POLYURETHANE FOAMS FROM NOVEL SOY-BASED POLYOLS

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Doctor of Philosophy

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by

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

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ABSTRACT

Polyurethane foams and molded plastic films were prepared by reacting isocyanates with polyols containing 50% of vegetable oil-based polyols and 50% of petroleum-based polyols. The vegetable oil-based polyols included epoxidized soybean oil, epoxidized soybean oil reacted with acetol, commercial soybean oil polyols (soyols), polyols derived from epoxidized soybean oil and diglycerides, etc. The petroleum-based polyols were Voranol® 490 for rigid foams and Voranol® 4701 for flexible foams in the B-side of foam formulation. For rigid water-blown polyurethane foams, density, compressive strength and thermal conductivity were measured. For flexible water-blown polyurethane foams, density, 50% compression force deflection, 50% constant force deflection, and resilience of foams were determined. A dynamic mechanical spectrometer (DMS) and a differential scanning calorimeter (DSC) were used to characterize the hard segment (HS) and soft segment (SS) ratio and thermal properties of plastic. Various functional groups in both flexible polyurethane foam and plastic film were characterized

using Fourier transform-infrared spectroscopy with attenuated total reflectance (FTIR-ATR).

Most foams made with polyols containing 50% of vegetable oil-based polyols were inferior to foams made from 100% petroleum-based polyol. However, rigid foams made with polyols containing 50% hydroxy soybean oil, epoxidized soybean oil reacted with acetol, and oxidized epoxidized diglyceride of soybean oil not only had superior thermal conductivity, but also better density and compressive strength properties than foams made from 100% petroleum polyol. Although the epoxidized soybean oil did not have any hydroxyl functional group to react with isocyanate, it showed interesting properties when used to replace the petroleum-based polyols in the B-side of foam formulation. For rigid polyurethane foams, no significant changes in density, compressive strength decreased and thermal conductivity decreased first and then increased with increasing epoxidized soybean oil. Similar to compressive strength, the foaming temperature decreased with decreasing isocyanate index and increasing ESBO replacement. Due to the lower reactivity of ESBO with isocyanate, the rate of foaming temperature decrease with decreasing isocyanate index was in the order of 0%>20%>50% ESBO replacement. For flexible polyurethane foams, when increasing epoxidized soybean oil, foam density decreased first and then increased, no changes in 50% compression force deflection first and then increased, increasing 50% constant force deflection, and decreasing resilience. When increasing the ESBO content, the peak of tanδ in DMS analysis and Δcp in DSC analysis of plastic films both decreased indicating the hard segment increased and the soft segment decreased in plastic film, respectively.

The FTIR-ATR results also show the hydrogen-bonded urethane group increased in plastic films with increasing ESBO content.

Chapter 1

INTRODUCTION

1.1 Background

Polyurethane is widely defined as a polymer material containing a huge amount of urethane group. Despite the chemical reaction between the NCO group and the hydroxyl compound that was originally found in the 19th century, the basic addition polymerization reaction of diisocyanate with alcohols to produce polymers, which is a polyurethane reaction, was not discovered and established until 1937 by Dr. Otto Bayer and co-worker in the laboratories of I. G. Farben Industrie. Chemical Co. in Germany. Between 1945 and 1947, millable elastomers, coatings and adhesives, the first commercial applications of polyurethane polymers, were developed. This was followed by the flexible polyurethane foams in 1953 and rigid polyurethane in 1957.

Polyurethanes can be manufactured in an extremely wide range of density and stiffness and have a broad range of applications. The densities of polyurethanes range from 6 to 1,220 kg/m^3 and polymer stiffness of polyurethanes range from elastomers to flexible, rigid, and hard plastics.[1] The global polyurethanes consumption has been growing at an average rate of over 7% annually for the last 15 years. Thus, it is not surprising that polyurethanes are all around us, from shoes to sofas, insulation panels to automobiles, playing an important role in many ways in our daily life.[1, 2]

In the past, polyurethanes were usually made with petroleum polyols. With the dwindling and non-renewable petroleum resource, some novel polyols made from vegetable and seed oil have been investigated for their potential of replacing the petroleum polyols. Of particular interest is a group of polyols derived from soybean oil. These new polyols, however, have some major disadvantages limiting its applications when compared with petroleum polyols:

1. The alcohol groups in the petroleum polyols are primary which are 3.3 times more reactive with isocyanates than the secondary ones in the new polyols.[2]
2. The saturated fatty acid in these new polyols is not reactive and adversely impacts the properties of polyurethane foams.
3. Most of these new polyols are not cost competitive against the petroleum polyols due to multiple steps involved and/or solvent consumption.

1.2 Polyurethane Chemistry

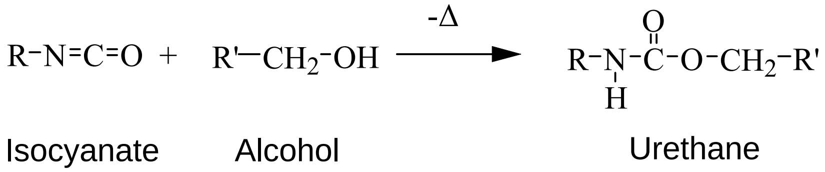
For the manufacture of high molecular weight polyurethanes, two groups of at least bifunctional substances are needed as reactants: 1) compounds with isocyanate groups (polyisocyanates) and 2) compounds with active hydrogen atoms (polyethers, polyesters, etc.). Polyurethane chemistry is based on the reactions of isocyanate groups with active hydrogen-containing compounds. Isocyanates are compounds having one or more highly reactive isocyanate groups (-N=C=O). These groups will readily react with hydrogen atoms that are attached to atoms that are more electronegative than carbon.

Commercial polyurethane products are usually formed by reactions of liquid isocyanate components with liquid polyol resin components.

In the polyurethane foaming process, two major reactions take place in the process: 1) polymerization reaction to form the three-dimensional network of polyurethane structure and 2) gas-producing reaction to expand the polyurethane structure from the polymerization reaction.

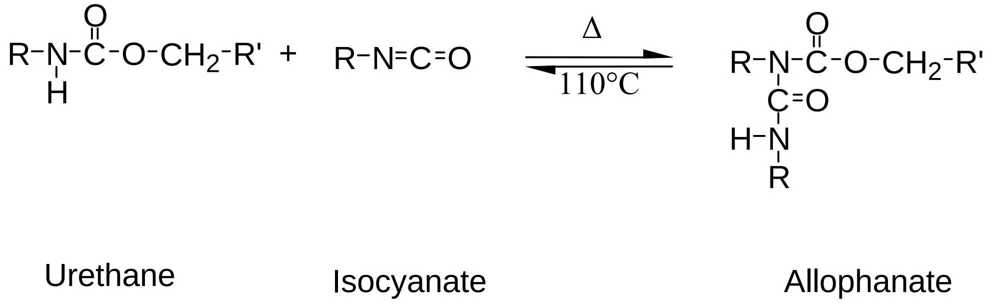
1.2.1 Polyurethane Polymerization Reaction

The polyurethane polymerization reaction occurs between an isocyanate and an alcohol as follows:



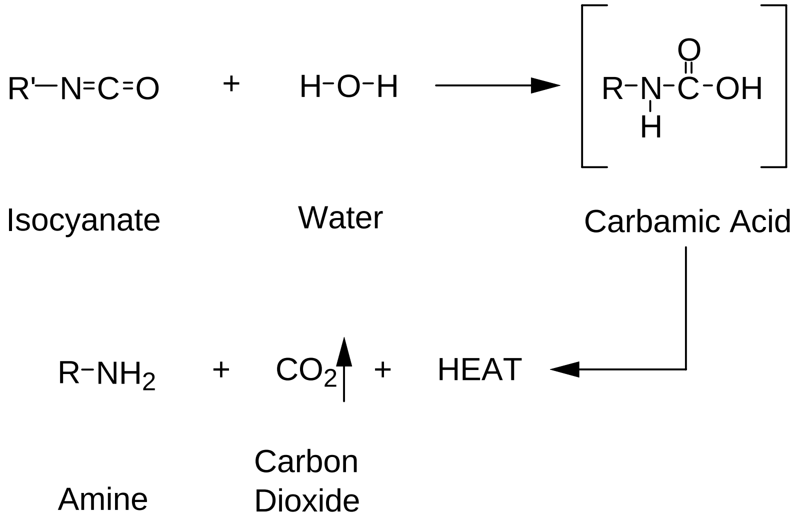
$$R-N=C=O + R'-CH_2-OH \xrightarrow{-\Delta} R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-CH_2-R'$$

This reaction is an addition reaction process and the heat of this reaction is approximately 100 kJ/mole of urethane.[3] The hydrogen next to the nitrogen atom in the urethane group is capable of reacting with additional isocyanate to form an allophanate group.

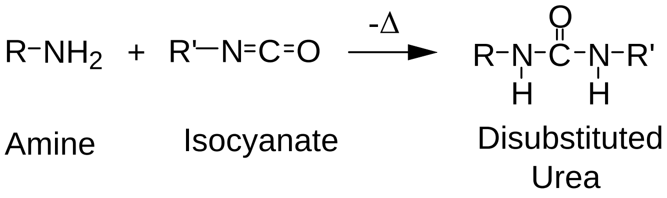


1.2.2 Gas-production Reaction

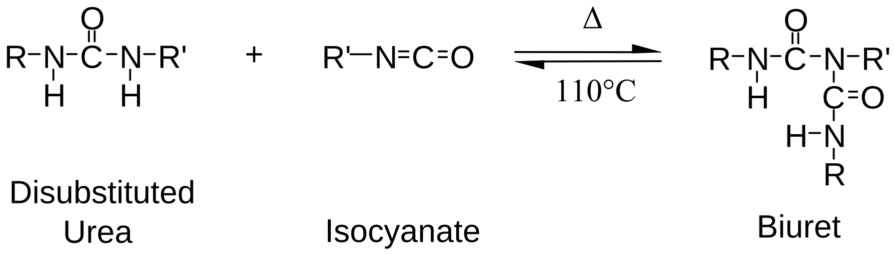
To make foam, the polyurethane polymer must be expanded or blown by gas or a gas-forming material. There are two different ways to produce gas during the polyurethane foaming process. One is called physical gas-production reaction process and the other is called chemical gas-production reaction process. In physical gas-production reaction, the gases are produced by vaporizing the blowing agent which is a low-boiling non-reactive liquid in the foam formulation, like CFC-11, CFC-22, HFC-245fa, pentane, and methyl formate, with heat generated from the polymerization reaction. Due to environmental issues, the CFC and HFC gases will either be reduced or forbidden to use[4] and due to safety issues, the hydrocarbon blowing agents might not be suitable for polyurethane foaming. The other method of generating gas during the foaming process is called chemical gas-production process. For example, carbon dioxide is produced from the reaction of an isocyanate group with water. The intermediate product of this reaction is a thermally unstable carbamic acid, which spontaneously decomposes to an amine and carbon dioxide.



Further reaction of amine with additional isocyanate will generate disubstituted urea.



The approximate total heat released per mole of water is 196 kJ. The disubstituted urea can further react with additional isocyanate to form a biuret linkage.



1.3 Raw Materials

The two major raw materials for making polyurethane foams are isocyanates and polyols.

