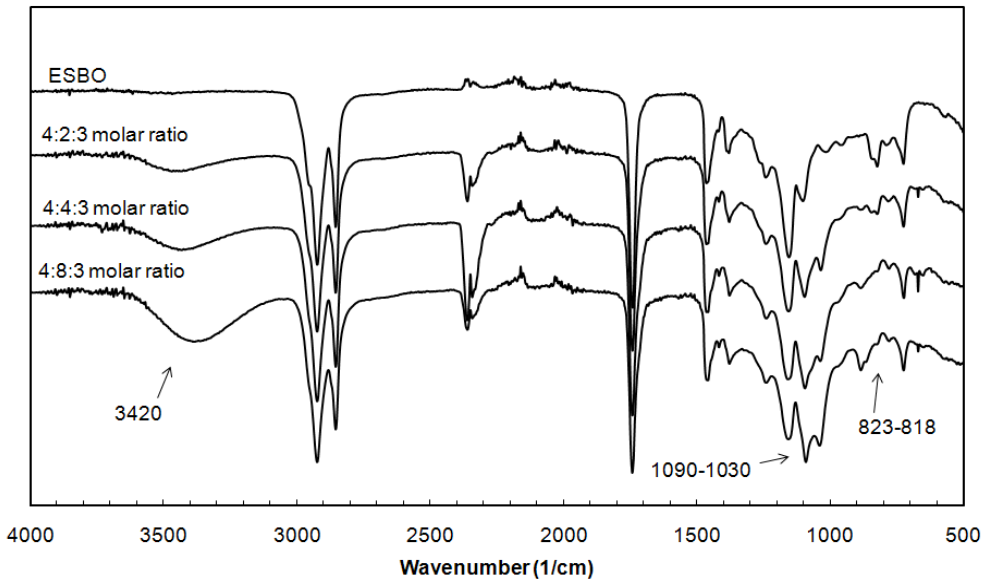

Figure 41. FT-IR spectra of epoxidized soybean oil (ESBO) and three molar concentration of ethylene glycol: 4:2:3, 4:4:3 and 4:8:3 (ESBO:EG:ME molar ration)

The mechanisms showed in Figure 35 were confirmed by the FT-IR spectra of each polyol sample, as shown in Figure 41 and Figure 42. The poly-alcohol compound formation was confirmed by a peak signal at 3420 cm^{-1}. The ether compound and poly-ether alcohol compound formation were confirmed by peak signals at 1090-1030 cm^{-1} and 1200 cm^{-1}.

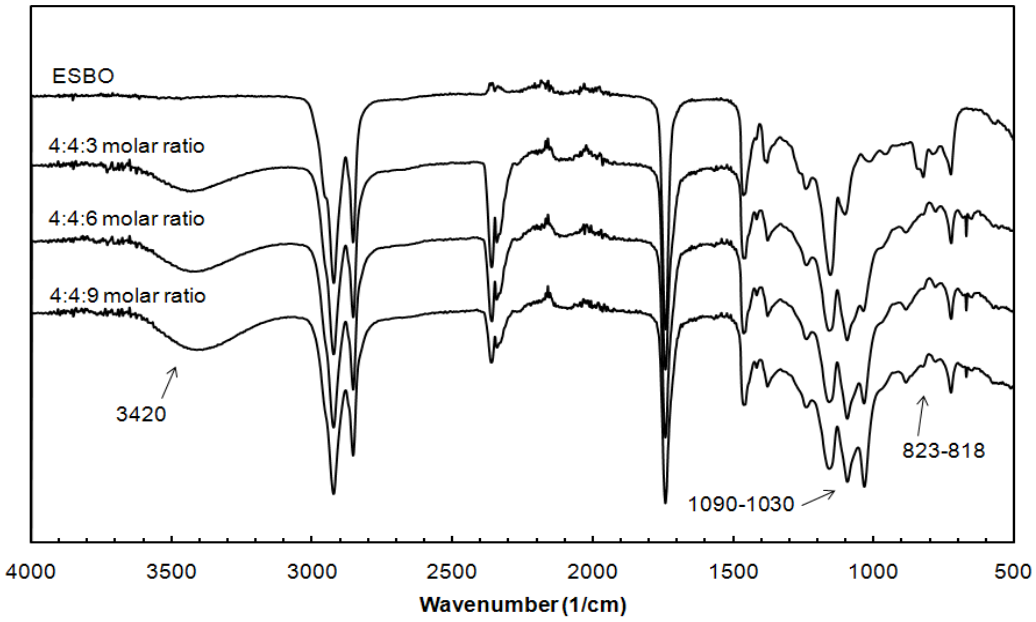

Figure 42. FT-IR spectra of epoxidized soybean oil (ESBO) and three different molar concentrations of methanol: 4:4:3, 4:4:6 and 4:4:9 (ESBO:EG:ME molar ratio)

5.4.3. Catalyst-Alcoholysis Study

A catalyst-alcoholysis study using methanol as opened reagent on the epoxy-ring opening reaction was conducted. The main purposes for this study was analyze and compare to the method proposed previously by Z. S. Petrovic and co-workers.[24, 25] In the U.S. Patent Application 2006/0041157 and U.S. Patent 6,686,435 Petrovic describe the use of several catalysts on the epoxy-ring opening reaction in combination with methanol and water. In the claims, he mentioned that the tetraflouroboric acid (THFB) was the preferred catalyst for the “methanolysis” reaction.

In terms of the art-technology comparison, our work demonstrates the utility of pTSA as a catalyst for the alcoholysis reaction, do not rely on water which allows for better control of the final hydroxyl number and uses ethylene glycol as a cross-linker

which provides greater tenability of the final product. It should be notice that the Petrovic published work includes few claims of non-specific method to make an oligomeric modified vegetable oil-based polyol, but only mention the pTSA catalyst on the epoxidation reaction. However, his procedure includes water and excess of alcohol like methanol or ethanol.

Table 23 shows the final results for the alcoholysis reaction at 150°C for 4 hours of reaction using three different catalysts. Additional samples using ethylene glycol in the formulation were made for comparison purposes. The p-toluenesulfonic acid shows better results compare to the other two catalysts, tetrafluoroacetic acid and tetrafluoroboric acid. Higher temperatures affect the catalytic behavior of tetrafluoroboric acid (sample 7 on Table 23) resulting on elastomeric solid product.

Table 23. Polyol properties for alcoholysis reaction using three different catalyst

no.	Sample (molar ratios)				Conditions		Polyol Properties			
	ESBO	EG	ME	Catalyst (grams)	Temp. (°C)	time (hrs)	Oxirane (%)	Acid no.	OH No. (mgKOH/g)	Viscosity (cP)
1	1	0	1.5	no	150	4	6.25	0.5	43.9	300
2	1	0	1.5	0.5 pTSA	150	4	4.29	0.7	44.9	514
3	1	0.5	1.5	0.5 pTSA	150	4	2.99	0.7	100.2	996
4	1	0.5	1.5	0.5 tFAA	150	4	5.73	3.3	138.7	496
5	1	1	1.5	0.5 pTSA	150	4	2.25	0.7	176.0	1109
6	1	1	1.5	0.5 tFAA	150	4	5.88	3.2	165.4	475
7	1	1	1.5	0.5 tFBH	150	4	**Solids**			

NOTE: pTSA: p-Toluenesulfonic acid, tFAA: tetraflouroacetic acid, tFBH: tetraflouroboric acid, EG: ethylene glycol and ME: methanol.

The final results on the polyol production using Petrovic Patent Application procedure was shown in Table 24. According to the hydroxyl equivalent weight calculations on the methanolysis reaction (patent application procedure) it is possible to reaches a hydroxyl number between 1100 to 1210 mg KOH/g; unfortunately, the hydroxyl number for these samples were lower than the value expected. Based on the data shown in Table 24, a higher viscosity was obtained using p-toluenesulfonic acid compared to tetraflouroacetic acid and tetrafluoroboric acid.

Table 24. Polyol properties for methanolysis reaction (Patent Application method)

no.	Sample (molar ratios)				Conditions		Polyol Properties			
	ESBO	ME	Water	Catalyst (grams)	Temp. (°C)	time (hrs)	Oxirane (%)	Acid no.	OH No. (mgKOH/g)	Viscosity (cP)
1	1	20.8	9.3	1.4 tFAA	70	5	4.24	3.3	60.1	699
2	1	20.8	9.3	1.4 tFAA	70	10	2.67	5.0	121.0	2352
3	1	20.8	9.3	1.0 pTSA	70	5	2.38	1.2	79.7	2059
4	1	20.8	9.3	1.4 tFBH	70	4	0.37	4.4	104.5	1299
5	1	20.8	9.3	1.4 tFBH	70	10	0.20	7.0	89.4	2209

NOTE: pTSA: p-Toluenesulfonic acid, tFAA: tetraflouroacetic acid, tFBH: tetraflouroboric acid and ME: methanol.

5.5. 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. Alcoholysis of ESBO with ethylene glycol and methanol using *p*-toluenesulfonic acid catalyst at 130, 150 and 170ºC was previously investigated. [22] Several molar ratios of the reactants (ESBO:EG:ME) and the reaction times were considered to obtain better-performing soy-based polyols.

High methanol ratios produced lower viscosity polyols while higher ethylene glycol ratio promoted oligomerization and produced higher viscosity polyols. The methanol ratio was identified as a tunable parameter to control the ratio of epoxy to alcohol moiety in the final product. The ethylene glycol is a tunable parameter that, in combination with reaction time, is able to control final product viscosity. For viscosities of 3,000 to 13,000 cP, the optimal ratios were 4:6:3 to 4:8:3 (ESBO:EG:ME).

5.6. Acknowlegdements

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CHAPTER 6

ONE-POT APPROACH: EPOXIDATION FOLLOWED BY ALCOHOLYSIS OF SOYBEAN OIL

6.1. Abtract

In this study, soy-based polyol was produced in one reactor by the sequence: epoxidation of soybean oil (SBO), water removal and alcoholysis reaction. Full and partially epoxidized soybean oils (PESBO) were developed by different molar ratios of formic acid (FA) and hydrogen peroxide (HOOH) used in the reaction. PESBO was formed with molar ratio of 1:0.4:0.7 (SBODB:FA:HOOH) obtaining a yield of 93% (based on double bonds –DB- in SBO). Alcoholysis with 4 wt-% of ethylene glycol and 0.5 wt-% of *p*-toluenesulfonic acid was effective at mild conditions to increase the reactivity of the PESBO and hydroxyl number around 100 mg KOH/g. FT-IR and ^{1}H-NMR characterization confirmed epoxy and alcohol formation. The extent of epoxidation and oligomerization are tunable to create polyol products for a range of applications.

Keywords: alcoholysis reaction, epoxy, oligomers, ring-opening polymerization, soy-based polyols

6.2. Introduction

In recent years, there has been a growing demand for vegetable oils for “greener” starting materials for the production of bio-based polymers like urethane products. Petroleum-based oils are used as the starting material for most polymers. Environmental and economic problems arise because petroleum is a finite resource. Environmental issues arise because the decomposition of these materials in nature is slow and sometimes generates byproducts that are public hazards.[1] The biopolymers offer the advantages of low cost, ready availability from renewable natural resources, and possible biodegradability.

Most of the work on polymeric materials derived from natural oils has involved functionalized oils. SBO consists primarily of triglycerides with long chains of saturated and unsaturated fatty acids. The presence of the double bonds makes this oil suitable for several chemical modifications. Polymerization of SBO was evaluated to improve the molecular weight and viscosity of SBO for future reactions. Oligomerized SBO has been used as a starting material for polyol production produced by enzyme hydrolysis, glycerolysis (transesterification) and acetol addition (alcohol addition). Epoxidized is a particularly useful starting material for oligomerization.[2-5]

Several processes for epoxidation of vegetable oils have been developed. One of the most widely used methods can be carried out in solution, with “*in-situ*” formed or preformed peracids, and with homogeneous or heterogeneous catalyst.[6-11] A kinetic model for *“in-situ”* epoxidation of anchovy oil with partially preformed peracetic acid in the presence of a resin catalyst was reported.[12]

Hydrolysis of epoxy moiety in the epoxidized soybean oil (ESBO) with the presence of organic acids was previously investigated.[13-16] Campanella and Baltanas' work described in detail the kinetics for the degradation of the oxirane ring of ESBO with sulfuric acid catalyst in two phase system.[17, 18] This work also includes the effect of the main process variables, such as pH, agitation speed, and concentration levels. Additional studies on degradation of the oxirane ring of epoxidized vegetables oils with solvated acetic acid over ion-exchange resins were investigated by Campanella and Baltanas.[19, 20] Guo and co-workers evaluated the ring-opening hydrolysis reaction of ESBO with water in the presence of phosphoric acid.[21] The phosphoric acid not only catalyzed the hydrolysis reaction, but combines chemically to form phosphate esters in the final soy-polyol.

A variety of lubricants have been made from ESBO by epoxy-ring opening hydrolysis reaction using alcohols.[22, 23] Hwang, Erhan and co-workers used ESBO as starting material in combination with different alcohols (Guerbet C12-C18 alcohols) to produce synthetic lubricants.[24] In addition, they used acids anhydrides with alcohols in the hydrolysis reaction.[25]

Kazemizadeh presents the method of epoxidation and hydroxylation reaction in a single reactor without acid-catalyst added.[26] The first reaction was performed with per-acids such as organic acid combinations (sulfuric acid, acetic acid and formic acid) and hydrogen peroxide. The hydroxylation reaction was carried out with one or a combination of alcohols (methanol and ethanol) and water as discussed in the patent. The polyol produced by this process is ion-free and can be used in the polyurethane application.

