SYNTHESIS AND TESTING OF SOY-BASED POLYOLS: PHOSPHATE AND GLYCEROLYSIS OLIGOMERS

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

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Presented by Arnold A. Lubguban

a candidate for the degree of Doctor of Philosophy

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ABSTRACT

Soy-based polyols are important industrial prepolymeric materials that use renewable resources. They react with isocyanates to produce polyurethanes (PU) and can be produced at costs less than polyols derived from petrochemicals. This project proposes new soy-based polyols with high hydroxy equivalent weights that produce significant reactivity with isocyanate in flexible and rigid polyurethane foams and bioelastomers. Biocatalytic, transesterification and polymerization processes were evaluated to increase equivalent weights and hydroxyl functionality of soy-based polyols used in polyurethane formulations.

Oligomeric soy-based polyols were synthesized using the following chemistries: 1) acidolysis of epoxidized soybean oil with phosphoric acid, 2) glycerol transesterification of bodied soybean oil, 3) ethylene glycol alcoholysis of epoxidized soybean oil, and 4) enzymatic functionalization.

Acidolysis reaction was carried out by mixing epoxidized soybean oil with up to 1.5% *o*-phosphoric acid. *In situ* oligomerization took effect almost instantly producing a clear, homogeneous, highly viscous, and a low-acid soy-phosphate polyol product with a high average functionality. The resulting soy phosphate-based bioelastomer showed an 80% decrease in extractable content and increased tensile strength at the same isocyanate loading relative to the non-catalyzed epoxide. The oligomerized epoxidized soybean oil materials exhibited ASTM hydroxyl values 40% less than the non-oligomerized starting material which translates to reduced isocyanate loadings in urethane applications.

Acylglycerol-based polyols were synthesized by thermally polymerizing (bodying) soybean oil followed by transesterification with glycerol. Transesterification with glycerol at temperatures greater than 200°C provided the desired polyol pre-polymers. Rigid foaming results of the processed soy-based polyol showed excellent physicochemical properties comparable with petroleum-based polyether polyols.

Catalyst-free polymerization and alcoholysis of epoxidized soybean oil with ethylene glycol was carried out in a closed batch reaction at 250°C. This temperature provided an adequate rate for cleavage of the oxirane rings and hydroxyl group attachment while not being so high as to cause product degradation. Results have shown excellent thermoinsulating and mechanical properties of the foams compared to epoxidized soybean oil alone or the petroleum-based polyether polyol alone. A reduction of up to 8% of the polymeric diphenylmethane diisocyanate was achieved using the synthesized epoxidized soybean.

Heat-polymerized soybean oil was functionalized by hydrolysis with free and immobilized *C. rugosa* lipase at a lower reaction temperature of 45°C

attaining up to 100% hydrolysis. The resulting hydrolyzed polyol products have high average hydroxyl functionality owing to the bodied soybean oil's high initial molecular weight and the attachment of primary alcohol moieties from enzymatic hydrolysis. The hydrolyzed polyol products were used to produce flexible foams that have properties comparable to most of the properties of the control aliphatic triglyceride-type polyol but less comparable with the control petroleum-based linear polyol.

Soy-based polyol products described in this study have physicochemical properties comparable to both commercial triglyceride-based and petroleum-based polyols. The reactions were performed at lower temperatures- 45℃ for enzymatic hydrolysis and room temperature (25˚C) for phosphate-ester formation. Also, glycerol transesterification and ethylene glycol reactions were one-pot processes and solvent-free processes. In general, results have shown that oligomeric soy-based polyols can be synthesized with moderate hydroxyl numbers that produce good reactivity with isocyanate and produce polyurethane products comparable to those made from petroleum-based polyols.

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

A polyol is a compound containing multiple hydroxyl functional groups available for organic reactions. In polyurethane chemistry, it is a major B-side monomer with active hydrogens that readily reacts with the N=C=O group of the isocyanate [1]. Polyols are mostly derived from petrochemical sources but in recent years emphasis on renewable content has reactivated interest on natural oil-based polyols to minimize dependency on petroleum sources [2].

Polyurethane foams and elastomers made from soy-based polyols have shown comparable properties with petroleum-based formulations [3-5]. Despite the soy-based polyols' valuable contribution to green chemistry there are several challenges of using soybean oil as base material for polyol production. The performances of most commercially available, soy-based polyols are limited by their low molecular weights, low alcohol reactivity due to the major presence of secondary alcohols, and large non-functional branches [6-9].

The main objective of this study was to functionalize soybean oil using enzymatic and chemical reaction routes to produce polyols with improved properties for polyurethane foams and bioelastomers. This objective included verification of synthesis and performance to allow for rapid commercialization of the products.

1.2. POLYURETHANES

Otto Bayer and his coworkers in 1937 were credited for the pioneering work on polyurethane polymers at the laboratories of I.G. Farben in Leverkusen, Germany. The condensation of difunctional hexane diisocyanate and 1,4-butanediol, monomers that were not commercially available produced the polyurethane product which seemed to point to special opportunities and has found special uses compared to already existing plastics [10]. Most urethane polymers are of the thermoset type which means that the A-side and B-side monomers react with each other to form a non-extrudable highly cross-linked network.

The Figure 1 reaction represents the general polyurethane polymer-forming reaction between an isocyanate as the A-side component and an alcohol or polyol as the B-side component as follows:

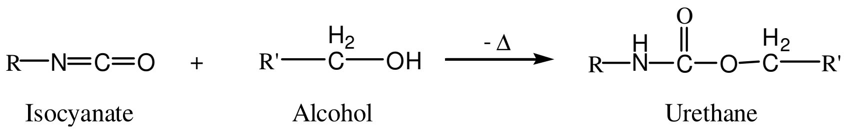


Figure 1. Typical reaction of urethane formation.

The major global consumption of polyurethane products is in the form of foams which come in two types, flexible and rigid, being roughly equal in market size. In 2007, the global consumption of polyurethane raw materials was above 12 million metric tons, the average annual growth rate is about

5%. Polyurethane products are used in many different ways as summarized in Table 1 below [11-12].

Table 1. Polyurethane products consumption (US Data 2004) [13].

Application	Amount of polyurethane used (millions of pounds)	Percentage of total
Building & Construction	1,459	26.8%
Transportation	1,298	23.8%
Furniture & Bedding	1,127	20.7%
Appliances	278	5.1%
Packaging	251	4.6%
Textiles, Fibers & Apparel	181	3.3%
Machinery & Foundry	178	3.3%
Electronics	75	1.4%
Footwear	39	0.7%
Other uses	558	10.2%
Total	5,444	100.0%

1.3. POLYOLS IN POLYURETHANE PRODUCTION

The polyol is a multifunctional source of hydroxyl groups in the synthesis of polyurethane products. For some of the soy-based polyols of this dissertation, other functional groups (e.g. epoxy groups) may be added to monomer to complement the reactivity of the hydroxyl groups. The majority of the commercially available polyols are petroleum-based distributed as polyether-type polyols (90%), polyester-type (9%), and others (1%). Petroleum-based polyols have mainly uniform and linear structures (with methyl group branches) with terminal hydroxyls which are three times more reactive than secondary alcohols [14]. Figure 2 shows the mechanism of a triol synthesis using a trifunctional initiator and an organic oxide [1].

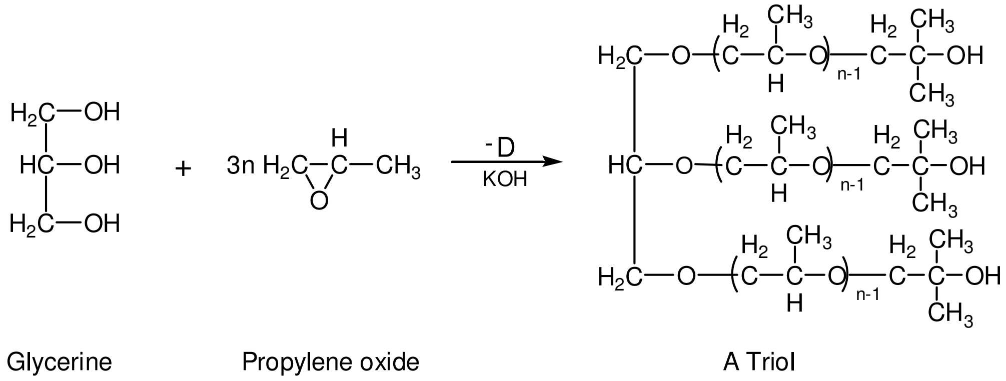


Figure 2. A triol synthesis using trifunctional glycerine initiator and propylene oxide.

Figure 3 shows a typical reaction of an example commercial soy-based polyol that involves soybean oil epoxidation and hydroxyl functionalization [15]. As illustrated, this soy-based polyol retains its triglyceride backbone but with an added hydroxyl functionality for an increased isocyanate reactivity.

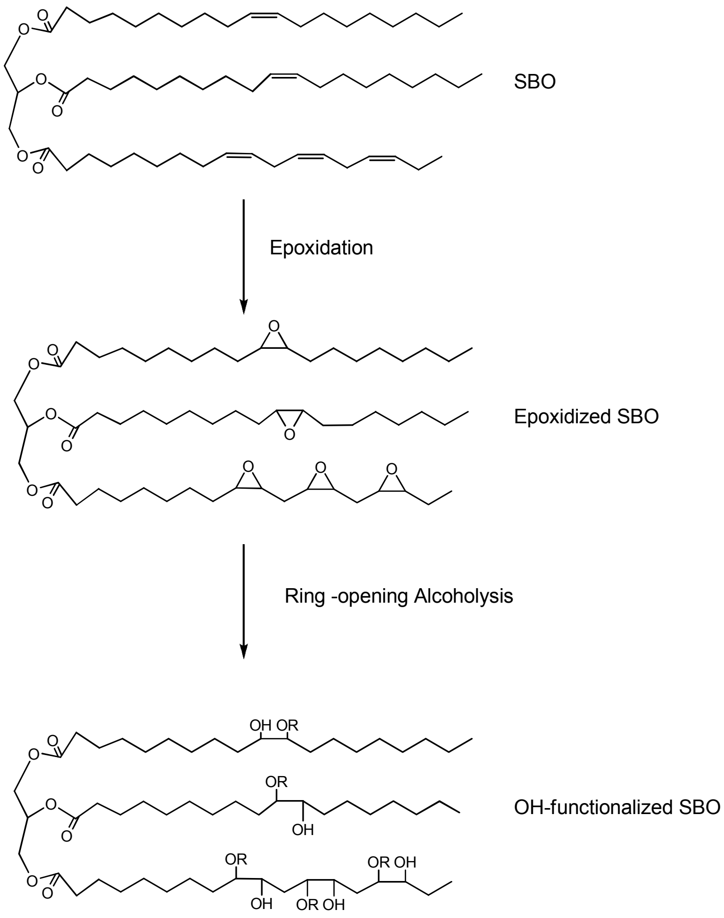


Figure 3. An example reaction route to produce commercial soy-based polyol.

BiOH™ polyols recently released by Cargill, Inc. are soy-based polyols used in flexible foam formulation for cushioning furniture, bedding, carpeting and flooring. They claimed that the manufacturing process involved produces 36% less global warming emissions (carbon dioxide), a 61% reduction in non-renewable energy use (burning fossil fuels), and a 23% reduction in the total energy demand. BiOH™ polyols are used in combination with less petroleum-based ingredients in a foam formulation [16].

BioBased Technologies® released its line of soy-based polyol called Agrol® with commercial and industrial polyurethane applications for flexible (slabstock and molded) and rigid (insulation), coatings, adhesives, sealants and elastomers. This polyol is odorless and residue-free, pH-neutral and with functionality of 2.0-7.0 [17].

Urethane Soy Systems Co. has marketed a series of two- and three-functional polyols with 50-60 and 160-180 mg KOH/g hydroxyl numbers, respectively. These polyols are made from unmodified soybean oil under the trade name Soyol™ and can be used in the production of flexible and rigid foams, coatings, adhesives, sealants and elastomers. Examples of two-functional polyols are Soyol™ R2-052-A to C and E to G; and three-functional includes R3-170-A to C, E to G [18].

1.3.1. Polyol properties

Polyols have different physicochemical properties that have direct effect on their performances in polyurethane formulations. The properties described below are important criteria for characterizing polyols.

Acid number (mg KOH/g) is defined as the amount in milligrams of potassium hydroxide required to neutralize the acid present in one gram of a polyol sample (usually present as acid residuals in the polyol). Typical values of acid number in commercially-available polyols are less than 10 mg KOH/g sample [15].

Hydroxyl Number is a measure of the amount of reactive hydroxyl groups available for reaction. This value is determined in a wet analytical method and is reported as mg KOH/g sample (amount in milligrams of KOH equivalent to the hydroxyl groups found in a gram of a polyol sample). The usual standard method used is ASTM D 4274-88 [1].

Hydroxyl equivalent weight is the amount in grams of sample required so that one equivalent weight (17.008 g) of hydroxyl will be present in the sample. The hydroxyl equivalent weight can be calculated from the hydroxyl number expressed in the following equation:

Hydroxyl equivalent weight = (56.1 x 1000)/Hydroxyl Number [14]

Functionality is defined as the average number of isocyanate reactive sites per molecule. These reactive sites could be a hydroxyl, amine, epoxy or hydroperoxy groups.

1.4. ISOCYANATES IN POLYURETHANE PRODUCTION

The isocyanate is the A-side component in the polyurethane chemistry as shown in Figure 1. It is a compound that provides the source of NCO groups to react with functional groups from the polyol, water, and cross-linkers in the formulation. The method used for the synthesis of isocyanate involves the phosgenation of an amine as shown in Figure 4 as follows:

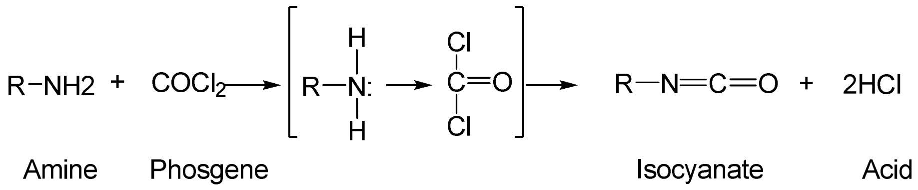


Figure 4. Phosgenation of an amine to produce isocyanate.

Isocyanates available in the industry today contain at least two isocyanate groups per molecule [1]. The Dow Chemical Company offers a broad range of isocyanates which include ISONATE® MDI (methylene diphenyl diisocyanate) and PAPI® polymeric MDI for polyurethane processing and solution applications in coatings, adhesives, sealants and elastomers. By example, PAPI® 27 is a polymeric MDI with a 31.4% weight NCO, 134 isocyanate equivalent weight, >204℃ flash point, and 180 cSt viscosity at 25℃. In polyurethane chemistry, an isocyanate index is the amount of isocyanate used relative to the theoretical equivalent amount [1].

1.5. SOY-BASED POLYOLS AND POLYURETHANES

Leading companies with research programs on soy-based polyols in the US include Cargill, Inc., The Dow Chemical Company, BioBased Technologies®, Arkema, Inc., Cognis Oleochemicals, Urethane Soy Systems Company and other smaller independent companies. Academic research-based soybean polyol and polyurethane development includes the laboratories of Drs. J. Massingill (Texas State University), R. P. Wool (University of Delaware), Z. Petrović (Pittsburg State University), R. Larock (Iowa State University), G. Suppes/F. Hsieh (University of Missouri-Columbia), and G. Wilkes (Virginia Tech. University).

U.S. Patents on soy-based polyols and polyurethane include patent numbers: 6,399,698, 6,686,435, 6,624,244, 6,573,354, 6,548,609, 6,476,244, 6,465,569, 6,433,121, 6,107,433, 5,932,336, 5,674,802, 5,482,980, 4,220,569, 4,025,477, 6,891,053, 4,640,801, 7,045,577, and 6,548,609.

1.6. SOY-BASED POLYOLS FOR POLYURETHANE APPLICATIONS

In this study four types of synthesis routes were investigated to produce polyols for rigid and flexible polyurethane foam production as well as bioelastomers as outlined in Figure 5. An overarching goal was to develop soy-based polyols of molecular weights between 1,000 and 3,000 and functionalities of 2-8 per molecule.

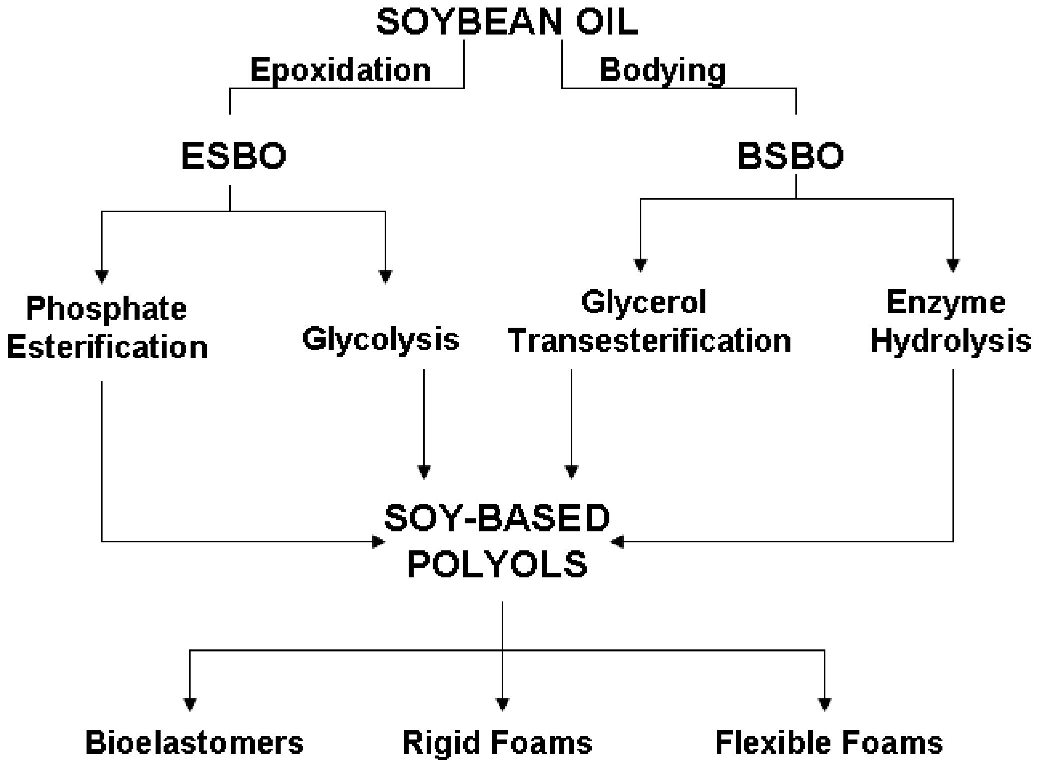


Figure 5. Overview of the soy-based polyol syntheses and polyurethane formulations.

Chapter 2 describes a room-temperature method of epoxy ring polymerization of epoxidized soybean oil by adding phosphoric acid to act not only as a catalyst but as a participant in the reaction. The homogeneous product phosphate ester has high viscosity and low acidity. The sample polyols were evaluated for bioelastomers formation and compared with the non-catalyzed sample.

Chapter 3 describes reacting glycerol and bodied soybean oil at high temperature. The mechanism involved glycerol transesterification with the bodied soybean structure, increasing the latter's hydroxyl functionality while retaining its high molecular weight. The polyols were evaluated in rigid polyurethane foam formulations with key foam properties being tested.

Chapter 4 explains an approach to incorporate modified epoxidized soy-based vegetable oil polyol to partially-replace petroleum-based polyether polyol and reduce the isocyanate loading in the rigid foam formulation. Epoxidized soybean oil was reacted with ethylene glycol to cleave the epoxy rings and incorporate the alcohol in the triglyceride structure increasing its molecular weight. The polyol products were evaluated and tested in rigid foam formulations.

In Chapter 5, enzymatic hydrolysis of bodied soybean oil with *C. rugosa* lipase was achieved at a lower temperature with less organic solvents added. The hydrolyzed bodied soybean oil has high molecular weight and hydroxyl functionality due to attachment of hydroxyls and selective cleaving of saturated fatty acid esters. The product polyol was used as the B-side in flexible polyurethane foam production and the foam properties were evaluated.

The chemical and enzymatic methods used in this study are simple, mostly one-pot, energy-conserving processes to produce better-performing polyols evaluated for polyurethane rigid and flexible foams and bioelastomer production. Chapter 6 will discuss the products produced from these processes and includes recommendations for future work.

1.7. REFERENCES

1. R. Herrington, K. Hock, Flexible Foams. The Dow Chemical Company, Midland, MI, 1997.
2. U. Biermann, W. Friedt, S. Lang, W. Luhs, G. Machmuller, J. O. Metzger, M. R. Klaas, H. J. Schafer, M. P. Schneider, Angewandte Chemie International Edition, 39, 2206 (2000).
3. Y.-C. Tu, G. J. Suppes, F.H.-Hsieh, Journal of Applied Polymer Science, 105, 453 (2007).
4. Y.-C. Tu, G. J. Suppes, F.H.-Hsieh, Journal of Applied Polymer Science, 109, 537 (2008).
5. S. Narine, X. Kong, L. Bouzidi, P. Sporns, Journal of the American Oil Chemists' Society, 84, 55 (2007).
6. P.- p. Kiatsimkul, G. J. Suppes, W. R. Sutterlin, Industrial Crops and Products, 25, 202 (2007).
7. P.- p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Z. Lozada, Y.- C. Tu, Industrial Crops and Products, *27*, 257 (2008).

8. T. W. Pechar, G. L. Wilkes, B. Zhou, N. Luo, Journal of Applied Polymer Science, 106, 2350 (2007).
9. A. Guo, W. Zhang, Z. S. Petrovic, Journal of Materials Science, 41, 4914 (2006).
10. R. B. Seymour, Journal of Chemical Education, 69, 909 (1992).
11. http://www.pfa.org/intouch/index.html.
12. G. Avar, Kunststoffe International, 10, 123 (2008).
13. http://en.wikipedia.org/wiki/Polyurethane
14. M. Szycher, Szycher's Handbook of Polyurethanes, CRC Press LLC, Boca Raton, Florida, 1999.
15. P. Kiatsimkul, Use of enzymes to produce soy-based polyols for polyurethane, PhD Thesis, University of Missouri, Columbia, Missouri, 2006.
16. http://www.greendaily.com/2008/03/21/cargills-bioh-polyols-make-comfy-more-earth-friendly/.
17. http://www.biobasedpolyol.com/.
18. http://www.soynewuses.org/ProductsGuide/Ingredients_IndustrialPlastics.aspx.

CHAPTER 2

ISOCYANATE REDUCTION BY EPOXIDE-SUBSTITUTION OF ALCOHOLS FOR POLYURETHANE BIOELASTOMER SYNTHESIS

2.1. INTRODUCTION

Polyurethane elastomers and industrial foams manufacturing rely significantly on fossil fuels and its derivatives as major reactants for the production of polyols. These non-renewable resources are rapidly being exhausted so a growing worldwide research effort is being focused on the understanding and using renewable resources to reduce dependence on petroleum-derived materials and to develop innovative technologies and competitive industrial products. Vegetable oils such as soybean oil (SBO) are increasingly replacing petroleum-derived products owing to its environment-friendly, biodegradable, and noncorrosive properties [1-3].

Although SBO-based polyols have shown promising results in the production of urethane-formulated products ranging from elastomers to flexible foams [2,4,5], replacement of substantial portions of polyol and isocyanate with soybean oil-derived epoxides is economically significant. SBO-derived epoxides which include epoxidized soybean oil (ESBO) and bodied ESBO are intermediates in much of the chemistry to create soy-based polyols [4,6-8], and so, they are less expensive than many soy-based polyols. High reactivity through cleavage of the oxirane ring makes epoxides very versatile both as chemical intermediates and as end-product. Epoxides are able to directly react with water to diols, with carboxylic acids to ester alcohols, and with alcohols to ether alcohols [9]. Moreover, epoxides have been reported to react with and partially displace isocyanate in urethane mixtures [6,10,11], hence, urethane formulations with increased bio-based content can be developed. A multi-functional monomer containing one or more epoxide moiety may thus to some extent displace alcohol and isocyanate in the regular urethane formulation.

Phosphoric acid (o-H_3PO_4) has been extensively used in the preparation of a series of soybean oil phosphate esters for rigid polyurethanes, coatings, surfactants and anti-wear additives [1,3,14-17]. Guo and coworkers [1] reported that soy-polyols having tunable hydroxyl content and phosphate ester functionality are possible by controlling the type and amount of polar solvent and phosphoric acid content added to the reactants. The authors claimed that phosphoric acid does not only catalyze ring-opening reaction of ESBO with water but also chemically combine to become part of the polyol product. Much of the work done to produce soybean oil phosphate ester polyols used water and significant amount of polar solvents to obtain high hydroxyl functionality while keeping the final acid values low [1,3,16,17].