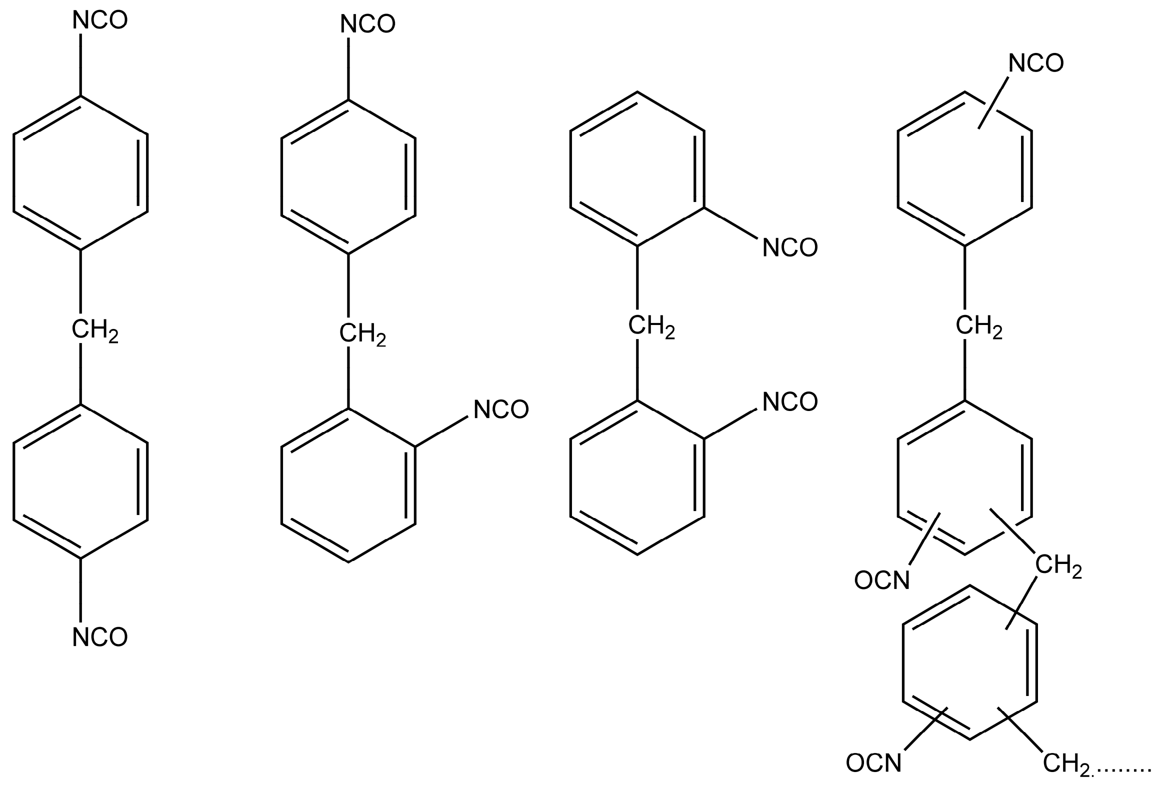
1.3.1 Isocyanates

The most common method of producing isocyanates is phosgenation of amines.

$$\underset{\text{Amine}}{R\text{-}NH_2} + \underset{\text{Phosgene}}{COCl_2} \rightarrow \underset{\text{Isocyanate}}{R\text{-}N{=}C{=}O} + \underset{\text{Acid}}{2HCl}$$

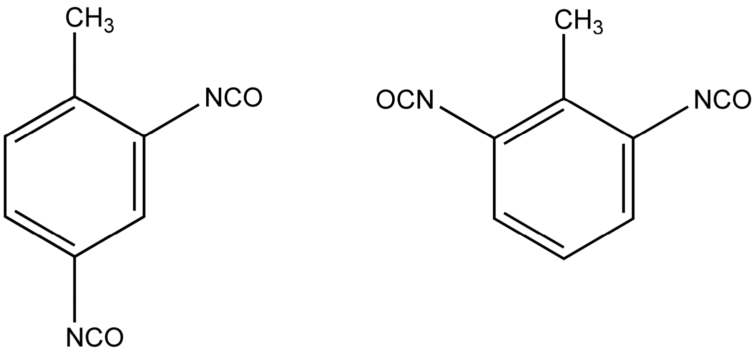
This reaction is usually completed in a chlorinated aromatic solvent. The chlorinated aromatic solvent is employed to remove excess phosgene in later purification steps.

Methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are two major kinds of isocyanates consumed in the global isocyanate market. In 2000, approximately 61.3% of isocyanates consumed in global isocyanate market were MDI, 34.1% were TDI, and approximately 4.6% were other types of isocyanate.[1] Other types of isocyanates, like 1,6-hexane diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,5-napthalene diisocyanate (NDI), 1,4-phenylene diisocyanate (PDI) are also used in different applications. Table 1.1[5] and Figures 1.1 to 1.3 show the physical properties and chemical structures of these isocyanates.



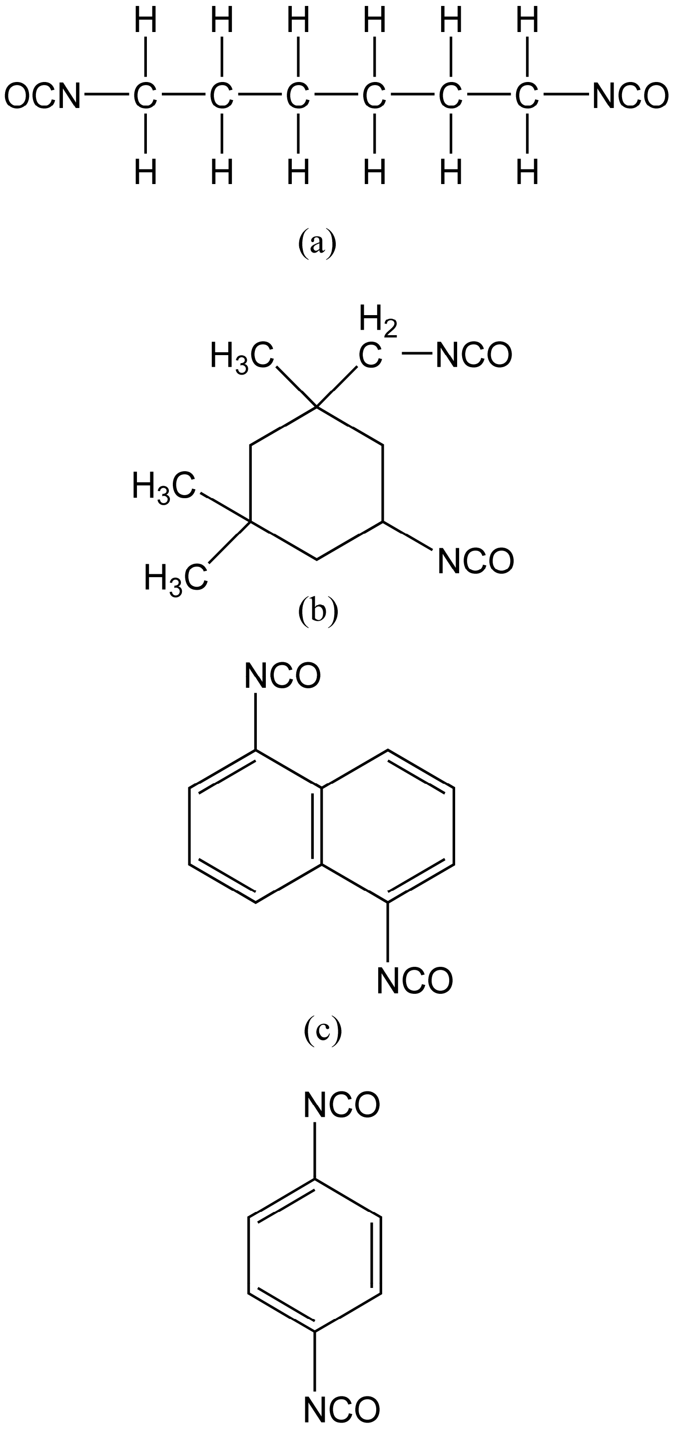
4,4'-MDI **2,4'-MDI** **2,2'-MDI** **Polymeric-MDI**

Figure 1.1. Chemical structure of methylene diphenyl diisocyanate (MDI).



2,4-TDI **2,6-TDI**

Figure 1.2. Chemical structure of toluene diisocyanate (TDI).



(a)

(b)

(c)

(d)

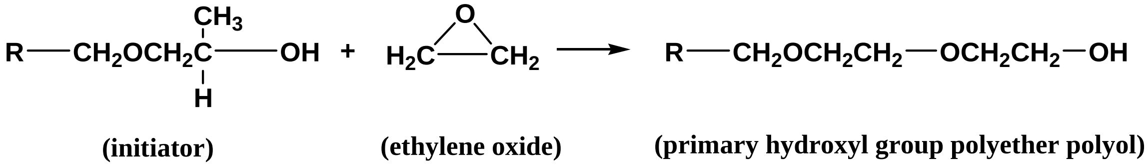
Figure 1.3. Chemical structure of (a) 1,6-hexane diisocyanate (HDI), (b) isophorone diisocyanate (IPDI), (c) 1,5-napthalene diisocyanate (NDI), and (d) 1,4-phenylene diisocyanate (PDI).

Table 1.1. Physical properties of polyisocyanates[5]

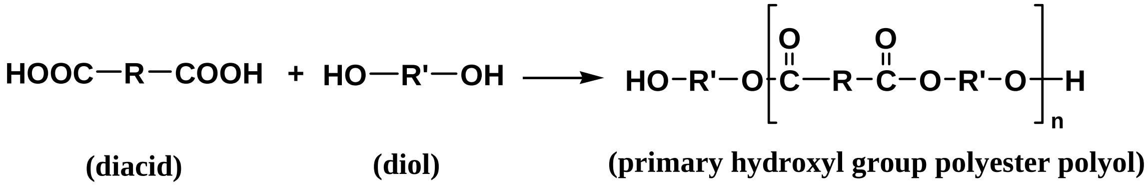
Designation	Formula	Molecular Weight	B.P. (°C/Torr)	Density (g/cm^3)
2,4-Toluene diisocyanate (TDI)	$C_9H_6O_2N_2$	174.2	121/10	1.2178/20°
2,6-Toluene diisocyanate (TDI)	$C_9H_6O_2N_2$	174.2	121/10	1.2271/20°
Toluene diisocyanate mixture 2,4:2,6=65:35 (TDI 65)	$C_9H_6O_2N_2$	174.2	121/10	1.222/20°
Toluene diisocyanate mixture 2,4:2,6=80:20 (TDI 80)	$C_9H_6O_2N_2$	174.2	121/10	1.221/20°
Diphenylmethane-4,4'-diisocyanate (MDI)	$C_{15}H_{10}O_2N_2$	250.3	208/10	1.183/50°
Diphenylmethane-2,4'-diisocyanate (MDI)	$C_{15}H_{10}O_2N_2$	250.3	154/1.3	1.192/40°
Diphenylmethane-2,2'-diisocyanate (MDI)	$C_{15}H_{10}O_2N_2$	250.3	145/1.3	1.188/50°
1,6-Hexane diisocyanate (HDI)	$C_8H_{12}O_2N_2$	168.2	127/10	1.047/20°
1-Isocyanto-3-isocyanatomethyl-trimethyl-cyclohexane (IPDI)	$C_{12}H_{18}O_2N_2$	222.3	158/10	1.0615/20°
1,5-Napthalene diisocyanate (NDI)	$C_{12}H_6O_2N_2$	210.2	183/10	1.450/20°
1,4-Phenylene diisocyanate (PDI)	$C_8H_4O_2N_2$	160.1	110-112/12	1.4407/20°

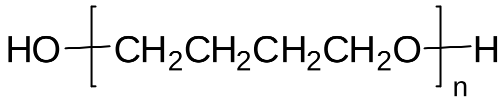
1.3.2 Petroleum Polyols

Polyether polyols and polyester polyols are two major kinds of polyols consumed in the global polyols market. In 1994, nearly 90% of four billion pounds of polyurethanes consumed in the United States were based on polyethers, 9% on polyesters and and 1% on other specialty polyols.[6] In polyether polyols, the initiator like ethylene glycol, propylene glycol, and glycerin reacts with alkylene oxide to produce polyether polyols with the primary hydroxyl group. Figure 1.4 shows the chemical structure of common polyether polyols.