This study presents the full and partially epoxidation of SBO by varying the amount of the reactants without heterogeneous catalysts or solvents. Water removal after epoxidation followed by alcoholysis of the epoxy moieties using ethylene glycol and *p*-toluenesulfonic acid was performed to produce hydroxyl functionalities in the SBO molecule. The primary purpose of this work was to create a 1,000-3,000 MW soy-based polyol through an epoxy intermediate with minimized separation costs.

6.3. Experimental set up

6.3.1. Materials

SBO (RBD grade, Iodine no. 127-130 cg I_2/g) was obtained in a local grocery store. Formic acid (88 wt.-%), hydrogen peroxide (30 wt.-% aqueous solution), *p*-toluenesulfonic acid monohydrate (98 wt.-%) and ethylene glycol (99 wt.-%, HPLC grade) were purchased from Sigma (St. Louis, MO.).

6.3.2. Epoxidation Reaction

An epoxidation reaction was carried out in a 500 mL two-necked round-bottom flask over a hot plate with a thermometer and condenser connected to a 100 mL round flask as a collector for product distillation, shown in Figure 43. SBO and formic acid were placed in the 500 mL two-necked flask with a magnetic stirrer. Hydrogen peroxide (30 wt.-% aqueous solution) was poured slowly into the flask over 30 minutes. The mixture was heated at 40°C and stirred at 300 rpm for 30 hours. The extent of the reactions were determined as the epoxy content or epoxidation degree desired. Partial and full ESBO were estimated at 5.0 and 7.0 % of epoxy content, respectively. Different molar ratios of formic acid (0.5 to 0.1 molar ratios) and hydrogen peroxide (1.2 to 0.7 molar ratios) were used in the epoxidation reaction.

When the reaction was completed, the resultant formic acidand water was removed by distillation at 100°C for about 4 hours or until the water was removed from the oil sample. A vacuum pump was connected (part 3 in the drawn) into the system to enhance the distillation process as illustrated on Figure 43.

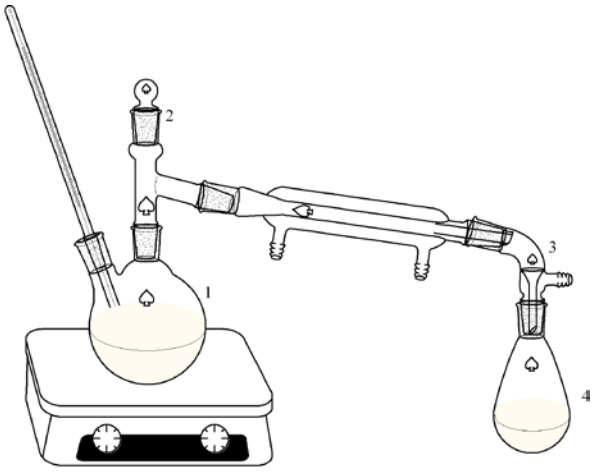

Figure 43. Reaction and distillation system

6.3.3. Alcoholysis Reaction

Ethylene glycol (4 wt.-%, 0.64 molar ratio: based on PESBO) and *p*-toluenesulfonic acid (0.5 wt.-%, 0.63 molar ratio: based on PESBO) were placed in the round-bottom flask with the prepared ESBO. The reactants were hold at 150°C for about 7 to 10 hours of reaction time (oxirane % less than 1%).

6.3.4. Analytical Methods

The final products were analyzed for acid number, iodine number, hydroxyl number, epoxy content 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). The epoxy content percent of a dry sample is analyzed by AOCS method Cd 9-57 (1997), oxirane oxygen in epoxidized materials. The dynamic viscosity of the samples was measured in centipoises (cP) at 22°C using a Model RS100 Rheometer Haake – Thermo electron (Newington, NH).

6.3.5. Characterization Analyses

A fourier transform infrared spectroscopy and a proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) were used to follow the change in chemical structure of the polyols. The FT-IR spectra were recorded on model Magna 550 using Omnic 5.1 software (Madison WI). The ^{1}H-NMR spectra were recorded in $CDCl_3$ using a Varian Unity spectrometer at 300 MHz (Palo Alto, CA).

6.4. Results and discussion

6.4.1. Reaction syntheses

In the epoxidation reaction there are two main reactions involved: peroxoacid formation and epoxy groups formation. The first reaction is the formation of peroxoformic acid from formic acid and hydrogen peroxide, while the second reaction is the uncatalyzed epoxidation of unsaturated SBO with the peroxoformic acid formed previously, shown in Figure 44. The peroxy acid transfers an oxygen moiety to the alkene in a cyclic (single-step) mechanism, resulting in a *Syn addition* of the oxygen to the alkene with the formation of an epoxide and a carboxylic acid. Simultaneous side

reactions such as epoxy ring opening followed by dimerization of hydroxy or acetoxy compounds previously formed may precede (illustrated in Figure 45).

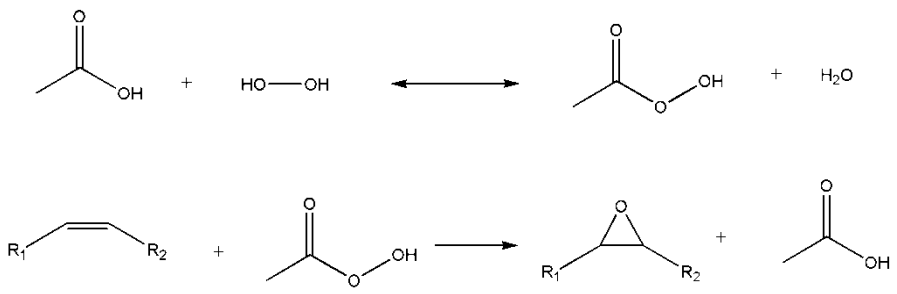

Figure 44. General epoxidation reaction mechanism

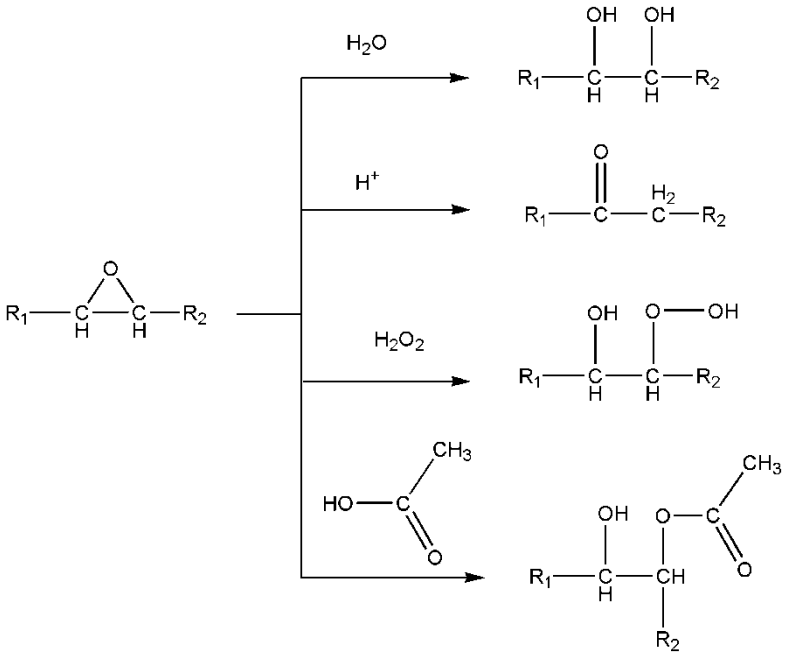

Figure 45. Possible side reaction of epoxy groups

As discussed in the experimental procedure, different molar ratios of formic acid and hydrogen peroxide were used in the epoxidation reaction of SBO. Table 25 summarizes SBO epoxidation results at molar ratios of 0.8 to 1.2 moles hydrogen peroxide per mole of carbon-carbon π-bond moieties in SBO. The properties are for

Table 25. Results for the epoxidation reaction of soybean oil (SBO) with different molar ratios of hydrogen peroxide (H_2-O_2) and the rotary evaporator removal of water and acid

no.	Molar Ratio			Properties of ESBO		Yield[b]	Acid and water removal	Final Properties		
	SBO[a]	F A	H_2O_2	Oxirane	Acid no.			Oxirane	AOCS OH	Iodine no
1	1	0.5	1.2	7.10	1.00	101.0	solvent removal	6.80	10.0	1.50
2	1	0.5	1.2	6.68	1.30	95.4	Rotary evaporator	6.68	31.5	1.30
3	1	0.5	0.9	6.45	2.00	92.1		5.01	67.2	5.00
4	1	0.5	0.9	6.78	1.50	96.8		6.78	34.6	1.50
5	1	0.5	0.8	6.80	2.00	97.1	100C/4hrs	5.50	42.2	11.00
6	1	0.5	0.8	6.89	2.00	98.4		5.60	62.4	10.00

NOTE: Reactions were performed at 40°C for 30 hours. [a]Molar ratio based on the double bond present in the soybean oil (SBO-DB, functionality of 4.6). [b] Yield is based on maximum possible epoxy content with complete conversion of hydrogen peroxide which is the limiting reagent.

ESBO product after the distillation process removes water and acid. Table 26 shows the results of PESBO obtained in the epoxidation reaction with lower hydrogen peroxide stoichometries prior to removal of water and formic acid.

Table 26. Results for the partially epoxidized soybean oil (PESBO) for different molar ratios of soybean oil (SBO), formic acid (FA) and hydrogen peroxide (H_2O_2).

no.	Molar Ratio			PESBO Product		Yield[b] (%)
	SBO[a]	F A	H_2O_2	Epoxy Content (%)	Acid no. (mg KOH/g)	
1	1	0.5	0.4	3.09	23.60	63.0
2	1	0.5	0.7	4.67	16.13	95.3
3	1	0.4	0.7	4.85	25.00	98.9
4	1	0.2	0.6	4.65	7.80	94.9
5	1	0.2	0.7	4.70	5.40	95.9
6	1	0.1	0.7	4.00	3.50	81.6

NOTE: Reactions were performed at 40°C for 24 hours. The results are prior to removal of water and formic acid. [a]Molar ratio based on the double bond present in the soybean oil (SBO-DB, functionality of 4.6). [b] Yield is based on maximum possible epoxy content with complete conversion of hydrogen peroxide which is the limiting reagent.

Reactions 1 and 2 of Table 25 provide base lines to which other reactions can be compared. Fully ESBO contains about 6.8% epoxy (based on oxygen of epoxy group) while the PESBO content varied from 3.09 to 4.85%. Lower molar ratios of formic acid in the reaction mixture resulted in a low acidity product and less consumption of formic acid. Formic acid loadings were reduced from 0.5 to 0.2 while maintaining yields greater than 95%. However, a reduction to 0.1 produced a significantly lower yield of 81.6%.

Factors such as temperature, type of reactants and reaction time had a minor impact on loss of epoxidation yield (~ 4% loss or less). Formic acid is crucial for

producing enough peroxy formic acid in the aqueous phase to deliver an oxygen atom to the carbon-carbon double bond in the organic phase. At higher temperatures the formic acid will react with the epoxy moieties to form alcohol-ester pairs. Hydrogen peroxide may also decompose due to the high activity of formic acid or the absence of solvent (as organic diluents). This is less of an issue with hydrogen peroxide is the limiting reagent in the pursuit of partial oxidation.

Possible side-reactions of the epoxy moieties with hydrogen peroxide, formic acid and water residuals are represented by Figure 45. The formation of hydroxyl groups during the epoxidation reaction are desired for future application studies. What might be a detrimental side reactions for some applications actually benefits epoxidation for polyol production.

To remove all the water and the acid content in the reaction vessel, the system was connected to a vacuum pump and heated at 100°C for 3 to 4 hours to vaporize these compounds. Table 25 demonstrates the results before and after devolatilization for full ESBO. A reduction in the epoxy content caused by the heat applied to the system indicates the formation of alcohol groups in the sample.If one epoxy-ring was opened, it will form at least one hydroxyl group and a substituent group in the molecule, as shown in Figure 45.

Table 27 summarizes the properties of PESBO after water and acid removal. PESBO shows the same characteristic behavior of epoxy-group openings during the water-removal process as with ESBO (see Table 25). Samples prepared with larger amounts of formic acid always produced higher hydroxyl numbers from this reaction as seen by the trends in Table 27 data.

Table 27. Final properties of PESBO after the rotary evaporator removal of water and acid (performed at 100°C for 4 hours)

No.	Molar Ratio			Final Properties			
	SBO[a]	F A	H_2O_2	Oxirane (%)	Acid no. (mg KOH/g)	Iodine no. (mg I_2/g)	OH no. (mg KOH/g)
1	1	0.5	0.4	1.88	8.20	26.5	49.2
2	1	0.5	0.7	3.08	4.08	25.4	41.5
3	1	0.4	0.7	3.80	4.10	22.4	34.2
4	1	0.2	0.6	3.22	3.85	22.5	33.5
5	1	0.2	0.7	3.73	2.40	23.2	21.5
6	1	0.1	0.7	3.54	2.40	27.1	16.8

[a]Molar ratio based on the double bond present in the soybean oil (SBO-DB, functionality of 4.6)

The acid number decreased during devolatilization. This can be attributed to both volatilization of the formic acid and reaction of the formic acid. Since the amount of alcohol formation is less than that targeted for the final polyols, this processing procedure is suitable, effective, and efficient.