The main objectives of this work were 1) develop catalyst formulations to specifically promote solventless epoxide reaction to obtain the epoxide-substituted polyol (ESP) and effectively replace substantial amounts of the petroleum-based polyol, and 2) develop urethane bioelastomer formulations using ESP to reduce total isocyanate content. Acid, hydroxyl, oxirane values, and viscosity of the ESP were measured to evaluate the effect of *o*-H_3PO_4 on ring-opening hydrolysis and oligomerization of the monomers.

2.2. METHODS

2.2.1. Synthesis of epoxide-substituted polyol (ESP)

Ortho-H_3PO_4 85% aqueous from Fisher Scientific, ESBO (Vikoflex®7170) 7.0% oxirane from Arkema, polymeric MDI (PAPI 27) 31.4wt% NCO from Dow Chemical and castor oil from AlnorOil. Full epoxidized soybean oil was reacted with 0.5-2.0% *o*-H_3PO_4 added drop wise in a beaker under vigorous mechanical stirring at room temperature. A homogeneous and highly viscous product is obtained after mixing for 5 minutes. The schematic of this reaction is shown in Figure 6. The next step was the preparation of a series of ESPs by varying the amount of the acid-catalyzed ESBO in castor oil. This was done by moderately mixing the catalyzed ESBO and castor oil at room temperature until a homogeneous ESP is obtained.

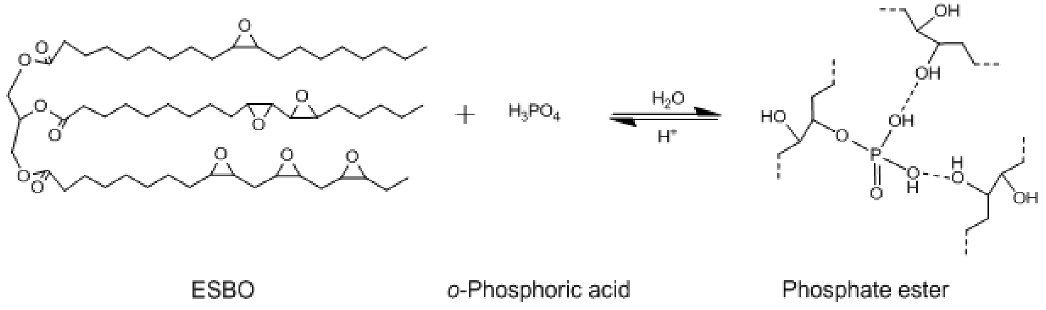


Figure 6. Schematic representation of phosphate ester formation.

2.2.2. Preparation of urethane bioelastomers

Two types of bioelastomers were prepared, ESPs using only 0.5% *o*-H_3PO_4 and acid-catalyzed ESBO using 0.5-2.0% *o*-H_3PO_4 without castor oil. The preparation procedure of ESP bioelastomer consists of the following steps: (1) Mixing 5.0 g ESP and 2.5 g pMDI in a 50-mL beaker on a hotplate equipped with stirrer (Moderate stirring at room temperature was employed to obtain uniform phase and consistency and also avoid bubbles formation); (2) Placing the samples in a 7cm x 11cm rectangular plastic mold and degassed for 10 mins at 45^{o}C vacuum oven to get rid of CO_2, air trapped, or gases evolved during reaction; and 3) Postcuring samples for about 48 h at 45^{o}C in an oven with no vacuum applied. Extractability of unreacted oil phase of the finely-cut samples was measured after 48 h of curing. The second type of bioelastomers was prepared the same way but the amount of *o*-H_3PO_4 was varied (0.5, 1.0, 1.5%) and no alcohol source (castor oil) was added. Polymeric MDI was added at 10%-30% by weight of the acid-reacted ESBO. After postcure, dumbbell-shaped specimens were cut from bioelastomer samples using an ASTM D638 Type V cutter.

2.2.3. Characterization of ESPs and bioelastomers

Hydroxyl values of ESPs were determined according to an American Oil Chemists' Society (AOCS) Official Method Tx 1a-66. Acid numbers (mgKOH/g sample) of all reaction products were evaluated according to the AOCS official method (AOCS Te 1a-64, 1997). Epoxy content of the ESP samples were measured according to AOCS official method (AOCS Cd 9-57, 1997). The dynamic viscosities (centipoise, cP measured at 20^{o}C) of the ESPs were determined using a Model RS100 Rheometer made by Haake–

Thermoelectron (Newington, NH) and Gardner color index was evaluated according to ASTM D1544 (edited D6166, 1998). Tensile properties of the bioelastomers were determined by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) following ASTM Procedure D 882-02. DSC measurements were carried out on a TA Instruments (New Castle, DE, USA) DSC Q100. All the DSC measurements were performed following the ASTM E 1356-03 standard. About 10 mg of the bioelastomer samples were heated at a rate of 10^{o}C/min from -60^{o}C to +100^{o}C under dry nitrogen gas atmosphere.

A Thermo Scientific Nicolet^{TM} 4700 (Thermo Electron Corp., Madison, WI) equipped with Smart Detectors^{TM} and multiple spectral range capability was used to characterize the functional groups of the bioelastomers. The sample was pressed against an ATR diamond to have a good contact. A total of 64 scans from 4000-400cm^{-1} wavenumber range were obtained at a resolution of 4 cm^{-1}. The functionality groups present in the control bioelastomer (non-catalyzed with *o*-H_3PO_4), with peak intensities corresponding to the wavenumbers were: epoxy at 824 cm^{-1} (high intensity), epoxy at 920 cm^{-1} (present), phosphate ester at 1020 cm^{-1} (absent), urethane bonds at 1730 cm^{-1} (present), 2-oxazolidone at 1760 cm^{-1} (absent), NCO groups at 2280 cm^{-1} (present), and urethane bonds at 3340 cm^{-1} (high intensity). In comparison, the functionality groups present in the sample bioelastomer (catalyzed with *o*-H_3PO_4) were: epoxy at 824 cm^{-1} (low intensity), epoxy at 920 cm^{-1} (present), phosphate ester at 1020 cm^{-1} (high intensity), urethane bonds at 1730 cm^{-1} (present), 2-oxazolidone at 1760 cm^{-1} (absent), NCO groups at 2280 cm^{-1} (present), and urethane bonds at 3340 cm^{-1} (low intensity).

The differentiation in structures of both unreacted and acid-reacted ESBO was confirmed by 13C NMR (Bruker DRX 500 MHz, $CDCl_3$). Both samples exhibited spectra of epoxy groups present in the δ 56.9-58.5 ppm region. The unreacted ESBO showed a slightly higher intensity in this region compared with the acid-reacted sample indicating more epoxidic carbons attached to the oxirane oxygen.

2.2.4. Extractability test

A single-step unreacted oil-phase extraction method was used to determine the extent of polymer crosslinking between pMDI and epoxides. Polymeric MDI and the sample epoxide in a specified weight ratio were well mixed in a small disposable aluminum pan. The resulting elastomeric wafer product was left to cure for 24 hours in a convection oven at 140°C in the case of samples evaluated for catalyst performance (Table 2) and 48 hours/45°C in the case of ESP bioelastomers. The cured wafer samples were then cooled to room temperature and cut into thin sheets for unreacted oil extraction. About a gram of each cut sample was soaked with occasional stirring in a 1:4 by volume *n*-hexane-cyclohexanol solution for 15 minutes after which the mixture is filtered. Both permeate and retentate were dried in a vacuum oven at 110°C for 2 hours. The percentage of unreacted oil phase was calculated by mass balance. This test is a straightforward reaction of epoxides and pMDI. This basic polymerization reaction is described elsewhere [18].

2.3. RESULTS AND DISCUSSION

In this work, a urethane bioelastomer formulation is studied following epoxide-substituted polyol (ESP) and polymeric diphenylmethane diisocyanate (pMDI) reaction, including physico-chemical characterization of the elastomer products. Catalysts were evaluated to specifically promote epoxide reaction. *Ortho*-phosphoric acid lowered the oxirane concentration of the epoxide even at room temperature with no solvents added. A simplified scheme of the process is shown in Figure 7.

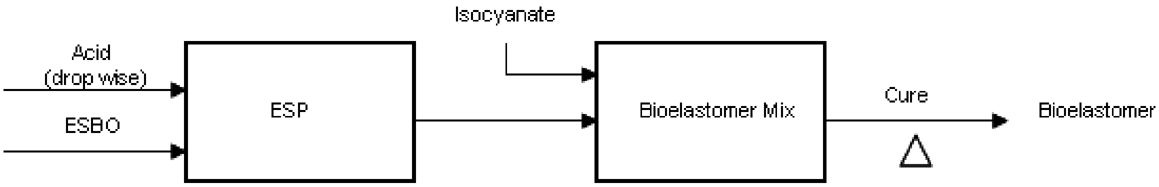


Figure 7. Schematic of bioelastomer synthesis. Oxirane opening reaction is performed at room temperature with constant stirring.

ESP reacted in an open glass vessel with the acid catalyst added drop wise until a homogeneous phase is obtained. Proper mixing was crucial in attaining a uniformly-catalyzed product. After completion of reaction, pMDI was added to ESP and the product degassed, then postcured in a convection oven. Bioelastomer products display different phase behavior ranging from viscous and tacky to hard and brittle. Variations in the elastomer properties are attributed mainly to isocyanate index used and hydroxyl equivalent weight of the ESP [7,12,13].

2.3.1. Extractability for evaluation of catalysts

An extractability analysis method was established in our previous work [19] to evaluate the reactivity of the polyol products with polymeric MDI. The test determined the percentage of the unreacted oil phase in the elastomer. Low extractability is believed to correlate with high crosslinking, whereas high extractability is believed to correlate with the presence of nonfunctional or single-functional components in the B-side (alcohol side) of the urethane formulation.

In this study the extractability method was used to evaluate the effect of different catalysts added in epoxidized soybean oil for promoting reaction with polymeric MDI. A lower extractable content value indicates higher crosslinking and better catalyst performance. Table 2a and 2b show the extractability values of samples using different catalysts. While presented as catalysts, in some instances the materials may participate in reaction.

More than 30 catalysts were evaluated. About half promoted minor increases in reactivity with isocyanate as shown in their extractable content. Phosphoric acid showed the lowest extractable content at 2.85% followed by a metal-based catalyst Tin(II) 2-ethylhexanoate at 10.0%. The former was the catalyst of choice owing to its effect in the reactivity of ESP with isocyanate.

Table 2a. Catalysts evaluation by extractable content method. A sample elastomeric wafer was a mixture of catalyzed ESBO (0.5% catalyst) and pMDI at 2:1 mass ratio then cured at 140℃/24h in a convection oven.

Sample	Catalyst Used	Extracted Oil Phase, %
CONTROL	None	16.0
1	K_2HPO_4	17.2
2	Tin(II) 2-Ethylhexanoate	10.0
3	Triethanolamine	15.1
4	***o*-Phosphoric acid**	**2.85**
5	Glycerol	15.6
6	DABCO 8154	21.1
7	Polycat SA-1	22.6
8	DABCO BL-17	21.6
9	Propylamine	18.9
10	Propionamide	17.9
11	Octadecanamide	19.5
12	N-methyl-N-nitroso-*p*-toluenesulfonamide (Diazald)	14.0
13	N-Bromo-succinimide	15.4
14	N,N-Dimethylformamide	15.9
15	KH_2PO_4	14.4

Table 2b. Catalysts evaluation by extractable content method. A sample elastomeric wafer was a mixture of catalyzed ESBO (0.5% catalyst) and pMDI at 2:1 mass ratio then cured at 140°C/24h in a convection oven.

Sample	**Catalyst Used**	**Extracted Oil Phase, %**
CONTROL	None	16.0
16	Calcium carbonate	15.1
17	*n*-Butanol	15.6
18	Methanol	16.2
19	Methanol + Sulfuric acid	17.0
20	Perfluoric acid-PTF prepolymer	13.8
21	Cobalt acetate	15.2
22	Phthalic acid	13.1
23	Acetic acid	19.8
24.	Formic acid	11.3
25	*p*-Toluenesulfonic acid	11.0
26	Titanocene Dichloride	10.2
27	Phenylenediamine	22.1
28	Potassium hydroxide	41.5
29	Ammonium chloride	16.1
30	Sulfuric acid	15.2

2.3.2. Mixing of epoxide and alcohol

Two mixing sequences were performed to investigate any changes in properties of the final ESP. In the first sequence, ESBO was made to react with *o*-H_3PO_4 separately before castor oil was added. The other sequence was performed by mixing ESBO, castor oil and *o*-H_3PO_4 simultaneously. All reactions were performed at room temperature. The chemical properties of the final ESPs are summarized in Table 3.

Based on Table 3 results, there were no significant changes in the chemical properties of the final ESPs using different mixing sequences; therefore, the alcohol did not significantly interfere in the phosphate-epoxy ring reaction. Under the conditions of the reaction, the *o*-H_3PO_4 is believed to react directly with the oxirane group as shown in Figure 6 causing an increase in viscosity and decrease in the oxirane oxygen concentration. Slight increases in hydroxyl values are attributed to increasing *o*-H_3PO_4 percentages where *o*-H_3PO_4 reacts to from an alcohol.

Table 3. Chemical properties of ESPs using two different mixing sequences. The Gardner color indices of the samples range from1 to 3. All reacted samples composition: 1:1 by wt ESBO and CO. "Separate" indicates acid reaction was done first before alcohol addition while "Simultaneous" indicates acid and alcohol reactions were done at the same time.

% *o*-H_3PO_4 based on ESBO	Acid Value, mg KOH/g (±0-5%)	Viscosity, cP (±0.2-1%)	%Oxirane Oxygen (±0.2-3%)	AOCS Hydroxyl Value, mg KOH/g (±2-4%)
Control				
0	1.54	434	3.44	84.10
Separate				
0.5	1.75	501	3.22	84.30
1.0	1.65	665	3.12	89.56
2.0	1.63	1240	2.69	95.36
Simultaneous				
0.5	1.90	507	3.30	87.70
1.0	1.80	660	3.04	89.30
2.0	1.90	1100	2.73	98.24

2.3.3. Extractability for ESPs

The schematic representation of the reaction of ESP/phosphate esters with pMDI is shown in Figure 8. For ESPs with higher alcohol concentration it is expected that the unreacted oil extractability is lower because the hydroxyl groups of castor oil readily react with the NCO functional group of pMDI forming crosslinked urethane polymer network.

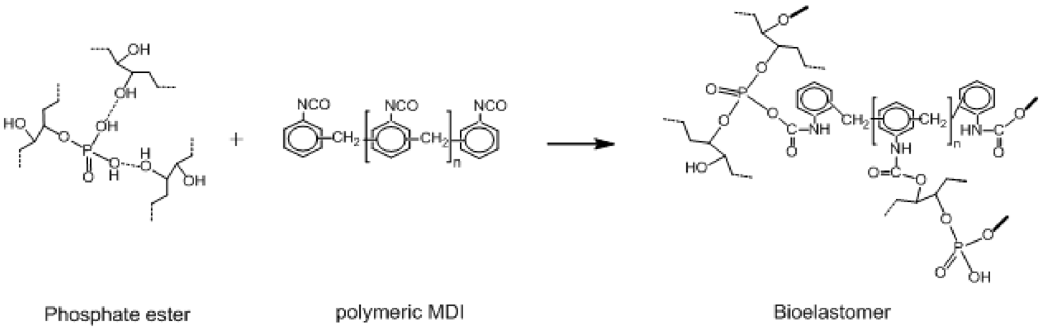


Figure 8. Schematic representation of bioelastomer formation.

The effect of catalysis and reaction of ESBO with *o*-H_3PO_4 is more pronounced at mass fractions between 0.5 to 1.0 ESBO in castor oil as shown in Figure 9. With no alcohol loading an increase from 4.1% (catalyzed) to 18.6% (non-catalyzed) unreacted oil phase is observed which means that the extent of ESP-pMDI reaction can be increased by increasing the amount of *o*-H_3PO_4. Lower extractability can be obtained by either increasing the alcohol loading in the bioelastomer mix or increasing the hydroxyl functionality (increase the hydroxyl equivalent weights at the same hydroxyl number) of the ESP which can be achieved by epoxy reaction with *o*-H_3PO_4.

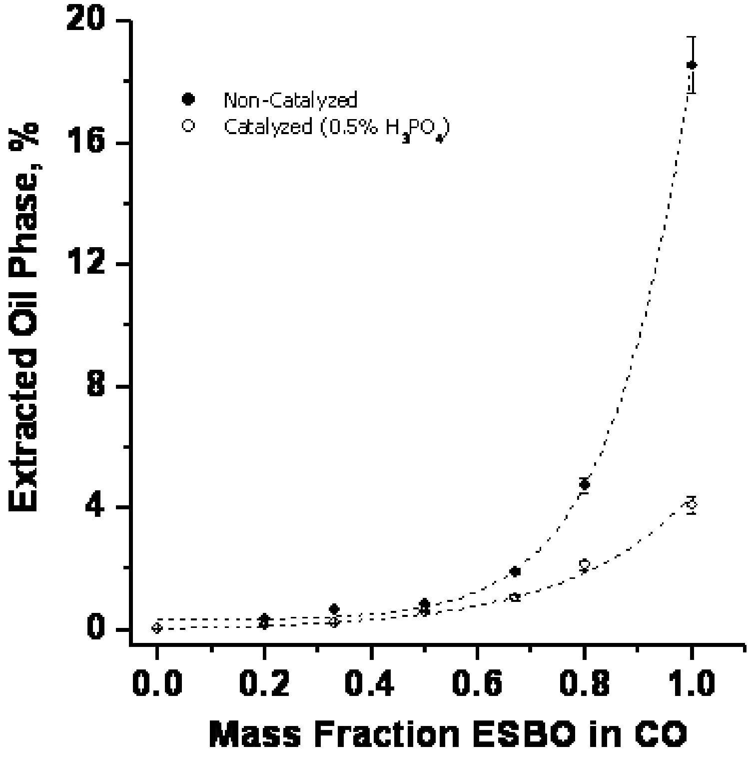


Figure 9. Extractability trend of urethane elastomers based on catalyzed and non-catalyzed ESBO. Urethane materials were formed from the reaction of ESPs, castor oil and polymeric MDI. Curing conditions were at 45°C for 48 h in a convection oven.

The ASTM hydroxyl value of the polyol is used in order to calculate the amount of isocyanate needed to react with the polyol. The acid-catalyzed epoxide sample C in Table 4 shows an ASTM hydroxyl value of 240 mg KOH/g. The amount of isocyanate can be reduced to about 40% relative to the control with a hydroxyl value of 404 mg KOH/g. *o*-H_3PO_4-catalyzed ESBO presents the following potential advantages: increased polymeric network (high average functionality), improved tensile properties and reduced pMDI loading for both urethane bioelastomer and rigid foaming formulations.

Table 4. Chemical properties of *o*-H_3PO_4-reacted ESBO (at RT) without solvent or alcohol source.

Sample Code	% *o*-H_3PO_4 based on ESBO	Acid Value, mg KOH/g (±0-5%)	%Oxirane Oxygen (±0.2-3%)	AOCS Hydroxyl Value, mg KOH/g (±2-4%)	ASTM Hydroxyl Value, mg KOH/g (±0.3-5%)	Viscosity, cP (±0.2-1%)
Control	0	<0.20	7.06	11.0	404	362
A	0.5	0.77	6.77	23.0	--	559
B	1.0	0.89	6.30	32.2	--	1020
C	1.5	0.95	5.34	38.4	240	3950

2.3.4. Acid-catalyzed epoxide

Urethane bioelastomers were also prepared by reacting ESBO with *o*-H_3PO_4 without solvent or alcohol source. Table 4 presents the chemical properties of these samples with untreated ESBO as a control. A reduction of about 25% oxirane oxygen content was observed upon reacting ESBO with 1.5% phosphoric acid. Gelation was observed at about 2.0% acid loading.

The epoxy ring-opening reaction was verified by FTIR with the untreated ESBO showing a more intense peak compared with acid-treated sample at wavenumber 824 cm^{-1}, characteristic of an epoxy signal. A steep increase in viscosity was also observed from 362 cP for untreated ESBO to about 4000 cP for the 1.5% acid-treated sample. This was indicative of the formation of phosphate esters which was verified by FTIR spectral intensity at wavenumber 1020 cm^{-1}. This characteristic signal was not observed with the untreated ESBO sample. The acid number did not increase significantly with increasing phosphoric acid loading which indicate that the phosphate molecules completely reacts with the epoxy molecules up to at most 1.5% phosphoric acid loading.

Higher residual acidity is an undesirable polyol property as it competes with hydroxyls to react with isocyanates and consumes catalysts when these samples are further processed to produce bioelastomers and urethane foams. All samples maintained non-problematic acid values less than 1.0. The increase in AOCS hydroxyl values from 11.0 to 38.4 was attributed wholly to the residual water that came from the aqueous o-H_3PO_4.

2.3.5. Bioelastomer formation

Physicochemical properties of bioelastomers synthesized from treated epoxides in Table 4 are presented in Table 5 with the actual bioelastomers shown in Figure 10. Urethane bond formation was verified by FTIR spectra at wavenumber 3340 cm^{-1} with a higher peak intensity observed with the bioelastomer synthesized from non-treated epoxide.

Table 5. Tensile and thermal properties of bioelastomers from reacted epoxides of Table 4.

Bioelastomers were evaluated at 10%-30% by weight pMDI based on acid-treated ESBO.

Sample Code	Description	Strength at Break, MPa	Strain at Break, %	Young's Modulus, MPa	T_g (DSC), °C
10A	A + 10% pMDI	Material too soft			---
10B	B + 10% pMDI	Material too soft			---
10C	C + 10% pMDI	Material too soft			---
15A	A + 15% pMDI	Material too soft			-10.2
15B	B + 15% pMDI	0.29 ± 0.01	4.34 ± 2.96	0.22 ± 0.03	-13.8
15C	C + 15% pMDI	0.42 ± 0.14	5.10 ± 2.89	0.47 ± 0.34	-17.4
25A	A + 25% pMDI	0.94 ± 0.12	9.00 ± 1.54	0.46 ± 0.09	-11.5
25B	B + 25% pMDI	1.32 ± 0.14	5.93 ± 0.83	0.95 ± 0.07	-15.9
25C	C + 25% pMDI	1.47 ± 0.12	5.13 ± 0.48	2.04 ± 0.36	-18.4

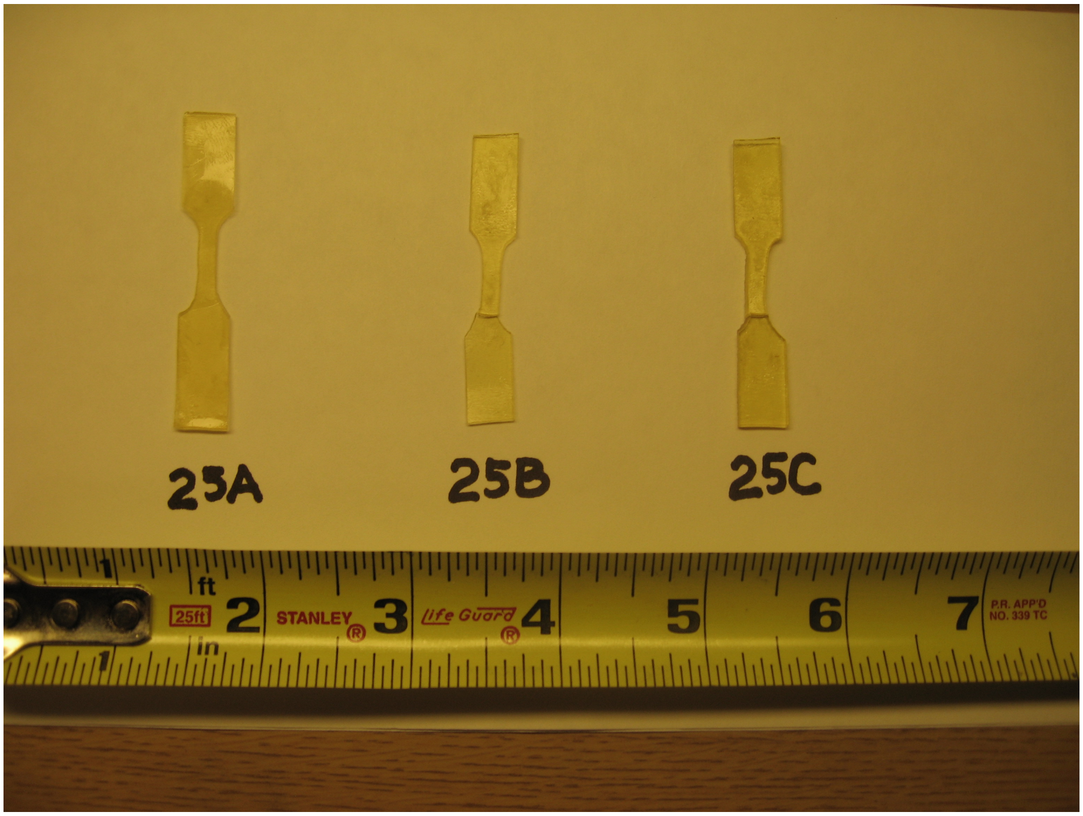


Figure 10. Phosphate ester-PU bioelastomer cut samples (Type V cutter).