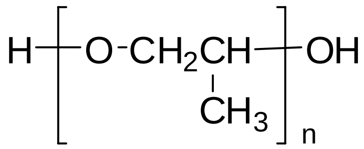
In polyester polyols, on the other hand, glycols such as 1,6 hexanediol or polyols such as glycerin react with diester or diacid to form primary polyester polyols





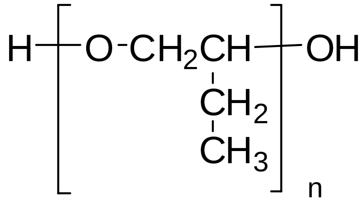
$HO\left[CH_2CH_2CH_2CH_2O\right]_nH$

Polytetramethylene etherglycol (PTMEG)



$H\left[O-CH_2\underset{CH_3}{CH}\right]_nOH$

Polypropylene oxide glycol (PPO)



$H\left[O-CH_2\underset{\underset{CH_3}{CH_2}}{CH}\right]_nOH$

polybutylene oxide glycol (PBO)

Figure 1.4. Chemical structure of common polyether polyols.

Two important properties of polyols play a dominant role in properties of the final product, polyurethane polymers. These properties are functionality and equivalent weight. The functionality of polyols can be defined as the average number of functional groups reacting to isocyanate per molecule of polyols. The equivalent weight of polyols can be defined as follows:

$$Equivalent\ weight = \frac{Molecular\ weight\ of\ polyols}{Functionality\ of\ polyols} = \frac{56100}{Hydroxyl\ number}$$

The hydroxyl number (mg KOH/g) is milligrams of potassium hydroxide equivalent to the hydroxyl groups found in one gram of polyols.[2] The relation between the properties of polyols and applications of polyurethane polymer is summarized in Table 1.2.

Table 1.2. The relation between the properties of polyols and applications of polyurethane polymer.

Applications	Functionality of polyols	Equivalent weight of polyols
Flexible Foams	2.5-3.0	500-3000
Semi-Rigid Foams	3.0-3.5	70-2000
Rigid Foams	3.0-8.0	70-800
Elastomers & Coatings	2.0	70-2000

In recent years, the price of petroleum polyols has escalated due to the continuous price increase in crude petroleum; moreover, consumption of petroleum products releases CO_2 and contributes to global warming, which is a serious environmental concern. These problems could be partially addressed by producing polyols from renewable resources.

1.3.3 Soy-based Polyols

Because soybean oil is a renewable resource, abundant in supply and relatively low in cost, it has become an alternative source to produce polyols. About 40% of standard petroleum polyols in spray-on polyurethane applications have now been replaced by soybean oil based polyols costing approximately 20% to 30% less than the conventional polyols.[7] Figure 1.5 shows a typical chemical method to produce soybean oil based polyol.

Soybean oil based polyol is now commercially available in the polyurethane market and more and more researchers and companies are getting involved in this area. Urethane Soy System Company (Volga, South Dakota) has produced two kinds of soybean oil based polyols and one is called Soyol™ R2 polyol which has two functionalities and another one is called Soyol™ R3 polyol which has three functionalities.[8]

Dr. Petrovic and his colleagues[9,10,11] have numerous publications about soybean oil based polyols and collaborate with Cargill Inc to produce commercially available soybean oil based polyols.[12]

Sovermol® polyols are also soybean oil based polyols that are made with soybean oil triglyceride and produced by Cogins Oleochemicals.

Dr. Suppes and his colleagues[13-16] are producing soybean oil based polyols using both the chemical method and enzyme technology. None of the existing commercial soybean oil based polyol is produced by the enzyme technology.

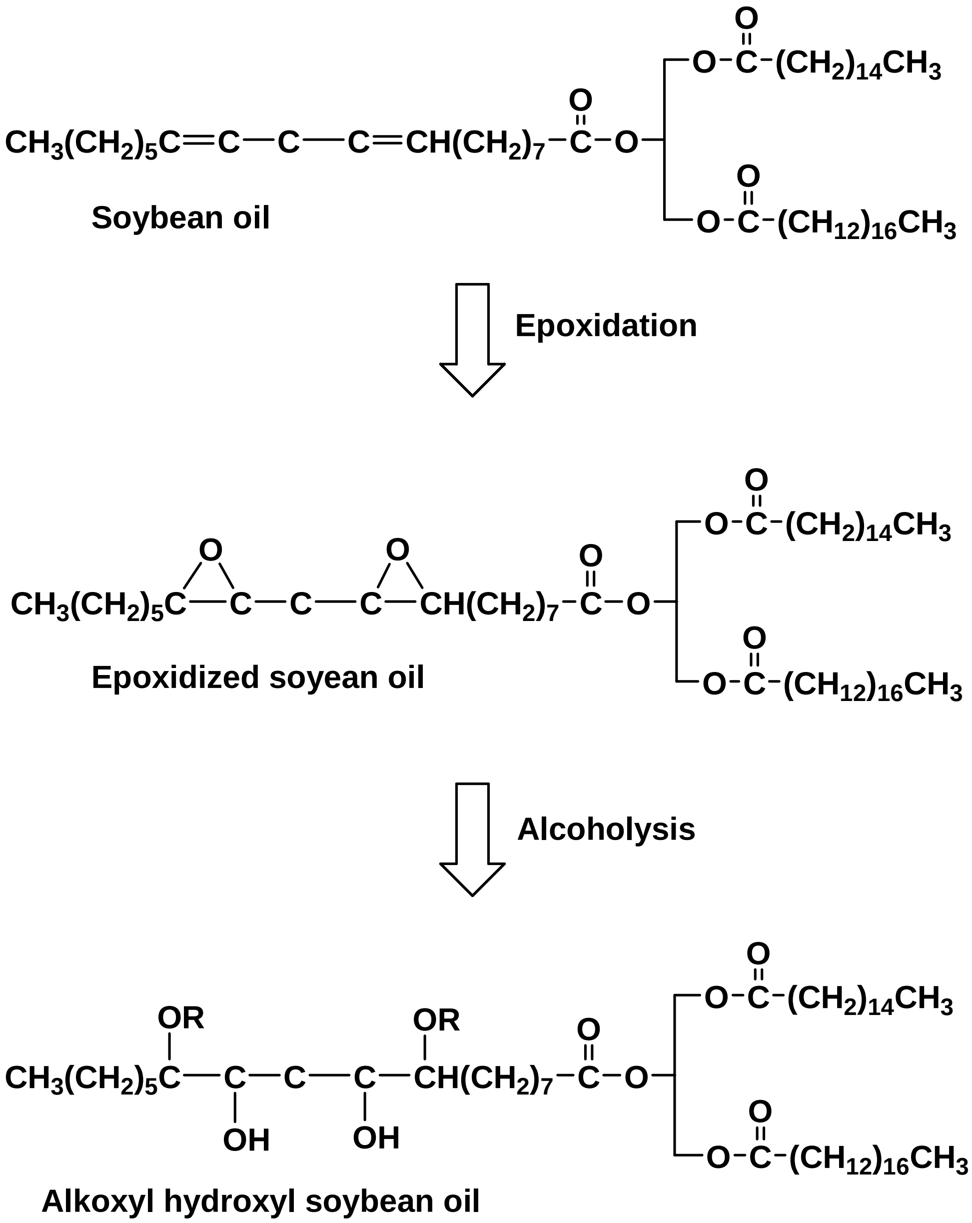


Figure 1.5. The chemical method to produce alkoxyl hydroxyl soybean oil.

In this study, several kinds of soybean oil based polyols provided by Dr. Suppes were used to synthesize either rigid or flexible polyurethane foams. The properties of these foams will be investigated. Epoxidized soybean oil, usually used as filler in polyurethane foam or as the raw materials of soybean oil based polyols, was used directly as a B-side material to make rigid polyurethane foams. A literature review revealed that epoxidized soybean oil has never been used directly as a polyol.

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CHAPTER 2

PHYSICAL PROPERTIES OF WATER-BLOWN RIGID POLYURETHANE FOAMS FORM VEGETABLE OIL BASED POLYOLS

2.1 Abstract

Fifty vegetable oil-based polyols were characterized in terms of their hydroxyl number and their potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications was evaluated. Polyurethane foams were prepared by reacting isocyanates with polyols containing 50% of vegetable oil-based polyols and 50% of petroleum-based polyol and their thermal conductivity, density, and compressive strength were determined. The vegetable oil-based polyols included epoxidized soybean oil reacted with acetol, commercial soybean oil polyols (soyols), polyols derived from epoxidized soybean oil and diglycerides, etc. Most foams made with polyols containing 50% of vegetable oil-based polyols were inferior to foams made from 100% petroleum-based polyol. However, foams made with polyols containing 50% hydroxy soybean oil, epoxidized soybean oil reacted with acetol, and oxidized epoxidized diglyceride of soybean oil not only had superior thermal conductivity, but also better density and compressive strength properties than foams made from 100% petroleum polyol. Although the epoxidized soybean oil did not have any hydroxyl

functional group to react with isocyanate, when used in 50:50 blend with the petroleum-based polyol the resulting polyurethane foams had density vs. compressive properties similar to polyurethane foams made from 100% petroleum-based polyol. The density and compressive strength of foams were affected by the hydroxyl number of polyols, but the thermal conductivity of foams was not.

2.2 Introduction

Polyurethanes, first produced in 1941, have a wide variety of commercial applications. They are present everywhere in our daily lives, such as seating, cars, insulations, packaging, footwear, construction, furniture[1] and rank fifth in the production volume of plastics in the world.[2] The consumption of polyurethanes is increasing rapidly throughout the world.

Polyurethanes 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). The raw materials of typical polyols, using a diol as an example, are ethylene glycol and propylene oxide; both are derived from petroleum, a nonrenewable and dwindling resource. To meet the need of rapidly increasing polyurethane volume and hence polyol consumption, many researchers are actively searching for alternative resources as raw materials for polyols.

Vegetable oils are renewable resources. They are triglycerides and often have at least one unsaturated fatty acid in its chemical structure. By using enzymes or chemicals to modify the unsaturated fatty acid moiety and introduce one or more hydroxyl functional groups, vegetable oils could be converted into polyols.[3] For example, Leitheiser[4] and Ehrilich[5] reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams. Lu[6] used waterborne polyurethane made from rapeseed oil-based polyol to modify glycerol-plasticized starch and develop biodegradable films. Chang[7,8] added commercial soy flours into water-blown rigid polyurethane foams to improve the physical properties and lower the cost of these foams. Petrovic and his colleagues[9-13] investigated the structure and properties of vegetable oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behavior and thermal stability. Although many types of vegetable oils have been tested and reported for polyol and polyurethane applications, soybean oil is the most promising one to partially replacing petroleum to make polyols due to its volume and price stability. Many innovative chemical and/or biological approaches are possible to convert soybean oil into polyols but not all will result in polyols with adequate functionality to be useful or considered as the B-side component for polyurethane application. The objectives of this study were to characterize various vegetable oil-based polyols, particularly those made with new chemical and/or biological approaches, in terms of their hydroxyl number, and explore their potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications. The replacement potential was evaluated based on three properties that are important for rigid polyurethane foams: density, compressive strength, and thermal conductivity.