Ethylene glycol was added as a co-reagent for the ring-opening hydrolysis reaction to increase the hydroxyl content and provide cross-linking of the PESBO. Ethylene glycol is relatively inexpensive and has a high hydroxyl number, 1807 mg KOH/g. Figure 46 summarizes a general reaction scheme for epoxy-ring opening hydrolysis of oxirane-containing compound with an alcohol compound followed by glycol formation and alcohol dehydration producing ethers and alkenes.

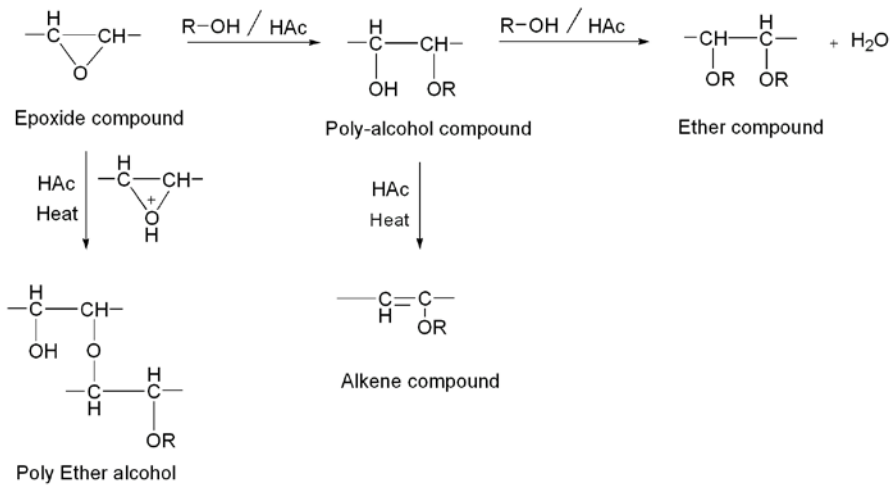

Figure 46. General mechanism for the epoxy-ring hydrolysis reaction

Ethylene glycol acts as a nucleophile with the *p*-toluenesulfonic acid monohydrate in the hydrolysis reaction forming equivalent hydroxyl functionalities in the final soy-polyol. Table 28 and Table 29 show the final properties for the alcoholysis reaction for PESBO and ESBO with ethylene glycol. The increase of hydroxyl numbers are showed in Table 27 and Table 28 for each sample. Insignificant changes in the iodine number were observed before and after the alcoholysis reaction, as illustrated in Table 27 and Table 28. This behavior indicates that the reactions undergo an ether and alcohol formation route rather than the alkene formation route. The viscosity for each sample increased gradually relative to the viscosity of the starting material (SBO ~ 80 cP).

Table 28. Results for the alcoholysis reaction of partially epoxidized soybean oil (PESBO) with 4 wt.-% of ethylene glycol (EG) using 0.5 wt.-% of p-toluenesulfonic acid (p-TSA) as catalyst.

no.	Molar Ratio			Rxn Conditions		Product Properties				
	PESBO[a]	EG	pTSA	Temp (ºC)	Time (hours)	Oxirane (%)	Acid no. (mg KOH/g)	Iodine no. (cg I_2/g)	Hydroxyl no. (mg KOH/g)	Viscosity (cP)
1	1	0.64	0.03	140	6	0.37	1.05	25.4	125	670
2	1	0.64	0.03	150	5	0.38	0.98	30.5	106	1491
3	1	0.64	0.03	140	8	0.80	1.50	24.8	102	2407
4	1	0.64	0.03	150	10	0.76	0.80	34.4	99	1817
5	1	0.64	0.03	150	6	0.93	0.90	40.5	104	2493
6	1	0.64	0.03	150	8	1.29	1.50	41.7	122	1635

[a] Molar ratio based on the epoxy moiety of PESBO.

Table 29. Results for the alcoholysis reaction of epoxidized soybean oil (ESBO) with 4 wt.-% of ethylene glycol (EG) using 0.5 wt.-% of p-toluenesulfonic acid (p-TSA) as catalyst

no.	Molar Ratio			Rxn Conditions		Product Properties				
	ESBO	EG	pTSA	Temp. (ºC)	Time (hrs)	Oxirane (%)	Acid no. (mg KOH/g)	Iodine no. (cg I_2/g)	Hydroxyl no. (mg KOH/g)	Viscosity (cP)
1	1	0.64	0.03	160	6	0.89	1.20	16.5	115	12424
2	1	0.64	0.03	145	4	1.28	2.55	10.4	105	7614
3	1	0.64	0.03	145	9.5	2.50	0.95	17.2	104	2989
4	1	0.64	0.03	145	13	1.05	0.90	26.5	116	8470
5	1	0.64	0.03	150	9	1.60	0.90	14.6	123	12440
6	1	0.64	0.03	150	8	1.50	0.70	16.5	107	4692

The amount of ethylene glycol addition is a tunable parameter to control cross-linking where the alcohols moieties of ethylene glycol limit the reaction. Since ethylene glycol is relatively non-volatile at 150 °C, this alcoholysis can be operated at ambient pressure.

6.4.2. Characterization Results

Figure 47 shows the ^{1}H-NMR spectra of SBO (a), PESBO (b) and alcoholysis of PESBO (c), respectively. The triglyceride of SBO has approximately 4.5 carbon-carbon double bonds per molecule according to the spectra. The three side chains are composed of ~ 20-30% oleic acid (ester), ~ 50-80% linoleic acid (ester) and ~5-10% linolenic acid (ester) and 15-25% of saturated fatty acids. The structure of PESBO is similar to that of the SBO, but with lower carbon-carbon double bonds (peak signals at 2.7-2.8 ppm bisallylic protons).

As shown in Figure 47(b), the appearance in the spectra of the peaks at 2.9-3.1 ppm in the PESBO implies an epoxy ring formation (-CH-CH-). The olefinic protons at 5.23-5.48 ppm nearly disappear. The hydroxyl group formation was confirmed in the ^{1}H-NMR spectra for the PESBO and the alcoholysis of PESBO in Figure 47 (b-c). In both spectra, the peaks at 3.6-3.7 ppm were the multiplet signal for the methyl group (–CH_2-) in the hydroxyl groups formed in the reactions. The spectra show a reduction in the epoxy ring group and the olefinic protons at 2.9-3.1 ppm and 5.23-5.48 ppm. Lee and co-workers report a detailed ^{1}H-NMR analysis for SBO and ESBO samples.[27]

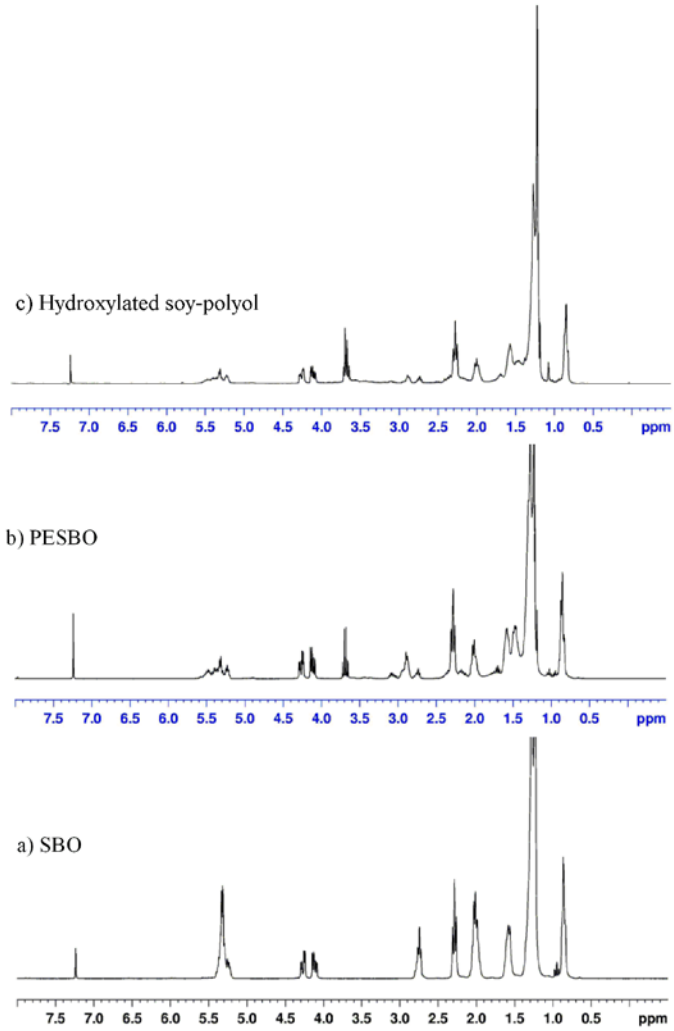

Figure 47. ^{1}H-NMR spectra of soybean oil (SBO), partially epoxidized soybean oil (PESBO), and hydroxylated soy-polyol

A FT-IR spectrum of the SBO, PESBO and the hydroxylated PESBO are presented in Figure 48. The spectra of PESBO (b) shows an appearance of the epoxy group at 825-845 cm^{-1} compared with the starting material, SBO (a). The hydroxylated PESBO (c) shows the characteristic signals at 1050 cm^{-1} indicating the presence of ester groups and the emergence of hydroxyl groups at 3450 cm^{-1}. The disappearances of the

epoxy groups at 825-845 cm^{-1} are obvious. The FT-IR spectra confirmed the epoxidation reaction and the pathway mechanism shown in Figure 44, Figure 45 and Figure 46. The poly-alcohol compound formation was confirmed at 3450 cm^{-1}. The ether compound and poly-ether alcohol compound formation were confirmed by peak signals at 1250-1040 cm^{-1}.

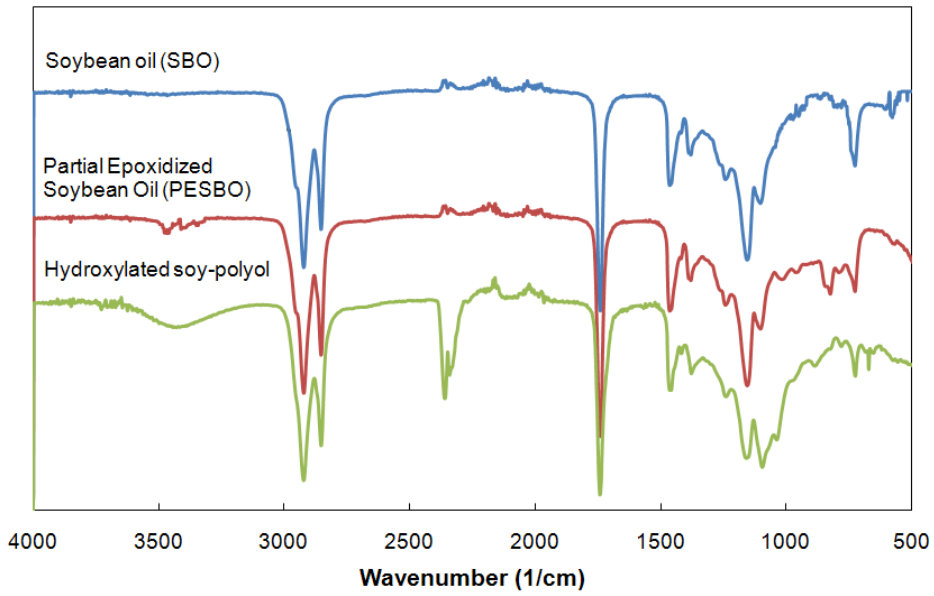

Figure 48. FT-IR spectra of SBO, PESBO and hydroxylated soy-polyol

6.5. Conclusion

SBO was fully and partially epoxidized using hydrogen peroxide and formic acid without organic solvent. Epoxy yields in excess of 90 % were obtained. The hydrogen peroxide, formic acid and water residuals in the epoxidation reaction can be converted to alcohol and carboxylic acid as illustrated previously in Figure 45. Higher concentrations of formic acid or hydrogen peroxide cause product degradation (particularly, the

carboxylic acid -in the epoxidation reaction-). This process alternative compares favorably to conventional processing which is conducted at 40°C by adding organic solvent with ion exchange resin catalyst; higher epoxide productivity are attainable.

An epoxy-ring opening hydrolysis of the PESBO was performed using a p-toluenesulfonic acid monohydrate and ethylene glycol as a co-reagent in the reaction. Ample degrees of freedom were observed in the alcohol addition to control the hydroxyl functionality and the viscosity (MW) in the final polyol. These soy-based polyols are potential monomers for rigid and flexible polyurethane foam synthesis. Reaction conversions were confirmed by FT-IR and ^{1}H-NMR spectra of the different samples.

6.6. Acknowlegdments

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CHAPTER 7

POLYURETHANE APPLICATIONS FOR SOY-BASED POLYOLS

7.1. Abstract

Several rigid and flexible water-blown polyurethane foams were made by replacing 50 to 100% of Voranol® 490 for rigid foams and Voranol®4701 for flexible foams in the B-side of the foam formulation by soybean oil derivatives. For rigid water-blown polyurethane foams, density, thermal conductivity and compressive strength were determined. For flexible water-blown polyurethane foams, density, 50% constant deflection compression, 50% compression force deflection, tear resistance and resilience were measured.