The greatest extent of crosslinking in elastomers will tend to happen with the A-side and B-side monomers are reacted in stoichiometric quantities. For urethane reactions, and especially for urethane reactions with expoxy moieties present, there is a complex network of reactions and reaction stoichiometry is not straight forward. However, even with this uncertainty. it is evident that at 10% PMDI there is an inadequate amount of isocyanate to completely react the B-side alcohol and epoxy moieties. At 10% pMDI loading the bioelastomeric materials were too soft to be measured with its tensile properties. NCO concentration was less compared to the available alcohol/epoxy reacting groups leaving more unreacted soy-phosphate molecules.

At 30% PMDI, the PMDI will tend to exhaust reaction with the alcohol moiteties and undergo reactions that form undesirable brittle elastomers. At 30% pMDI loading, bioelastomers were observed to be hard and brittle. This seemed to be the opposite of the 10% loading at the same curing temperature. Excess amounts of pMDI relative to the epoxy/alcohol groups may result in the formation of the hard segment of isocyanurate, biurets and allophanates which would lead to brittleness and fragility of the urethane product. The T_g values of the bioelastomers in Table 5 shows consistent trend, an increasing T_g value as OH/NCO molar ratio increases. Each bioelastomer sample show only one glass transition temperature which reflects a high degree of phase mixing between the hard segment and the soft-segment domains.

Optimal combinations of strength and strain performances were attained at about 25% PMDI loadings.

At the same pMDI loading tensile strength increased with increasing mass percentage of phosphoric acid added to ESBO. The higher *o*-H_3PO_4 loading in ESBO led to increased viscosities which are associated with increased average molecular weights. The higher average molecular weight of the B-side monomer translates to more crosslinking and increased tensile strength.

At different pMDI loadings (e.g. samples 15C and 25A) the Young's Modulus of the samples are comparatively similar, which means that both samples have the same resistance to elastic deformation under load (see Figure 11).

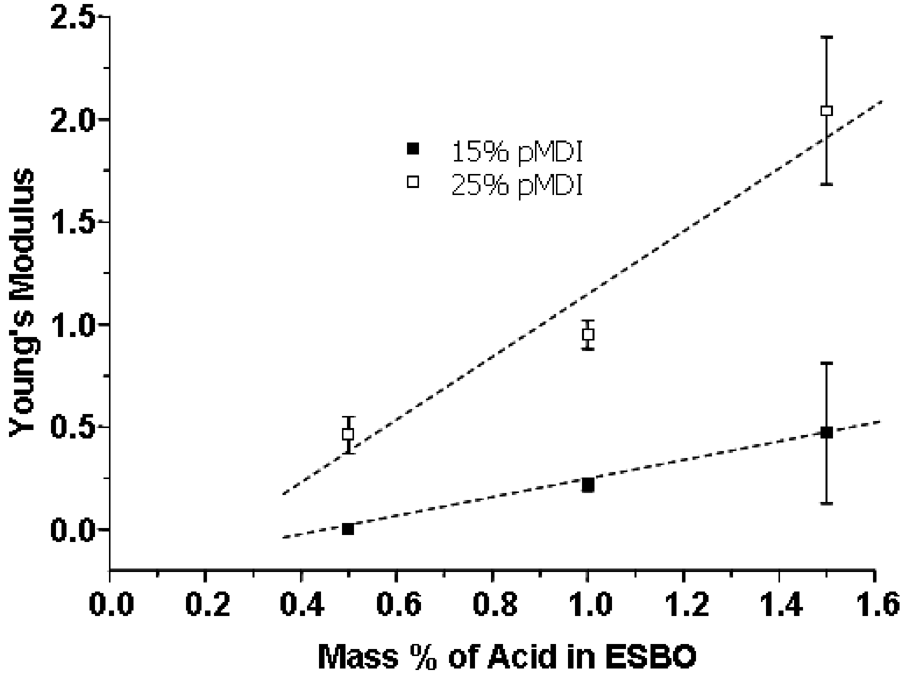


Figure 11. Effect of the amount of *o*-H3PO4 on Young's modulus of bioelastomers with 15% and 25% pMDI loading.

2.4. CONCLUSIONS

Polymerized epoxidized soybean oil were synthesized by phosphate ester formation carried out by mixing epoxidized soybean oil with up to 1.5% *o*-phosphoric acid at room temperature (25˚C). The product produced was homogeneous, highly viscous, low-acid and with a high average functionality. The resulting phosphoric acid-catalyzed epoxide-based bioelastomer showed up to 80% decrease in extractable content and increased tensile strength at the same isocyanate loading relative to the non-catalyzed epoxide.

With the same catalyzed epoxide used as a B-side reactant in the rigid foam formulation, the amount of isocyanate can be reduced to about 40%

compared with the non-catalyzed epoxide reactant. There was no significant increase in the hydroxyl number of the polyols but its relatively lower extractable content indicates a higher hydroxyl equivalent weight due to its high molecular weight.

2.5. REFERENCES

1. Y. Guo, J. Hardesty, V. Mannari, J. Massingill, Journal of the American Oil Chemists' Society, 84, 929 (2007).
2. S. Narine, X. Kong, L. Bouzidi, P. Sporns, Journal of the American Oil Chemists' Society, 84, 55 (2007).
3. Y. Guo, V. Mannari, P. Patel, J. Massingill, Journal of Coatings Technology and Research, 3, 327(2006).
4. Y.-C. Tu, P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 105, 453 (2007).
5. L. Zhang, H. K. Jeon, J. Malsam, R. Herrington, C. W. Macosko, Polymer, 48, 6656 (2007).
6. Y.-C. Tu, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 109, 537 (2008).
7. P.-p. Kiatsimkul, G. J. Suppes, W. R. Sutterlin, Industrial Crops and Products, 25, 202 (2007).
8. P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Z. Lozada, Y.-C. Tu, Industrial Crops and Products, 27, 257 (2008).

9. G. Knothe, J. T. P. Derksen, Recent Developments in the Synthesis of Fatty Acid Derivatives, AOCS, Champaign, 1999.

10. T. I. Kadurina, V. A. Prokopenko, S. I. Omelchenko, European Polymer Journal, 22, 865 (1986).

11. T. I. Kadurina, V. A. Prokopenko, S. I. Omelchenko, Polymer, 33, 3858 (1992).

12. M. Modesti, A. Lorenzetti, European Polymer Journal, 37, 949 (2001).

13. Huntsman Int. LLC, Patent Application 20000801, USPTO, USA, 2002.

14. J. P. L. Dwan'Isa, A. K. Mohanty, M. Misra, L. T. Drzal and M. Kazemizadeh, Journal of Polymers and the Environment, 11, 161 (2003).

15. B. Zhong, C. Shaw, M. Rahim, J. Massingill, Journal of Coatings Technology, 73, 53 (2001).

16. R. B. Cracknell, A. J. Moore, Patent Application 5414103, USPTO, USA, 1995.

17. S. Sato, R. Carielo Bueno, A. Bueno, A. W. Bueno De, Patent Application 6274750, USPTO, USA, 2001.

18. R. Herrington, K. Hock, Flexible Foams. The Dow Chemical Company, Midland, MI, 1997.

19. A. A. Lubguban, Y.-C. Tu, Z. R. Lozada, F.-H. Hsieh, G. J. Suppes, Journal of Applied Polymer Science, 112, 19 (2009).

CHAPTER 3

FUNCTIONALIZATION via GLYCEROL TRANSESTERIFICATION OF POLYMERIZED SOYBEAN OIL

3.1. INTRODUCTION

Polymers derived from plant oils have gained major commercial interest and significant attention in scientific research owing to the availability, biodegradability and unique properties of the triglycerides. Triglycerides rich in unsaturated fatty acids, like soybean oil, are particularly susceptible to chemical modification to the desired polymeric materials.

Various physicochemical and even biological methods have been used to functionalize unsaturated vegetable oils to yield industrially-useful polymer derivatives and polyols. In a study done by Kiatsimkul et al. [1], bodied soybean oil was used as a starting material for polyol production by enzyme hydrolysis. This method is suggested to yield a soy-based polyol with high molecular weight, reduced saturated fatty acid moieties, increased primary alcohol moieties, and a tunable hydroxy equivalent weight.

Relatively higher molecular weight polyols with corresponding higher hydroxyl equivalent weights are desired in polyurethane production because they lead to larger amounts of B-side components in the urethane formulation. Enzymatic approaches that reduce the use of inorganic catalysts, reduce amounts of organic reagents or co-reagents, and operate at lower temperatures are considered to be more desirable, greener processes.

However, the high costs and relatively low operational productivities of the lipases create economic barriers that offset the advantages.

Epoxidation with oxirane opening reactions are effective for converting soybean oil to polyols secondary hydroxyl moieties. These secondary hydroxyl moieties react slower than primary moieties. Alternatively, ozonolysis of canola and soybean oil yields polyols with primary, terminal hydroxyls [2] that are more reactive with isocyanate [3]. Primary hydroxyl moieties require lower catalyst quantities, and this reduces the cost of the urethane formulation. Drawbacks of ozonolysis include energy-intensive separations and disposal issues related to the generation of low molecular weight monofunctional by-products.

This paper is on a two-step process starting with heat polymerization (bodying) of soybean oil, which promotes crosslinking of acylglycerols generally through a Diels-Alder reaction. The Diels-Alder reaction is possible because of the diene functionality in linoleic acid (C18:2) and linolenic acid (C18:3) [1]. During heat polymerization, double-bond migration (producing the more reactive conjugated dienes), other isomerizations, and transesterification lead to a complex product mixture [4]. An increase in viscosity is observed during bodying due to the participation of conjugated dienes in the Diels-Alder crosslinking reaction [5].

After bodying of soybean oil, transesterification is used to impart hydroxyl functionality. Transesterification of fats and oils with glycerol has long been used in the commercial manufacturing of the chemically versatile monoglycerides. This physicochemical process, also known as glycerolysis, requires high temperatures (210-260^{o}C), inorganic catalysts and organic solvents. In addition to monoglycerides, di- and triglycerides; water and alcohol are also formed [6].

There is mounting worldwide pressure to move toward renewable, inexpensive, domestic, and more environment-friendly raw materials. One result of this is the burgeoning biodiesel industry, which has led to a considerable amount of crude glycerol in the market. An advantage of this two-step process including a second glycerolysis step is the generation of value-added polyols from natural glycerol.

In this paper, a series of polyols are presented based on variation in bodying and amount of glycerol added during transesterification. Extractability characterization was performed in elastomer test-wafers. Rigid foams were prepared with characterization of their density, compressive strength, and thermal conductivity.

3.2. METHODS

3.2.1. Materials

Voranol®490 polyether polyol (a petroleum-based polyol made from polypropylene oxide and a sucrose/glycerin base and with the following properties: 4.3 alcohol functionality, 460 average molecular weight, and 490 hydroxyl number) and PAPI® 27 (a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4 wt % of NCO content) were obtained from Dow Chemical (Midland, MI). Epoxidized soybean oil (ESBO) (Vikoflex® 7170) was supplied by ATOFINA

Chemicals (Philadelphia, PA). Glycerol was obtained from Procter & Gamble Co. (Ivorydale, OH). Catalysts (POLYCAT® 5 and POLYCAT® 8) and a surfactant (Dabco® DC 5357) were from Air Products and Chemicals (Allentown, PA), gratis. Distilled water was used as the blowing agent. Refined food-grade soybean oil (SBO) having an iodine value (IV) of 129 cg I_2/g SBO and viscosity (η) of 28 cP (at 40°C) was obtained from a local wholesaler.

Bodied soybean oil (BSBO) was synthesized to provide an intermediate that could be further reacted with glycerol to increase the hydroxyl content. The BSBO was prepared by heat-polymerization of soybean oil in batch and continuous processes as described in the Methods section below. A GPC (Gel Permeation Chromatography) analysis of the BSBO intermediate revealed the following components by weight; oligomer: 57.23%, monomer: 34.68%, and FFA: 8.09% with an average molecular weight of 2422 g/mol (SBO has 948 g/mol).

3.2.2. Physicochemical analyses

Hydroxyl values of polyols were determined according to an American Society for Testing and Materials (ASTM) Procedure E222-00 (reapproved 2005) Method A [7]. Acid numbers (mgKOH/g sample) of all reaction products were evaluated according to the AOCS official method (AOCS Te 1a-64, 1997)[8]. Iodine values (mgI_2/g sample) of the polyol samples were determined using ASTM Designation: D1959-97 [9]. Epoxy content of the samples were measured according to AOCS official method (AOCS Cd 9-57, 1997) [10]. The dynamic viscosities (cP, measured at 20°C) of the samples were determined using Model RS100 Rheometer (Haake–Thermoelectron).

A single-step plastic extraction method was used to determine the extent of polymer crosslinking between the polymeric MDI (PAPI® 27) and polyol products. Polymeric MDI and polyol in a weight ratio of 1:2 was well mixed in a small tin cup. The resulting product was left to dry for 10 hours in a convection oven at 110°C. The dry sample was then cooled to room temperature and cut to thin sheets for unreacted oil extraction. About 1 gram of the cut sample was soaked in a 1:4 by volume cyclohexanol-hexane solution for 15 mins. after which the mixture was filtered. Both permeate and retentate were dried in a vacuum oven at 110°C for 2 hours. The percentage of unreacted oil phase was calculated by mass balance.

A Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA) was used to measure the thermal conductivity of the PUs according to ASTM Procedure C518-04 [11]. Densities of foam samples were determined according to ASTM Procedure D 1622-03 [12]. Compressive strengths of foam samples were measured using a TA.Hdi Texture Analyser (Texture Technologies, Scarsdale, NY) according to ASTM Procedure D 1621-04a [13]. Thermal conductivity measurements were performed after curing the foams for 24 hours while density and compressive strength measurements were performed after 7 days sample storage.

3.2.3. Methods for heat polymerization of soybean oil

Thermal polymerization of soybean oil was carried out using batch and continuous processes. The batch process was performed in a 2-L Bench Top Model 4526 Parr stirred vessel. About 1500 grams of refined soybean oil was heated in a closed Parr reactor vessel for 6 hours at 260°C with constant stirring. A convection oven was used in a single-pass continuous bodying of soybean oil with a flow rate of about 0.32 mL/min at 355°C. The downstream product was cooled to below 30°C by direct water-cooling of the discharge tube before product collection in an open vessel. The final collected bodied soybean oil (BSBO) was well-mixed with a stirring rod to ensure uniform chemical properties. Decreases in iodine values and increases in viscosities of the batch- and continuous-processed soybean oils were observed. The actual measured values are: Batch (IV = 107, η = 200), and Continuous (IV = 96.6, η = 438). The mechanism was explained elsewhere [1].

3.2.4. Synthesis of glycerol-transesterified bodied soybean oil

Glycerol-transesterification of bodied soybean oil for polyurethane production was done in a 2-L Bench Top Model 4526 Parr stirred vessel while transesterification of bodied soybean oil for kinetic study was done in a smaller 300-mL Bench Top Model 4561 Parr stirred vessel. About 1500 grams of bodied soybean oil was poured into the 2-L Parr reactor vessel. Pure glycerol was added to the same vessel at varying quantities from 5% to 10% by weight based on bodied soybean oil. The mixture reacted in a closed Parr vessel with constant stirring at a temperature range of 200-225°C at 1-5hr reaction times. Kinetic studies were performed on the samples to evaluate the effects of glycerol concentration and reaction conditions on the chemical properties of the glycerol-transesterified bodied soybean oil (GLYC-BSBO) products.

3.2.5. Polyurethane formation

A foaming procedure described by Tu et al. [14] was used in this study. VORANOL® 490, soybean oil-based polyol, catalysts, surfactant, and blowing agent were added by weighing into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s and then PAPI® 27 was rapidly added while continuously stirring for another 10–15 s at the same speed. The mixture was 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).

3.3. RESULTS AND DISCUSSION

3.3.1. Effect of reaction time

Figures 12 and 13 summarize the dynamics of the transesterification of bodied soybean oil (BSBO) with 5% glycerol. Viscosity increased during the 5-hour reaction time approaching asymptotic values at 5 hours—this is consistent with cross-linking that is promoted with the 3-functional glycerol.

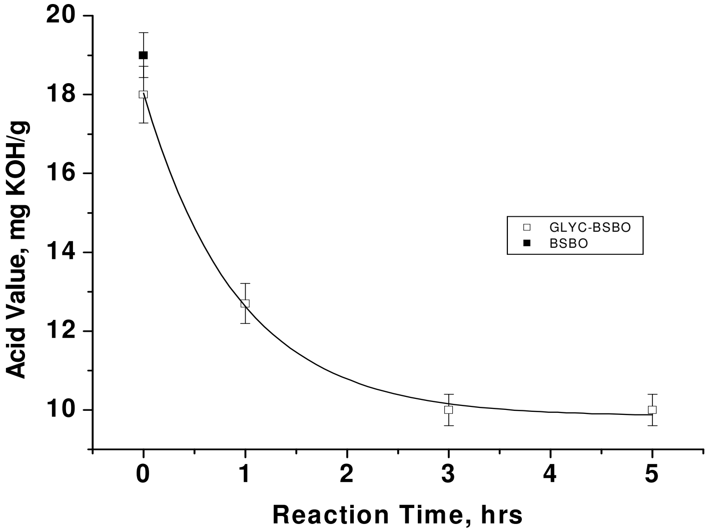


Figure 12. Effect of reaction time on polyol acid number for the reaction of BSBO with 5% Glycerol at 225°C. The control BSBO (batch-processed) indicated above has the following chemical properties: Acid Number: 19.0 mg KOH/g polyol, Hydroxyl Value: 13.2 mg KOH/g polyol, Viscosity: 200 cP.

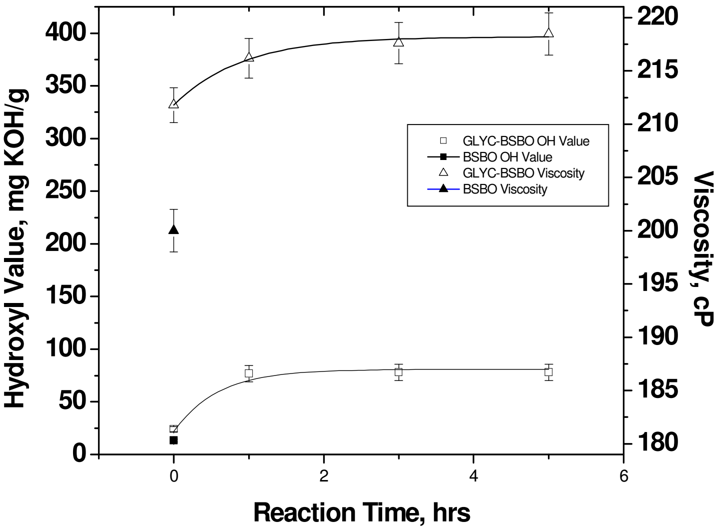


Figure 13. Effect of reaction time on polyol hydroxyl value and viscosity for the reaction of BSBO with 5% Glycerol at 225°C. The control BSBO (batch-processed) indicated above has the following chemical properties: Acid Number: 19.0 mg KOH/g polyol, Hydroxyl Value: 13.2 mg KOH/g polyol, Viscosity: 200 cP.

During soybean oil bodying reaction, the acidity increased such that the resulting BSBO reagent acidity was 19 mg KOH / g sample. The acidity decreased rapidly during glycerol-transesterification with a near-constant value of about 10 obtained at 5 hours (see Figure 12). These trends are consistent with the glycerol alcohol moieties esterifying with the acid moieties and thereby reducing the acid number. Low acidity in polyols is important because high acid number polyols tend to neutralize the urethane formulation catalysts.

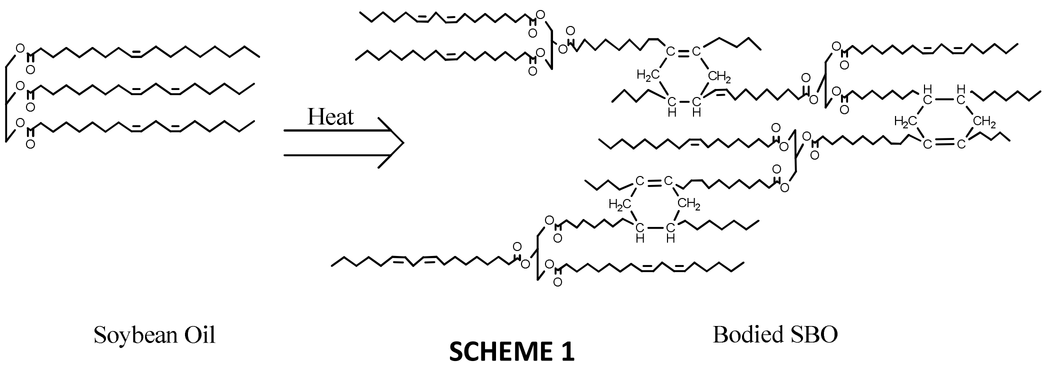
The hydroxyl groups were introduced primarily by the glycerol reagent to the mixture. Consequently, the hydroxyl number remained essentially constant through reaction as shown in Figure 13. The primary reaction impacting the hydroxyl content was esterification with acid in the solution. The amount of alcohol moieties lost by reaction with the acids had a negligible impact on the hydroxyl number. Starting with the same BSBO as control (Hydroxyl Value = 13.2 mgKOH/g, η = 200 cP) transesterification with 5% glycerol produced a polyol with a hydroxyl value of 78 and viscosity of about 400 after a 5-hr reaction time.

A study done by Erhan et al. [5] confirmed through GC-MS analysis of volatile by-products (from bodying of SBO) that the more reactive linolenic and linoleic acids are consumed at an early stage of the bodying process to produce the polymeric materials. This was evident by the decrease in IV (from 129 to 107) and increase in viscosity (from 29 to 200) of SBO after the bodying process.

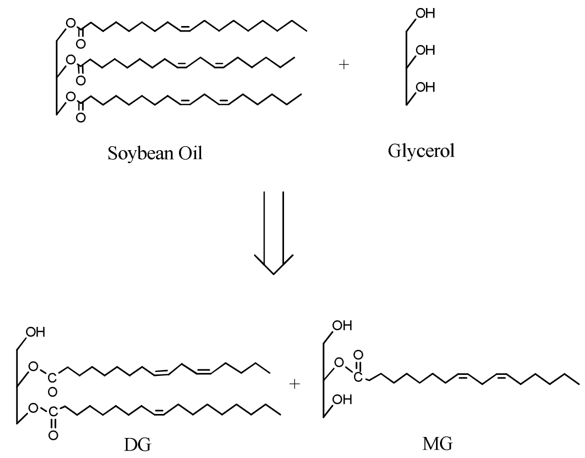
The three reaction schemes shown in Figures 14 (SCHEMES 1 and 2) and Figure 15 (SCHEME 3) are possible when glycerol is reacted with BSBO at 225°C; they include: 1) further polymerization of unreacted SBO triglycerides (TG) to BSBO, 2) formation of SBO monoglycerides (MG) and diglycerides (DG), and 3) transesterification of BSBO to GLYC-BSBO. The latter is assumed to be the dominant, but not sole, reaction when the amount of moisture (water) is negligible.

The free fatty acids (FFA) in the BSBO will react with glycerol to form acylglycerols as illustrated in SCHEME 2 of Figure 14. This is an important reaction as it results in a product with two functional alcohols, which react with isocyanates to propagate a urethane reaction. Residual triglyceride and diglyceride in the BSBO would be converted to similar acylglycerols. Trace amounts of diglyceride and triglyceride would be expected with the reaction products [15].