2.3 Materials and Methods

2.3.1 Materials

Voranol® 490 polyether polyol, a petroleum-based polyol with 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% part by weight of NCO content were obtained from Dow Chemical Co. (Midland, MI). Soybean oil-based polyols (GC5N, P38N, R2-052, and R3-170) were obtained from Urethane Soy System Co. (Volga, SD). Soybean oil and diglyceride soybean oil (ENOVA®) were from ADM (Decatur, IL). Epoxidized soybean oil (Vikoflex® 7170) was supplied by ATOFINA Chemicals (Philadelphia, PA). Castor oil was from Alnor Oil Company (Valley Stream, NY). Catalysts (POLYCAT® 5 and POLYCAT® 8) and a surfactant (Dabco® DC 5357) were from Air Products & Chemicals (Allentown, PA) gratis. Distilled water was used as the blowing agent.

The derivatives of soybean oil, epoxidized soybean oil, and castor oil (Table 2.1) were prepared in the lab of Chemical Engineering Department, University of Missouri-Columbia and briefly described as follows.

1. DG SBO. ENOVA® oil contains >80% of diglycerides (DGs) used and designated as diglyceride soybean oil (DG SBO).
2. Epoxidized DG SBO. DG SBO was epoxidized using the method developed by Suppes and Dasari[14].
3. Oxidized SBO, oxidized DG SBO and oxidized epoxidized DG SBO. The starting raw materials (SBO, DG SBO and epoxidized DG SBO) were oxidized by oxygen bubbling

and heating at 100-110ºC for 30 h. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng *et al*[15].

4. Blown SBO. Blown SBO (680 Blown SBO) was from Cargill (Chicago, IL). It contains soybean oil-based oligomers produced by heat polymerization and oxygen oxidation. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng *et al*[15].

5. Bodied soybean oil (BSBO). To produce bodied soybean oil (BSBO), non-oxidized soy-based oligomers, soybean oil was heated at 330ºC for 30-60 min with vigorous stirring in a closed system (no air/oxygen circulation). The process of making bodied soybean oil was reported by Erhan *et al*[16, 17]. The bodying process increased viscosity by 23% and reduced the iodine number by 45%. The iodine value and viscosity of BSBO were 67 and 80 cS, respectively.[18]

6. Epoxidized BSBO. The method used to prepare epoxidized BSBO was similar to that for epoxidized DG SBO except the staring raw material was BSBO.

7. Selectively hydrolyzed BSBO. This polyol was derived from BSBO by enzyme hydrolysis. Lipase from *Candida rugosa* ("Amano" AY, Amano Enzyme, Elgin, IL) was used at a loading unit of 1 mg enzyme per g of BSBO and the weight ratio of BSBO to phosphate buffer (pH 7.0) was 1:1. The reaction was carried out in a well-mixed reactor at 45ºC for 4 h. The lipase selectively hydrolyzed saturated fatty acids, especially palmitic acid from BSBO, and introduced hydroxyl functional groups. Sodium bicarbonate solution (0.5 M) was used to wash and remove fatty acids from the polyol products after the enzyme hydrolysis.

8. SBO/Acetol and BSBO/Acetol. They were synthesized in a closed, well-mixed reactor. SBO (or BSBO) was mixed with acetol (20% by wt.) at 180ºC for 9 h with rigorous agitation to produce SBO/Acetol (or BSBO/Acetol). The reason to use acetol is that Acetol is expected to be an inexpensive material due to high volume of glycerin in the market from the expanding of biodiesel manufacturing.[19] The products were washed by water to remove unreacted acetol and then neutralized.

9. DG of castor oil. Diglycerides (DG) of castor oil were produced by transesterification of castor oil triglycerides and glycerol. Sulfuric acid was used as the catalyst at a high temperature (>120ºC) in a closed well-mixed reactor.

10. Oxidized DG castor oil. To produce oxidized DG castor oil, DG products from the transesterification of castor oil were oxidized for 30 h by heating (100-110ºC) and oxygen bubbling. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng *et al*[15].

11. Oxidized ESBO. It was synthesized by applying heat and oxygen bubbles to ESBO at 100-110ºC for 30 h. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng *et al*[15].

12. Hydroxy methoxy SBO. It was produced via alcoholysis of epoxidized soybean oil (ESBO) by reacting ESBO with methanol using an acid catalyst according to the method of Suppes and Dasari.[14] One epoxy group in ESBO was opened producing one hydroxyl group and one methoxyl group.

13. Hydroxy SBO. It was produced by reacting ESBO with water using an acid catalyst according to the methods of Suppes and Dasari.[14] One epoxy group in ESBO was opened producing two hydroxyl groups.

14. ESBO/Acetol. It was synthesized similarly to the production of SBO/Acetol, or BSBO/Acetol except ESBO was used instead of SBO or BSBO.

15. Selectively hydrolyzed ESBO. It was derived from ESBO by enzyme hydrolysis using lipase from *Burkhloderia cepacia* (a gift from Amano Enzyme, Inc. Elgin, IL) according to the methods of Kiatsimkul, Sutterlin and Suppes.[20] ESBO triglycerides and phosphate buffer pH 7.0 (1:1) was mixed with the lipase (67.5 enzyme units per g of ESBO) in a well-mixed reactor at 50ºC for 2-4 h. The lipase selectively replaced saturated fatty acid (palmitic and stearic) moieties with hydroxyl functional groups. The product was washed and neutralized by sodium bicarbonate solution (0.5 M).

2.3.2 Hydroxyl Number Test

The American Society for Testing and Materials (ASTM) procedure E222-00 (reapproved 2005) method A was used to determine the hydroxyl value (hydroxyl number) of polyols. If the sample contained a free acid or base, a correction factor was applied. If sodium hydroxide was required to neutralize the sample, the correction factor, which is also called acid value, was added to the hydroxyl number. If hydrochloric acid was used to neutralize the sample, the correction factor was subtracted from the hydroxyl number.

2.3.3 Experimental Design and Formulations

The effect of the different kinds of soybean oil, epoxidized soybean oil, castor oil and their derivates in the foam formulation on the properties of water-blown rigid polyurethane foams were studied. Other factors in the foam formulation such as water content, catalysts, surfactant, and isocyanate index were kept constant. The foam formulation for water-blown rigid polyurethane foam is shown in Table 2.2. The amount of isocyanate in each formulation was based on the total hydroxyl content of VORANOL® 490, vegetable oil-based polyols, and distilled water.

2.3.4 Foaming Procedures

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used.[21] The petroleum polyol (VORANOL® 490), vegetable oil based polyol, catalysts, surfactant, and blowing agent (B-side materials) were added by weighing into a 500 mL disposable plastic cup and mixed at 3450 rpm for 10-15 s. The mixture was allowed to degas for 120 s. PAPI® 27 (A-side material) was then added rapidly and stirring was continued for another 10-15 s at the same speed. The mixtures were poured immediately into a wooden mold (11.4×11.4×21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23ºC). Figure 2.1 illustrates the foaming procedures.

2.3.5 Foam Property Measurements

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

2.4 Results and Discussion

2.4.1 Hydroxyl Number

Fifty different polyol samples were tested for their hydroxyl numbers. These samples were classified into 8 different categories based on their raw materials. Table 2.3 shows the results of the hydroxyl number test of various vegetable oil polyols as compared against the control, Voranol® 490, a common polyol for rigid polyurethane foams.

As expected, lower hydroxyl numbers were found for soybean oil and bodied soybean oil. On the other hand, some vegetable oil polyols made from epoxidized soybean oil reacted with acetol, diglycerides, and epoxidized soybean oil had a relatively high hydroxyl number. It is interesting to note that even though epoxidized soybean oil does not have the alcohol functional group in its chemical structure as shown in Figure 2.2, its hydroxyl number of 404 is close to that of Voranol® 490. However, when hydroxyl number of epoxidized soybean oil was test in the hydroxyl number determination process, the epoxidized soybean oil was placed in acid solution (mixture of pyridine and acetic anhydride) for 2 to 4 hours and then titrated with 0.5N of sodium hydroxide for a very short period of time (30 to 60 seconds). The further study will be needed to investigate the role of epoxidized soybean oil in polyurethane foaming.

2.4.2 Thermal Conductivity

Figure 2.3 shows the thermal conductivity of the foams that were made with 50 different vegetable oil polyol samples. All samples used a combination of 50% Voranol® 490 and 50% vegetable oil polyol as the polyol component (B-side) for the polyurethane foam, except the first one, which was 100% Voranol® 490 and served as the control for comparison. In addition, 3% of distilled water, based on the amount of polyol, was used as the blowing agent. It is interesting and encouraging to note that some foams made with 50% of epoxidized SBO series polyols, DG (ENOVA) series polyols, commercial soyols, and ESBO reacted with acetol polyols had a thermal conductivity as low as foams made with 100% Voranol® 490.

Most foams, however, had a thermal conductivity higher than foams made with 100% Voranol® 490. This could be attributed to the slower reaction rate of soybean oil polyols with isocyanate. Unlike Voranol® 490 which has the majority of its functional group (OH group) as primary alcohols, the majority of functional group in soybean oil polyols is secondary. The reaction rate of primary alcohols with isocyanate is about 3.3 times faster than that of secondary ones in the polyurethane reaction.[22] During polyurethane foaming reaction, carbon dioxide is generated by the reaction between water and isocyanate which is faster than the reaction between the primary hydroxyl group in Voranol® 490 and isocyanate. Since the soybean oil polyols in this study contain only secondary hydroxyl group, they react with isocyanate at a slower rate than the primary hydroxyl group in Voranol® 490. A slower reaction rate might weaken the three-dimensional network of the polyurethane foam which is less capable of holding up the pressure of carbon dioxide generated from the polyurethane reaction and cells in polyurethane foam are more open (data not shown). Carbon dioxide contributes to the low thermal conductivity in water-blown rigid polyurethane foam and open cells increases air convection and increases thermal conductivity. Therefore, foams with a lower carbon dioxide content and more open cells would have a higher thermal conductivity.

2.4.3 Density and Compressive Strength

Figure 2.4 shows the density and compressive strength of polyurethane foams made with 50 different soybean oil polyols. The data shown as solid square symbols are polyurethane foams made with 100% Voranol® 490 with 2% to 5% of distilled water as the blowing agent. The compressive strength of these foams increased linearly with foam density. This is a commonly observed phenomenon in many cellular foam systems.[23]

Increasing the water content, which acted as a blowing agent, expanded the foam volume resulting in thinner foam cell walls and larger foam cells. Therefore, the compressive strength decreased. Similar results have been reported.[24] The data shown on the left side of solid square symbols had inferior density and compressive strength property to foams made with 100% Voranol® 490 while the data on the right side had superior one.