7.2. Introduction

Polyurethanes are polymers containing urethane functional groups synthesized from the reactions of isocyanates (A-side materials) and polyols (B-side materials). The polyols are compounds containing active hydrogen (typically alcohol or hydroxy functional groups).

The major application of polyurethanes is in the area of flexible foams and rigid foams, with significant application in coatings, adhesives, sealants, and elastomers. World consumption of polyurethanes in 2005 was 8.8 million tons. According to 2005 industry estimates by IAL Consultants, the global polyurethanes market is a $30–35 billion industry with approximately 30.3 billion pounds of total production.[1]

7.2.1. Polyol Properties for Foaming

There are several physical and chemical properties of polyols; namely, hydroxyl number, acid number, molecular weight and functionality. The polyol properties have significant effects on the final foam properties.

7.2.1.1. Functionality

Functionality is the number of functional groups reacting with isocyanate per molecule of the functional polyols. The reactive groups could be hydroxy groups, epoxy groups, hydroperoxy groups or amine groups.

7.2.1.2. Hydroxyl number

The ASTM E 222-00 (2005 reapproved) method covers the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and alicyclic compounds and phenols. The AOCS Tx 1a-66 (1997) method covers the

determination of hydroxyl groups in oil and their derivatives that contain an oxirane ring structure in the molecule.

7.2.1.3. Oxirane Oxygen Content (%)

This method determines oxirane oxygen which is the oxygen contained in the epoxy group. In this test method, the oxygen is titrated directly with hydrogen bromide solution in acetic acid. It is applicable to epoxidized fatty materials and epoxy compounds in general, according to AOCS Official method Cd 9-57 (1997).

7.3. Water-blown Polyurethane Rigid Foam

Polyols for rigid foams differ from polyols for flexible foams in molecular weight (below 1000) and functionality (varies from 3 to 6). Especially significant is equivalent weight (molecular weight per mol of hydroxyl groups), which is typically between 100 and 200. Some rigid applications may require the presence of aromatics, especially when high compressive strength of foams and low flammability is desired. Functional groups in these compounds may come from the low molecular weight agents and fatty acids may play the role of a diluent or plasticizer. Part of the rigidity may come from ureas obtained by reacting isocyanates with amines generated from isocyanates by addition of water. Structural imperfections in highly cross linked systems are tolerated more easily than in flexible applications.

7.3.1. Foam Formulation

The effect of replacing the B-side polyether polyol (VORANOL® 490) with 50 to 100% of soy-based polyol in the foam formulation on the properties of water-blown rigid polyurethane foam was studied.[2, 3] A few isocyanate indexes were measured 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, soy-based polyol and distilled water used. The amount of the soy-based polyol used in the foam formulation was based on the hydroxyl number obtained by 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. The foam formulations for water-blown rigid polyurethane foam for different isocyanate index are shown in Table 30.

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 each into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 seconds. The mixture was allowed to degas for 2 minutes. PAPI® 27 (A-side material) was then added rapidly and stirring was continued for another 10–15 seconds at the same speed. The mixtures were poured immediately into a wooden mold (11.4 x 11.4 x 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C).

7.3.2 Foam Properties

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23°C) for 24 hr, using a Fox 200 heat flow meter instrument (Laser Comp, Wakefiled, MA) and ASTM procedure C 518-04. The dimension of the foam samples was 20 x 20 x 2.5 cm. Density of the 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 x 6.35 x 3.81 cm.

Table 30. Formulation for water-blown rigid polyurethane foam with different isocyanate index

Ingredients	Parts by weight
B-side materials	
VORANOL® 490	100, 50, 25, 0
Soy-based Polyol	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.

7.4. Water-blown Polyurethane Flexible Foam

There are two basic markets for flexible foams: slabstock foams and molded foams. Slabstock foams are produced continuously by pouring the formulation mixture on a conveyor belt, which foams in open air to form a bun. The foams are cut to desired shapes such as mattresses etc. Molded foams are formed in closed molds and have higher technical requirements: they are used for car seats and must be light (low density) and

have high load bearing properties (support a passenger without large deformation, and show good elastic recovery). Flexible foam characteristics depend on the degree of cell opening, which should be complete for desirable properties. Two foaming formulations differ in several ways. First, slabstock foam cells must be opened spontaneously, while molded foams are usually crushed to achieve complete cell opening.

Polyols for slabstock flexible foams are usually polyether triols with secondary hydroxyl groups (polypropylene oxide, or random propylene oxide, ethylene oxide, copolymers-based), but the reactivity for molded application must be higher.

7.4.1. Foam Formulation

The effect of replacing the B-side polyether polyol (VORANOL® 4701) with 50% to 100% of soy-based polyol in the foam formulation on the properties of water-blown flexible polyurethane foam was studied.[3] An isocyanate index of 80 was used for soy-based polyol replacement in the foam formulation, including a 100 % of Voranol® 4701 as control for comparison purposes. The amount of isocyanate was based on the total hydroxyl number of the Voranol® 4701 and the soy-based polyol. Other factors in the foam formulation such as water content, catalysts and surfactant were kept constant. Table 31 shows the foam formulation for water-blown flexible polyurethane foam.

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used. The petroleum polyol (Voranol® 4701), soy-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 seconds. The mixture was allowed to degas for 2 minutes. PAPI® 27 (MDI, A-side material) was then added rapidly and stirring continued for another 10–15 seconds at the same speed. The mixtures

were poured immediately into a wooden mold (11.4 x 11.4 x 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C).

Table 31. Formulations for water-blown flexible polyurethane foam

Ingredients	Parts by weight
B-side materials	
VORANOL® 4701	100, 50, 25
Soy-based polyol	0, 50, 75
DABCO® 33-LV	0.6
DABCO® BL-17	0.2
Stannous octoate	0.3
Dibutyltin dilaurate	0.3
Diethanolamine	2.2
DABCO® DC 2585	1.0
Blowing Agent (distilled water)	5.0
A-side materials	
PAPI® 27	Index[a] 80

[a] The quantity of isocyanate was based on an isocyanate index 80, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

7.4.2. Foam Properties

The density, 50% compression force deflection, 50% constant force deflection, tear resistance and resilience (ball rebound test) of flexible polyurethane foams were measured according to ASTM procedure D 3574-05. Fifty percent compression force deflection was determined by a TA.HDI Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). For 50% constant force deflection or compression set, the initial foam thickness was measured. The foam was then pressed to 50% of initial thickness and

placed in a VersaTenn III Temperature-Humidity Chamber (Tenney Engineering Inc., Williamsport, PA) set at 70 ºC and 6% RH for 22 hours. The final thickness was measured after foam was removed from the constant temperature-humidity chamber and placed in ambient environment (23 °C and 50% RH) for 30 to 40 minutes. The compression set was calculated by the following equation:

$$C_t = \left(\frac{t_o - t_f}{t_o} \right) x100$$

where:

C_t= compression set expressed as a percentage of the original thickness, t_o= original thickness of test specimen, and t_f = final thickness of test specimen.

7.5. Polyurethane Foam Results

7.5.1. Water-blown Rigid PU Foams

The mechanical properties of polymers are of key importance in all applications where polymers are used as structural materials. The prime consideration in determining the utility of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. Also, the thermal stability of a polymer has important role in its application.

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:

$$OH_m = \left(OH_{Voranol\,490} \cdot A\right) + \left(OH_{soy-polyol} \cdot B\right)$$

Where OH_m is the hydroxyl of the mixture, $OH_{voranol490}$ is 484.4 mg KOH/g, $OH_{soy\text{-}polyol}$ isthe hydroxyl number obtained from ASTM E 222-00, A is the mass percent of VORANOL® 490 and B is the mass percent of soy-based polyol sample.

Generally, the density of the cellular materials is the main factor for determining properties. The density of water-blown rigid foam is dominated by the weight and volume of the plastics consisting of the matrix of the foam and the gases trapped in the foam cells. The solid-phase composition contains all additives such as the surfactant, catalysts and stabilizers, as well as the pure polymer.[4] Table 32 shows the effect of isocyanate index on the density, thermal conductivity and compressive strength of the PUF samples. Figure 49 shows the effect on foam density on the compressive strength of several polyurethane foam formed with soy-based polyol samples (from chapter 4). As the density of the foam increases, the mechanical strength increases, illustrated on Figure 49. Most of the foams made from vegetable based polyol with a lower OH_m usually shrank within a few days of storage at room temperature. This effect reduced the dimensions of foam resulting in higher density foams. A linear behavior of the 50% soy-based polyol with a smaller change in density and compressive strength compared to the control polyol (Voranol®490).

The foaming study demonstrated that the compressive strength of the PUF samples increased with the isocyanate index, even with a slight increase in the densities. The increase in the compressive strength of the PUF samples may be attributable to the additional networks that arise from allophonate and biuret formation by the supplementary reactions of excess PMDI (isocyanate), shown by the results in Table 32 and Figure 49.

Table 32. Final properties of polyurethane rigid foam samples from soy-based polyol sample G (Chapter 4) at different percent of replacement in the formulation

No.	*% Replacement*	*Iso Index*	*OH_m no. (mg KOH/g)*	*Thermal Conductivity (W/mK)*	*Density (Kg/m^3)*	*Compressive Strength (kPa)*
0	0%(100%V490)	110	484	0.02692	45.55	430.47
1	50% soy-polyol	110	381	0.02601	48.11	415.03
2	50% soy-polyol	100	381	0.02571	45.16	359.08
3	50% soy-polyol	90	381	0.02558	42.35	293.12
4	50% soy-polyol	80	381	0.02614	41.40	250.27
5	75% soy-polyol	110	330	0.02662	46.70	313.52
6	75% soy-polyol	100	330	0.02620	49.13	275.61
7	75% soy-polyol	90	330	0.02600	42.60	200.74
8	75% soy-polyol	80	330	0.02948	N/A	N/A
9	100% soy-polyol	110	278	0.04327	48.77	223.08

The apparent thermal conductivity (k value) of a material is characterized by its ability to transport heat from one side of the material to the other for a unit difference in temperature. The insulating capacity increases as the k value decreases. The thermal conductivity of foams is contributed by the thermal conductivity of gas trapped in the foam cells, thermal conductivity of the foam cell membrane material, convection of cell gas, cell size, cell orientation, closed cell content, foam density and thermal radiation.[5] It is interesting that most of the foams made with 50 and 75% soy-based polyol have nearly the same thermal conductivity as the control foam made with 100% Voranol®490.

The foam made with 100% of soy-based polyol has a much higher thermal conductivity than the control foam made with 100% of Voranol®490.

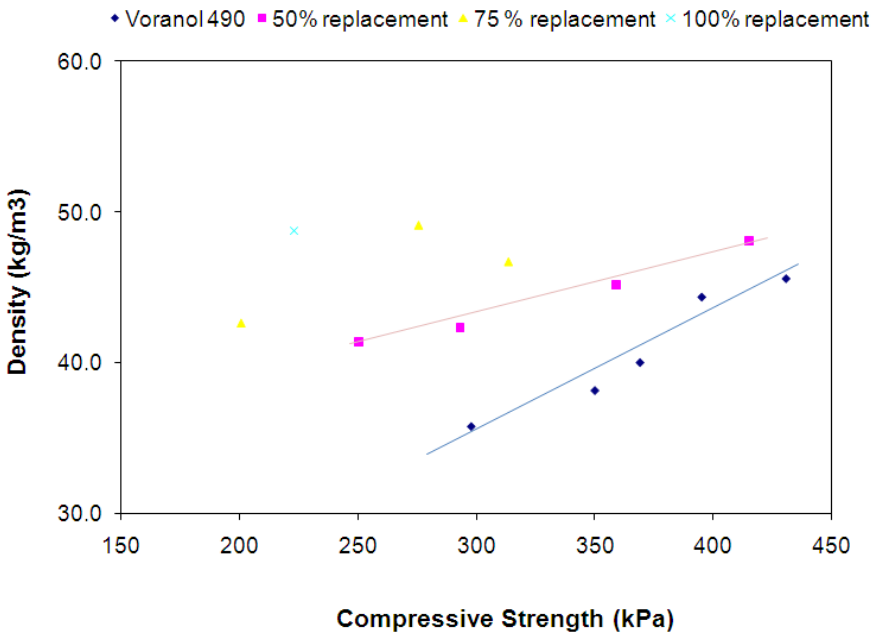

Figure 49. Effects on compressive strength related with density of PU rigid foams from soy-based polyol sample G (Chapter 4)

Table 33 shows the mechanical properties for the rigid polyurethane foams made with 50% and 100% of soy-based polyol formulations described in Chapters 3, 5 and 6. The foam samples 5, 6, 7, 8 and 19 have thermal conductivities about the same foam made with Voranol®490 (see on Table 33). However, most of the foam made with 50% and 100% soy-based polyol has higher thermal conductivity due to the higher content of secondary alcohols in the molecule. The secondary alcohol reacts with isocyanate at a slower reaction rate than the primary alcohols in Voranol®490 and this effect can change the three-dimensional network in the polyurethane foam.