A number of factors can contribute to the formation of free fatty acids in the bodying process of soybean oil. The presence of moisture in the reaction mixture would yield free fatty acids by triglyceride hydrolysis [16]. Fatty acids with no olefin groups could also incorporate into the end product as they can easily volatilize at high bodying temperatures [5].The presence of water would lead to esterification equilibrium of fatty acids balanced with water and glycerides [17]. The decrease and eventual plateau in the acid number value of the polyol in Figure 12 may be indicative of residual water content; however, this is unlikely. The residual acid was present in batch and flow reactor BSBO product. In the batch reactor product the combination of a nitrogen purge and temperatures in excess of 300 °C would drive off essentially all water.



SCHEME 1



Consecutive Steps:

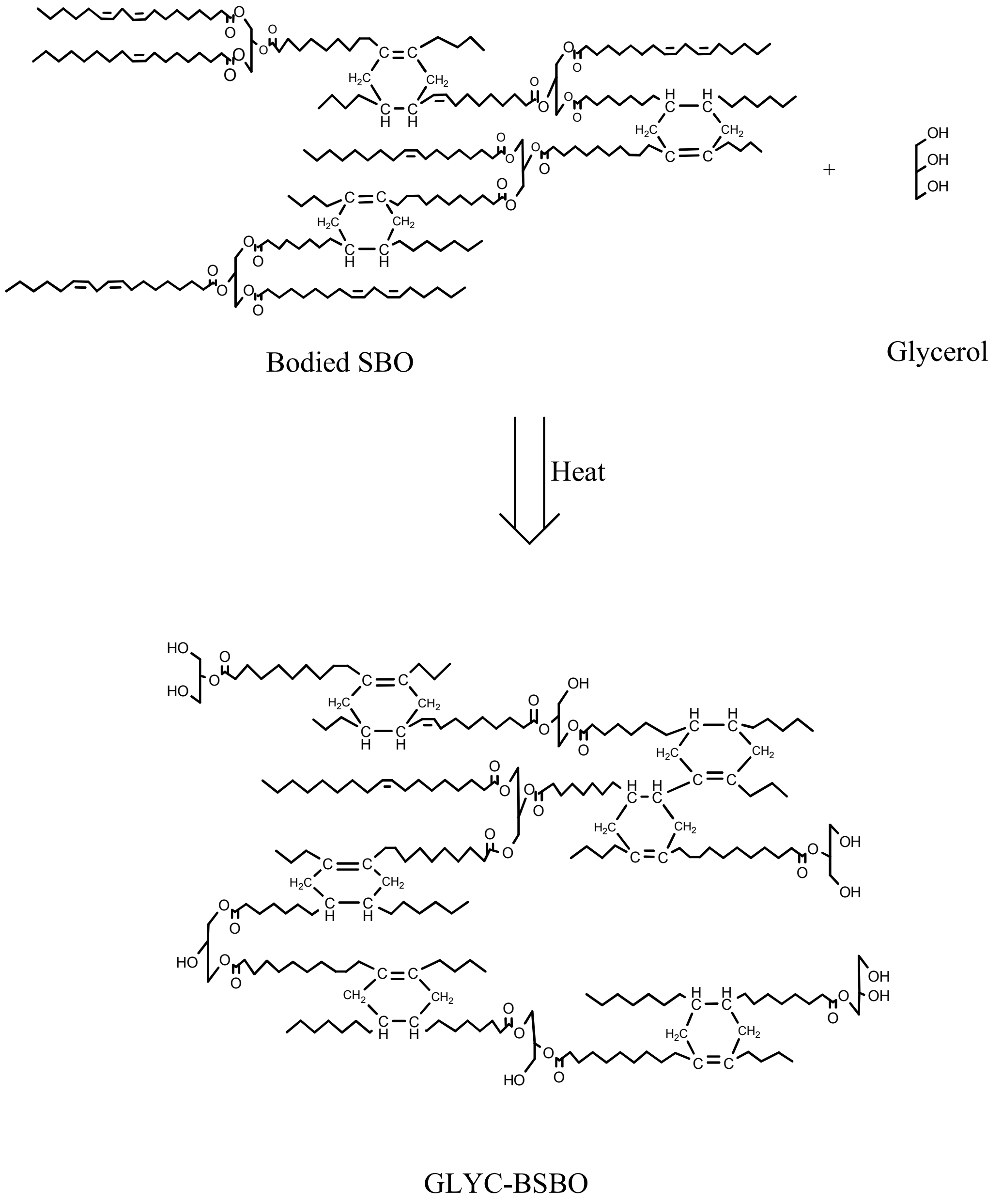
$$\text{TG} + \text{Glycerol} \rightleftharpoons \text{MG} + \text{DG}$$

$$\text{DG} + \text{Glycerol} \rightleftharpoons 2\,\text{MG}$$

$$\text{TG} + \text{MG} \rightleftharpoons 2\,\text{DG}$$

SCHEME 2

Figure 14. Reaction schemes in the hydroxylation process of BSBO: SCHEME 1) where the unreacted SBO is polymerized to BSBO, and SCHEME 2) where SBO and glycerol reacts to form acylglycerols of SBO (MG, DG, and TG).



SCHEME 3

Figure 15. Major reaction in the hydroxylation process where BSBO and glycerol reacts to form GLYC-BSBO.

The major reaction in the glycerol-transesterification process is the reaction between BSBO and glycerol shown as SCHEME 3 in Figure 15. BSBO is a macromolecule of polymerized SBO with a moderate molecular weight, which can be readily cleaved by glycerol at the ends of its branches. Since BSBO has a higher molecular weight than SBO, it requires less glycerol per mole to achieve a given average functionality.

For every mole of glycerol reacting with a glyceride, the concentration of alcohol moieties in solution remains the same. This explains the nearly constant hydroxyl value as a function of reaction time illustrated by Figure 13. Alcohol moiety on a triglyceride is known to increase viscosity (e.g. castor oil versus SBO). The trend in viscosity of Figure 13 reflects an increase in viscosity due to the alcohol functionality. The leveling-off of viscosity after the first hour could reflect nearly complete transesterification at one hour.

3.3.2. Preliminary crosslinking test on GLYC-BSBO

The reactivities of GLYC-BSBO products were evaluated by reacting of the GLYC-BSBO with polymeric MDI. The percent unreacted oil phase (GLYC-BSBO) was determined by an extraction phase described in the mehods section (3.2.2). The extraction test results are summarized in Table 6 with a graphical comparison of the different product-categories in Figure 16. A low extractability is believed to correlate with high crosslinking while a high extractability is believed to correlate with the presence of non-functional or single-functional components in the B-side (alcohol side) of the urethane formulation.

Table 6. Polyol product synthesis details for polyurethane production. Different extractability values expressed as percent-unreacted oil phase of the synthesized soy polyols and controls.

Polyols	Description	% Unreacted Oil Phase (±5-25%)
Voranol™490	Commercial	0.38
GLY-10	10% by wt Glycerol in BSBO and heat processed at 220°C/2 hrs, Parr	0.77
BSBO	Heat treatment of SBO at 355°C, continuous-flow process at 0.32 mL/min	4.92
ESBO	Commercial	17.78
SBO	Soybean Oil	~100
SBOGLY-10	SBO + 10% Glycerol, 220°C/2 hrs	did not cure (liquid state)
GLY5-BO	GLY-5 neutralized with stoic. amount of 1,2-butylene oxide at 170°C/2 hrs, Parr	5.20
GLY10-BO	GLY-10 neutralized with stoic. amount of 1,2-butylene oxide at 170°C/2 hrs, Parr	1.77
GLY10-ESBO	GLY-10 neutralized with stoic. amount of ESBO at 170°C/1 hr, N_2 flowing	0.81
GLY10-KOH	GLY-10 with 1% KOH, 225°C/5 hrs, Parr	1.90

Table 6, Continued

GLY-5 with Varying Viscosities of Starting BSBO (Figure 6)

SBOGLY-5	SBO (cP =57) + 5% Glycerol, 220°C/2 hrs	did not cure
GLY-5a	BSBO (cP = 384) + 5% Glycerol, 220°C/2 hrs	4.70
GLY-5b	BSBO (cP = 438) + 5% Glycerol, 220°C/2 hrs	4.58
GLY-5c	BSBO (cP = 451) + 5% Glycerol, 220°C/2 hrs	4.40
GLY-5d	BSBO (cP = 510) + 5% Glycerol, 220°C/2 hrs	4.10
GLY-5e	BSBO (cP = 984) + 5% Glycerol, 220°C/2 hrs	3.42
GLY-5f	BSBO (cP = 3936) + 5% Glycerol, 220°C/2 hrs	3.05

Table 7. Chemical properties of polyols used in the preparation of polyurethanes.

Polyols	**Acid Number (mg KOH/g)**	**Viscosity (cP at 22°C)**	**Hydroxyl Number (mg KOH/g)**	**Epoxy Content (%)**
Voranol®490	<1.0	11240	484.4	<0.10
ESBO	<1.0	362	403.8	6.1
BSBO	30.4	438	16.0	<0.10
GLY-5	2.1	732	91.1	<0.10
GLY-10	1.4	2000 (gelled)	162.2	<0.10
GLY5-BO	2.5	732	91.2	0.10
GLY10-BO	1.4	997	163.0	0.13
GLY10-ESBO	1.6	1664	90.3	<0.10
GLY10-KOH	8.0	2791 (gelled)	153.4	<0.10

Based on Figure 16, the crosslinking of GLY-10 (synthesis and property details shown in Table 6 and 7, respectively, and extraction result details in Table 6) is greater than that of GLY-5. In view of the amount of fatty acid groups in the BSBO, 5% glycerol is apparently not adequate to assure that most of the molecules have at least two functional alcohol groups.

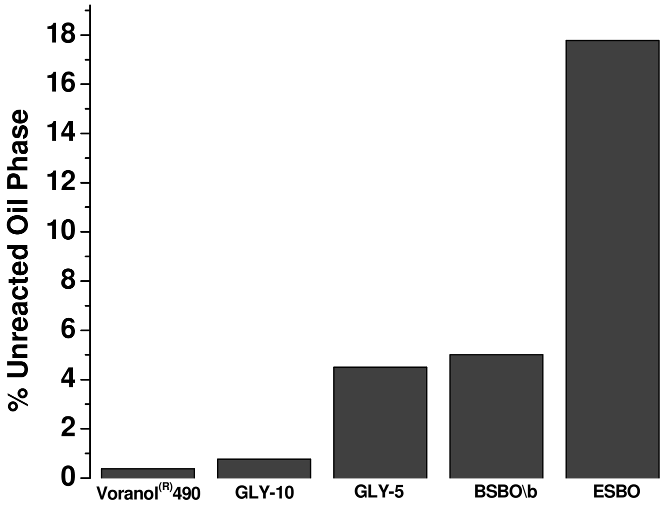


Figure 16. Preliminary crosslinking test results represented by percent-unreacted oil phase recovered after organic solvent extraction. Extractability of GLY-5 and GLY-10 are shown in comparison with controls.

A series of controls were run to evaluate the crosslinking performance of the GLYC-BSBO polyols. Petroleum-based Voranol® 490 achieved the highest reactivity with polymeric MDI based on its 0.38% unreacted oil phase. Its crosslinking performance reflects its high hydroxyl functionality and ordered polymeric structure.

Epoxidized soybean oil (ESBO) exhibited the lowest crosslinking (of the systems that set to polymers) with 17.8% unreacted oil phase. Depending upon the means of evaluating hydroxyl value, each epoxy group in ESBO can register as two alcohol groups as corresponding to the cleavage of the epoxy group with water to yield a diol. The fact that the epoxy polymerizes is an interesting artifact of these results. When soybean oil (SBO) is used as the B-side in the wafers used for extraction tests, the system does not set (100% extractability).

Bodied soybean oil (with 4.92% unreacted oil phase) has shown considerable reactivity and crosslinking with polymeric MDI, especially as compared to SBO, which does not set upon curing. BSBO has a higher molecular weight than SBO, and so, fewer reactive moieties go farther in reducing extractability. At least some of the functionality in BSBO is attributed to cleaved ester bonds, which results in an alcohol and acid group—both of which will react with MDI.

When BSBO is transesterified with glycerol, alcohol functionality is imparted and some of the acids is reacted to esters. A decrease of about 7% in extracted oil phase is observed when BSBO was further processed by adding 5% glycerol. The 5% glycerol increases the hydroxyl value of BSBO by about 80%. Addition of 10% glycerol to BSBO enhances its hydroxyl value by 90% and further decreases the extracted oil phase.

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. To evaluate this, SBO and BSBO various degrees of oligomerization (via viscosity) were evaluated after transesterification with 5% glycerol.

Figure 17 illustrates the correlation between percent unreacted oil phase and the viscosity of the starting BSBO used to prepare GLY-5 polyol. As expected, higher degrees of oligomerization result in reduced unreacted oil phase. Better crosslinking performance is related to higher hydroxy equivalent weights of the soy polyols (at the same hydroxyl number), which can be achieved primarily by initially bodying the soybean oil and addition of glycerol to increase alcohol functional groups. This clearly illustrates that the primary goal of the bodying process is achieved—a larger molecular weight monomer is produced.

A control was performed with 5% and 10% glycerol transesterification with SBO. The resulting extractability test wafer did not set. At 5% and 10% glycerol, the bodying process transforms the soy-based monomer from a non-viable to a viable monomer for urethane applications.

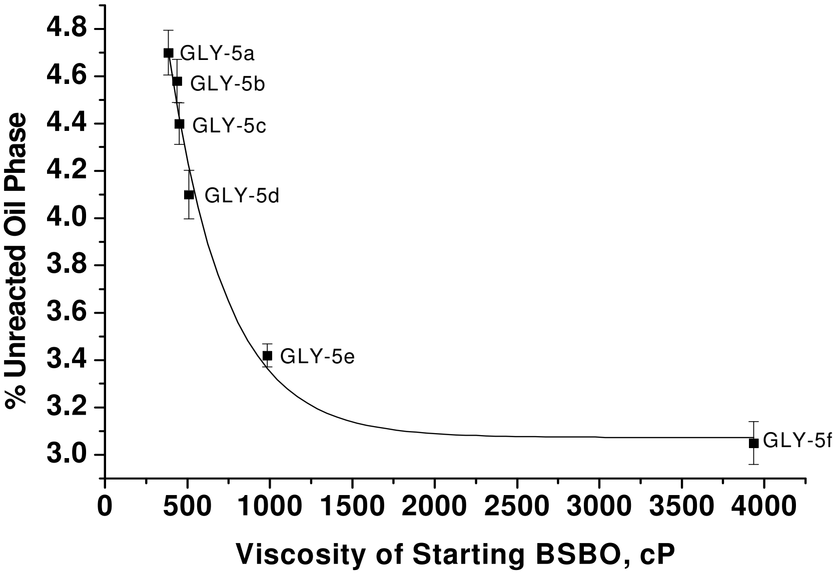


Figure 17. Effect of viscosity of the starting BSBO on the extractability of the final GLY-5 polyol.

3.3.3. Properties of polyurethanes based on GLYC-BSBO polyols

Rigid foams were prepared using the GLYC-BSBO polyols and several controls as summarized in Table 6. In each case, 50% by mass of the B-side was the indicated polyol and 50% was Voranol®490. Table 8 summarizes the foaming performances and graphically in Figure 18 where the traditional trade-off in compressive strength versus density can be observed. The line indicates the Voranol®490 which was created by varying the water content (water at 2.5%-4.5% as a blowing agent) in the formulation.

The BSBO control was inferior to the other polyols. The very low hydroxyl functionality (16.0 mg KOH/g) created poorly cross-linked foam with a very low compressive strength (121 kPa).

The GLY5-BO product was also, debatably, inferior to the other polyols (aside from BSBO). The hydroxyl number, viscosity, and acid number of GLY5-BO and GLY-5 were essentially identical. One possible difference in these products is that the butylene oxide converted the primary functionality available with the glyceride into an ether link and secondary functionality. This would lead to a lower reactivity for the GLY5-BO and higher density.

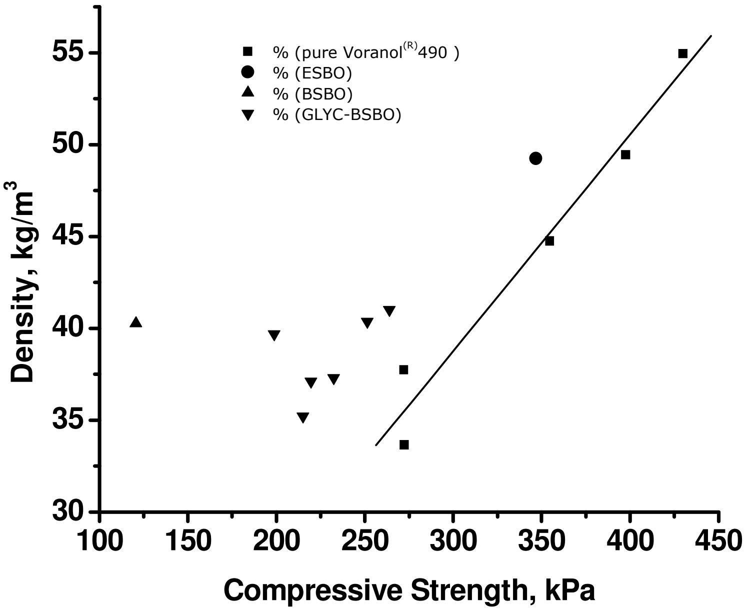


Figure 18. Soy polyol foam properties plotted against control (pure Voranol® 490) at varying quantities of water as blowing agent (2.5, 3.0, 3.5, 4.0, and 4.5%)

The remaining five soy-based polyols (GLY-5, GLY-10, GLY10-BO, GLY10-ESBO, and GLY10-KOH) exhibited similar behavior when the dependence of rigid foam density on urethane-formulation water content is taken into account. The products exhibited a decrease in compression strength of about 17%. In some applications, the lower compression strengths are acceptable. The advantage of these products is that they can be synthesized at nearly 100% yield from relatively inexpensive renewable materials in a relatively simple process.

A comparison of the GLY-10 product to the GLY10-BO reveals that only minor changes in physical properties occurred when butylene oxide was used to neutralize residual acidity. Both samples eventually gelled and both had similar viscosities prior to gelling. The butylene oxide is believed to slow down the reactivity of the alcohol groups (converts primary alcohols to secondary alcohols) and this results in higher densities. In the case of GLY10-BO versus GLY5-BO, the higher glycerol content of the GLY10-BO product could have provided enough added functionality to maintain crosslinking at a level consistent with the better of the other products.

Table 8. Properties of polyurethane products obtained from the synthesized soy-based polyols. Three percent water is used as blowing agent.

Polyols	**Thermal Conductivity (W/mK)**	**Density (kg/m^3)**	**Compressive Strength (kPa)**
Voranol™490	0.02660	49.44	398
ESBO	0.03247	49.25	347
BSBO	0.03326	40.27	121
GLY-5	0.02930	37.11	219
GLY-10	0.02820	37.31	232
GLY5-BO	0.02805	39.70	199
GLY10-BO	0.02955	41.02	264
GLY10-ESBO	0.02665	40.38	251
GLY10-KOH	0.03058	35.23	215

When ESBO rather than butylene oxide was used to neutralize residual acidity (GLYC10-ESBO versus GLYC10-BO), a more-viscous polyol was formed. The high functionality of the ESBO (4-5 versus 1) resulted in crosslinking of the polyol prior to the urethane formulation with a corresponding increase in viscosity. ESBO is effective for both neutralizing acidity and joining smaller low-functional alcohols into larger more-functional polyols.

The GLY10-KOH material had the lowest of all densities. It also had the highest viscosity and acid number. The viscosity was similar to the GLY-10 product indicating that the potassium hydroxide may not have been needed to promote transesterification (it is a catalyst). The differences in performance between the GLY-10 and GLY10-KOH products can be attributed to the differences in acidity. And the differences in acidity may be attributable to slightly different workups after reaction.

From best to worst thermal conductivity, the GLY10-ESBO and Voranol®490 control had similar, good thermal conductivities. The GLY-10 product also had a good thermal conductivity with acceptable combinations of density and compressive strength. Good thermal conductivity appeared to correlate with the molecules having the highest average functionality (reflected on the polyols' viscosity values). In the complex gelling and blowing reactions of the rigid foaming process, an early high degree of crosslinking is critical to keep the foam cells closed (which leads to low thermal conductivities).

3.4. CONCLUSIONS

Polyurethanes made from the transesterification of glycerol with BSBO exhibited good physicochemical properties. The better attainable performances were comparable to those of petroleum-based Voranol®490 except for an 18% reduction in compressive strength. The advantages of a GLYC-BSBO polyol series include: 1) simple non-hazardous processing to form polyols, 2) yields to polyols approaching 100%, and 3) feedstock costs that are considerably less than the propylene oxide and butylene oxide used to prepare petroleum-based polyols.

Use of 10% glycerol versus 5% glycerol with the BSBO led to a marked increase in crosslinking as evaluated in extraction results from test wafers. The best-performing soy-based derivatives were the GLY10-ESBO and GLY-10 products.

When compared to the synthesis and use of monoglycerides in rigid foams, the 10% BSBO materials require less glycerol (10% versus 30%) and have the potential for attaining functionalities in excess of two. It is noted that free fatty acids formed during the BSBO preparation, and so, some monoglycerides were in most of the formulations evaluated in this study. A reduction in free fatty acid content of the BSBO should lead to improved performances.

The results of these studies represent the first report of polyols based on the transesterification of BSBO and glycerol. In view of this, the 18% lower compressive strengths are a very reasonable entry point for this technology. Reduction of fatty acid content in the BSBO and optimization of the rigid foam formulation are two of many possible methods to improve the compressive strengths.

3.5. REFERENCES

1. P.-p. Kiatsimkul, G. J. Suppes, W. R. Sutterlin, Industrial Crops and Products, 25, 202 (2007).
2. Z. S. Petrović, W. Zhang, I. Javni, Biomacromolecules, 6, 713 (2005).
3. R. Herrington, K. Hock, Flexible Foams. The Dow Chemical Company, Midland, MI, 1997.
4. P.O Powers, Journal of the American Oil Chemists' Society, 27, 468 (1950).
5. S. Z. Erhan, Q. Sheng, H.-S. Hwang, Journal of the American Oil Chemists' Society, 80, 177 (2003).
6. H. Noureddini, V. Medikonduru, Journal of the American Oil Chemists' Society, 74, 419 (1997).
7. American Society for Testing Materials. Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols, Designation: Procedure E222-00 (reapproved 2005) Method A; West Conshohocken, PA, 2005.
8. AOCS. Official Methods and Recommended Practices of the American Oil Chemists' Society, Acid Value, AOCS Te 1a-64, Champaign, IL, 1997.
9. American Society for Testing Materials. Standard Test Method for Iodine Value of Drying Oils and Fatty Acids, Designation: E222-00 (reapproved 2005) Method A; Philadelphia, PA, 1997.

10. AOCS. Official Methods and recommended Practices of the American Oil Chemists' Society, Oxirane Oxygen in Epoxidized Materials, AOCS Cd 9-57, Champaign, IL, 1997.

11. American Society for Testing Materials. Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus, Designation: C518-04 (reapproved 2004); West Conshohocken, PA, 2004

12. American Society for Testing Materials. Standard Test Method for Apparent Density of Rigid Cellular Plastics, Dessignation: D 1622-03 (revised 2003); West Conshohocken, PA, 2003.

13. American Society for Testing Materials. Standard Test Method for Compressive Properties Of Rigid Cellular Plastics, Designation: D 1621-04 (revised 2004); West Conshohocken, PA, 2003.

14. Y.-C. Tu, P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 105, 453 (2007).

15. H. Noureddini, D. W. Harkey, M. R. Gutsman, Journal of the American Oil Chemists' Society, 81, 203 (2004).

16. N. K. Guthalugu, M. Balaraman, U. S. Biochemical Engineering Journal, 29, 220 (2006).

17. P. H. L. Moquin, F. Temelli, J. W. King, M. M. Palcic, Journal of the American Oil Chemists' Society, 82, 613 (2005).

CHAPTER 4

NON-CATALYTIC POLYMERIZATION OF ETHYLENE GLYCOL AND EPOXY MOLECULES FOR RIGID POLYURETHANE FOAM APPLICATIONS

4.1. INTRODUCTION

Polyols derived from vegetable oils have gained major commercial interest and significant attention in scientific research owing to the availability, biodegradability and unique properties of the triglycerides. These triglycerides have at least one unsaturated fatty acid moiety, which can be modified by catalytic or non-catalytic means to introduce the desired hydroxyl functional groups in the polyol structure. A number of physicochemical approaches and even biological methods have been used to functionalize unsaturated vegetable oils to yield industrially useful polymer derivatives and polyols [1,2]. Soybean oil has been most promising as starting material for polyol conversion due to its volume and price stability in addition to its versatility for chemical modification.