The ellipse area contains foams made with 50% of Voranol® 490 and 50% epoxidized soybean oil. The diamonds are foams made with 50% of Voranol® 490 and 50% of hydrolyzed epoxidized soybean oil. As shown, foams made with both epoxidized soybean oil and hydrolyzed epoxidized soybean oil had similar density and compressive strength properties and were only slightly inferior to foams made with the control polyol, Voranol® 490. Further optimization in the foam formulation may result in foams with density and compressive strength property similar to the control. It is interesting to note that the epoxidized soybean oil does not have the hydroxyl functional group in its chemical structure. Although the epoxy ring will react with isocyanate to form oxazolidone, the reaction rate of this reaction is too slow at the room temperature. However, it appears there were some unknown cross-linking reactions between epoxidized soybean oil and isocyanate based on the foam density and compressive strength results that were only slightly inferior to foams made with 100% Voranol® 490. Further research on reaction of epoxidized soybean oil with isocyanate is needed since it is beyond the scope of this study.

Some foams had encouraging and better density and compressive strength properties than foams from 100% Voranol® 490 as shown in Figure 2.4. These foams were made with 50% replacement of Voranol® 490 by: 1) hydroxy SBO, 2) ESBO/Acetol, and 3) oxidized epoxidized DG SBO. Therefore, some derivatives of epoxidized soybean oil and diglyceride show the potential to make high quality rigid polyurethane foams. Again, additional study is needed to elucidate the reaction chemistry of these new soyol polyols with isocyanate.

2.4.4 Hydroxyl Number Effects

Figures 2.5 to 2.7 show the results of thermal conductivity, density, and compressive strength of foams from polyols with various hydroxyl numbers. Except the control foam which used 100% Voranol® 490, all foams were made with 50% of Voranol® 490 and 50% of vegetable oil based polyols as the B-side components and 3% water was used as a blowing agent. The OH number of each mixture was calculated as follows:

$$OH_m = \frac{OH\ of\ Voranol®\ 490 \times 50 + OH\ of\ Vegetable\ Oil\ Based\ Polyols \times 50}{100}$$

where

OH_m= The hydroxyl number of polyol mixture

OH of Voranol® 490 = 484.4 mgKOH/g

Figure 2.5 shows the relationship between thermal conductivity of foams and the hydroxyl number of polyol mixtures. As shown, the hydroxyl number did not significantly affect the thermal conductivity of foams (r = -0.46). This is not surprising since the hydroxyl number alone does not provide information whether the hydroxyl group in polyol mixture is primary or secondary, which has very different reaction rates with isocyanate causing differences in open cell content. The thermal conductivity of foams is contributed by the thermal conductivity of gas trapped in the foam cells, thermal conductivity of foam cell membrane material, convection of cell gas, cell size, cell orientation, closed cell content, foam density, and thermal radiation.[23] While the hydroxyl number of polyol mixtures (OH_m) influences the cross-linking density of foams, the convection of gas is mainly governed by the open cell content.

It is interesting to note that while the majority of foams made with 50% vegetable oil based polyols and 50% Voranol® 490 had inferior or higher thermal conductivity than the control foam made with 100% Voranol® 490, some were equal or superior and show the potential for further study. These polyols were: 1) hydroxy SBO, 2) ESBO/Acetol, and 3) oxidized epoxidized DG SBO. It is also interesting to note that the foams made with 50% of these three vegetable oil based polyols and 50% Voranol® 490 also had encouraging and better density and compressive strength properties than foams made from 100% Voranol® 490 as shown in Figure 2.4.

Figure 2.6 shows the relationship between density of foams and the hydroxyl number of polyol mixtures. As shown, the hydroxyl number of polyol mixtures seems did not significantly affect density of foams ($r = 0.58$). However, it was noted that foams made from vegetable oil based polyols having hydroxyl number below 100, or polyol mixtures having OH_m lower than 292, usually shrank within a few days of storage at room temperature. The shrinkage reduced the dimensions of foams resulting in higher density of foams (Figure 2.6). If these data (having OH_m lower than 292) were ignored, foams made from a higher OH_m number of polyol mixture appeared to have a higher density ($r = 0.68$).

Figure 2.7 shows the relationship between OH_m number of polyols and compressive strength of foams. It is evident that compression strength of foams increased with increasing OH_m number of polyols ($r = 0.86$). As mentioned previously, a higher OH_m number of polyols will consume more isocyanate causing foams to have a higher cross-linking density of foams. Both higher cross-linking density and higher foam density (Figure 2.6) will result in foams with a higher compressive strength.[1] In addition, it should be noted here that density and compressive strength should be used together to compare the foams made from 50% vegetable oil based polyols and 50% Voranol® 490 against foams made from 100% Voranol® 490 as shown in Figure 2.4.

2.5 Conclusions

In summary, novel water-blown rigid polyurethane foams were successfully prepared by blending petroleum polyol and vegetable oil based polyol together as the B-side component. Some polyols that derived form soybean oil had a lower thermal conductivity than petroleum polyol, such as epoxidized SBO series polyols, DG (ENOVA) series polyols, commercial soyols, and polyols made by reacting ESBO with acetol. Foams made from other soybean oil polyols had a higher thermal conductivity because the hydroxyl group in their chemical structure is secondary. The hydroxyl number of polyols affected the density and compressive strength of foams but not the thermal conductivity. Foams made with hydroxy SBO, ESBO/Acetol, and oxidized epoxidized DG SBO not only had superior thermal conductivity, but also better density and compressive strength properties than the petroleum polyol. These three vegetable oil based polyols appear to have the potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications. Foams made from epoxidized soybean oil, despite not having any hydroxyl groups in its chemical structure, surprisingly had density vs. compressive strength properties similar to those of petroleum polyol in polyurethane foams. Further studies are needed to investigate the reaction mechanism of epoxidized soybean oil with isocyanate in rigid polyurethane foam applications.

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Table 2.1. The derivatives from soybean oil, epoxidized soybean oil, and castor oil used in this study.

Raw Materials	Derivatives
Soybean Oil (SBO)	Diglyceride Soybean Oil (DG SBO)
	Oxidized DG SBO
	Oxidized Epoxidized DG SBO
	Blown SBO
	Oxidized SBO
	Bodied SBO (BSBO)
	Epoxidized BSBO
	Selectively Hydrolyzed BSBO
	SBO/Acetol
	BSBO/Acetol
Epoxidized SBO (ESBO)	Oxidized ESBO
	Hydroxy Methoxy SBO
	Hydroxy SBO
	ESBO/Acetol
	Selectively Hydrolyzed ESBO
Castor Oil	DG Castor Oil
	Oxidized DG Castor Oil

Table 2.2. Formulations for Water-blown Rigid Polyurethane Foam with 50% of soybean oil based polyols.

Ingredients	Parts by weight
B-side materials	
VORANOL® 490	50
Vegetable Oil based Polyol	50
Polycat® 5	1.26
Polycat® 8	0.84
Dabco® DC 5357	2.5
Blowing Agent (distilled water)	3.0
A-side material	
PAPI® 27	Index 110[a]

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

Table 2.3. Hydroxyl numbers of soybean oil, epoxidized soybean oil, and castor oil based polyols.

Polyols	OH number
Voranol® 490 (1)	484.4
Castor oil series (3)	152.4-176.2
Soybean oil series (6)	6.2-177.7
Epoxidized soybean oil series (14)	131.1-455.98
Diglyceride series (ENOVA) (7)	79.86-347.9
Commercial soybean oil polyols (4)	61.5-178.0
Bodied soybean oil series (11)	10.6-198.72
Epoxidized soybean oil reacted with acetol (4)	172.7-271.3

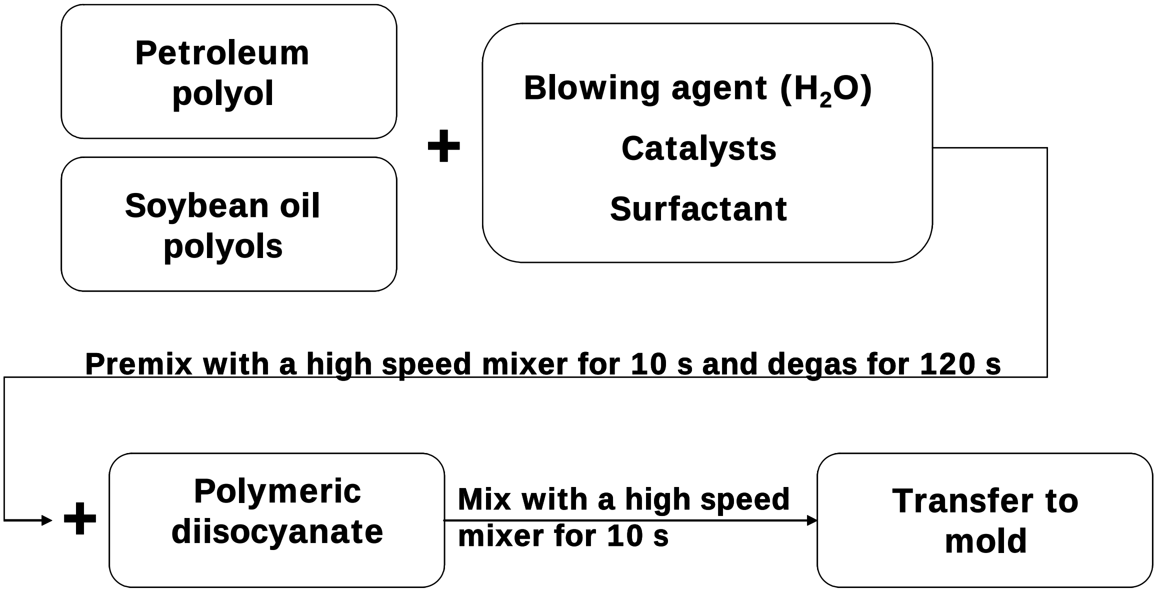

Figure 2.1. Procedures of preparing polyurethane foams in the laboratory.

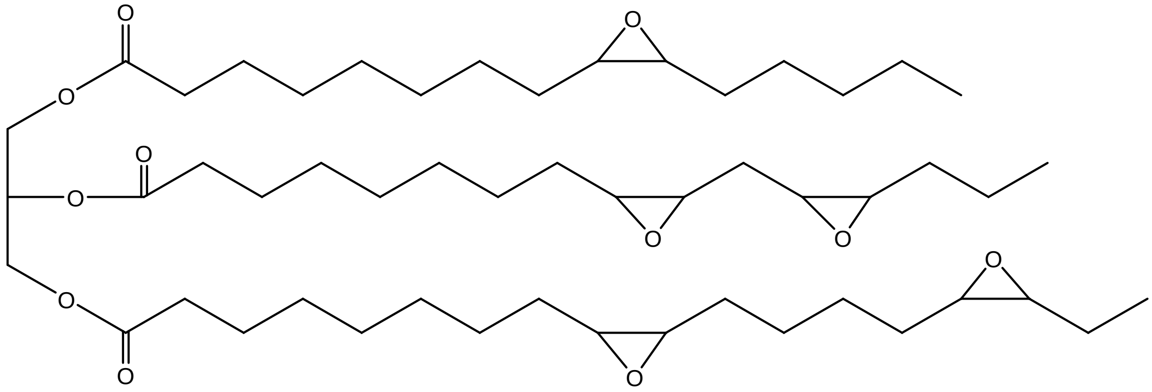

Figure 2.2. Representative chemical structure of epoxidized soybean oil (ESBO).