Figure 50 show the effect of compressive strength with density for rigid polyurethane foam made with 50 and 100% of soy-based polyol compared to the control foam made with Voranol®490. Most of the polyurethane rigid foam samples made with soy-based polyols show a lower compressive strength than the control. The ellipse area contains the data from soy-based polyols with similar density and compressive strength properties and was slightly inferior to foam made with control polyol, Voranol®490. However, the polyurethane rigid foam made with 100% soy-based polyol shows significant reduced compressive strength.

Table 33. Final properties of polyurethane rigid foam samples from soy-based polyol samples (Chapters 3, 5 and 6)

No.	*Sample Description*	*ASTM[a] OH (mg KOH/g)*	*AOCS[b] OH (mg KOH/g)*	*Thermal Conductivity (W/mK)*	*Density (Kg/m^3)*	*Compressive Strength (kPa)*	*Replacement (%)*
C1	Voranol 490 (Iso Index 110)	484	n/a	0.0272	45.6	430	50
C2	Voranol 490 (Iso Index 90)	484	n/a	0.0266	40.0	369	50
C3	Voranol 490 (Iso Index 70)	484	n/a	0.0266	36.0	298	50
1	BPESBO (ark)+ 5% EG	121	98.5	0.0286	41.4	252	50
2	BPESBO (ark)+ 10% EG	209	189	0.0328	43.4	328	50
3	PESBO + 4% EG + 0.5% pTSA	186	107	0.0293	40.9	245	50
4	50% Vikoflex+50% ESBO(4% EG,0.5% pTSA)	229	101	0.0326	41.5	222	50
5	ESBO:EG:ME (0.5%wt p-TSA, 4:4:3, 150C/2d)	286	158	0.0265	47.6	374	50
6	ESBO:EG:ME (0.5%wt p-TSA, 4:2:3, 150C/6hr)	341	106	0.0265	44.6	311	50
7	ESBO:EG:ME (0.5%wt p-TSA, 4:6:3, 150C/4hr)	294	163	0.0254	42.3	326	50
8	ESBO:EG:ME (0.5%wt p-TSA, 4:8:3, 150C/4hr)	285	188	0.0257	41.1	305	50
9	ESBO:EG:ME (0.5%wt p-TSA, 4:2:6, 150C/5hr)	310	182	n/a	43.9	305	50
10	ESBO:EG:ME (0.5%wt p-TSA, 4:6:3, 150C/6hr)	209	236	n/a	43.8	346	50
11	ESBO:EG:ME (0.5%wt p-TSA, 4:2:9, 150C/6hr)	302	206	n/a	42.3	291	50
12	Alcoholysis ESBO-3.90% (4% EG+0.5%p-TSA, 145C/6hr)	223	104	0.0323	36.5	244	50

13	Alcoholysis ESBO-3.90% (4% EG+0.5%p-TSA, 145C/4hr)	250	105	0.0266	36.0	320	50
14	Alcoholysis ESBO-5.50% (4% EG+0.5%p-TSA, 145C/9.5hr)	230	104	0.0292	45.7	364	50
15	Alcoholysis ESBO-5.50% (4% EG+0.5%p-TSA, 145C/13hr)	231	116	0.0301	44.7	379	50
16	Alcoholysis ESBO-5.60% (4% EG+0.5%p-TSA, 150C/9hr)	199	123	0.0328	43.9	343	50
17	ESBO:EG:ME (0.5%wt p-TSA, 4:2:3, 150C/6hr)	341	106	0.0431	48.8	143	100
18	ESBO:EG:ME (0.5%wt p-TSA, 4:6:3, 150C/4hr)	294	163	0.0371	44.5	193	100
19	ESBO:EG:ME (0.5%wt p-TSA, 4:8:3, 150C/4hr)	285	188	0.0371	44.9	191	100
20	ESBO:EG:ME (0.5%wt p-TSA, 4:2:6, 150C/5hr)	310	182	n/a	47.6	177	100
21	ESBO:EG:ME (0.5%wt p-TSA, 4:6:3, 150C/6hr)	209	236	n/a	42.3	222	100
22	ESBO:EG:ME (0.5%wt p-TSA, 4:2:9, 150C/6hr)	302	206	n/a	41.8	163	100

[a] Hydroxyl number experimentally obtained by the ASTM D 4274-2005. [b]Hydroxyl number experimentally obtained by AOCS method Tx 1a-66-1997.

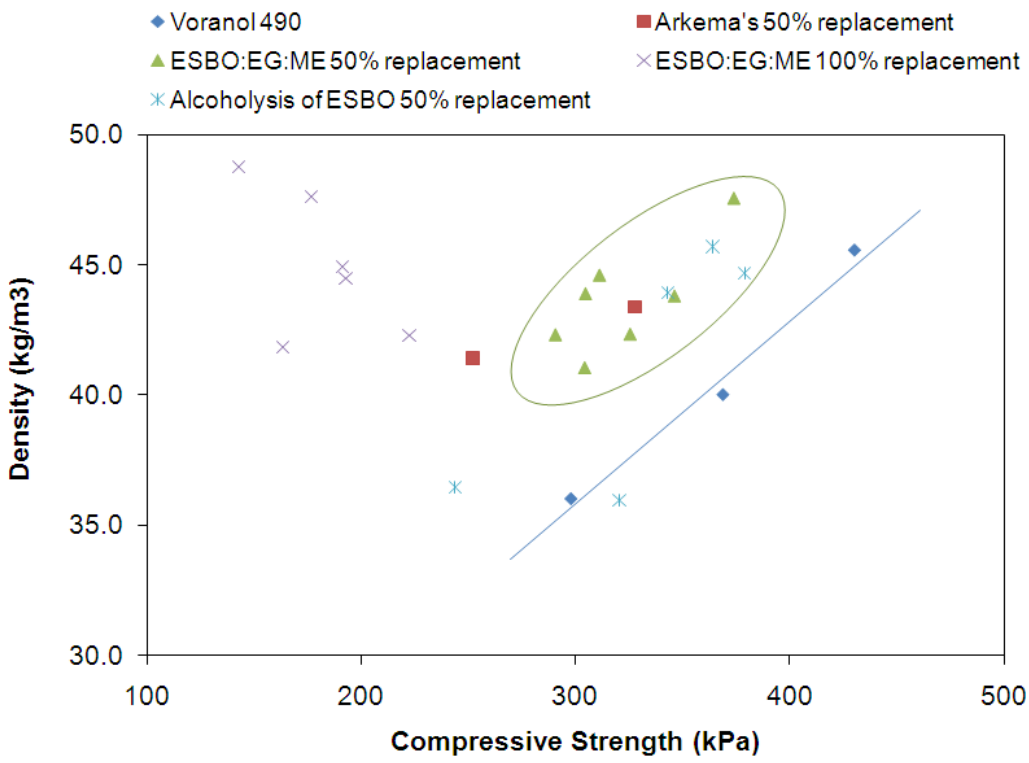

Figure 50. Effects on compressive strength related with density of PU rigid foams from soy-based polyols (Chapter 3, 5 and 6) using 50 and 100% replacement in the foam formulation

7.5.2. Water-blown Flexible PU Results

The effect on replacing the B-side polyether polyol, Voranol® 4701, in the foam formulation was studied. The compression force deflection (CFD), constant deflection compression set (CDC), foam density, tear strength (or resistance) and resilience were experimentally determined.

Compression force deflection (CFD) test measures the force necessary to produce a 50% compression over the entire top surface area of the foam specimen. A higher compression force deflection indicates the foam is firmer resulting from either a higher

cross-linking density or a higher foam density or both. Constant deflection compression (CDC) test consist of deflecting the foam specimen to 50% initial thickness, exposing it to 70ºC and 6% RH for 22 hours and measuring the change in the thickness of the specimen after recovery at 23 ºC and 50% RH for 30 to 40 minutes. A lower constant deflection compression set indicates the foam is more flexible and recovers its thickness better after deflection compression.

Density is important to the performance and economics of foam because it measures how much foam is air and how much is polymer. The density is simply the mass divided by the volume and is commonly measured in kilograms per cubic meter (kg/m^3). The tear resistance is the resistance to a growth of a cut or nick in the foam specimen when tension is applied. Resilience is measured by dropping a steel ball on a foam sample and measuring the height of the rebound. The ball rebound test is different from other tests because it indicates the instantaneous feel of the foam.or an indicator of the surface elasticity or "springiness" of the foam.

Table 34 shows the final foam properties for 50% replacement of soy-based acetol polyol samples (soy-based polyol samples from Chapter 2) compared to the petroleum-based polyurethane foam samples with 100% of Voranol®4701 and Voranol®3136. Table 34 shows the final foam properties for 50% replacement of soy-based PESBO polyol samples (soy-based polyol samples from Chapter 3) compared to the petroleum-based polyurethane foam samples with 100% of Voranol®4701 and Voranol®3136. Table 34 shows the final foam properties for 50, 75 and 100% replacement of soy-based polyol samples (soy-based polyol samples from Chapter 6) compared to the petroleum-based polyurethane foam samples with 100% of Voranol®4701 and Voranol®3136.

Most of the polyurethane flexible foam made with 50% of vegetable polyols had higher constant deflection compression (CDC) values than the two control foam samples made with Voranol®3136 and Voranol®4701, indicating a loss of the initial thickness and less flexible foam than the controls. The polyurethane flexible foam samples 4, 11 and 13 (samples from Table 34) have comparable values on compression force deflection (CDF), constant deflection compression (CDC), tear and resilience as the control foam made with 100% of Voranol 3136. These polyurethane foam samples appear to have a medium to small size of open cell structure.

The majority of the polyurethane flexible foam samples made with 50% of replacement from Table 34 and Table 35 show a higher foam density than the control foams. It was noted that foam made with 200 or lower hydroxyl number usually shrinks, affecting the dimensions of the foam resulting in higher density foam. The polyurethane foams made from soy-based PESBO polyols have similar compressive force deflection values as the control foams made from petroleum-based polyols (Table 35).

Table 34. Final properties for polyurethane flexible foam samples from soy-based acetol polyols (Chapter 2) using 50% replacement in the formulation

No.	*Sample description*	*ASTM[a] OH*	*Iso Index*	*Density (Kg/m^3)*	*CFD (kPa)*	*CDC (50%)*	*Tear (N/m)*	*Resilience %*
C1	Voranol 4701	34	80	44.8	8.8	5.5	142	44.9
C2	Voranol 3136	54	80	42.3	15.5	13.0	149	46.4
1	ESBO:acetol(V27)(1:0.5)	119.42	80	37.7	12.8	38.1	160	27.7
2	Sample AE	136.25	80	41.2	10.1	48.1	126	33.8
3	Sample BE	120.57	80	45.4	16.4	41.5	175	19.9
4	Sample CE	104.74	80	51.4	16.1	27.3	173	28.0
5	Sample DE	108.15	80	49.5	19.5	34.2	200	26.7
6	Sample EE	94.43	80	45.9	16.7	39.4	168	18.7
7	Sample FE	105.85	80	42.4	13.6	32.4	192	27.6
8	Sample GE	112.62	80	53.4	16.1	32.8	131	20.0
9	Sample IE	98.42	80	63.8	31.8	29.0	262	33.0
10	Sample HE	104.99	80	59.7	22.7	32.1	201	27.0
11	Sample JE	103.59	80	54.3	17.8	27.4	157	30.8
12	Sample KE	104.76	80	50.8	21.7	31.8	257	24.7
13	ESBO: acetol (V89), 1:0.7	92.55	80	50.8	13.4	27.1	108	19.4
14	ESBO: acetol (V93), 1:0.7	99.61	80	63.5	26.9	27.6	n/a	25.1

[a] Hydroxyl number experimentally obtained by the ASTM D 4274-2005.

Table 35. Final properties for polyurethane flexible foam samples from soy-based PESBO polyols (Chapter 3) using 50% replacement in the formulation

No.	*Sample Description*	*ASTM[a] OH*	*Iso Index*	*Density (Kg/m^3)*	*CFD (kPa)*	*CDC (50%)*	*Tear (N/m)*	*Resilience (%)*
C1	Voranol 4701	34	80	44.8	8.8	5.5	142	44.9
C2	Voranol 3136	54	80	42.3	15.5	13.0	149	46.4
1	BPESBO (ark)+3.4 % EG	93	80	36.3	8.8	44.1	147	27.6
2	BPESBO (ark)+ 5 % EG	105	80	36.7	8.7	42.7	146	26.3
3	BPESBO (ark)+ 10 % EG	183	80	37.2	11.4	48.5	144	24.0
4	BPESBO (ark)+ 10 % EG (250/2)	113	80	36.7	7.7	41.9	129	27.7
5	BPESBO (ark)+ 10 % EG (250/2)	213	80	38.4	10.0	49.6	138	24.7
6	BPESBO (ark)+ 10% EG (250/5)	140	80	40.8	10.3	44.9	131	27.2
7	BPESBO (ark)+ 5 % EG (250/2)	126	80	36.8	7.3	42.6	148	29.2
8	BPESBO (ark)+ 5 % EG (250/7)	128	80	38.4	10.4	40.4	164	28.6
9	BPESBO (ark)+ 5 % EG (250/10)	126	80	40.3	11.5	39.1	176	28.4
10	BPESBO (ark)+ 5 % EG (250/15)	127	80	41.4	10.8	44.1	172	29.1

[a] Hydroxyl number experimentally obtained by the ASTM D 4274-2005.