More recently, epoxidized soybean oil has received increased attention because they are of interest both as chemical intermediates and as end-products. A wide variety of ring-opening reactions are possible because of the high reactivity of the oxirane group. Cleavage of the epoxy functional group by reaction with carboxylic acids leads to ester alcohols, with water to diols, and with alcohols to ether alcohols [3]. Different epoxidized soybean oil-based polyols were evaluated in terms of its potential to replace up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications. Results have shown that the polyurethane foams not only had superior thermal conductivity but better density and compressive strength properties than had foams made from 100% petroleum polyol. The epoxidized soybean oil alone when used in a 50:50 blend with a petroleum-based polyol had similar density versus compressive strength properties with foams made from 100% petroleum-based polyol [4].

Palm oil-based epoxidized diethanolamides were used to produce a new type of rigid polyurethane foam. The epoxides retained in the diethanolamides reacted with isocyanate during foam production in the presence of $AlCl_3$-THF complex catalyst to form oxazolidone linkages in the polyurethane network. The resulting foams had improved thermal and mechanical properties but required high isocyanate loading to produce quality rigid foams [5]. Rigid polyurethane foams are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate) [4]. Rigid foam formulation typically requires a high hydroxyl value (OH Number) in the 400-500 mg KOH/ g range to obtain the necessary rigidity [6].

Based upon these previous studies, higher isocyanate loading was often required to react with vegetable oil-based polyols to obtain polyurethane foams with comparable mechanical and thermoinsulating properties to that of petroleum-based polyols. The objectives of this study were to evaluate an approach for preparing a high average equivalent weight soy-based epoxy polyol, test its potential to replace up to 75% of the petroleum-based Voranol®

490 in waterborne rigid polyurethane foam applications, and evaluate the reduction in isocyanate loading in the rigid foam formulation (pure epoxidized soybean-oil compared with the synthesized soy-based epoxy polyol). Epoxidized soybean oil (ESBO) is reacted with ethylene glycol (EG) at optimum reaction conditions without catalyst keeping the acid number less than 1 and a Gardner color index less 7 for product quality.

An increase in viscosity and a decrease in weight percentage of oxirane oxygen were observed with different EG loading (for the same reaction time and temperature), which is indicative of oxirane ring opening and polymerization. In this paper, a series of polyols are presented based on variation in the amount of ethylene glycol added to ESBO. Extractability characterization was performed in elastomer test-wafers. Rigid foams were prepared with characterization of density, compressive strength, and thermal conductivity.

4.2. METHODS AND MATERIALS

4.2.1. Materials

Voranol® 490 polyether polyol (a petroleum-based polyol made from propylene oxide and a sucrose /glycerin base with the following properties: 4.3 alcohol functionality, 460 average molecular weight, and 490 hydroxyl number) and PAPI® 27 (a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4 wt % of NCO content) were obtained from Dow Chemical (Midland, MI). Epoxidized soybean oil (ESBO) (Vikoflex® 7170) was supplied by ATOFINA Chemicals

(Philadelphia, PA). Ethylene glycol (≥99% *ReagentPlus*) was purchased from Sigma Aldrich (St. Louis, MO). Catalysts (POLYCAT® 5 or pentamethyldiethylenetriamine is a liquid tertiary amine mainly used as a blowing catalyst; and POLYCAT® 8 or dimethylcyclohexylamine is a standard liquid amine catalyst used in rigid foaming formulation) and a silicone surfactant (Dabco® DC 5357) were from Air Products and Chemicals (Allentown, PA) gratis. Single-distilled water (4 MΩ.cm) was used as the blowing agent.

4.2.2. Chemical analyses

Hydroxyl values of polyols were determined according to an American Society for Testing and Materials (ASTM) Procedure E222-00 (reapproved 2005) Method A [7]. Another method of hydroxyl content determination was performed according to American Oil Chemists' Society (AOCS) Official Method Tx 1a-66 [8]. Acid numbers (mgKOH/g sample) of all reaction products were evaluated according to the AOCS official method (AOCS Te 1a-64, 1997) [9]. Iodine values (centigram, cg I_2/g sample) of the polyol samples were determined using ASTM Designation: D1959-97 [10]. Epoxy content of the samples were measured according to AOCS official method (AOCS Cd 9-57, 1997) [11]. The dynamic viscosities (centipoise, cP measured at 20℃) of the samples were determined using Model RS100 Rheometer (Haake–Thermoelectron). Gardner color index of the polyol samples were evaluated according to ASTM D1544 (edited D6166, 1998) [12].

A Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA) was used to measure the thermal conductivity of the polyurethanes (PUs) according to ASTM Procedure C518-04 [13]. Densities of foam samples were determined according to ASTM Procedure D 1622-03 [14]. Compressive strengths of foam samples were measured using a TA.Hdi Texture Analyser (Texture Technologies, Scarsdale, NY) according to ASTM Procedure D 1621-04a [15]. Thermal conductivity measurements were performed after curing the foams for 24 hours while density and compressive strength measurements were performed after 7 days sample storage.

4.2.3. Soy-based polyol synthesis

Non-catalytic batch synthesis of ESBO-EG polyols was carried out in a 300-mL Bench Top Model 4561 Parr stirred vessel. About 200 grams of ESBO was poured into the Parr reactor vessel. Pure EG was added to the same vessel at varying quantities (0%, 2%, 7% and 9% by weight based on ESBO). The mixture reacted in a closed Parr vessel with constant stirring at a temperature range of 150^{o}C-300^{o}C at 1-10hr reaction times. Kinetic studies were performed on the samples to evaluate the effects of EG concentration and reaction conditions on the chemical properties of the ESBO-EG polyol products. Table 9 presents relevant chemical physicochemical properties of these polyol products.

Table 9. Physicochemical properties and reaction conditions for the synthesized polyols.

Polyol Code	Description[a]	Acid Value, mg KOH/g (±0-5%)	Oxirane Oxygen, % (±0.2-3%)	Viscosity, cP (±0.2-1%)	Gardner Color Index[b]	Unreacted Oil Phase, % (±0-38%)	AOCS Hydroxyl Value, mg KOH/g (±2-4%)	ASTM Hydroxyl Value, mg KOH/g (±0.3-5%)
Ctrl A	pure ESBO	<0.20	7.18	362	1	17.8	11.0	352
Ctrl B	Voranol® 490	<0.20	<0.10	>10,000	1	0.38	484	484
EG-3	ESBO+7%EG, 250°C/1h	0.18	5.71	467	4	1.83	153	370
EG-4	ESBO+7%EG, 250°C/3h	0.20	5.59	512	5	1.65	158	363
EG-5	ESBO+2%EG, 250°C/5h	0.45	5.98	530	3	5.28	81.0	320
EG-6	ESBO+7%EG, 250°C/5h	0.66	4.86	600	6	1.34	169	322
EG-7	ESBO+9%EG, 250°C/5h	0.68	4.22	647	6	0.92	202	325
EG-8	ESBO+9%EG, 250°C/10h	0.72	2.53	1360	6	0.47	211	268

[a] Reactions in a closed Parr reactor. All reaction products were one-phase.

[b] Gardner color index of water is 1 and carbon black is 16.

4.2.4. Extractability test

A single-step plastic extraction method was used to determine the extent of polymer crosslinking between the polymeric MDI (PAPI® 27) and polyol products. Polymeric MDI and the sample polyol in a weight ratio of 1:2 was well mixed in a small disposable aluminum pan. The resulting product was left to dry for 10 hours in a convection oven at 110°C. The dry sample was then cooled to room temperature and cut into thin sheets for unreacted oil extraction. About 1 gram of the cut sample was soaked in a 1:4 by volume *n*-hexane-cyclohexanol solution for 15 minutes after which the mixture was filtered. Both permeate and retentate were dried in a vacuum oven at 110°C for 2 hours. The percentage of unreacted oil phase was calculated by mass balance.

4.2.5. Fourier-transform infrared spectroscopic analyses

A Thermo Scientific Nicolet™ 380 FT-IR equipped with Smart Orbit diamond ATR Attachment (Thermo Electron Corp., Madison, WI) was used to characterize the functional groups in ESBO-EG polyols. A total of 64 scans of each sample from 4000 to 400 cm^{-1} wavenumber range were obtained at a resolution of 2 cm^{-1}.

4.2.6. Polyurethane formation

A foaming procedure described by Tu et al. [4] detailed in Table 10 was used in this study. Voranol® 490, ESBO-EG polyol, catalysts, surfactant, and blowing agent were added by weighing into a 500-mL disposable plastic drinking cup and mixed at 3450 rpm for 10–15 seconds. The mixture was allowed to degas for 120 s and then PAPI® 27 was rapidly added while continuously stirring for another 10–15 seconds at the same speed. The mixture was 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). Fifty and seventy-five percent replacements of Voranol® 490 by the ESBO-EG polyol were performed using isocyanate index of 100 (where both alcohol and epoxy is used to calculate the index). Modification in the foaming was done to evaluate the effect of heating the polyols prior to foaming. The polyols were placed in a microwave oven for 9 seconds at high power. Higher peak foaming temperatures were achieved (measured by infrared temperature sensor). Catalysts, surfactant, and water were then added and mixed. The plastic cup containing the B-side components was then subjected to a 50°C convection oven for 5 minutes before adding the A-side component.

Table 10. Water-blown rigid polyurethane formulation

Materials	Parts by weight (per 100)
B-side	
Voranol®490	50
ESBO-EG Polyol	50
Polycat®5	1.26
Polycat®8	0.84
DABCO DC 5357	2.5
Blowing Agent (Water)	3.0
A-side	
PAPI®27	100*

*Isocyanate index is the percentage of the actual amount of isocyanate used over the theoretical amount of isocyanate required.

4.3. RESULTS AND DISCUSSION

4.3.1. Polyol physicochemical properties

High residual acidity is an undesirable polyol property. Acid numbers more than 10 mg KOH/g polyol will have a significant impact on polyurethane foam synthesis as it competes with hydroxyls to react with isocyanates and consumes catalysts [16]. Industry standard requires acid numbers to be less than 4. Table 9 shows that a reaction temperature of 250°C yields a polyol with an acid number less than 1 even at longer reaction times up to 10 hours. EG-5, EG-6, EG-7, and EG-8 polyols were selected for foaming studies. Two methods of polyol hydroxyl value determination were used in the study as mentioned above. ASTM Procedure E222-00 Method A measures both the epoxy and the hydroxyl group content of the polyol. This hydroxyl value is used in the calculation of the amount of polymeric MDI (PMDI) to be added in the rigid foam formulation. AOCS Official Method Tx 1a-66 measures only the hydroxyl group content of the polyols which evaluates the quantity of the hydroxy funtionality of the polyols. Only the latter method was used to explain the kinetics of polymerization via oxirane opening.

4.3.2. Oxirane opening polymerization

Near-constant hydroxyl values were observed with respect to time as shown in Figure 19 for polyol products obtained from a starting mixture of 7% EG loading in ESBO at 250^{o}C reaction temperature. Longer reaction times did not significantly affect the hydroxyl values of the polyols with EG loading and reaction temperature kept constant at 250^{o}C.

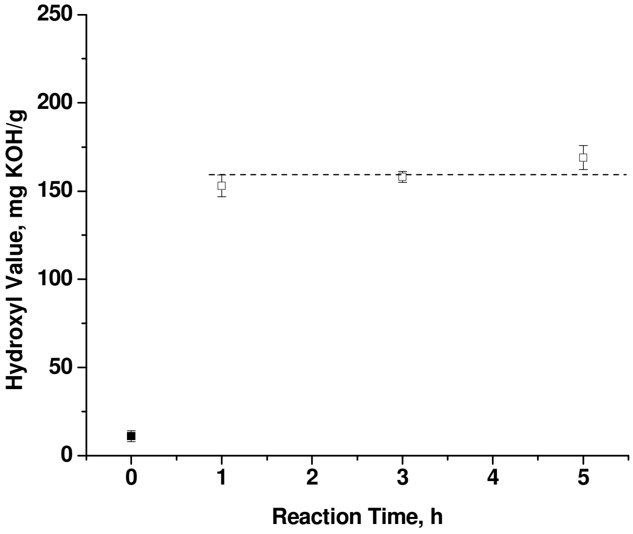


Figure 19. Dependence of hydroxyl value on reaction time for the batch processing of ESBO-EG polyols. EG loading (7%) and reaction temperature (250°C) were kept constant (■ - pure ESBO, □ - ESBO-EG polyols).

The polyols underwent oxirane opening polymerization to some extent as evidenced by the reduction of oxirane oxygen content from 7% (no reaction- 0 hr) to 4.86% (5 h reaction time), which is about 30% decrease in oxirane oxygen content confirmed by the wet analytical method. Viscosity values of these polyols have also increased with pure ESBO as reference. Longer reaction times will mean more oxirane-ring opening (decrease in epoxy group content) and higher conversion to ESBO-EG complex with conservation in hydroxyl group content. An EG molecule with two terminal hydroxyls reacts with ESBO and yields two hydroxyls.

Figure 20 shows a steep increase in hydroxyl values of the resulting polyol products as the concentration of EG was increased from 2% to 9%. It is important to note that these products (EG-5, EG-6, and EG-7) were reacted completely as observed by the polyols' uniform phase appearance.

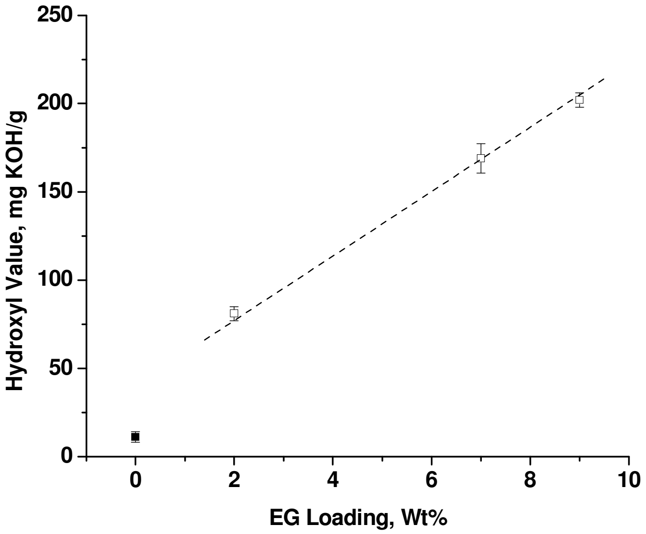


Figure 20. Dependence of hydroxyl value on EG loading for the batch processing of ESBO-EG polyols. Reaction time (5 h) and reaction temperature (250°C) were kept constant (■ - pure ESBO, □ - ESBO-EG polyols).

Viscosity values were observed to have increased and oxirane oxygen decreased as well. This phenomenon was still attributed to the ring-opening reaction of the epoxy groups in ESBO and the simultaneous formation of an ESBO-EG complex suggested in the reaction scheme shown in Figure 21.

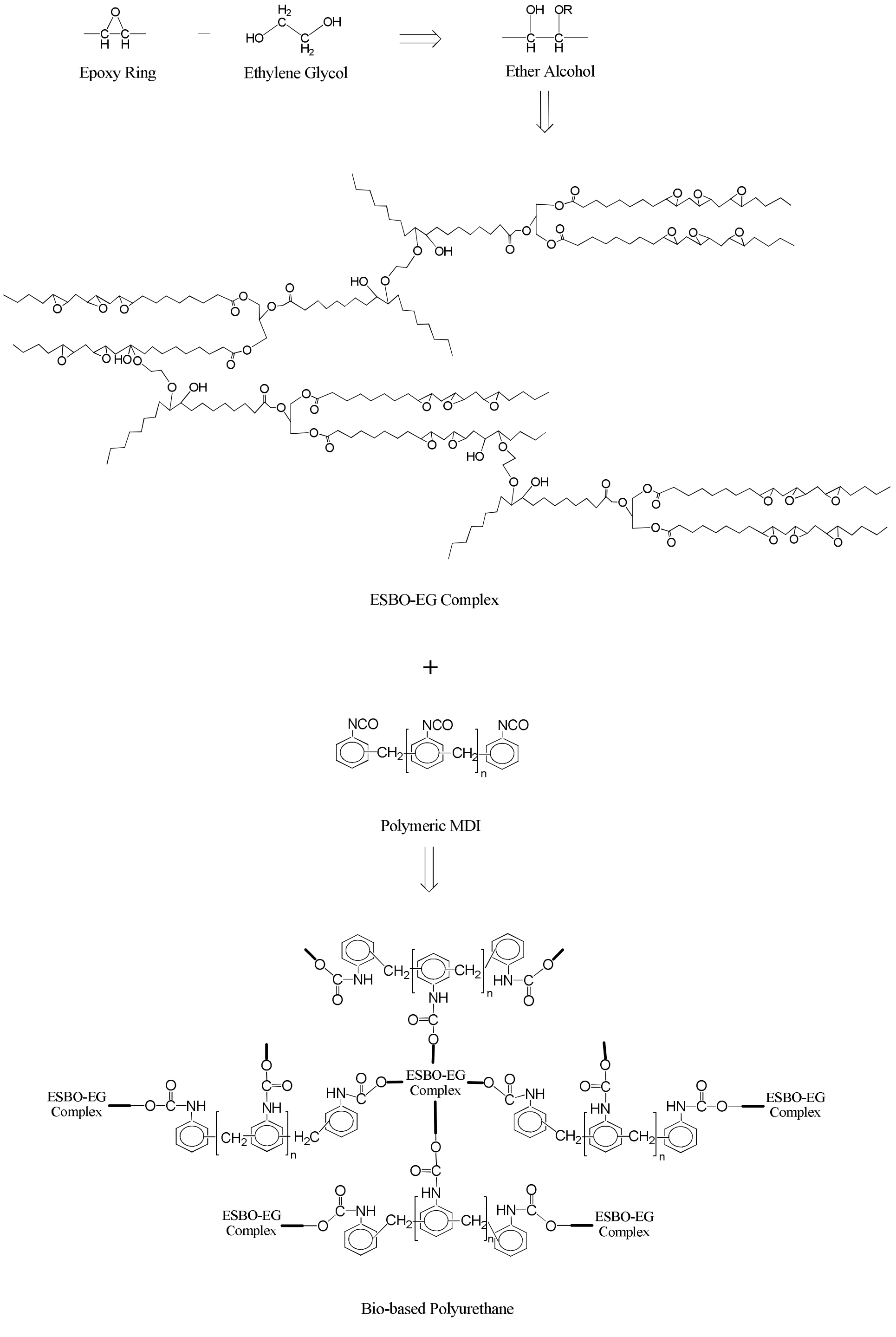


Figure 21. Two-step reaction schemes from the formation of ESBO-EG complex to the synthesis of bio-based polyurethane foam.

An epoxy ring reacts with ethylene glycol to form an ether alcohol. In the bigger scheme, simultaneous conversion of the reacting species into ether alcohol will effect a complexation between ESBO and EG, thus the polymerization. The resulting increase in viscosity and consumption of oxirane oxygen content were mainly attributed to this complexation which is suggested to be the main product.

4.3.3. FTIR analysis of ESBO-EG polyols

A comparison of FTIR spectra [17-19] of both pure ESBO and EG is shown in Figure 22. Symmetric/asymmetric methyl or C-H stretching for both ESBO and EG are shown at different but closer wavenumbers. The absorption intensity of hydroxyl groups at 3000-3700 cm^{-1} which represents the OH vibration band is much stronger in EG spectra than ESBO which showed a flat line in this region, indicative of less or absence of H-bonded OH and other –OH groups. Most of the –OH groups found in EG were attributed to the terminal alcohol groups, which also exhibit COH bending at 1396 cm^{-1}. The characteristic oxirane absorption peak at 823.3 cm^{-1} and the ester carbonyl band (C=O) centered at 1734.5 cm^{-1} of the ESBO spectra are obviously not present in EG.

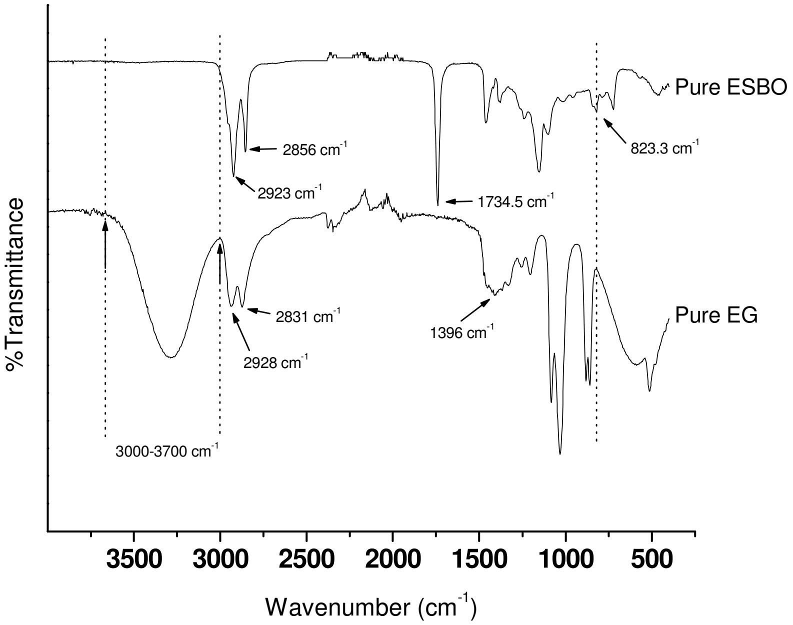


Figure 22. FTIR spectra of pure ESBO and EG.

Figure 23 shows the spectra of ESBO-EG polyols processed at different times (1, 3, and 5h, corresponding to EG-3, EG-4, and EG-6) but the same EG loading and reaction temperature of 7% and 250°C, respectively. The oxirane absorption peaks and the OH vibration bands of these ESBO-EG polyols have shown almost the same intensity. This seems to indicate reaction time does not significantly affect oxirane opening polymerization as reflected by close hydroxyl (Figure 19), viscosity and oxirane oxygen content (Table 7) values of the polyols.

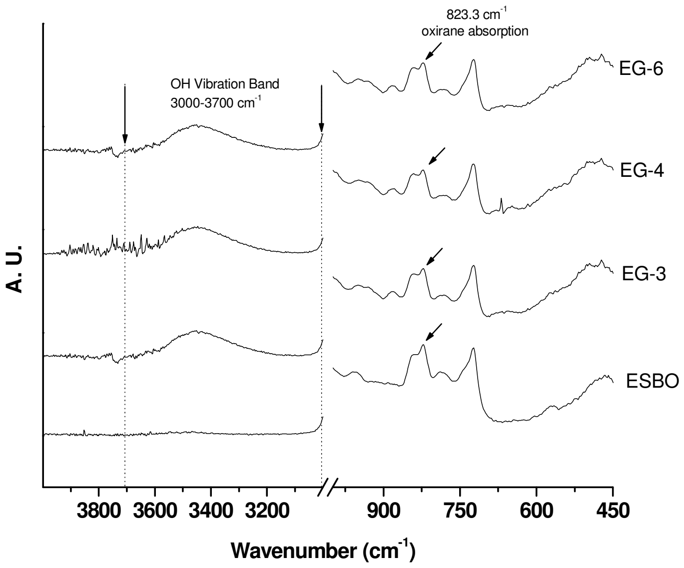


Figure 23. FTIR spectra of ESBO-EG polyols processed at different times with EG loading (7%) and reaction temperature (250°C) kept constant.

Figure 24 shows the spectra of ESBO-EG polyols processed at different EG loading (2, 7, and 9%, corresponding to EG-5, EG-6, and EG-7) but the same reaction times and temperature of 5 h and 250°C, respectively. The reaction products were observed to be one-phase, indicative of a complete reaction. At higher EG loading such as sample EG-7 (at 9%) it seems there is greater tendency for oxirane ring polymerization compared to EG-5 (at 2%). This is consistent with their corresponding oxirane absorption band at 823.3 cm^{-1} wavenumber. A steep change in both viscosity and hydroxyl values of these samples indicate a high degree of polymerization, thus, a high average functionality of the polyols. The plot of hydroxyl values versus EG loading shown in Figure 20 is consistent with the OH vibration band at 3000-3700 cm^{-1} which showed the highest intensity for EG-7 and lowest intensity with EG-5.