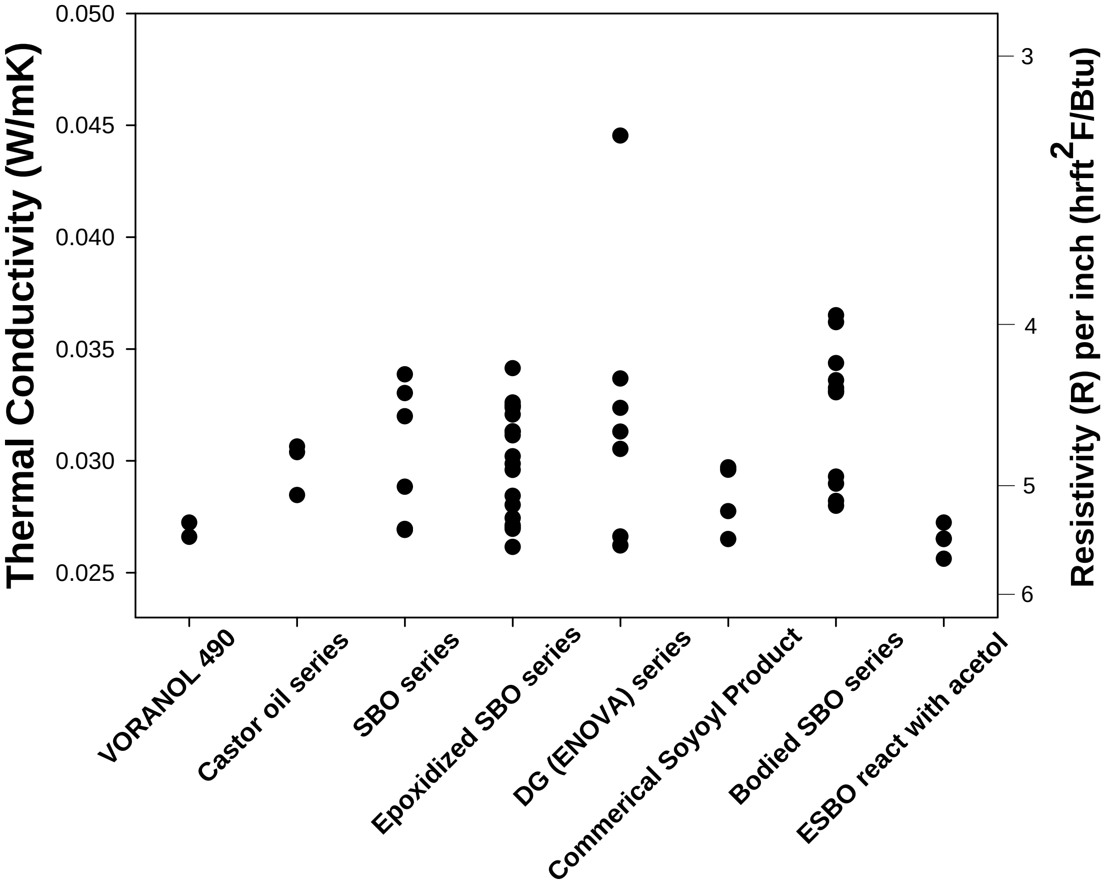

Figure 2.3. Thermal conductivity of foams made with polyols containing 50% Voranol® 490 and 50% of various vegetable oil based polyols.

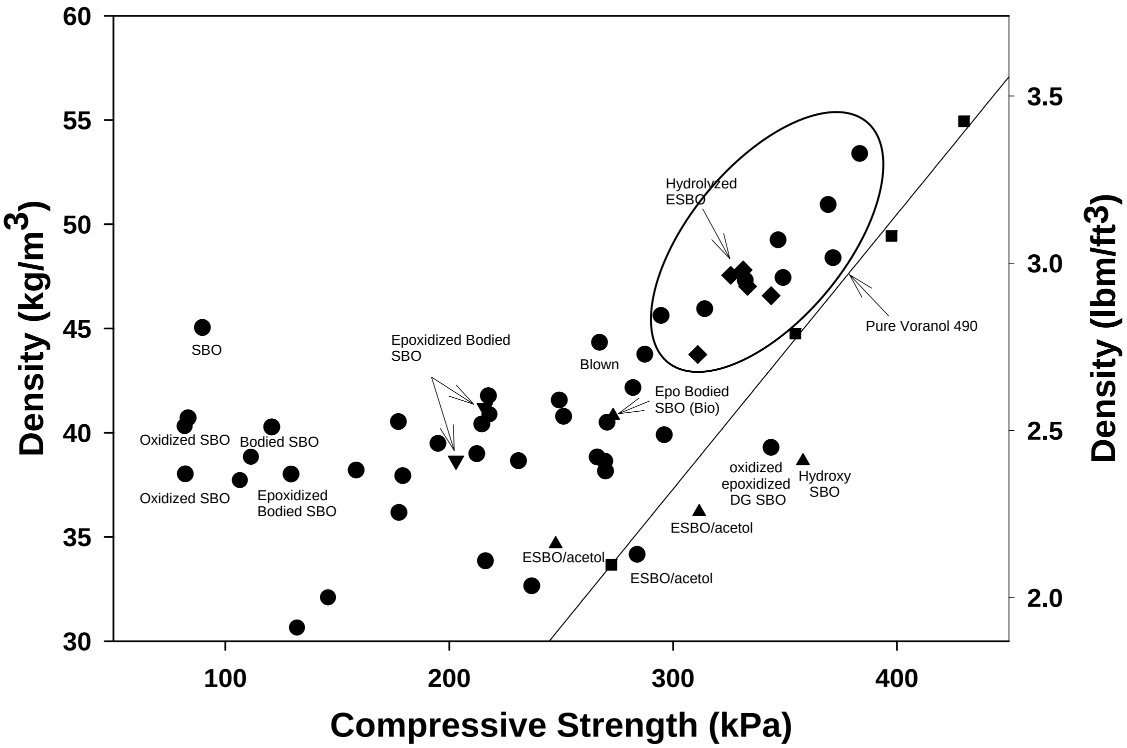

Figure 2.4. Density vs. compressive strength of polyurethane foams made with soybean oil polyols.

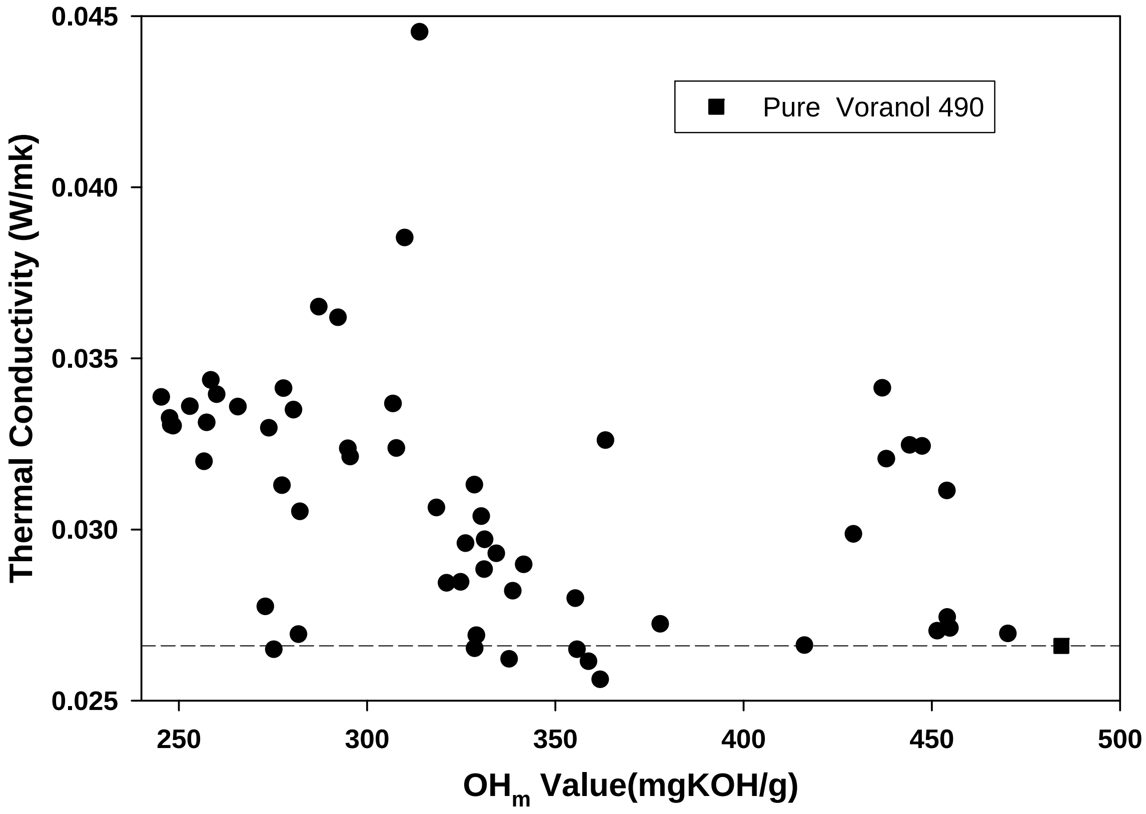

Figure 2.5. Thermal conductivity of foams vs. hydroxyl number of soybean oil polyols.

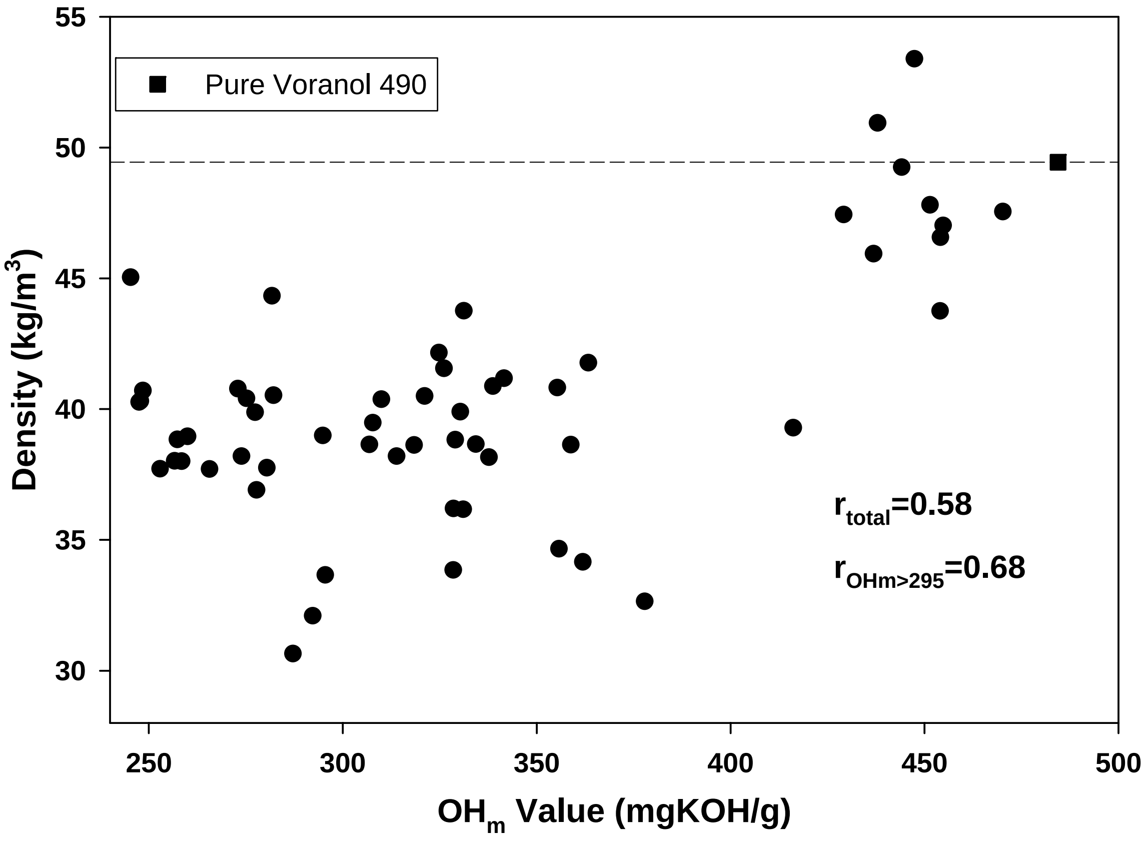

Figure 2.6. Density of foams vs. hydroxyl number of soybean oil polyols.