Table 36. Final properties for polyurethane flexible foam samples from soy-based polyols (Chapter 6) using 50, 75 and 100% replacement in the formulation

No.	*Sample description*	*ASTM[a] OH*	*AOCS[b] OH*	*Density (kg/m^3)*	*CFD (kPa)*	*CDC (50%)*	*Tear (N/m)*	*Resilience (%)*	*Replacement (%)*
C1	Voranol 4701	34		44.8	8.8	5.5	142	44.9	50
C2	Voranol 3136	54		42.3	15.5	13.0	149	46.4	50
1	Alcoholysis ESBO-3.9% (1:0.5:0.8, molar ratio) 4% EG,0.5%p-TSA	288	116	34.6	13.4	46.9	140	24.4	50
2	ESBO (3.90%ox.)(1:0.5:0.80, molar ratio)	254	29	35.1	12.6	48.3	145	24.7	50
3	Alcoholysis ESBO-3.9% (4% EG, 0.5% p-TSA, 145C/6hr)	223	109	34.8	14.1	45.6	133	26.2	50
4	Alcoholysis ESBO-3.9% (4% EG, 0.5% p-TSA, 145C/4hr)	250	107	34.7	14.1	45.9	133	25.8	50
5	Alcoholysis ESBO-5.5% (4% EG, 0.5% p-TSA, 145C/9.5hr)	230	105	32.2	9.4	42.7	126	29.3	50
6	Alcoholysis ESBO-5.5% (4% EG, 0.5% p-TSA, 145C/13hr)	231	117	37.2	14.3	46.7	141	25.0	50
7	Alcoholysis ESBO-5.6% (4% EG, 0.5% p-TSA, 145C/9hr)	199	123	39.7	14.8	47.7	163	28.8	50
8	Alcoholysis PESBO(1:0.2:0.7, molar ratio) 4%EG,0.5% p-TSA	135	105	32.7	9.9	n/a	138	25.0	50
9	Alcoholysis PESBO(1:0.1:0.7, molar ratio) 4%EG,0.5% p-TSA	131	97	32.0	9.6	n/a	137	26.5	50
10	Alcoholysis PESBO(1:0.5:0.7, molar ratio) 4%EG,0.5% p-TSA	124	101	32.5	9.8	n/a	135	26.5	50

11	Alcoholysis PESBO(1:0.2:0.6, molar ratio) 4%EG,0.5% p-TSA	120	107	32.5	9.9	n/a	139	25.3	50
12	Alcoholysis PESBO(1:0.2:0.6, molar ratio) 4%EG,0.5% p-TSA	133	101	35.7	10.4	44.6	116	30.0	75
13	Alcoholysis PESBO(1:0.2:0.7, molar ratio) 4%EG,0.5% p-TSA	128	102	34.1	9.7	45.4	106	28.3	75
14	Alcoholysis PESBO(1:0.5:0.4, molar ratio) 4%EG,0.5% p-TSA	129	127	31.0	6.8	48.0	95	0.0	100
15	Alcoholysis PESBO(1:0.2:0.7, molar ratio) 4%EG,0.5% p-TSA	143	124	32.6	13.8	48.8	92	17.0	100
16	Alcoholysis PESBO(1:0.1:0.7, molar ratio) 4%EG,0.5% p-TSA	129	101	42.9	16.7	44.4	89	25.0	100
17	Alcoholysis PESBO(1:0.4:0.7, molar ratio) 4%EG,0.5% p-TSA	139	129	33.6	13.3	49.5	n/a	19.2	100
18	Alcoholysis PESBO(1:0.2:0.6, molar ratio) 4%EG,0.5% p-TSA	118	112	34.0	12.4	48.4	n/a	21.3	100
20	Alcoholysis PESBO(1:0.1:0.7, molar ratio) 4%EG,0.5% p-TSA	127	100	36.8	7.5	47.8	n/a	14.7	100
21	Alcoholysis ESBO-5.5%(1:0.5:0.8, molar ratio) 4%EG,0.5% p-TSA	180	117	35.2	18.2	48.8	117	19.6	100

[a] Hydroxyl number experimentally obtained by the ASTM D 4274-2005. [b] Hydroxyl number experimentally obtained by AOCS method Tx 1a-66-1997.

The polyurethane flexible foam made with 50, 75 and 100% of soy-based polyols do not show a significant change on the foam properties such as CDC and CFD, illustrated on Table 36. The tear and resilience decreases as the amount of soy-based polyol increases. Most of the foam samples shown lower foam density compare to the control foam made with 100% petroleum-based polyol.

7.6. Conclusion

Several rigid and flexible water-blown polyurethane foam samples were successfully prepared by blending petroleum-based polyol and vegetable-based polyol together as the B-side component. The hydroxyl number of the soy-based polyols affects the density and compressive strength but not the thermal conductivity of the rigid water-blown polyurethane foams. Foam samples made with alcoholysis of ESBO (samples 5 and 7, Table 33) and one-pot alcoholysis of ESBO (sample 19, Table 33) have similar thermal conductivities as samples made with Voranol®490. These three soy-based polyols appears to have the potential to replacing up to 50% of the petroleum based polyol in the rigid water-blown polyurethane foam application.

Most of the polyurethane flexible foam made with 50, 75 and 100% of vegetable oil based polyols has higher constant deflection compression (CDC) values compared to foam samples made with Voranol®3136 and Voranol®4701, indicating a loss of the initial thickness and a less flexible foam than do the controls. The polyurethane flexible foam samples from soy-based acetol polyol (samples 4, 11 and 13, Table 34) have comparable values on compression force deflection (CDF), constant deflection compression (CDC), tear and resilience as the control foam made with 100% of Voranol®3136. These three

soy-based polyol samples appear to have the potential to replacing up to 50% of the petroleum based polyol in the flexible water-blown polyurethane foam application.

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CHAPTER 8

OIL EXTRACTION FROM SOYBEAN SEEDS

8.1. Abstract

Extraction treatment of oil from soybean seeds is an important industrial process. Two experimental methods were evaluated: mechanical compression extraction and use of water-soluble enzymes extraction. N-hexane extraction served as the basis for comparison because it is usually used commercially. The effects of soybean particle size, three temperatures (45, 55, and 70°C), and four concentrations (1.0, 3.0, 4.0, and 6.0%) of ten hydrolytic enzymes were assumed. *Bacillus subtilis proteases* (NL and N) provided the best extraction; optimum conditions for extraction were 4.0% (w/w) enzyme in contact with the soybeans for 20 hours at 55°C. These enzymes promote the release of 10.0% of the oil, compared to 18.0% oil removal by n-hexane. Seven enzymes were found to be ineffective for soybean oil extraction. The soybean particle size was evaluated for the organic solvent and mechanical press method. By mechanical pressing of 0.25 mm soybean particles, 16.0% of oil was extracted at constant pressure and temperature. A limited number of enzymes enhance oil extraction from soybean seeds.

Keywords: Soybean, oil extraction, enzymes, solvent extraction, pressing extraction

8.2. Introduction

Soybeans are the dominant oilseed in the USA and world markets. There are a variety of factors: economics, high quality protein meal and edible oils, a plentiful, dependable supply of soybeans in both domestic and export markets at competitive prices. Soybeans protein and oil contain amino acids and fatty acids, components that fulfill many applications. We focus on enhanced oil extraction that may offer fewer undesirable by-products.

8.2.1. Composition of soybean seeds

The soybean seed consists of three major parts: 1) the seed coat or hull, 2) two cotyledons, and 3) germ or hypocotyls (Table 37). By weight, the hull is about 8 %, cotyledon 90 %, and hypocotyls 2 % of the soybean. The cotyledon contains practically all the oil and protein in its palisade-like cells. Microscopic examinations of these cells reveal the presence of protein and lipid bodies which store proteins and oil. Protein bodies, average 10 microns while the lipid bodies are typically, 0.2 to 0.5 microns in diameter. The hull holds the cotyledons together and provides an effective protective layer. [1, 2]

Table 37. Approximate composition of soybean seed

Seed Part	Whole seed	Protein	Lipid	Carbohydrate	Ash
	% (w/w)				
Cotyledon	90	43	23	29	5
Hull	8	9	1	86	4.3
Hypocotyls	2	41	11	43	4.4
Whole seed	100	40	20	35	5

NOTE: % (w/w) is a moisture free basis percent.

Soybean protein is made up of 18 amino acids: Ala, Arg, Asp, Cys, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr and Val in varying amounts. The lipids of crude soybean oil consist of 96% triglycerides, 2% phospholipids, 1.6% unsaponifiables, 0.5% free fatty acids and trace carotenoid pigments. Soybeans contain about 35% carbohydrates. These can be divided into two groups: soluble sugars (sucrose 5%, stachyose 4%, raffinose 1%, and others) and insoluble "fiber" (20%). The mineral content of soybeans, determined as ash, is about 5%. The major mineral constituents are potassium, calcium and magnesium.

8.2.2. Extraction Process

Industrial processes for the extraction of edible oil from oilseed involve several steps: dehulling, grinding or flaking, pre-heating, cooking, organic solvent extraction, and mechanical pressing. Health and safety considerations using organic solvents have prompted attempts to develop alternative methods for oil extraction; mechanical pressing, aqueous enzymatic treatment, and a combinations of these treatments.

8.2.3. Solvent Extraction Mechanism

Solvent extraction of oils is standard practice in the vegetable fats and oils industry. Solvent extraction processes tends to be costly, involving high capital equipment cost and operational expenditures. [2] Residual solvent, such as hexane in the meal can also make the meal unfit for some feed applications. The extraction of oil from oilseeds by non-polar solvents is basically a solid-liquid unit operation.

This separation of oil from the solid to the oil-solvent solution may be divided into three steps:

1. Diffusion of the solvent into the solid particle (mainly cotyledon)

2. Dissolution of the oil into the solvent

3. Diffusion of the oil-solvent out of the solid particle into the surrounding liquid

Due to the high solubility of the oil in the commonly used solvents (n-hexane), the dissolution step is not a rate limiting factor. [1, 3] The rate-limiting process is diffusion, much can be gained by reducing the size of the solid particles. These extractions are diffusion controlled and several studies confirm that the key controllable factor is the oilseed particle size. [2, 3]

8.2.4. Press Extraction

Another extraction method is based on the use of the mechanical / hydraulic press. It is one of the oldest pressing methods. The mechanical / hydraulic press extraction breaks the cell walls to release the oil. [4, 5] Pressing equipment include extruders, expellers, or continuous screw pressing equipments. Expeller pressing has replaced the hydraulic press procedure for extraction of oils. [2] Mechanical presses are still used in some countries for small volume production or for special purposes. The press technique has several parameters to consider: pre-heating, pressing time, particle size and moisture content in the grain. At low moisture and small particle size it is possible to achieve maximum oil release from soybeans.

8.2.5. Enzyme Extraction

Enzymatic oil extraction is the newest method for treating ground soybean seeds. Enzymes work by opening the oil cell walls by bio-degeneration or degradation. The cell wall is very complex, which at the level of various strata (lamella and tonoplast) contains different kinds of substances: pectin, hemicelluloses, cellulose, protein substances and lipids. The key for oil extraction is the rupturing of the seed to render the cell wall more

porous. [6, 7] Due to cell wall complexity the extent of enzyme degradation is determined by the structural details, such as the chemical constituents, and the type and source of the enzymes. Glycosylases are the most widely used enzymes for this application.[8-10] The choice of glycosylases depends on the overall chemical structure of the target cell wall. The degree of cell wall rupture during processing influences the rate of oil recovery with solvents; maximal extraction requires that every oil cell was broken before the oil extraction. The mass transfer is improved when the diffusion distance is shortest.

Enzymatic oil extraction has not been previously evaluated as a pre-treatment before a press oil extraction or solvent extraction. In this work, enzymes are used with excess water to generate a free oil phase. Published reports indicate that enzymes can promote the release of 16-88 % of the oil in soybean seeds, and 32-87 % of the oil in corn germ. [9-11, 13-15]

The objective of this study was to compare the various extraction methods used to free oil from soybean seeds. The extraction methods include: the press-oil extraction, solvent-oil extraction (n-hexane), and enzymatic-oil extraction. The effects of selected experimental parameters were evaluated as follows: 1) press-oil extraction using high pressure and varying soybean particle size, 2) solvent-oil extraction at three particle sizes, and 3) enzymatic-oil extraction using four enzyme concentrations and three temperatures as experimental parameters. Initially, ten enzymes were quantitative compared for the amounts of oil released to the aqueous phase. In addition, the same enzymes were used with a different substrate, corn germ, to observe the effect on oil released with different cell wall composition.

8.3. Experimental Set-up

8.3.1. Materials and Equipment

Hexane (HPLC grade) was purchased from Fisher Scientific Co. Soxhlet extractor equipment (glassware with reflux Figure 51), Denver Instrument weight balance model XP 300, and a hotplate were used in the solvent extraction procedure. A SPEX CertiPrep* Automated X-Press* 35 Ton Laboratory Press, and Denver Instrument weight balance model XP 300 were used for the press extraction experiment.