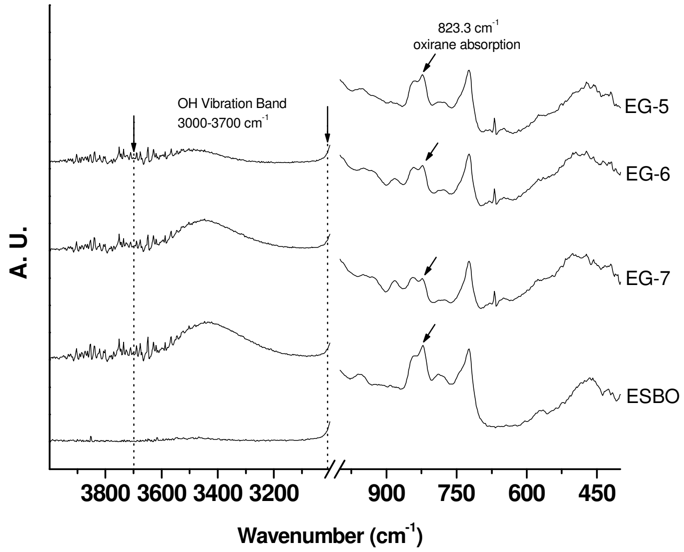


Figure 24. FTIR spectra of ESBO-EG polyols processed at different EG loading with reaction time (5h) and reaction temperature (250°C) kept constant.

4.3.4. Extractability tests

An initial crosslinking performance test or extractability test was done on the ESBO-EG polyols as well as the controls. This test is a straightforward reaction of the polyol and PMDI described in the Methods part. The basic polymerization reaction of this test is described elsewhere [20] and is shown in the reaction scheme-second step in Figure 21. Figure 25 shows a correlation of the % unreacted oil phase of the polyol and its viscosity.

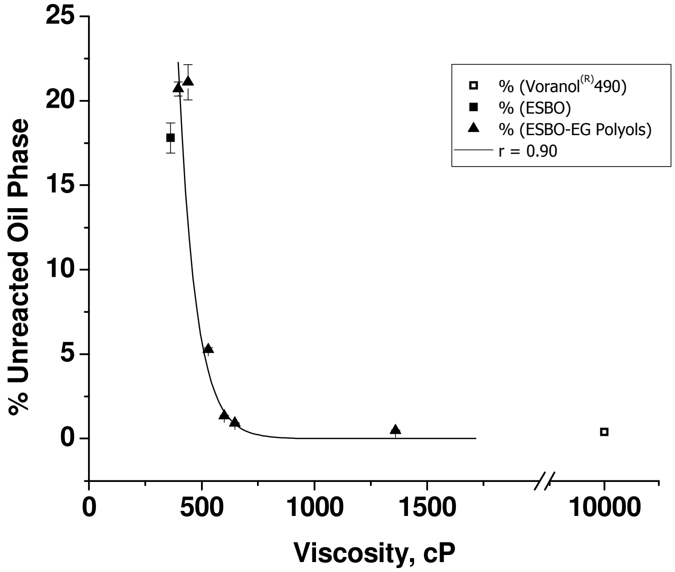


Figure 25. Crosslinking performance and viscosity relationship of ESBO-EG polyols.

A high viscosity polyol product indicates a higher degree of oligomerization or complexation between ESBO and EG. . The trend shows that the higher the viscosity of the ESBO-EG polyol the lower its extracted unreacted oil phase. Viscosity is significantly related to the hydroxyl content of the polyol as shown in Figure 26.

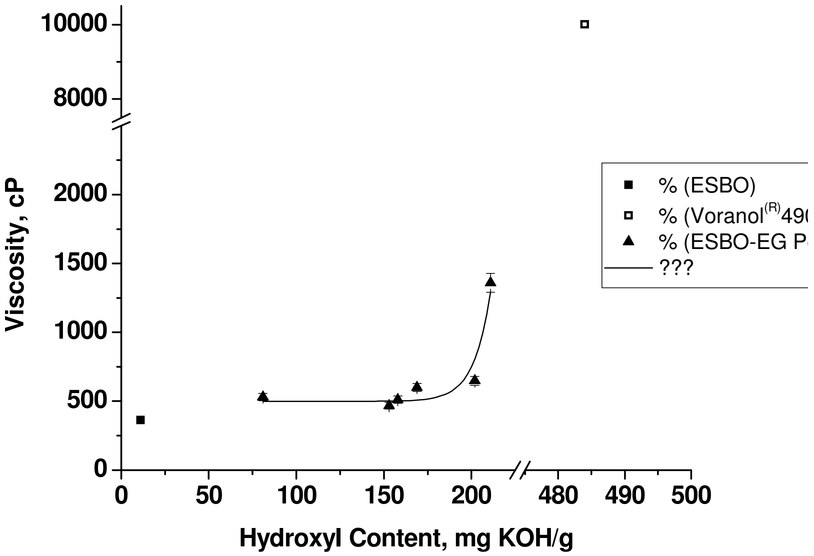


Figure 26. Hydroxyl content dependence of the viscosities of ESBO-EG polyols.

Viscosity generally increases with an increase in the hydroxyl content of the polyol. At the same quantity of PMDI, there are more reactive hydrogen sites for the isocyanate to react with in the case of EG-8 (OH# = 211) than with EG-5 (OH# = 81.0) to form the polymer network, therefore, higher hydroxyl content means lower unreacted oil extractability. Both the unreacted polyol and unreacted PMDI will be extracted by hexane-based solution as weight percentage of unreacted oil phase. For the ESBO-EG polyols tested, the highest hydroxyl content of EG-8 achieved the lowest mass percentage of the unreacted oil phase at 0.47% while EG-5 achieved the lowest mass percentage at 5.28%. The control Voranol® 490 presents the lowest (0.38%) extractability not only due to its high hyroxyl content (484 mg KOH/g) but that most of its hydroxyl groups are primary, which is 3.3 times more reactive than secondary hydroxyl groups which made up most of the ESBO-EG polyols. ESBO has the lowest hydroxyl content (11.0 mg KOH/g) of all polyols tested, which translates to its highest (17.78%) unreacted oil extractability value.

Polyol average equivalent weights (average molecular weights at the same hydroxyl content) increase with increasing complexation of the starting components. A more efficient crosslinking performance is related to higher average weights of the ESBO-EG polyols. Higher viscosity ESBO-EG polyols have higher average equivalent weights achieved by increasing the degree of oligomerization reflected in the increased hydroxyl content of the polyols as shown in Figure 26. Voranol$^{®}$ 490 exhibits the highest viscosity of about 10,000 cP and highest hydroxyl content most of which are primary as oppose to ESBO with the lowest viscosity of 362 cP and hydroxyl content (lowest average equivalent weight)..

4.3.5. Foam thermal conductivity

Thermal conductivity of the foam samples can be affected by many factors including the polyol's $\mathrm{OH_m}$, or the combined ASTM hydroxyl values of the polyol and Voranol$^{®}$ 490 replacement. For a 50% Voranol$^{®}$ 490 replacement, the $\mathrm{OH_m}$ of the polyol blend is computed as follows:

$$\mathrm{OH_m} = \frac{[(\text{ASTM OH Value of Voranol}^{®}\text{ 490})*50] + [(\text{ASTM OH Value of Polyol})*50]}{100}$$

The $\mathrm{OH_m}$ values of the ESBO-EG polyols ranges from 376 to 463 mg KOH/g compared to pure Voranol$^{®}$ 490 with 484 mg KOH/g and ESBO with an $\mathrm{OH_m}$ of 418 mg KOH/g. A higher $\mathrm{OH_m}$ means higher reactivity of the polyos with isocyanate due to a higher concentration of the active hydrogen sites. Rigid foam made with 100% Voranol$^{®}$ 490 exhibits lower thermal conductivity

(0.026 W/mK) than ESBO-EG and ESBO foams (0.026-0.030 W/mK). This could be attributed to the fact that in addition to the petroleum-based polyol's higher OH_m, it has also most of its hydroxyl functional group as primary compared to the soy-based polyols which have mostly secondary. A faster reaction rate could be expected with Voranol® 490 and PMDI resulting in a stronger three-dimensional polyurethane network capable of holding up most of the carbon dioxide evolved in the reaction of PMDI and water.

Secondary hydroxyl group has slower reaction rate with PMDI resulting in a weaker polymer network and increased number of open cells which would be susceptible to air convection and escape of carbon dioxide, both of which contribute to a higher thermal conductivity [4]. Other factors that affects foam thermal conductivity includes thermal conductivity of gas trapped inside the foam cells, thermal conductivity of the foam cell mebrane material, convection of cell gas, cell size and orientation, closed cell content, foam density, and thermal radiation [21]. ESBO presenting the highest thermal conductivity (0.032 W/mK) can be attributed to its chemical structure which contains the lowest hydroxyl groups (all secondary) at 12 mg KOH/g. ESBO has the potential to form oxazolidone with PMDI but at a higher temperature.

Foaming reaction rates can be evaluated by measuring the peak foaming temperatures of the polyols. Higher peak foaming temperature reflects higher heat generation of the polyols foamed at the same isocyanate index. ESBO-EG polyols foamed at 50% Voranol® 490 replacement and 100 isocyanate index have lower peak temperatures (range = 88.3 –93.3°C) than the peak temperature of Voranol® 490 (104°C). This can be attributed to the presence of primary hydroxyls as the majority of its hydroxyl functional group which react faster with PMDI than do polyols with most of its hydroxyl functional groups as secondary hydroxyls. In addition, Voranol® 490 has a higher OH_m value than any of the ESBO-EG polyols as mentioned earlier, therefore a higher tendency of the PMDI to react with the hydrogen reactive sites. ESBO has the lowest peak foaming temperature (78°C) of the polyols tested and is therefore suggested to have the lowest PMDI reactivity and is reflected in its high thermal conductivity.

4.3.6. Foam density

ESBO-EG polyols have a foam density values in the range of 42.4-46.6 kg/m^3, lower than the control Voranol® 490 (46.7 kg/m^3) and ESBO (47.3 kg/m^3). An increase in density may be governed by the rate of reaction of the polyol and isocyanate that would eventually make up the polyurethane network after curing of the rigid foams. A faster reaction and higher conversion rate would make up a denser crosslinked three-dimensional polyurethane network that eventually gives a higher foam density and volume. A slower reaction and conversion rate translates to a weak three-dimensional polyurethane network which consequently results in a higher density of the final foam due to the shrinkage of the dimensions making it heavier for the same volume. OH_m alone does not give enough information as to the type of hydroxyls present in the polyols or polyol blends. In the case of Voranol® 490 which has most of its hydroxyls as primary, a higher foam density is expected. ESBO presenting the highest foam density can be attributed to poor polymer network causing shrinkage of the structure.

4.3.7. Foam compressive strength

Like foam density, compressive strength is also governed by the rate of reaction of the polyol and isocyanate [22]. A faster reaction and higher conversion of the A-side and B-side reactants would make up a denser and stronger crosslinked three-dimensional polyurethane network that eventually gives a denser and stronger final foam property as exemplified by the petroleum-based control Voranol® 490. Figure 27 presents a strong correlation (r =0.80) between the extractability of the starting ESBO-EG polyol and the compressive strength of its resulting rigid foam.

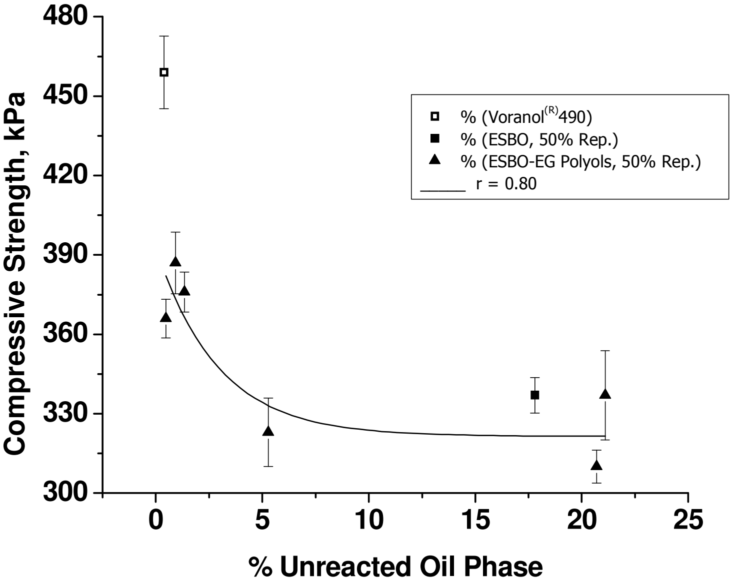


Figure 27. Compressive strength and polyol extractability relationship of the rigid polyurethane foams.

The lower the unreacted oil phase of the starting polyol the higher compressive strength of its rigid foam (at 50% Voranol® 490 replacement and 100 isocyanate index) will be expected. Lower extractability translates into a higher viscosity ESBO-EG polyol (higher degree of polymerized ESBO and EG proposed in Figure 21) resulting in a complex with the hydroxyl groups distributed throughout the macromolecule. This high equivalent weight complex will react with PMDI forming an even denser complex that consequently gives a stronger structure in the final rigid foam. Higher compressive strength rigid ESBO-EG foam can be achieved by increasing the average equivalent weight of its starting polyol. Initial crosslinking test was necessary in order to predict the final compressive strengths of the rigid foam. The highest compressive strength achieved by the ESBO-EG polyol tested was 387 kPa with % unreacted oil phase of 0.92. Comparatively, Voranol® 490 has a compressive strength of 459 kPa with 0.38% unreacted oil phase. Although, these two polyols have close extractability values, their hydroxyl content (primary and secondary alcohol content) varies which made a significant impact in the final compressive strength.

4.3.8. Reduction in PMDI

Table 11 presents the summary of the foam properties of the controls and the synthesized ESBO-EG polyol specifically EG-8. EG-8 was evaluated at 50% and 75% Voranol® 490 replacement and a modification in the foaming procedure was done on EG-8 at 50% replacement by heating the polyol blend as described in the Methods section. In the regular foaming of EG-8 at 50% replacement, better foam properties were achieved: a lower thermal conductivity value at 0.027 W/mK, a value close to the thermal conductivity of

Table 11. Comparison of polyurethane foam properties.

Polyols	% PMDI Used (100 iso-index)	Thermal Conductivity, W/mK	Density, kg/m^3	Compressive Strength, kPa
Voranol® 490	61.6	0.026	46.6	459
ESBO (50R)*	60.0	0.032	47.3	337
EG-8 (50R)	57.4	0.027	42.0	366
EG-8 (50R) – heated	57.4	0.028	41.5	336
EG-8 (75R)*	55.0	0.030	41.8	311

Voranol® 490 (0.026 W/mK), and a higher compressive strength than ESBO. A higher density was measured for ESBO, although there was no evident collapse of the foam observed after curing. The ESBO may act as a “filler” for the interaction between the highly reactive primary hydroxyl groups of

Voranol® 490 and PMDI. Oxazolidone formation between the epoxy rings and isocyanate is unlikely at lower temperatures. A 5% reduction of PMDI was achieved for the regular foaming of EG-8 with ESBO as the basis.

The heated EG-8 polyol produced rigid foam with almost similar thermal conductivity and density values with the unheated EG-8 polyol. The objective of the polyol heating was to achieve a higher peak foaming temperature to boost the reaction rate between the A-side and B-side components. A significant drop in the compressive strength value was observed for the heated EG-8 foam. This might be due to the collapse of the polyurethane cells caused by an imbalance of gelling and blowing rates. Foaming of EG-8 at 75% replacement of the Voranol® 490 was also possible and displayed better thermal conductivity than ESBO foam.

There was no significant change in the density of the foam with respect to EG-8 at 50% replacement but the compressive strength dropped to about 15%. As the Voranol® 490 replacement increases, there is also a corresponding decrease in the amount of primary hydroxyl functional group which made up most of the petroleum-based polyol. This will slow down the reaction rate between the polyol blend and PMDI resulting in a less dense and weaker polyurethane network that will cause a weaker compressive strength. A reduction of about 8% was achieved for EG-8 foams at 75% replacement.

4.4. CONCLUSIONS

In conclusion, high average equivalent weight polyols were synthesized by non-catalytic polymerization of ESBO and EG. A high molecular weight ESBO-EG complex was the major component of the polyols tested for waterblown rigid polyurethane foams. EG-8 polyol at 50% Voranol® 490 replacement displayed closer thermal conductivity (0.027 W/mK) compared with that of 100% Voranol® 490 and better compressive strength compared with that of ESBO foam at 50% replacement. EG-8 polyol at 75% replacement was also possible and displayed a better thermal conductivity (0.030 W/mK) compared with that of ESBO at 50% replacement. The compressive strength dropped significantly by about 15% which was mainly attributed to a slower reaction rate of the polyol blend and PMDI (decreased primary hydroxyl content). The variation in hydroxyl content (primary and secondary alcohol content) of the polyols made a significant impact in the final compressive strength. EG-8 polyols at 50% and 75% replacement reduced PMDI quantity used by about 5% and 8% based on ESBO foam (at 50% replacement). Heating the polyols did not significantly improve foam properties.

4.5. REFERENCES

1. L. Zhang, H. K. Jeon, J. Malsam, R. Herrington, C. W. Macosko, Polymer, 48, 6656 (2007).
2. P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Z. Lozada, Y.-C. Tu, Industrial Crops and Products, 27, 257 (2008).

3. G. Knothe, J. T. P. Derksen, Recent Developments in the Synthesis of Fatty Acid Derivatives, AOCS, Champaign, 1999.
4. Y.-C. Tu, P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 105, 453 (2007).
5. C. S. Lee,T. L. Ooi, C. H. Chuah, S. Ahmad, Journal of the American Oil Chemists Society, 84, 1161 (2007).
6. A. Guo, I. Javni, Z. Petrovic, Journal of Applied Polymer Science, 77, 467 (2000).
7. American Society for Testing Materials. Polyurethane raw materials: determination of hydroxyl numbers of polyols, Designation: Procedure E222-00 (reapproved 2005) Method A; West Conshohocken, PA, 2005.
8. AOCS. Official Methods and Recommended Practices of the American Oil Chemists' Society. Hydroxyl value of epoxidized oils, AOCS Tx 1a-66, Champaign, IL,1997.
9. AOCS. Official Methods and Recommended Practices of the American Oil Chemists' Society. Acid value, AOCS Te 1a-64, Champaign, IL,1997.
10. American Society for Testing Materials. Standard test method for iodine value of drying oils and fatty acids. Designation: E222-00 (reapproved 2005) Method A; Philadelphia, PA, 1997.
11. AOCS. Official Methods and recommended Practices of the American Oil Chemists' Society. Oxirane oxygen in epoxidized materials, AOCS Cd 9-57, Champaign, IL,1997.
12. American Society for Testing Materials. Standard test method for color of transparent liquids. Designation: D6166 (reapproved 1998); Philadelphia, PA, 1997.

13. American Society for Testing Materials. Standard test method for steady-state thermal transmission properties by means of the heat flow meter apparatus, Designation: C518-04 (reapproved 2004); West Conshohocken, PA, 2004

14. American Society for Testing Materials. Standard test method for apparent density of rigid cellular plastics. Designation: D 1622-03 (revised 2003); West Conshohocken, PA, 2003.

15. American Society for Testing Materials. Standard test method for compressive properties of rigid cellular plastics. Designation: D 1621-04 (revised 2004); West Conshohocken, PA, 2003.

16. Kiatsimkul, P.; Suppes, G. J.; Sutterlin, W. R. Industrial Crops and Products, 25, 202 (2007).

17. A. A. Lubguban, J. A. Lubguban, M. T. Othman, R. V. Shende, S. Gangopadhyay, R. D. Miller, W. Volksen, H.-C. Kim, Thin Solid Films, 516, 4733 (2008).

18. Y.-C. Tu, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 111, 1311 (2009).

19. G. Biresaw, Z. Liu, S. Z. Erhan, Journal of Applied Polymer Science, 108, 1976 (2008).

20. R. Herrington, K. Hock, Flexible Foams. The Dow Chemical Company, Midland, MI, 1997.

21. F. Oertel, Polyurethane Handbook, Macmillan: New York, 1985, p.323.

22. Y. Lin, F. Hsieh, H. E. Huff, E. Iannotti, Cereal Chemistry, 73, 189 (1996).

CHAPTER 5

C. RUGOSA HYDROLYSIS OF POLYMERIZED SOYBEAN OIL FOR FLEXIBLE POLYURETHANE FOAM APPLICATIONS

5.1. INTRODUCTION

Soybean oil (SBO) is the world's most widely used edible agricultural product derived from soybean, a major oil plant which is cultivated worldwide. The United States alone has the potential to produce about 30 billion pounds of soybean oil which is considered an inexpensive commodity. Refined soybean oil contains more that 99% triglycerides and about eight major fatty acids with different degrees of unsaturation, including linoleic, oleic, linolenic, palmitic, and stearic acids.

The physical and chemical properties of the soybean oil reflect the difference in composition of these fatty acids in terms of chain length, composition, distribution and location [1]. A certain variety of soybean has been developed to contain high oleic oil using enhanced breeding technology [2]. Primarily, soybean oil is used for food applications but in recent years a number of research and development efforts have advanced the use of soybean oil in a wide range of applications including thermosetting resins [3], biodiesel [4], polyols for polyurethane applications [5-8] coating material for Li battery [10], nanoshells for targeted molecular delivery [11], and many others.

Polyols are one of the major components in polyurethane foam production. Recent emphasis on renewable content has reactivated interest on natural oil-based polyols to minimize dependency on petrochemical sources and promote green chemistry while taking advantage of the vegetable oil's low cost and unique properties [11]. Various physicochemical and biochemical methods were employed to functionalize the generally less reactive, low molecular weight, and structurally-inconsistent plant oils to produce competitive bio-based polyols.

Lipases have been widely researched and used to promote hydrolysis reaction with natural oils. Kiatsimkul et al. [6] have reported the preparation of high hydroxyl equivalent weight polyols from free enzyme hydrolysis of bodied soybean oil. In their method, soybean oil is polymerized at high temperature prior to low-temperature catalysis with different free and immobilized enzymes to attach hydroxyl functionality for urethane-based applications. Among the enzymes tested, *C. rugosa* has shown to have significantly hydrolyzed palmitic acid and was recommended to be used for soy-based polyol production.

Aside from free-enzyme hydrolysis of bodied soybean oil, immobilized enzymes are mostly used for organic synthesis especially lipases used for esterification reactions in organic media [12]. Immobilization of enzymes has been widely researched because of their advantages over using free enzymes in biocatalysis. Immobilized enzymes improve storage and operational, thermal and conformational stabilities. Also, immobilization allows for easier recovery for reuse.

A number of research articles have reported the use of chemically-functionalized soybean oil for flexible foam production including: replacement of up to 50% petroleum-based polyol with epoxidized soybean oil [13, 14]; substitution with a polyol synthesized from epoxidation and epoxy-ring opening reaction of soybean oil [15]; and production of flexible slabstock polyurethane foam solely from soy-based polyols [16] but none on the polyols were made from bodied soybean oil hydrolyzed by *C. rugosa* lipase.

One of the objectives of this paper was to synthesize high hydroxyl equivalent weight soy-based polyol by initially bodying the soybean oil, a process of heat-polymerization by Diels-Alder mechanism by which double bond migration (producing the more reactive conjugated dienes), other isomerizations, and transesterification lead to a complex product mixture with an increased viscosity [17, 18]. Another significant objective was to functionalize the bodied soybean oil by *C. rugosa* hydrolysis to impart hydroxyl functionality through free and immobilized enzyme methods, and lastly, to test the hydrolyzed bodied soybean oil in a flexible polyurethane foam formulation and compare foaming results with both petroleum-based polyol and soy-based polyols.

5. 2. METHODS

There are three distinct processes in this section. The first step is the heat polymerization of the bodied soybean oil and its analyses. The second step is the *C. rugosa* hydrolysis of the polymerized soybean oil followed by the last which is the flexible foam production.

5.2.1. Bodying of soybean oil

5.2.1.1. Materials

Soybean oil of RBD grade (refined, bleached, deodorized) with an iodine value of 130-136 was obtained from a local supplier. Anthraquinone or AQ (90%) and chemicals for iodine number determination which include sodium thiosulfate solution (0.1N), potassium iodide, and Wijs solution were purchased from Sigma-Aldrich (St. Louis, MO). The ethanol (95% aq.) used for acid number analysis was purchased from the university (Chem Store, Dept. of Chemistry) and high purity grade nitrogen was obtained from Praxair (St. Louis, MO).

5.2.1.2. Methods

Two established methods of soybean oil batch bodying were performed in our laboratories; one was thermal and the other catalytic. In the non-catalytic method, bodied soybean oil was produced by heating soybean oil up to 330^{o}C under a nitrogen gas environment until the desired bodied soybean oil properties are obtained. The heating process was performed in 2-L Parr reactor with volatile matter being removed during the reaction by a nitrogen purge. Typical values obtained for a process at 330^{o}C for 1 h were: iodine number = 100 cg I_2/g, acid number = 15 mg KOH/g, viscosity = 68 cP.

In the catalytic method, 2.0-5.0% anthraquinone was added as catalyst to promote soybean oil polymerization at a lower temperature relative to the non-catalytic process. Typical values obtained for a process at 280^{o}C for 6 h and 2.5% AQ were: iodine number = 91 cg I_2/g, acid number = 15 mg KOH/g, viscosity = 1158 cP [19].