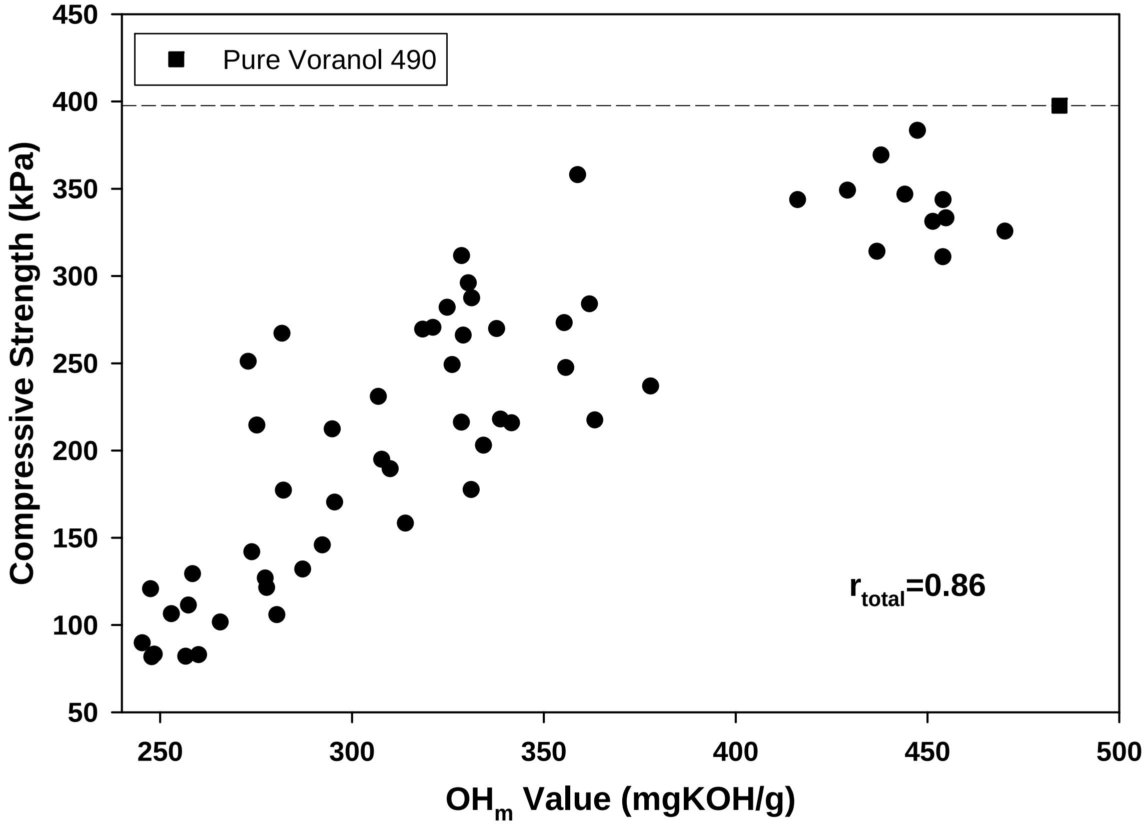

Figure 2.7 Compressive strength of foams vs. hydroxyl number of soybean oil polyols.

CHAPTER 3

WATER-BLOWN RIGID AND FLEXIBLE POLYURETHANE FOAMS CONTAINING EPOXIDIZED SOYBEAN OIL TRIGLYCERIDE

3.1 Abstract

Both rigid and flexible water-blown polyurethane foams were made by replacing 0-50% of Voranol® 490 for rigid foams and Voranol® 4701 for flexible foams in the B-side of foam formulation by epoxidized soybean oil. For rigid water-blown polyurethane foams, density, compressive strength and thermal conductivity were measured. While there were no significant changes in density, compressive strength decreased and thermal conductivity decreased first and then increased with increasing epoxidized soybean oil. These results could be explained by differences in the hydroxyl number between Voranol® 490 and epoxidized soybean oil as well as in the reactivity between the primary hydroxyl groups in Voranol® 490 and the secondary reactive functional groups in epoxidized soybean oil. For flexible water-blown polyurethane foams, density, 50% compression force deflection, 50% constant force deflection, and resilience of foams were measured. Density decreased first and then increased, no changes in 50% compression force deflection first and then increased, increasing 50% constant force deflection, and decreasing resilience with increase in epoxidized soybean oil. These results could be explained by differences in the hydroxyl number and

equivalent weight between Voranol® 4701 and epoxidized soybean oil. It appears that up to 20% of Voranol® 490 could be replaced by epoxidized soybean oil in rigid polyurethane foams. When replacing up to 20% of Voranol® 4701 by epoxidized soybean oil in flexible polyurethane foams, density and 50% compression deflection properties were similar or better than control but resilience and 50% constant deflection compression properties were inferior.

3.2 Introduction

With numerous advantages like light weight, good heat insulation, excellent strength and weight ratio, and good force and sound absorbing properties, the consumption of polyurethane foams has grown rapidly and they become indispensable part in our daily life.[1] Effort to use alternative resources to replace finite petroleum for making polyurethane foams has been accelerated in recent years. The major alternative and renewable resources are vegetable oils such as soybean oil. Soybean oil is a triglyceride which contains several unsaturated π bonds as shown in Figure 3.1. Several methods have been reported for converting soybean oil triglyceride into polyols. For example, the hydroxyl functionalities[2-4] or the epoxy group[5-7] can be attached directly to the unsaturated π bonds in the soybean oil triglyceride. Unlike the group with hydroxyl functionalities, the epoxy group does not react directly with the isocyanate.[8] Therefore, the epoxy rings in the epoxidized soybean oil triglyceride will need to be converted further into hydroxyl groups through other methods.[9-13] In a previous study, we found that epoxidized soybean oil triglyceride can be blended with a commercial polyether polyol and used in polyurethane foaming directly, however. The epoxidized soybean oil triglyceride has a high hydroxyl number (403.8) and the resulting foam has excellent density versus compressive strength properties.[14] Epoxidized soybean oil appears to have participated in the polyurethane foaming reaction and formed the cross-linking structure. The objective of this study is to further investigate the role of epoxidized soybean oil in both rigid and flexible water-blown polyurethane foams.

3.3 Materials and Methods

3.3.1 Materials

Epoxidized soybean oil (Vikoflex® 7170) used in this study was supplied by ATOFINA Chemicals (Philadelphia, PA) with a hydroxyl number of 403.814,15. Voranol® 490 and Voranol® 4701 are petroleum-based polyether polyols with a hydroxyl number of 490 and 34 for rigid and flexible foam applications, respectively. PAPI® 27, a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, has 340 average molecular weight, and 31.4% part by weight of NCO content. Voranol® 490, Voranol® 4701, and PAPI® 27 were obtained from Dow Chemical Co. (Midland, MI). The catalysts for rigid polyurethane foaming were POLYCAT® 5 and POLYCAT® 8. A surfactant, DABCO® DC 5357, was used in rigid polyurethane foaming. DABCO 33-LV®, DABCO® BL-17, stannous octoate, dibutyltin dilaurate were used as catalysts and DABCO® DC 2585 was the surfactant for flexible polyurethane foaming. A cross-linker, diethanolamine, was used in flexible polyurethane foaming. POLYCAT® 5, POLYCAT® 8, DABCO 33-LV®, DABCO® BL-17, Dabco® DC 5357, and DABCO®

DC 2585 were from Air Products & Chemicals (Allentown, PA) gratis. Both stannous octoate and dibutyltin dilaurate were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). Diethanolamine was from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

3.3.2 Experimental Design and Formulations

The effects of replacing the B-side polyether polyols (Voranol® 490 and Voranol® 4701) with 0-50% of epoxidized soybean oil in the foam formulation on the properties of water-blown rigid and flexible polyurethane foams were studied. Other factors in the foam formulation such as water content, catalysts, surfactant, and isocyanate index were kept constant. Tables 3.1 and 3.2 show the foam formulations for water-blown rigid and flexible polyurethane foams. The amount of isocyanate was based on the total hydroxyl content of Voranol® 490, Voranol® 4701, epoxidized soybean oil, and distilled water.

3.3.3 Foam Property Measurements

3.3.3.1 Rigid Polyurethane Foam Properties

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23ºC) for 24 h, by a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA), using American Society of Testing and Materials (ASTM) Procedure C 518-04. The dimension of the foam samples was 20×20×2.5 cm. Density of foam samples was measured according to ASTM procedure D 1622-03. Compressive strength of foams was determined by a TA.HDi Texture Analyzer (Texture Technologies

Corp., Scarsdale, NY) following ASTM Procedure D 1621-04a. Both density and compressive strength were conducted after foams were stored for 7 days at room temperature (23°C and 50% RH) and the dimension of the foam sample was 6.35×6.35×3.81 cm. Five measurements were made for each treatment and the average reported.

3.3.3.2 Flexible Polyurethane Foam Properties

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

$$C_t = \left(\frac{t_o - t_f}{t_o} \right) \times 100\%$$

where:

C_t = compression set expressed as a percentage of the original thickness,

t_o = original thickness of test specimen, and

t_f = final thickness of test specimen.

3.3.4 Extractable Oil of Water-blown Rigid Polyurethane

The determination of extractable oil in polyurethane foams was based on ASTM Procedure C 613-97 (Reapproved 2003) using Soxhlet's procedure. Rigid foams containing 0% (control) and 50% of epoxidized soybean oil were prepared and aged at ambient environment for 12, 36, 60, 84, 108, 132, and 156 h, respectively. Hexane obtained from Fisher Scientific (Hanover Park, IL) was used as the extraction reagent. The extraction time is 6 hours. Then the extraction thimble placed into 100°C oven overnight for drying. The extractable oil was calculated as follows,

$$Extractable\ Oil\ (\%) = \frac{W_o - W_e}{E} \times 100\%$$

where

W_o = Sample weight before extraction

W_e = Sample weight after extraction

E = Weight of B-side polyols in sample

3.3.5 Morphology of Water-blown Rigid Polyurethane Foams

A Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM, Tokyo, Japan) was used to examine the surface of water-blown rigid polyurethane foams containing 0-50% of epoxidized soybean oil. The water-blown rigid polyurethane foams were first cut into 3 mm cubes and then attached to the substrate with silver glue. Each sample was coated with gold by plasma sputter due to the non-conductivity of polyurethane. Samples were placed into the outer vacuum chamber and vacuumed after coated with gold. They were then moved into the inner chamber and under an electron gun after the pressure was balanced between outer and inner chambers. The accelerating voltage and emission current of FESEM were 5000 V and 9700 nA, respectively.