Sodium hydroxide pellets, sodium acetate trihydrate, sodium phosphate (monobasic), sodium phosphate (dibasic), and phosphoric acid were purchase from Sigma Aldrich, St. Louis, MO. Enzymes: Acid Protease (*A. niger*), Cellulase DS (*A. niger*), Protease M (*A. oryzae*), Protease NL (*B. subtilis*), Protease N (*B. subtilis*), and Protease S (*B. stearothermophilus*) were supplied by Amano Enzyme Co., Elgin IL. Enzymes: Cellulase GC 220 (*T. reesei*), Cellulase Multifect GC (*T. reesei*), Protease GC 106 (*A. niger*), and Multifect Xylanase (*T. reesei*) were supplied by Genencor Inc., Rochester NY. The enzymes evaluated are listed in Table 38. A Psycotherm controlled environmental incubator shaker and a Thermo IEC Centra CL3R centrifuge were used in the enzymatic extraction procedure.

Table 38. Enzyme properties used in the oil extraction

Enzyme Source	Commercial Name	Optimal pH	Enzyme Activity
A. niger	Acid Protease II	3	15 k units/g
A. niger	Cellulase DS	4	100 k units/g
A. oryzae	Protease M	3	5.5 k units/g
B. subtilis	Protease NL	7	20 k units/mL
B. stearothermophilus	Protease S	7	10 k units/g
B. subtilis	Protease N	7	150 k units/g
T. reesei	Cellulase GC 220	4	6.82 k IU/mL
T. reesei	Cellulase Multifect GC	4	98.4 GCU/mL
A. niger	Protease GC 106	4	1.18 k SAPU/mL
T. reesei	Multifect Xylanase	4	8 k GXU/mL

NOTE: k represents 1000.

8.3.2. Solvent Extraction Procedure

Using the Soxhlet procedure, oil and fat from solid material were extracted by repeated washing with an organic solvent, usually hexane or petroleum ether, under reflux in special glassware (Figure 51). In this method, the sample is dried and ground into small particles. Ten grams of this soybean flour was placed in a porous cellulose thimble. The thimble was placed in an extraction chamber, suspended above a flask containing the organic solvent-hexane and below the condenser.

The flask was heated and the solvent evaporates moving to the condenser where it is converted into a liquid that trickles into the extraction chamber containing the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask. This extraction cycle is then repeated as long as heat is applied. At the end of the extraction

process, which lasts a few hours, the flask containing the solvent and lipid is removed. The solvent in the flask is then evaporated and the mass of the extracted lipid is measured. The percentage of lipid in the initial sample can then be calculated.

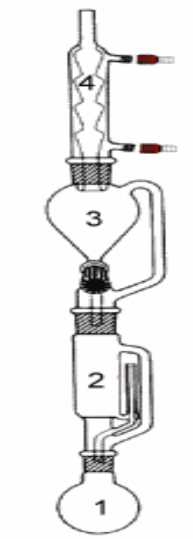

Figure 51. Soxhlet extractor glassware

8.3.3. Mechanical Press Extraction Procedure

Seven grams of dry soybean flour were pressed in the mechanical press with 44 MPa for one hour. The difference in sample weight (initial and final) represents the amount of oil extracted. Four different particle sizes were used: 1.8 mm, 1.2 mm, 0.75 mm, and 0.25 mm.

Solvent (n-hexane) was used to clean the oil remaining in the die. The sample was it 44 MPa and then increased by 66 MPa to get thet total of 110 MPa. The sample was weighed to calculate the oil extracted in the second press. The two values were added to determine the final amount of oil was extracted.

8.3.4. Enzymatic Extraction Procedure

Soybean seeds were ground to obtain about 200 μm (80 to 85 mesh) particle size. Samples of soybean flour of six grams were placed into 150 mL glass flasks. To each sample, depending on the enzyme type, 40 mL of appropriate buffer was added, 0.05 M sodium acetate pH 4.0, 0.01 M sodium phosphate pH 3.0, or 0.1 M sodium phosphate pH 7.0. Enzyme was dissolved in distilled water to the desired concentration. Enzyme concentrations of 1, 3, 4, and 6 % (w/w based on the enzyme weight or density) were used in the experiments.

Flasks were incubated at 45, 55, and 70°C and stirred at 2000 rpm in the incubator shaker for 20 hours. After incubation, the flasks were allowed to cool for 60 minutes. To adjust the pH of the enzyme solution, 0.5 mL phenolphthalein indicator (5 % by volume in ethanol solution) was added to the samples which were titrated with 0.2 M sodium hydroxide to get a pH of 10. The samples were centrifuged at 4000 rpm for 20 minutes, and the top layer (aqueous phase) was removed. Ten milliliters of n-hexane was added to the aqueous phase to coalesce the dispersed oil, and the samples were centrifuged at 1500 rpm for approximately 50 minutes. The n-hexane-oil phase (top layer) was removed and evaporated to determine the mass of oil extracted.

8.4. Results and disscusion

8.4.1. Solvent Extraction

The particle size of soybean flour is an important parameter in the extraction of oil. In the solvent extraction method, about 18 % of mass of the soybean seed is extracted as oil, this is about 90% of the oil in soybean. The amount of oil extracted with hexane

increased from 13.93 to 17.63% by decreasing the particle size of the soybean flour from 1.8 to 0.5 mm, as shown in Table 39.

Table 39. Oil extracted from soybean flour at different particle sizes using n-hexane solvent for 6 hours

Soybean Flour Samples (particle sizes mm)	Oil Extracted Weight (g)	Oil Extracted (% w/w dw)	Oil Extracted (g)	Std. Dev.
1.8	0.97	13.86	13.93	0.16
1.8	0.98	14.00		
1.8	0.96	13.71		
1.8	0.99	14.14		
1.0	1.71	17.07	16.86	0.22
1.0	1.69	16.90		
1.0	1.70	16.97		
1.0	1.65	16.50		
0.5	1.75	17.43	17.63	0.22
0.5	1.75	17.40		
0.5	1.78	17.80		
0.5	1.79	17.90		

8.4.2. Mechanical Press Extraction

Pressure oil extraction exhibits parametric trends similar to solvent extraction. Table 40 shows the effect on oil released with the particle size at the same applied pressure. The particles sizes were: half seed (1.8 mm), medium (1.2 mm), small (0.75 mm), and micro particles (0.25 mm). At small particle sizes highest amounts of oil were released in the pressure extraction method.

Table 40. Oil extraction quantities from soybean flour at different particle sizes using 44 MPa of pressure at ambient temperature for one hour

Soybean Flour Samples (particle sizes)	Oil Extracted Average (% w/w dry basis)	Std. Deviation
1.8 mm (half seed)	12.45	1.06
1.2 mm (medium)	13.76	0.51
0.75 mm (small)	14.49	0.15
0.25 mm (micro)	15.70	0.15

The pressure applied to the sample has a large effect on the amount of oil extracted. Figure 52 shows the percent oil extracted at two different pressures applied to the 0.25 mm particle size. The press oil extraction is an efficient technique to replace the conventional solvent method. The yield difference in oil extraction between the two methods, solvent and press extraction is about 2% of oil removed.

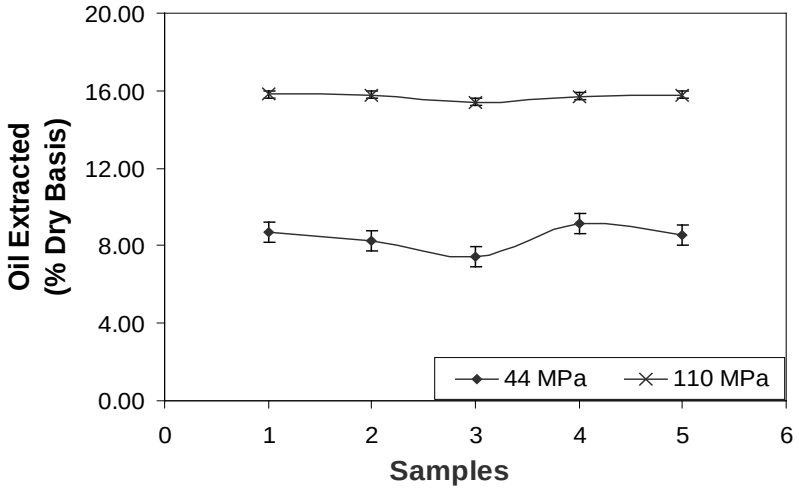

Figure 52. Oil extraction quantities from 0.30 mm particle size of soybean flour, at two different pressure applied, 44 and 110 MPa, at ambient temperature for one hour

8.4.3. Enzymatic Extraction

Table 41, Table 42 and Table 43 summarize the oil released by enzymatic extraction at different temperatures, enzyme concentration and substrate for soybeans and corn germ. Table 41 presents the oil extracted at three temperatures (45, 55, and 70°C) using six different enzymes. Other enzymes that were tested and showed essentially no enhancements of released oil were: Multifect Xylananse, Cellulase Multifect GC, Protease GC 106, and Cellulase GC 220.

At the lowest enzyme concentrations, 1.0% (w/w), enzyme activity is low for degraded soybean cell walls. This trend is consistent with most of the observations of other enzymes, as shown in Table 41.

The results show that the enzymes Protease NL (*B. subtilis*) and Protease N (*B. subtilis*) facilitate the release of about 50% of the total oil in the soybean seed, results shown in Table 42 and Table 43. These enzymes promote hydrolysis at 45 and 55°C at a concentration of 4.0 % (w/w), as shown in Figure 53.

Table 41. Oil extraction amounts for six different enzymes at different concentrations and temperatures for 20 hours

Oil Extracted (% dw)				
Enzymes by Commercial Name		Incubation Temperature (°C)		
	Enzyme Concentration (% w/w)	45	55	70
Acid Protease II	1.0	0.29	0.29	0.25
	3.0	0.67	0.50	0.17
	4.0	0.67	0.50	0.33
	6.0	1.17	0.67	0.67
Cellulase DS	1.0	0.14	0.29	0.00
	3.0	0.17	0.33	0.33
	4.0	0.33	0.33	0.33
	6.0	0.33	0.33	0.33
Protease M	1.0	0.29	0.43	0.25
	3.0	3.83	2.00	1.17
	4.0	2.33	2.83	2.00
	6.0	6.17	2.50	2.50
Protease NL	1.0	0.43	0.43	0.38
	3.0	5.00	8.50	4.00
	4.0	8.67	9.67	6.00
	6.0	9.50	7.67	7.33
Protease S	1.0	0.29	0.29	0.25
	3.0	0.67	0.50	0.67
	4.0	0.83	0.50	1.00
	6.0	0.33	0.33	0.33
Protease N	1.0	0.71	0.71	0.50
	3.0	5.33	7.83	4.33
	4.0	9.17	9.50	6.83
	6.0	9.17	5.50	6.00

The most effective enzymes were Protease NL, and Protease N. Cellulase GC 220 and Multifect Xylanase were the least effective. Table 42 summarizes the hexane extraction of residual seed oil after enzyme treatment. This is an analytical approach to

evaluate the accuracy of the data in Table 42 and is not a suggested as a production process. The total oil recovered from enzyme extraction plus the oil recovered by subsequent hexane extraction ranged from 17.38 to 18.13%. While the variation in these values is greater than the sum of any two standard deviations, the data are consistent and indicate that there was minimal unaccounted oil in the experimental procedure.

Table 42. Oil extracted from soybean flour using Protease NL and Protease N (B. subtilis) 0.25 mm particle size, at 45° C for 20 hours with each enzyme

Commercial Enzyme	Enzyme concentration (% w/w)	Oil Extracted (Enzyme) (% dw)	Residual Oil Extracted (n-hexane) (% dw)	Total Oil Extracted (% dw)	Std. Dev.
Protease NL	3.0	10.88	6.58	17.46	0.23
Protease NL	4.0	11.63	6.29	17.92	0.09
Protease N	3.0	10.50	6.88	17.38	0.16
Protease N	4.0	11.08	7.04	18.13	0.06

Table 43 show the impact on oil released from corn germ using different enzymes. Multifect Xylananse, Cellulase Multifect GC, Protease GC 106, and Cellulase GC 220, were not effective with soybean seeds, but promoted oil release in corn germ. Cellulase DS and Protease S had a minor impact on oil released with soybean seeds, but inverse behavior with corn germs. Acid protease enzyme was ineffective with both soybean flour and corn germ.

In the corn wet milling industry, Cellulase GC 220 enzyme can be used to improve separation of starch, gluten and fiber fractions and to make the filtration of individual product streams easier. In the wheat starch industry, GC 220 enzyme can be used to improve the separation of starch and gluten of poor and medium quality wheat

crops; in the fuel alcohol industry, it is used when milled grain is used as raw material to hydrolyze non-starch carbohydrates. GC 220 is especially effective on cellulose, hemicellose and β-glucan substrates. Multifect GC cellulose is designed for treatment of fibrous material consisting of non-starch polysaccharides (especially glucans).