Acid numbers (mg of KOH/g of sample) of all reaction products were evaluated according to the American Oil Chemists' Society (AOCS) method (AOCS Te 1a-64). Iodine values, IV (cg of I_2/g of sample) of the polyol samples were determined with ASTM D 1959-97. The dynamic viscosities, η (cP) of the samples, measured at 20°C, were determined with a model RS100 rheometer (Haake-Thermoelectron, Newington, NH).

5.2.2. Hydrolysis of bodied SBO (BSBO) by C. rugosa lipase

5.2.2.1. Materials

C. rugosa lipase (Lipase AY "Amano" 30) was from Amano Enzyme, USA (Elgin, IL). Prepared phosphate buffer solution and distilled water (both at pH 7) were used as mixing medium for the hydrolysis reaction. Bodied soybean oil was obtained using the process described above. Na_2CO_3 solid powder used in free fatty acid-removal washing was purchased from Sigma-Aldrich (St. Louis MO, USA). Epoxidized soybean oil (Vikoflex 7170) or ESBO used in the neutralization reaction of the hydrolyzed products was supplied by Atofina Chemicals (Philadelphia, PA). Rexyn$^{®\text{-}203}$ (OH) weak base anion exchanger, Na-alumino-silicate molecular sieve, and Amberlite$^{®}$IR-120-P strong acid cation exchanger were purchased from Fisher Scientific (Pittsburgh, PA).

5.2.2.2 Methods

For the kinetic study, bodied soybean oil was partially hydrolyzed by the commercial *C. rugosa* lipase without any surfactant or organic solvent. Bodied soybean oil (40 g), phosphate buffer at pH 7.0 (40 g), and *C. rugosa* lipase (40 mg - 0.1% by wt based on BSBO) were placed in a 250-ml flask equipped with a heating ring and a magnetic stirrer. The reaction conditions were controlled by an external computer-controller (NI simulator). The batch reaction sample was constantly stirred and kept at one-phase consistency at optimum temperature of 45°C. Samples were collected for chemical analyses at 0, 2, 4, 8, 18 and 24 hrs. After each collection, the reaction products were left at room temperature to cool, and then washed with water or a base solution of Na_2CO_3 (pH 9-10) and analyzed for acid numbers and extent of hydrolysis. The latter variable was defined by Kiatsimkul, et al. [6] by the following equation:

$$\%\ \textit{Hydrolysis} = \frac{\textit{acid number of reaction product before product workup (mg KOH/g)}}{\textit{190 mg KOH/g sample.}} \times 100$$

This equation is based on the premise that during the hydrolysis, the lipases will react with the carbonyl group to produce one free fatty acid and one hydroxy functional group.

In the synthesis of hydrolyzed products for flexible foam production, about 0.3-0.4% *C. rugosa* lipase was used and mixed with 250 g BSBO, 500 g water (pH 7) at 45°C with constant stirring in a 1-L reaction flask. After free fatty acid removal by base washing, the samples were analyzed for acid number and percent hydrolysis before neutralization. Hydrolyzed BSBO was then neutralized by ESBO at 170°C for several hours in a constantly-stirred partially-covered flask. The amount of ESBO added was based on a 1:0.5 epoxy per acid molar ratio. Typical acid number and epoxy content values for the neutralized polyols were <10.0 and <0.60, respectively. Epoxy contents of the samples were measured according to the official AOCS method (AOCS Cd 9-57). ^{1}H and ^{12}C NMR spectra of SBO, BSBO and hydrolyzed BSBO were recorded at room temperature using Bruker ARX 250MHz spectrometer (Billerica, MA).

Three different carrier supports were tested in the immobilization of C. rugosa lipase: Rexyn® 203 (anion exchanger), Sodium-Alumino-Silicate, and Amberlite®IR-120-P (cation exchanger). All supports were oven-dried prior to use. About 0.04 g of free lipase of *C. rugosa* in powder form was dissolved in 4 mL buffer 7.0 phosphate buffer solution. Enough quantity of each support was mixed directly with the lipase suspension and allowed to soak for 24 hours. The support materials were drained and dried in a dessicator for about 3 days prior to use.

Immobilization was carried out by preparing an equal weight percentage of buffer solution and BSBO. Reaction proceeded in a single-pass packed bed reactor (PBR) with the immobilized enzyme. PBR reactor properties: Bedlength = 12.5 cm, ID = 0.5 cm, Packed bed void fraction = 2%, Void volume = 0.047 mL, The feed was an equal weight percentage of the buffer solution and BSBO well-mixed to one-phase before starting the feed pump. The average flowrate measured was 0.17 mL/min in the course of 24 hours hydrolysis reaction. The control used free *C. rugosa* lipase of the same amount (0.04 g) to hydrolyze the same amount of BSBO.

5.2.3. Flexible polyurethane foam production

5.2.3.1. Materials

Hydrolyzed BSBO was obtained using the method described above and was used as 50% replacement for Voranol® 4701, a petroleum-based polyether polyol with a hydroxyl number of 34. PAPI® 27 was the A-side in the foam formulation. PAPI® 27 is a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO-functionality, has an average molecular weight of 340, and has 31.4% part by weight of NCO content. Voranol® 4701 and PAPI® 27were obtained from Dow Chemical (Midland, MI). Catalysts added include DABCO® 33-LV, DABCO® BL-17, stannous octoate, and dibutyltin dilaurate. DABCO® DC2585 was used as surfactant and diethanolamine was used as a crosslinker. All DABCO® chemicals were from Air Products and Chemicals (Allentown, PA). Stannous octoate and dibutyltin dilaurate were purchased from Sigma-Aldrich (St. Louis, MO) and diethanolamine from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

5.2.3.2. Methods

An initial extractability test was performed on the neutralized polyol to evaluate its isocyanate reactivity with the alcohol groups. An extractability method was established in our laboratory [20] using hexane-cyclohexanol solution to extract the unreacted oil phase. Polymeric MDI and polyol in a weight ratio of 1:2 were well mixed in a small disposable aluminum pan. The resulting product was left to dry for 10 hours in a convection oven at 110°C.

The dry sample was then cooled to room temperature and cut to thin sheets for unreacted oil extraction. About 1 gram of the cut sample was soaked in a 1:4 by volume cyclohexanol solution for 15 minutes after which the mixture was filtered. Both permeate and retentate were dried in a vacuum oven at 110°C for 2 hours. The percentage of unreacted oil phase was calculated by mass balance.

Flexible polyurethane foaming was performed according to the procedure used by Tu, et al. [13] using the hydrolyzed BSBO as the bio-based polyol replacement (50%). The density, 50% compression force deflection (CFD), 50% constant deflection compression (CDC), 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, 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, Williamsport, PA) set at 70°C and 6% RH for 22 h. 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 30–40 min. The compression set was calculated by the following equation:

$$C_t = (t_o - t_f)\ (100\%)\ / t_o$$

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.

5.3. RESULTS AND DISCUSSION

5.3.1. Heat-polymerization of soybean oil

Heat-polymerization or bodying of soybean oil has provided two important advantages, mainly, to promote crosslinking of SBO acylglycerols by interaction between the reactive double-bonds in the fatty acid components and to provide high equivalent weight molecule before any further alcohol functionalization. Heat-polymerization of soybean oil was done with and without catalyst (AQ). The advantage of catalytic bodying is that the same iodine number value can be attained at a lower temperature or a shorter time compared to non-catalytic SBO polymerization. However, catalytic bodying must undergo tedious downstream processing (separation process) to recover AQ from the product mass.

Figure 28a shows the proposed mechanism of heat-polymerization of SBO. It is generally a Diels-Alder reaction because of the presence of the diene functionality in linoleic acid (C18:2- 18 carbons, 2 double bonds) and linolenic acid (C18:3). In the course of heat bodying, double bond migrations produce the more reactive conjugated dienes, initiating an interaction between the conjugated diene and a substituted alkene or dienophile of another SBO acylglycerol to form a substituted cyclohexene system. This interaction decreases the overall iodine number with an observed increase in viscosity due to branching. Other possible interactions in heat-bodying include isomerization and transesterification reactions with the production of volatile components.

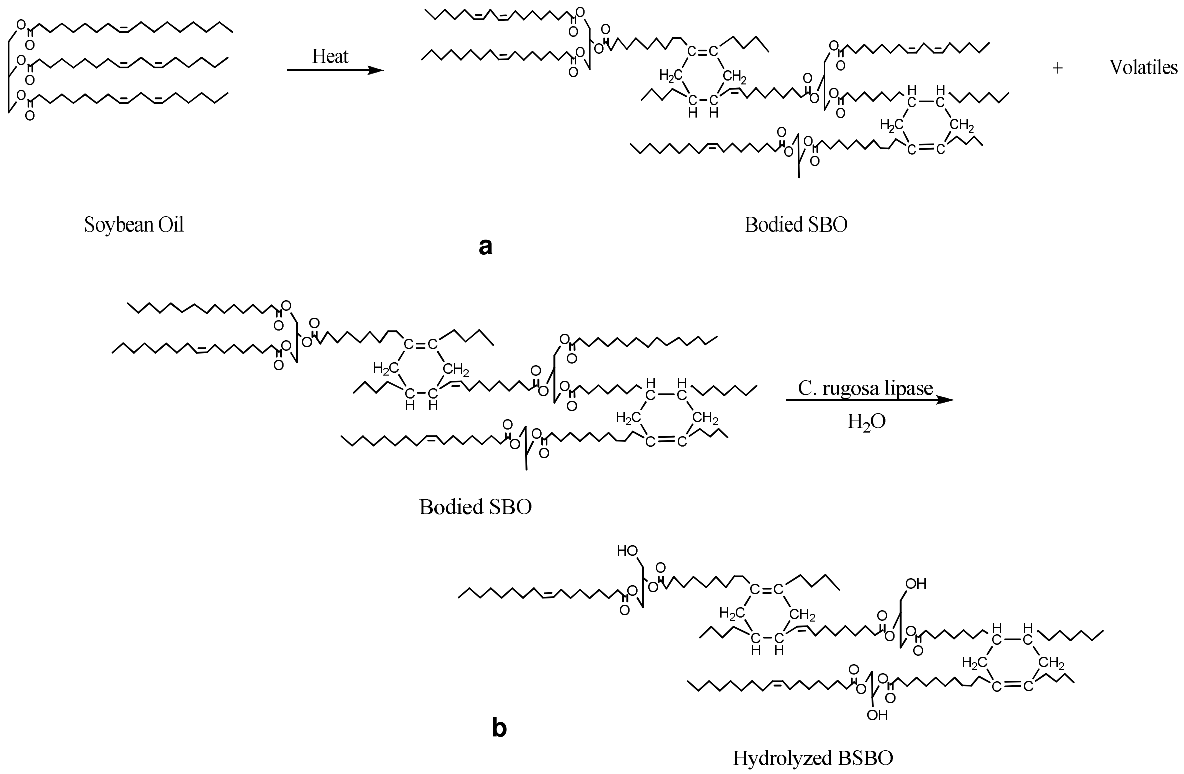


Figure 28. Reaction mechanism of a) heat-polymerization of soybean oil, and b) hydrolysis of bodied soybean oil by *C. rugosa* lipase.

In Figure 29 (^{1}H NMR) and Figure 30 (^{13}C NMR), spectra A and B compare the difference in structures of SBO [21, 22] and BSBO, respectively. In Figure 29A, five different spectra regions of proton chemical shifts indicate changes in the structure of SBO after heat-bodying. In region **a**, no significant changes in signal at 0.863-0.873 ppm of the terminal methyl protons of the ester components occurred; while in region **b**, disappearance of signal at 0.910-0.961 ppm of the bodied soybean oil indicates rearrangement of protons in the double bond between C-15 and C-16 of α-linolenic ester component due to either double bond disappearance or bond migration.

In region **c**, a decrease in signal intensity at 1.962-2.062 ppm can be observed from the spectra after heat-bodying. Protons in this region were slightly changed for all three unsaturated oleic, linoleic, and linolenic fatty esters. A more significant change in proton chemical shift can be observed in both regions **d** and **f**. The former being the characteristic signal of vinylic protons in succession found in both linoleic and linolenic ester components at 1.962-2.062 ppm and the latter, alyllic protons in all three unsaturated ester components with chemical shifts at 5.192-5.385 ppm.

This shows a major participation of linoleic and linolenic double bonds taking part in double bond rearrangement and oleic acid acting as dienophile to initiate Diels-Alder mechanism. There is no significant signal change in the proton chemical shift at 4.074-4.287 ppm, characteristic of protons in the triacylglycerol backbone, an indication of proton preservation after bodying.

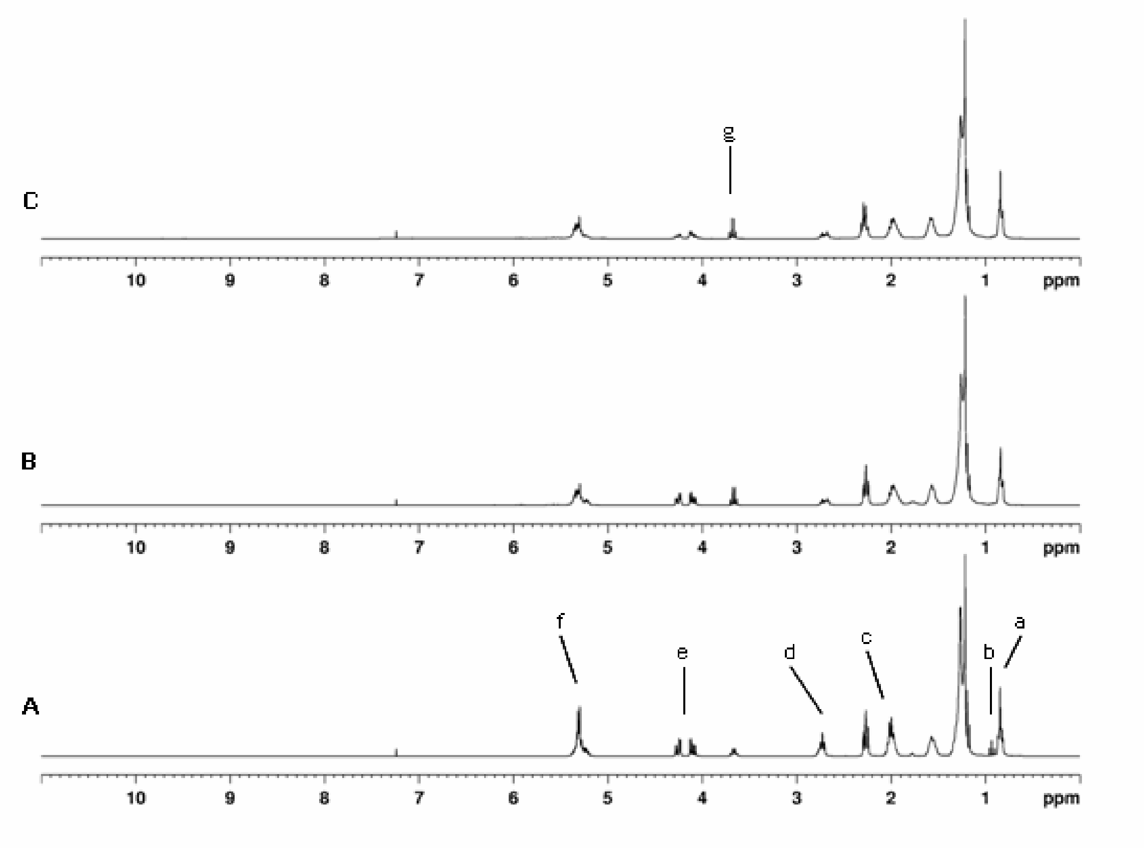


Figure 29. ^{1}H NMR spectra differentiation of (A) SBO, (B) BSBO, and (C) *C. rugosa*-hydrolyzed BSBO. Regions of chemical shifts include: a) δ 0.863-0.873 ppm –(CH2)n-CH3, b) δ 0.910-0.961 ppm –CH=CH-CH2-CH3, c) δ 1.962-2.062 ppm –(CH2)n-CH2-CH=CH-, d) δ 2.711-2.784 ppm -CH=CH-CH2-CH=CH-, e) δ 4.074-4.287 ppm protons in TG backbone, f) δ 5.192-5.385 ppm–CH=CH-, g) δ 3.632-3.703 ppm-suggests presence of hydroxyls.

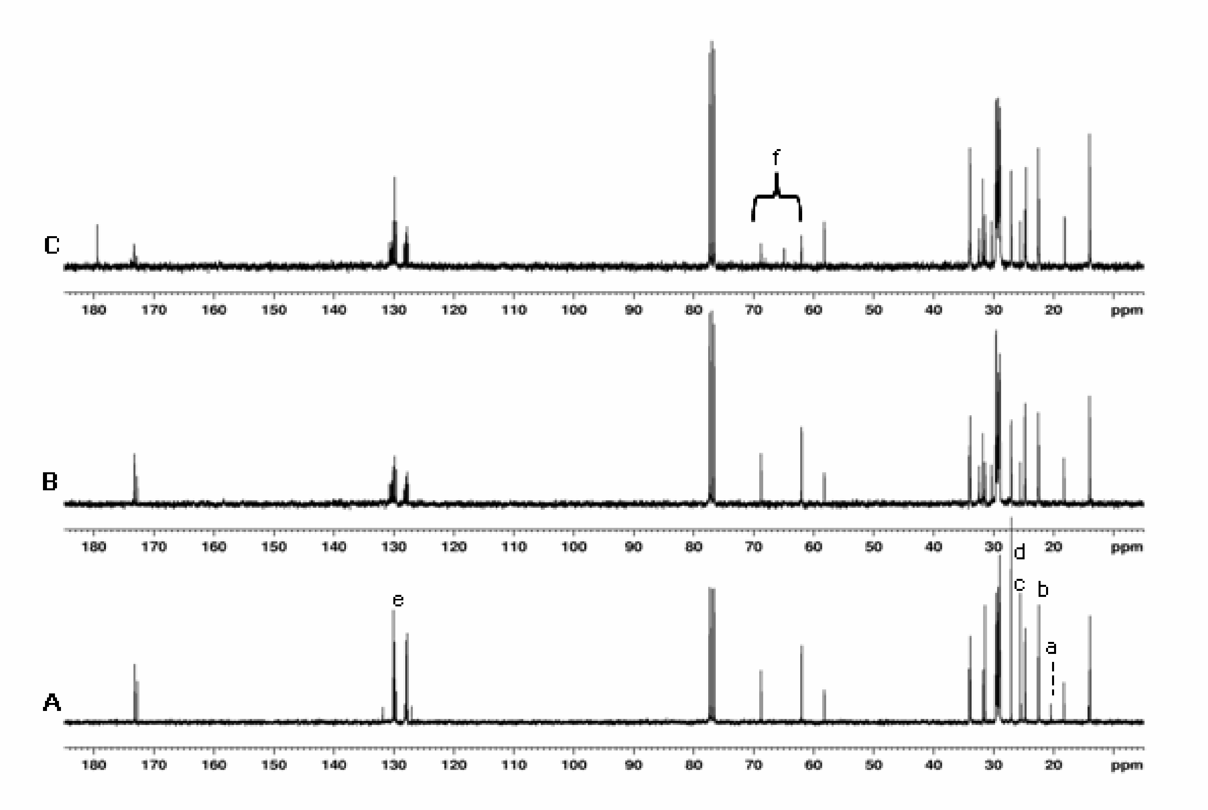


Figure 30. 13C NMR spectra differentiation of (A) SBO, (B) BSBO, and (C) *C. rugosa lipase* -hydrolyzed BSBO. Regions of chemical shifts of C in glycerol ester include: a) δ 20.47 ppm C-17 (α, β)-Linolenic, b) δ 22.50-22.61 ppm C-17 (α,β)-Linoleic, c) δ 25.45-25.55 ppm C-11, C-14 (α,β)-Linolenic, C-11 (α,β)-Linoleic, d) δ 27.12 ppm C-8 (α,β)-Oleic, Linoleic, Linolenic, e) δ 129.87-129.90 ppm C-10 (α,β)-Linolenic, δ 130.11 ppm C-9 (α,β)-Linolenic, f) δ 64.94-68.84 ppm-glycerol carbons.

The mechanism of SBO polymerization is further elucidated in the ^{13}C NMR spectra of the SBO before and after heat-polymerization. Five regions of significant chemical shifts are shown in Figure 30A and B which present C signals of oleic, linoleic, and linolenic fatty esters in the α and β chains. In region **a** at 20.47 ppm, position C-17 disappears completely after bodying. This indicates that the closest C=C relative to this carbon position almost always participate in either bond migration to form the conjugated diene or act as a dienophile. Regions **b**, **c**, **d**, and **e** show the same decrease in signal intensity of carbon positions closest to the C=C double bonds. Most carbon position rearrangements occur in the linoleic and linolenic fatty ester components as shown in the spectra which suggest that these two fatty esters were the major participants in the bodying process.

The effect of initial bodying of soybean oil was evident in the extractable content experiment done on both samples. The end-use of the soybean oil acylglycerols will be in the polyurethane applications so that an initial reactivity test with the A-side component (polymeric MDI) is significant. Using the extractability method described above, SBO and bodied SBO were each separately reacted with pMDI in a 2:1 polyol to isocyanate mass ratio. Table 12 shows the % extractable content of SBO and BSBO at 99.7% and 4.92%, respectively. This presents a significant finding on the effect of initially bodying SBO with A-side reactivity. Higher equivalent weight acylglycerol translates to a lower extractable content which reflects higher reactivity with the A-side component.

Table 12. Extractability values of some hydrolyzed soy-based polyol samples after neutralization. Lesser value indicates greater reactivity of the polyol with isocyanate.

Polyol	Substance	Extractable material, %
C1	SBO	99.7
C2	ESBO	17.8
C3	BSBO (IV = 91, η = 1158 cP)	4.92
S	Hydrolyzed BSBO (HBSBO, OH value = 121)	0.83
T	HBSBO (OH value = 101)	0.36
P1	HBSBO (OH value = 92.5)	0.91

5.3.2. Hydroxyl-functionalization of BSBO by C. rugosa lipase

Previous results in our laboratory has shown that *C. rugosa* lipase was the biocatalyst of choice [6] to largely hydrolyze palmitic acid, thus, lowering the concentration of the less reactive saturated fatty acids while promoting attachment of primary hydroxyl functionality. The proposed reaction mechanism of the hydrolysis of BSBO catalyzed by *C. rugosa* lipase is shown in Figure 28b. The figure presents the shortest fatty acid (palmitic acid) in the polymerized SBO being hydrolyzed and replaced by a primary hydroxyl. Hydrolysis of fatty acid lowers the molecular weight of SBO but can be countered by increasing its molecular weight by an initial heat-bodying. Primary hydroxyls formed as a result of selective hydrolysis by *C. rugosa* is a significant effect in the polyol's reactivity with isocyanate. Primary hydroxyls are threefold more reactive with isocyanate compared to other hydroxyl positions in the fatty acid.

Figure 31 shows the extent of hydrolysis of BSBO by *C. rugosa* lipase in the course of 72 hours of constant-stirred batch reaction at the optimum temperature of 45℃. It can be observed that the steepest increase in % hydrolysis occurs between 0-10th- hour of reaction and continues to increase up to the 20th-hour. Hydrolysis then slowed down starting at the 20th-hour and seems to plateau up to the 72nd-hour where it attained about 40% hydrolysis. Decreased enzyme activity through time and steric hindrance due to the released fatty acid moieties crowding are possible causes of decreased hydrolysis of BSBO.

Higher enzyme loading and longer reaction times are suggested to attain polyol products with hydroxyl numbers greater than 50 mg KOH/g which is typical value for commercial soy-based polyols. Hydroxyl values can be approximated as equal to the acid number of the hydrolysis product before neutralization because one hydroxy is formed when one fatty acid is hydrolyzed. Removal of free fatty acids released during hydrolysis is necessary in the product workup to lower the acid number which is an undesirable property in the final polyol for urethane application. Polyol neutralization step is necessary because high acid number polyol delays reaction times and competes with functionalized hydroxyls for isocyanate consumption.