Table 43. Enzymatic oil extractions from corn germ using 3.0 % (w/w) of enzyme concentration at 45°C for 20 hours

Enzyme Commercial Name	Enzyme Concentration (% w/w)	Oil Extracted (% dry basis)	Average Oil Extracted (% dry basis)	Std. Deviation
Multifect GC	3.0	39.2	37.9	0.88
Multifect Xylanase	3.0	13.3	12.9	0.29
GC 220	3.0	19.5	18.8	0.53
GC 106	3.0	15.8	15.3	0.35
Protease N	3.0	20.0	13.8	4.42
Protease NL	3.0	15.5	15.6	0.06
Protease S	3.0	13.2	10.9	1.59
Protease M	3.0	11.2	10.9	0.18
Acid Protease	3.0	5.0	3.9	0.77
Cellulase DS	3.0	30.7	29.8	0.65

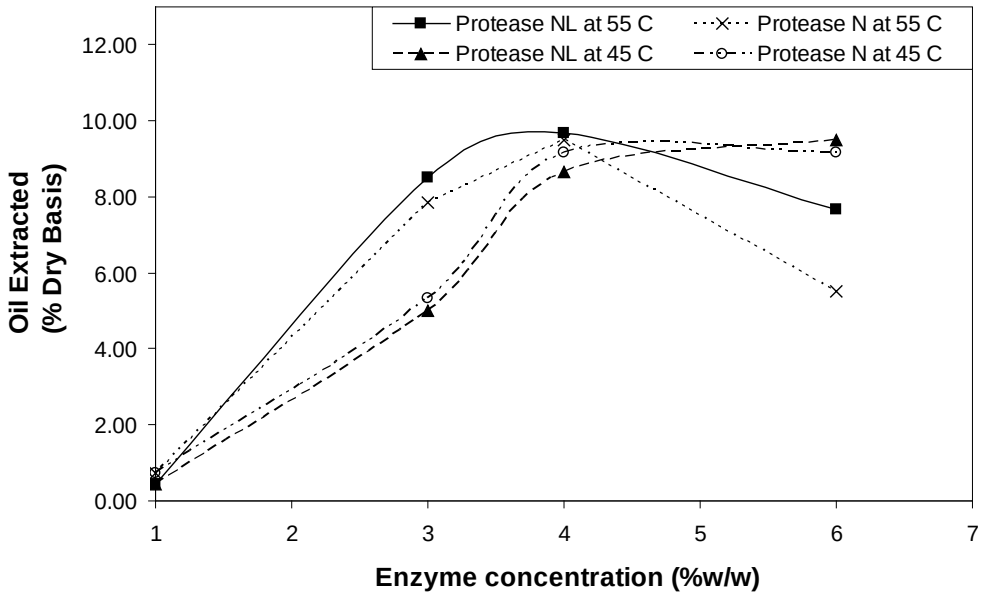

Figure 53. Effect on the oil amount extracted at different enzyme concentration of Protease NL and Protease N (*B. subtilis*) at 45 and 55°C for 20 hours

At enzyme concentrations between 3.0 to 4.0% (w/w), produced the best extraction at 55°C. When the enzyme concentration was increased, the amount of oil extracted decreased, as shown in Figure 53.

8.5.Conclusion

Mechanical press, hexane extraction, and enzyme-enhanced aqueous extraction were evaluated as a means to remove oil from soybean flour and corn germ. Hexane solvent recovered the most oil as expected based on its commercial prevalence. However, hexane creates health and safety issues that could be avoided with pressing, enzymatic, or combined enzymatic-pressing methods.

Repeated oil pressing can approach the recovery of hexane extraction to 15.7% versus 17.6%. For both pressing and hexane extraction, the particle size of the flour in the range from 1.8 to 0.25 mm had significant impact on oil recovery.

In this study, enzymes were able to release 9.2% of the oil compared to hexane extraction which recovered 17.6%. Xylananse, Cellulase Multifect GC, Protease GC 106, Cellulase GC 220, Cellulase DS, and Protease S were ineffective with soybean flour, but were effective with corn germ. Different and more-robust cellulose structures in soybeans require a more-targeted attack than is required for corn germ.

8.6. Acknowlegdments

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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

Triacylglycerols are excellent renewable raw materials for a range of products including polymers. Vegetable oil-based polymers are gaining popularity due to attractive properties related to the specific structure of oils, as well as concerns about the environment and sustainability. Determining factors for the applicability of oils are their composition and price.

Soybean oil is the most attractive raw material in North and South America since it combines stable low price with a relatively high degree of unsaturation. The US produces about 60% of the world's soybean oil. Soybean oil has a heterogeneous triglyceride structure (variety on carbon-carbon double bonds) and this should be considered when designing polymers for different applications. The polyol research group is focus on doing a range of vegetable-based polyols to use on polyurethane foam (flexible and rigid) syntheses.

Soybean oil has been polymerized at high temperatures (about 330ºC) with or without catalyst to create a higher molecular weight feedstock for synthesizing polyols. Bodying reactions increase the average molecular weight of SBO from 948 to 1000-2400 for bodied products. In the polymerization studies, the two reactor configurations follows the same conversion trends as a function of temperature and residence time as was expected.

Relative to the non-catalyzed reaction, the use of (9, 10)-anthraquinone as a catalyst led to decreased reaction times for the same increase in viscosity, led to lower

iodine values, and to a decrease in acidity for a given decrease in iodine number (or increase in viscosity).

Bodying reaction increased the average molecular weight of PESBO from its starting value of 960 to 2500-7050 for the bodied products. Low reactivity was identified as a problem with the bodied PESBO and was attributed to the prominence of secondary alcohols with stearic hindrance. Alcohol addition to the oxirane was evaluated to improved hydroxyl functional groups content. Higher temperatures were used in the alcohol addition reaction led to increased amount of mono FFA esters formed in the final products.

Ring opening of epoxy groups can be achieved with alcohols or water in the presence of acid catalysts, with organic acids, inorganic acids, and by hydrogenation. The studies in chapter 4 identified 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 one soy-polyol to use in the water-blown rigid polyurethane foam formulation study. *p*-Toluenesulfonic acid monohydrate (pTSA) shows a high catalytic reactivity that promotes the ring-opening reaction.

Better control of oxidation is achieved by epoxidation where epoxy groups are inserted exactly at the position of double bonds. One pot reaction studies were proposed for epoxidation reaction followed by alcoholysis reaction of soybean oil to produce a high hydroxyl equivalent weight polyols. This process alternative compares favorably to conventional processing which is conducted at 40°C adding an organic solvent with an ion exchange resin catalyst; higher epoxide productivity was attained.

An epoxy-ring opening hydrolysis of the PESBO and ESBO was performed using a p-toluenesulfonic acid monohydrate and ethylene glycol as a co-reagent in the reaction. Ample degrees of freedom were observed in the alcohol addition to control the hydroxyl functionality and the viscosity (MW) in the final polyol. These soy-based polyols are potential monomers for rigid and flexible polyurethane foam syntheses.

All ring-opened above had few or no double bonds and are very stable and resistant to oxidation. The price for this is higher viscosity compared to petrochemical polyols is due to higher rigidity of the hydrocarbon chains compared to polyether chains. While soybean oil has viscosity of about 60 cP, epoxidized soybean oil viscosity is around 220 cP and that of the corresponding polyol between 5,000 and 10,000 cP, depending on the number of OH groups and the degree of oligomerization.

Vegetable oil polyols must satisfy some structural requirements in order to compete with petrochemical polyols, such as the right functionality, molecular weight, and OH number. Several soy-based poyols from ring-opened reactions (Chapters 4 to 6) were used between 50 to up 100% as petroleum-based polyol replacement in the rigid water-blown polyurethane foam synthesis. A few soy-polyols from oligomerization reaction (Chapters 2, 3, 5 and 6) were used up to 50% replacement in the flexible water-blown polyurethane foam synthesis. Soy-polyol from ESBO ring-opened reaction (Chapter 4) was used to replace up to 100% of Voranol 490 in the rigid water-blown polyurethane foam synthesis, producing a completely closed cell structure.

Future investigations are recommended on the performance of rigid foam formulation from soy-based polyols toward the goal of obtaining similar properties to control foams of petroleum-based polyols. The soy-based polyols of this dissertation

would accurately be described as first generation materials based on new approach to production, and as such, there is ample opportunity to optimize the synthesis and targeted properties to match specific applications. New approach should be evaluated for the partial or complete substitution of MDI or TDI (isocyanate) in the polyurethane foam formulation, such as the addition of aromatic amines in the soybean oil molecule.

VITA

Zuleica Lozada-Rodríguez was born on April 6, 1981 in Rio Piedras, Puerto Rico. She attended public elementary, junior-high and high school in Canóvanas, Puerto Rico. She was a member of the honor students group from 5th to 12th grade. She obtained her Bachelor Degree on Science of Chemical Engineering (Second Honor Award) in the Polytechnic University of Puerto Rico, Hato Rey, Puerto Rico. Since January 2005, she initiated her graduate studies in Chemical Engineering at University of Missouri, Columbia, MO under the supervision of Dr. Galen J. Suppes. She received her Doctor of Philosophy degree in August 2009.

APPENDIX

Appendix A. Estimate of hydroxyl number

The hydroxyl number can be estimated by the amounts of the reagents used in the polyol formulation for the reaction. The soybean oil has only the amounts of oxygen in the carboxylic carbons in the trygliceride. Therefore for several reactions involving alcohol additions it is possible to estimate the amounts of hydroxyl groups or the hydroxyl number for the final product. Also, the hydroxyl number can be pronosticate for epoxidized vegetable oil through the experimental results on the oxirane content (%) in the sample, such full epoxidized soybean oil. The following equations are used for these calculations:

1. Weight of Epoxy = % Oxirane/1.6
2. Equivalent Weight Epoxy =(43*100)/ Weight of Epoxy
3. Hydroxyl number by Epoxy group = (56*1000)/Eq. Wt. Epoxy
4. Hydroxyl number total by Oxygen = OH by epoxy group * % Oxirane
5. Equivalent Weight for polyol = Molecular Weight/functionality

Appendix B. Calculations for Alcoholysis Reaction

ESBO properties:

Molecular weight: 1000 g/mole

Acid number: 0.5 mg-KOH/g

Functionality: 7-7.2

Hydroxyl number (ASTM D4274-05): 403.8 mg-KOH/g

Oxirane Oxygen (%): 7.0 %-wt.

Hydroxyl number (AOCS Tx 1a 66-1997): 8 -10 mg-KOH/g

Ethylene Glycol properties

Molecular weight: 62.07 g/mole

Functionality: 2

Acid number: 1.5 mg-KOH/g

Hydroxyl number (ASTM D4274-05): 1810 mg-KOH/g

Methanol properties

Molecular weight: 32.04 g/mole

Acid number: 2 mg-KOH/g

Functionality: 1

Hydroxyl number (ASTM D4274-05): 1750 mg-KOH/g

Stoichiometries for reagents in the alcoholysis reaction

1. Moles ESBO = mass ESBO/molecular weight ESBO
2. Mass of EG = moles of ESBO*(moles of EG/moles of ESBO)*Molecular weight EG

3. Mass of ME= moles ESBO*(moles of ME/moles of ESBO)* Molecular weight of ME
4. Mass of catalyst (pTSA) = 0.005*mass ESBO
5. Total mass = mass of ESBO + mass of EG + mass of ME

<u>Predictions of final hydroxyl number based on mass fraction</u>

6. Hydroxyl numer of polyol =(mass fraction of ESBO *10) + (mass fraction of EG*1810) + (mass fraction of ME*1750)
7. Mass fraction = mass of reagent/ total mass

<u>Example for calculations:</u>

Stoichiometry (ESBO:EG:ME molar ratios): 4:4:3

Moles ESBO = 200 g/1000 g/mole = 0.2 mole

Mass of EG =0.2 moles ESBO*(4moles of EG/4moles of ESBO)*62.07 g/mole EG = 12.41 g of EG

Mass of ME = 0.2 moles ESBO*(3 moles of ME/ 4 moles of ESBO)*32.04 g/mole of ME = 6.73 g of ME

Mass of catalyst (pTSA) = 0.005*200 g= 1.0 g of pTSA

Total mass = 200 g+ 12.41 g + 6.73 g= 219.4 grams

<u>Predictions of final hydroxyl number based on mass fraction</u>

Hydroxyl numer of polyol =(0.92 *10) + (0.06*1810) + (0.03*1750)= 170.3 mg-KOH/g

Appendix C. Calculations for Single reactor

SBO properties:

Molecular weight: 873-930 g/mole

Functionality: 4.4-4.6 (based on carbon-carbon double bond)

Formic acid properties:

Molecular weight: 46.02 g/mole

Hydrogen peroxide properties:

Molecular weight: 34.02 g/mole

Stoichiometry for reagents in the epoxidation reaction

1. Moles of SBO:DB = (Mass of SBO *4.6)/Molecular weight SBO
2. Mass of Formic Acid (FA)= (moles SBO:DB*moles of FA*Molecular weight of FA)/(moles of SBO:DB * concentration by mass of FA)
3. Mass of hydrogen peroxide (H2O2)= (moles of SBO:DB* moles of H2O2* Molecular weight of H2O2)/(moles of SBO:DB * concentration by mass of H2O2

Appendix D. Pictures of equipments

Few pictures of laboratory equipment used for the soy-based polyol production.

Batch reactor system

Batch reactor systems (glassware)

Appendix E. Pictures of samples

A few pictures of polyol and polyurethane foam samples did on the Biomaterials & Bioprocessing Laboratory

General picture for the application process: soybean oil, polyol, elastomer and flexible foam.

Water-blown flexible polyurethane foam samples using 100% of soybased polyol in the formulation.

Water-blown flexible polyurethane foam samples using 100% soy-based polyol in the formulation.