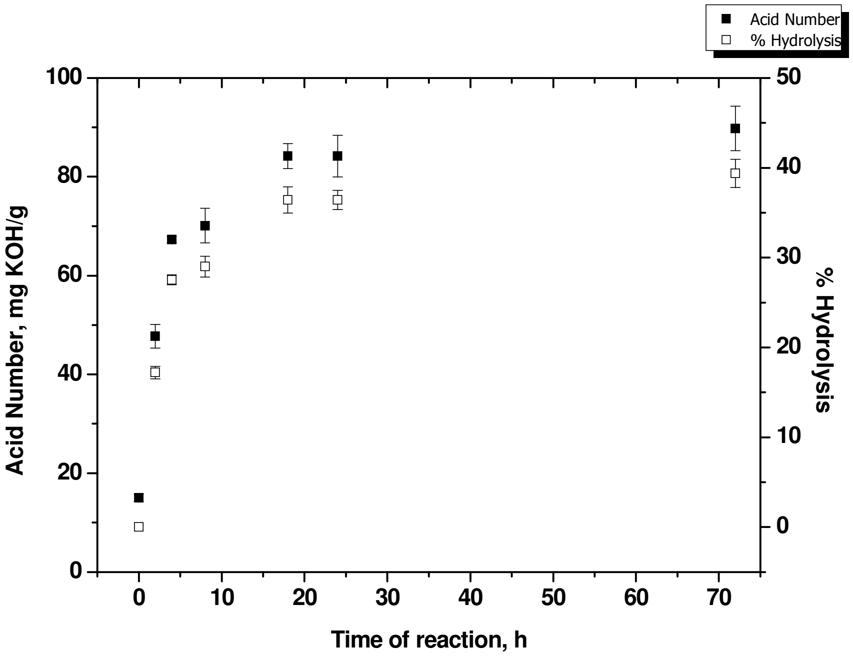


Figure 31. Hydrolysis kinetics of BSBO by free C. rugosa lipase at 45℃ constant-stirred batch reaction. The BSBO had a starting acid value of 15 mg KOH/g, iodine value of 100 cg I2/g, and viscosity of about 70 cP.

Polyol neutralization methods include the initial base-washing of the hydrolysis product and epoxy reaction at higher temperature. Base washing with aqueous Na_2CO_3 (0.5 M, pH 11.0) easily removed the fatty acids soaps which were mostly short-chain free fatty acids which separates as another phase from the ester glyceride phase. In the experiment a reduction of about 10 mg KOH/g acidity was observed with multiple base-washing with the aqueous carbonate solution. Although base washing removes most of the free fatty acids of the hydrolysis products, some acid moieties supposedly released from the hydrolysis reaction might still be bound to other fatty acid attached to other ester glycerides so that another neutralization step is necessary to substantially reduce the undesirable high acidity of the polyol.

Epoxy reaction with the hydrolyzed BSBO (HBSBO) was carried out at 170℃ for several hours depending on the amount of acidity of the hydrolyzed BSBO. Epoxidized soybean oil was added as an epoxy source to neutralize acidity of samples using 1:0.5 epoxy per acid molar ratio. The epoxy groups of ESBO start to open at temperatures equal to or greater than 170℃ and react with the carboxylic acids and considerably lower the acidity of the sample. Possible side reactions include epoxy-epoxy and epoxy-hydroxyl reaction.

Figure 29 and 30 include the proton and carbon NMR spectra of BSBO after hydrolysis with *C. rugosa* lipase. Figure 29B and C show a spectral comparison of the proton chemical shifts of BSBO before and after enzyme hydrolysis. Two regions of significant proton shift changes can be observed in the spectra of BSBO and hydrolyzed BSBO. In region **g** at 3.632-3.703 ppm, more intense spectra were observed which suggests the presence of hydroxyl groups and at region **e** at 4.074-4.287 ppm, a considerable reduction in signal intensity can be observed of BSBO after hydrolysis. This suggests reduction of protons in the TG backbone after attachment of primary hydroxyls in the BSBO. The increase of hydroxyl content was reflected in the increase of signal intensity in region **g.** Figure 30B and C show one region of significant chemical shift at **f** (64.94-68.84 ppm) which is a characteristic signal of glycerol carbons. Significant reduction in signal intensity can be observed in this region which suggests that glycerol carbons of BSBO were significantly affected after hydrolysis either by hydroxyl attachment or cleavage.

For the immobilization studies, *C. rugosa* lipase was immobilized in three granular carriers: an anion exchanger, cation exchanger and a silicate molecular sieve material. Figure 32 shows the extent of hydrolysis for each support used compared to the free enzyme.

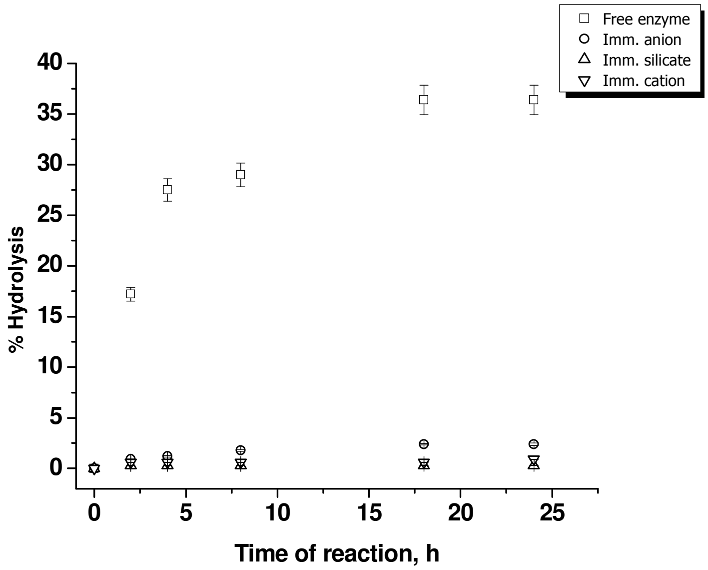


Figure 32. Immobilization of C. rugosa lipase using different supports including anionic and cationic exchange resins, and molecular sieve. Reaction was done in a packed-bed reactor at 45°C/24 h at an average flowrate of 0.17 mL/min.

In Figure 32 shown above, the free enzyme shows the highest hydrolysis percentage (36.4%) after 24 hours of reaction compared to the samples from the immobilized enzyme (2.4%). This high hydrolysis activity is reasonable since the enzyme was all in solution and was not diminished in quantity compared to the immobilized enzyme. C. rugosa lipase has different affinity with the different supports used which can be reflected in their activities. Among the carriers used, only the anion exchanger resin seemed to have some hydrolytic activity, the rest have plateau phase after 2 hours of reaction time which indicate less or no enzyme binding to the support. It is recommended that supports have the ability to entrap or covalently-bind to the lipase, among other methods.

5.3.3. Flexible polyurethane foaming of hydrolyzed BSBO

Table 13 summarizes the flexible foam properties derived from hydrolyzed BSBO with Voranol®4701 used as the control and replacement. SOVERMOL®1068 and Voranol®3136 were other commercial polyol controls used with flexible foam property values already previously known. SOVERMOL®1068 is an aliphatic triglyceride-type polyol with a higher hydroxyl number and Voranol®3136, a triol polyether polyol with lower hydroxyl number.

Table 13. Physical properties of flexible foams made from hydrolyzed BSBO by C. rugosa lipase batch-processed at 40℃ with constant stirring. The resulting product was neutralized with ESBO at an epoxy per acid ratio of 1:0.5. Flexible polyurethane foams were made by 50% Voranol® 4701 replacement.

Polyol	% Hydrolysis	ASTM OH No., mg KOH/g	Density, kg/m^3	CFD, kPa	CDC, %	Tear, N/m	Resilience, %
Voranol®3136	CONTROL	54.0	42.3	15.5	13.0	149	46.4
SOVERMOL®1068	CONTROL	193	51.1	8.4	45.7	333	18.2
Voranol®4701	CONTROL	34.0	44.8	8.8	5.50	142	44.9
S	92.0	121	59.4	27.9	34.1	216	25.2
T	100	101	46.2	12.0	37.2	148	18.7
P8	44.3	107	65.1	25.7	42.5	216	34.4
P14	48.7	140	51.1	28.2	26.1	272	25.8
P15	45.8	131	40.7	17.5	35.2	202	26.3
P24	48.7	111	52.2	22.1	33.1	228	26.2
P25	48.7	115	56.5	24.8	31.8	195	33.3

Figure 33 shows the trend in foam density of the HBSBO-based polyol mixed with 50% Voranol®4701 relative to the control flexible foams. The independent variable, OH_m is the total hydroxyl number of the polyol mix taken as half the sum of the hydroxyl numbers of a particular HBSBO polyol and Voranol®4701. The OH_m values of the HBSBO polyols range from 65 to 87 mg KOH/g. The controls were used without replacement.

From Figure 33, foam density of the HBSBO polyols varies greatly with a lowest value of about 40 and highest of about 68 kg/m^3 relative to 44.8 of Voranol®4701 (see ellipse). There was no observable pattern in the density values of the HBSBO-derived flexible foams with respect to OH_m mainly because of inconsistency in the hydrolyzed BSBO polyol structure. Bodied SBO alone was formed by a complex mechanism of polymerization with final product a mixture of different triacylglycerol structures. Hydrolysis of BSBO is a non-selective catalytic action of the *C. rugosa* lipase so that cleavage of the fatty esters will be non-uniform.

The significance of Figure 33 is that a broad range of foam densities can be attained with flexible foams derived from HBSBO polyols and in this case, about 90% of these foams have higher density values relative to Voranol®4701. Higher foam density could be a result of slower reaction rate of the HBSBO polyol resulting in a lower volume. Although Voranol®4701 has a lower hydroxyl value compared to all of the HBSBO polyols used in the experiment; it has a uniform structure for the isocyanate to directly and easily react with its available hydroxyls compared to the complex and highly-branched structure of HBSBO. High acidity and unneutralized bound fatty acid moieties unnecessarily consume isocyanate and contribute to loose structures in the polyurethane network.

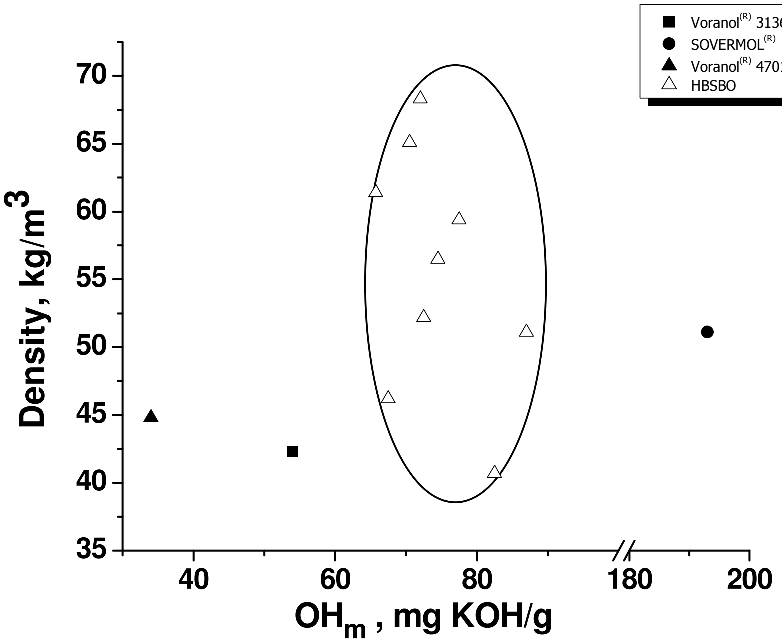


Figure 33. HBSBO foam density (50% Voranol® 4701 replacement) relative to petroleum-based and triglyceride-type control foams(no replacement).

Figure 34 shows the effect of applying compression force to the flexible foams. Figure 33a presents the compression set of the flexible foams which reflects thickness recovery of the foam after being pressed 50% of its original height for 22 hrs. Lower compression set value usually means higher resilience for flexible foam suggesting its better flexibility or ability to regain its original shape. In Figure 33a, the compression set of HBSBO-based flexible foams have higher compression set values than Voranol®4701-based foam.

The HBSBO polyol was a complex mixture of polymers with different molecular weight distribution (short and long chains) creating a discontinuous polyurethane network upon reaction with isocyanate. The resulting foams would be more easily crushed and destroyed by constant compression force.

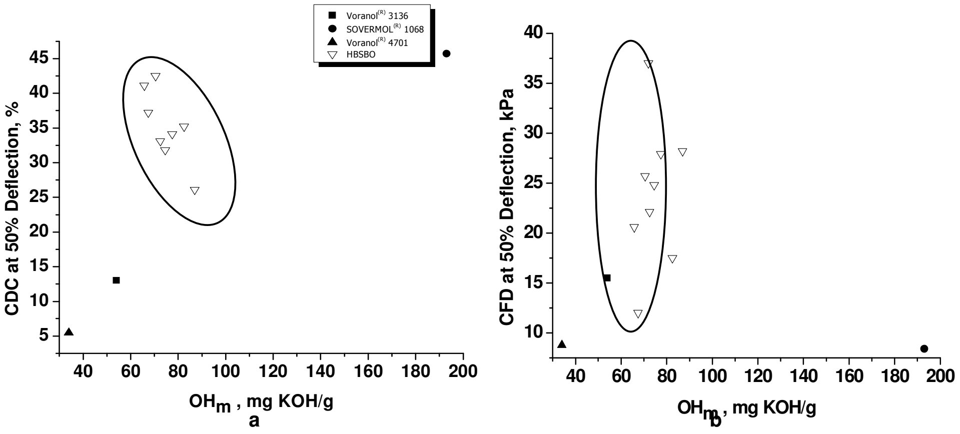


Figure 34. Compression force tests made on HBSBO foams (50% Voranol® 4701 replacement) with a) CDC at 50% deflection or compression set, and b) CFD at 50% deflection relative to petroleum-based and triglyceride-type control foams (no replacement).

This type of foams also have low resiliency resulting in a non-uniform polymer structure as presented in Figure 35b. All of the HBSBO-based foams also show lower resiliency compared to the Voranol®4701-based flexible foam. The triglyceride-type commercial SOVERMOL®1068 has compression set higher than all of the HBSBO-based foams and lower resiliency than most of the HBSBO-based samples. This suggests better flexibility of the HBSBO foams at 50% Voranol®4701 replacement than the commercial triglyceride-based flexible foam.

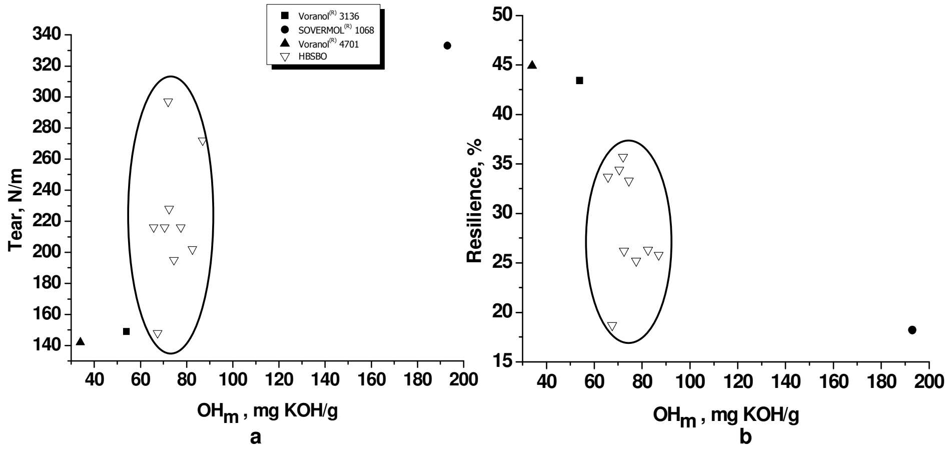


Figure 35. Strength and recovery tests made on HBSBO foams (50% Voranol® 4701 replacement) with a) Tear to evaluate foam strength, and b) Resilience to evaluate in-use recovery performance.

Figure 34b shows the effect of polyol OH_m to the CFD of the foams at 50% deflection. There is no general trend within the BSBO polyols with respect to its combined hydroxyl values due to its complex and non-uniform structures of the polymer mix. The general observation is the same with that of the compression set with all CFD values higher than that of Voranol®4701-based foams. Figure 35a shows the tear resistances of the HBSBO-based foams higher than that of Voranol®4701. Although tear resistance are not necessarily related to tensile strength, results could also vary with the sharpness of the cutting die. Voranol®4701 has a long linear chemical structure so that its polymer network with isocyanate would create a continuous and uniform structure in the final foam. An introduction of continuous stress at one point in the polymer network would easily cut through the mass compared to the highly-branched structure of the triglyceride-based foams including SOVERMOL®1068.

5.4. CONCLUSIONS

In this study, hydroxyl-functionalized BSBO was synthesized to create a high average functionality polyol by enzymatic hydrolysis using *C. rugosa* as biocatalyst done through free- and immobilized-enzymes. Hydrolyzed HBSBO products were neutralized by base washing and epoxy reaction to reduce acidity in the polyols.

Flexible foams were successfully made from these hydrolyzed soy-based polyols and exhibited foam properties comparable to commercial triglyceride-based SOVERMOL®1068. The HBSBO-based foams appeared to have inferior foam properties compared to Voranol®4701 due to differences in chemical structures. The petroleum-based polyol has long uniform structure compared to the complex and highly-branched HBSBO polyol.

5.5. REFERENCES

1. R. P. Wool and X. S. Sun, Bio-Based Polymers and Composites, Elsevier Academic Press, Burlington, MA, 2005, p. 56.
2. I. Debruyne, Lipid Technology, 19, 128 (2007).

3. J. Lu, R. P. Wool, Composites Science and Technology, 68, 1025 (2008).
4. J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias, D. Briones, Energy & Fuels, 23, 539 (2008).
5. D. F. Mielewski, C. M. Flanigan, C. Perry, M. J. Zaluzec, P. C. Killgoar, Industrial Biotecnology, 1, 32 (2005).
6. P.-p. Kiatsimkul, G. J. Suppes, W. R. Sutterlin, Industrial Crops and Products, 25, 202 (2007).
7. Y.-C. Tu, P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 105, 453 (2007).
8. P.-p. Kiatsimkul, G. J. Suppes, F.-H. Hsieh, Z. Lozada, Y.-C. Tu, Industrial Crops and Products, 27, 257 (2008).
9. K. Kim, J. H. Jeong, I. J. Kim, H.-S. Kim, *Journal of Power Sources,* 167, 524 (2007).
10. H. T. Schmidt, M. Kroczynski, J. Maddox, Y. Chen, Y. R. Josephs, A. E. Ostafin, Journal of Microencapsulation, 23, 769 (2006).
11. A. A. Lubguban, Y.-C. Tu, Z. R. Lozada, F.-H. Hsieh, G. J. Suppes, Journal of Applied Polymer Science, 2009, In Press.
12. E. M. Anderson, M. Karin, O. Kirk, Biocatalysis and Biotransformation, 16, 181 (1998).
13. Y.-C. Tu, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 109, 537 (2008).
14. Y.-C. Tu, G. J. Suppes, F.-H. Hsieh, Journal of Applied Polymer Science, 111, 1311 (2009).

15. L. Zhang, H. K. Jeon, J. Malsam, R. Herrington, C. W. Macosko, Polymer, 48, 6656 (2007).
16. J. John, M. Bhattacharya, R. B. Turner, Journal of Applied Polymer Science, 86, 3097 (2002).
17. P.O Powers, Journal of the American Oil Chemists' Society, 27, 468 (1950).
18. S. Z. Erhan, Q. Sheng, H.-S. Hwang, Journal of the American Oil Chemists Society, 80, 177 (2003).
19. Z. Lozada, G. J. Suppes, F.-H. Hsieh, A. Lubguban, Y.-C. Tu, Journal of Applied Polymer Science, 2009, In press.
20. A. A. Lubguban, Y.-C. Tu, Z. R. Lozada, F.-H. Hsieh, G. J. Suppes, Journal of Applied Polymer Science, 112, 19 (2009).
21. Y. Miyake, K. Yokomizo, N. Matsuzaki, Journal of the American Oil Chemists' Society, 75, 15 (1998).
22. G. Vlahov, A. D. Shaw, D. B. Kell, Journal of the American Oil Chemists' Sociey, 76, 1223 (1999).

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Polyols derived from soybean oil are alternative materials for polyurethane applications including rigid and flexible foams and elastomers. Soy-based polyols are important industrial prepolymeric materials that use renewable resources and with isocyanates they produce polyurethanes (PU) that can compete in many aspects with polyols derived from petrochemicals. Their impact in the future of polyurethane chemistry will be significant.

Soy-based polyols synthesized from enzymatic biocatalysis is a fairly new technology that has the advantage of high lipase selectivity with the potential for yielding primary hydroxyls which are known to be highly reactive, thus, increasing hydroxyl functionality for polyurethane production. Although the use of *C. rugosa* lipase is economical in some aspects (less organic solvents, low temperature process) and leaves less carbon footprint, the prices of enzymes are expensive. Enzyme immobilization is necessary to improve storage stability, recovery ability, and length of hydrolytic activity.

A packed-bed reactor (PBR) was applied to contain immobilized C. rugosa lipase during hydrolysis of bodied soybean oil. Results have shown less hydrolytic activities of the immobilized enzyme as compared to the free lipase possibly due to low covalent binding of the enzyme to the carrier surface and mass transfer problems. It is recommended that a more porous support be used to encourage lipase entrapment and improve lipase binding through covalent immobilization, among others.

The flexible polyurethane foams reported here based on C. rugosa-catalyzed polyol product have not been reported elsewhere. The high hydroxyl equivalent weight of the polyols due to initial bodying of the soybean oil and the suggested attachment of mostly primary hydroxyls made it possible for the neutralized polyol to be highly reactive in the polyurethane formulation. In addition to the drawbacks brought about by enzyme use, the downstream processing of the hydrolyzed BSBO products made it more expensive to produce the final polyol. Multiple base washings (to remove fatty acids) and epoxy reaction to reduce acidity due to the free fatty acids cleaved off during hydrolysis are reasons for these. It is recommended that other possible routes be investigated to eliminate these flaws.

An alternative to enzymatic process using BSBO was described in one chemical route described in this study. Bodying of the soybean oil is an effective method to increase the average equivalent weight of the final polyol. This was shown in the lower extractable content of the material compared to non-bodied samples. Functionalization was made possible by one-pot process of glycerol transesterification attaching hydroxyl-functionality to BSBO, thus, increasing the average hydroxyl functionality. Although the rigid foams were comparable to the control petroleum-based foams, the former was replaced with 50% of the petroleum-based polyol.

In this study, other methods to increase equivalent weight in soybean oil used ethylene glycol and phosphoric acid to oligomerize epoxidized soybean oil. The ethylene glycol-reacted polyols displayed better rigid foam properties with up to 75% petroleum-polyol replacement. The phosphoric acid-reacted polyols exhibited better extractability and tensile strengths in bioelastomer application as compared to epoxidized soybean oil alone. Although both chemical routes increase the polyol's equivalent weight the reactive hydroxyls were conserved in the reactions. It is recommended that new possible routes be investigated to increase both equivalent weight and hydroxyl functionality in the soy-based polyols.

Another potential focus for future research is to reduce isocyanate use either by increasing reactivity of the soy-based polyols or synthesizing polyols that mimic the chemical structure of the urethane linkage of soy-based polyol and isocyanate. MDI has a central benzene ring attached to -NCO and -CH_2 groups while soy-based urethane linkage has polymeric MDI attached to the reactive sites of the polyol. A search for reactants that would provide similar structure in the polyols product will be a worthwhile pursuit in product development.

In general, the soy-based polyol products described in this study have physicochemical properties comparable to both commercial triglyceride-based and petroleum-based polyols. These soy-based polyls are also potentially good with respect to commercialization prospects.

VITA

Arnold Ano-os Lubguban was born on October 24, 1976 in Malabang, Lanao del Sur, Philippines, where he also grew up. He graduated from Our Lady of Peace High School in 1994, and began his studies at the University of the Philippines (UP) under UP-Government Scholarship award. While attending UP, he majored in Chemical Engineering, and worked in the laboratories of the National Institutes of Molecular Biology and Biotechnology in College, Laguna Philippines working on his undergraduate thesis entitled "Consequential Semi-Batch Fermentation of Coconut Water into Acetic Acid" in 1998.

Arnold received his Bachelor of Science degree in April, 1999 and began working as a lecturer at Colegio de San Juan de Letran, Laguna, Philippines. He has also worked as a laboratory analyst in Pilmico Foods Corporation before initiating graduate studies.

Arnold began his graduate studies at the University of Missouri, Dept. of Chemical Engineering in 2003. He joined Gangopadhyay Research Group in the spring of 2004, mentored by Dr. Shubhra Gangopadhyay. On September 2006, Arnold graduated with a Master of Science degree in Chemical Engineering at the University of Missouri-Columbia. He joined Bio-based Polyols Research Group in the fall of 2006, mentored by Dr. Galen Suppes to pursue his PhD in Chemical Engineering. Arnold appreciates the financial support received from the National Science Foundation, the Consortium for Plant Biotechnology Research, Inc., and the United Soybean Board throughout his graduate study.