3.4 Results and Discussion

3.4.1 Density and Compressive Strength of Rigid Foam

Figure 3.2 shows the effect of epoxidized soybean oil on the density of water-blown rigid polyurethane foams. As shown, there was no significant difference in foam density as epoxidized soybean oil was increased from 0 to 50%. The density of plastic foam is dictated by the weight and volume of the plastics making up the foam matrix and the gases trapped in the foam cells. The plastic phase includes polyol, epoxidized soybean oil, isocyanate and all additives such as surface active agents, stabilizers, cross-linking agents, or processing aids (catalysts). The gas phase includes carbon dioxide, generated from the chemical reaction between the blowing agent (water) and isocyanate, and air which is either introduced during mixing or diffuses into the cells during the aging process. The blowing agent (water) was set at 3% for all foams. Although the isocyanate index was set at 110, the quantity of PAPI® 27 (isocyanate) in the foam formulation decreased slightly (about 6%) when increasing the epoxidized soybean oil from 0 to 50%. This was because the hydroxyl number of epoxidized soybean oil (403.8) is less than 490 of Voranol® 490. The reduction in isocyanate content might have not been sufficient to cause changes in foam density. On the other hand, the compressive strength of foams decreased with increasing epoxidized soybean oil percentage (r=-0.98) as shown in Figure 3.2. This was most likely caused by: 1) the slight reduction in isocyanate content when increasing epoxidized soybean oil lowered the foam cross-linking density and 2) a weaker three-dimensional foam network when increasing epoxidized soybean oil content due to a lower reaction rate of epoxidized soybean oil (containing secondary reactive functional groups) with isocyanate than Voranol® 490 (containing primary hydroxyl groups).[14-16]

3.4.2 Thermal Conductivity of Rigid Foam

Figure 3.2 also shows the effect of replacing Voranol® 490 with 0-50% of epoxidized soybean oil on thermal conductivity of water-blown rigid polyurethane foams. It is interesting to note that the foam thermal conductivity decreased with increasing epoxidized soybean oil up to 30%. This might be due to decreased polymer phase or solid structure with increasing epoxidized soybean oil content. As explained earlier, when increasing epoxidized soybean oil, the corresponding isocyanate content in the foam formulation decreased because epoxidized soybean oil had a lower hydroxyl number than Voranol® 490. When epoxidized soybean oil content was more than 30%, the polyurethane solid structure might have decreased to such an extent that the foam cells became more open and trap less carbon dioxide inside the foams. In addition, the reaction rate of epoxidized soybean oil with isocyanate was slower than Voranol® 490. This could lead to a weaker three-dimensional network causing cells to become more open[14,17]. As a result, the thermal conductivity would increase.

3.4.3 SEM Images of Rigid Foam

Figure 3.3(a) to (f) show the SEM images of water-blown rigid polyurethane foams with different epoxidized soybean oil contents. As shown, the bubbles appeared on the polyurethane foam when epoxidized soybean oil was incorporated. In addition, the number of bubbles increased with increasing epoxidized soybean oil up to 30%. Figure 3.4(a) to (d) shows the effect of epoxidized soybean oil on the bubbles size. It is evident that the bubble size increased with epoxidized soybean oil content. Thus, both number and size of bubbles increased with epoxidized soybean oil content. The presence of bubbles in the polyurethane foam structure seemed to indicate poor miscibility between epoxidized soybean oil and petroleum polyol which caused phase separation. In addition, epoxidized soybean oil reacted with isocyanate in much slower rate than Voranol® 490. Both poor miscibility and slower reaction rate might have weakened the three-dimensional network of the polyurethane foam, in particular, when epoxidized soybean oil was more than 30% in the foam formulation. Therefore, decreases in foam compressive strength and increases in thermal conductivity were observed as shown in Figure 3.2.

3.4.4 Oil Extraction of Rigid Foam

Table 3.1 shows that Voranol® 490 and epoxidized soybean oil were the sources of oil present in the water-blown rigid polyurethane foam. If the reaction between Voranol® 490 or epoxidized soybean oil and isocyanate were complete, extractable oil would be nil in the foam system. Figure 3.5 shows the effect of aging time of water-blown rigid polyurethane foams containing 0% and 50% of epoxidized soybean oil in the B-side of foam formulation on the percentage of extractable oil. As shown, most of Voranol® 490 (~92%) reacted with isocyanate at first 12 h for the foam containing 100% Voranol® 490 (i.e., 0% epoxidized soybean oil) in the B-side.[18] The extractable oil percentage decreased with aging time and Voranol® 490 almost fully reacted with isocyanate after 7 days. For foams containing 50% epoxidized soybean oil and 50% Voranol® 490 in the B-side, about 80% of them reacted with isocyanate at first 12 h. In addition, the extractable oil percentage also decreased with aging time and it took about 170 h for all epoxidized soybean oil and Voranol® 490 to complete their reaction with isocyanate. These results indicate: 1) similar to the petroleum polyol, Voranol® 490, epoxidized soybean oil also participated in the polyurethane reaction and contributed to the properties of polyurethane foam and 2) the reaction rate of epoxidized soybean oil with isocyanate was slower than Voranol® 490. The latter was not unexpected because the reactive functional groups in epoxidized soybean oil were secondary and less reactive than the primary hydroxyl groups in Voranol® 490.

3.4.5 Density of Flexible Foam

Figure 3.6 shows the effect of epoxidized soybean oil on the density of water-blown flexible polyurethane foams. The density decreased with increasing epoxidized soybean oil up to 30% and then increased. Because the hydroxyl number of epoxidized soybean oil (403.8) was much greater than Voranol® 4701 (34) and the isocyanate index was fixed at 80 (Table 3.2), the quantity of isocyanate (PAPI® 27) used in the foam formulation increased with epoxidized soybean oil. Thus, the foam matrix would weigh more with increases in epoxidized soybean oil. At the same time, foam volume would also increase due to more carbon dioxide from the reaction of isocyanate with the blowing agent (water) and maybe better gas retention of the foam matrix. The increase of foam volume exceeded the increase of foam weight up to 30% epoxidized soybean oil. Thus, the foam density decreased. Above 30% epoxidized soybean oil, the volume increase effect might have reached its limit and the gas retention deteriorated in the foam matrix. Both could be caused by the slower reaction rate of epoxidized soybean oil with PAPI® 27 than Voranol® 4701. Therefore, the foam density increased.

3.4.6 Compression Force Deflection of Flexible Foam

This test measures the force necessary to produce a 50 % compression over the entire top surface area of the foam specimen. A higher compression force deflection indicates the foam is firmer resulting from either a higher cross-linking density or a higher foam density or both. Figure 3.6 also shows the effect of epoxidized soybean oil on 50% compression force deflection of water-blown flexible polyurethane foams.

Similar 50% compression force deflection was observed for foams containing 0 to 30% epoxidized soybean oil. This could be explained by changes in foam density and cross-linking density. As epoxidized soybean oil increased from 0 to 30%, foam density decreased which would reduce the 50% compression force deflection. However, the cross-linking density increased, because epoxidized soybean oil had a higher hydroxyl number than Voranol® 4701 leading to using more isocyanate in the foam formulation, which would increase the 50% compression force deflection.[18] These two effects might have counteracted and cancelled each other. Thus, there was no significant change in 50% compression force deflection. When epoxidized soybean oil in foam exceeded 30%, both foam density and cross-linking density increased resulting in firmer foams. Therefore, the 50% compression force deflection would increase as shown.

3.4.7 Constant Deflection Compression Set of Flexible Foam

This test consists of deflecting the foam specimen to 50% initial thickness, exposing it to 70ºC and 6% RH for 22 h and measuring the change in the thickness of the specimen after recovery at 23°C and 50% RH for 30 to 40 min. A lower constant deflection compression set indicates the foam is more flexible and recovers its thickness better after deflection compression. Figure 3.7 shows the constant deflection compression set increased sharply when increasing epoxidized soybean oil from 0 to 10%. The increase then became less and the change was almost linear when increasing epoxidized soybean oil from 20 to 50%. It appears that the foams became less flexible and lost more of their initial thickness after deflection compression with increasing epoxidized soybean oil replacement of Voranol® 4701 in the foam formulation.[19]

The equivalent weights of Voranol® 4701 and epoxidized soybean oil are 1650 and 139, respectively. Equivalent weight is the molecular weight of polyol divided by its functionality, or 56100 divided by the hydroxyl number of polyol. The equivalent weight of polyol relates to or gives an indication of the length or distance between two adjacent hydroxyl functional groups in a polyol molecule. The polyol with a higher equivalent weight is expected to have a greater length or distance between two adjacent hydroxyl groups resulting in a longer "soft segment" in the polyurethane foam. In addition, the backbone of the epoxidized soybean oil is a triglyceride while Voranol® 4701 is linear in chemical structure. Because of the significant differences in the distance between two adjacent hydroxyl groups and the chemical structure, it is expected that the cell walls and struts in the polyurethane foam became stiffer, due to much shorter "soft segments" in the foam structure, and more easily be crushed or damaged by compression when more Voranol® 4701 is replaced by epoxidized soybean oil in the foam formulation. Therefore, constant deflection compression set increased with epoxidized soybean oil content in the foam.

3.4.8 Resilience (ball rebound test) of Flexible Foam

Figure 3.7 also shows effect of epoxidized soybean oil on the resilience of water-blown flexible polyurethane foams. It is apparent that the resilience of foams decreased steadily with increase in epoxidized soybean oil. Again, the loss of resilience was most likely due to significant differences in the equivalent weight between Voranol® 4701 and epoxidized soybean oil and their chemical structure. As a result, the foam containing more epoxidized soybean oil became stiffer and less resilient under the ball rebound testing conditions.

3.5 Conclusions

In conclusion, water-blown rigid and flexible polyurethane foams were successfully prepared by introducing epoxidized soybean oil in the foaming system. It appears that up to 20% of Voranol® 490 could be replaced by epoxidized soybean oil in rigid polyurethane foams without compromising the properties of rigid foams. It remains to be challenging when replacing up to 20% of Voranol® 4701 by epoxidized soybean oil in flexible polyurethane foams. While density and 50% compression deflection properties were similar or better than control flexible foams, resilience and 50% constant deflection compression properties were inferior.

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Table 3.1. Formulations for water-blown rigid polyurethane foam with different percentages of epoxidized soybean oil.

Ingredients	Parts by weight
B-side materials	
Voranol® 490	100, 90, 80, 70, 60, 50
Epoxidized Soybean Oil	0, 10, 20, 30, 40, 50
Polycat® 5	1.26
Polycat® 8	0.84
Dabco® DC 5357	2.5
Blowing Agent (distilled water)	3.0
A-side material	
PAPI® 27	Index 110[a]

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

Table 3.2. Formulations for water-blown flexible polyurethane foam with different percentages of epoxidized soybean oil.

Ingredients	Parts by weight
B-side materials	
Voranol® 4701	100, 90, 80, 70, 60, 50
Epoxidized Soybean Oil	0, 10, 20, 30, 40, 50
DABCO® 33-LV	0.6
DABCO® BL-17	0.2
Stannous octoate	0.3
Dibutyltin dilaurate	0.3
Diethanolamine	2.2
Dabco® DC 2585	1.0
Blowing Agent (distilled water)	5.0
A-side material	
PAPI® 27	Index 80[a]

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

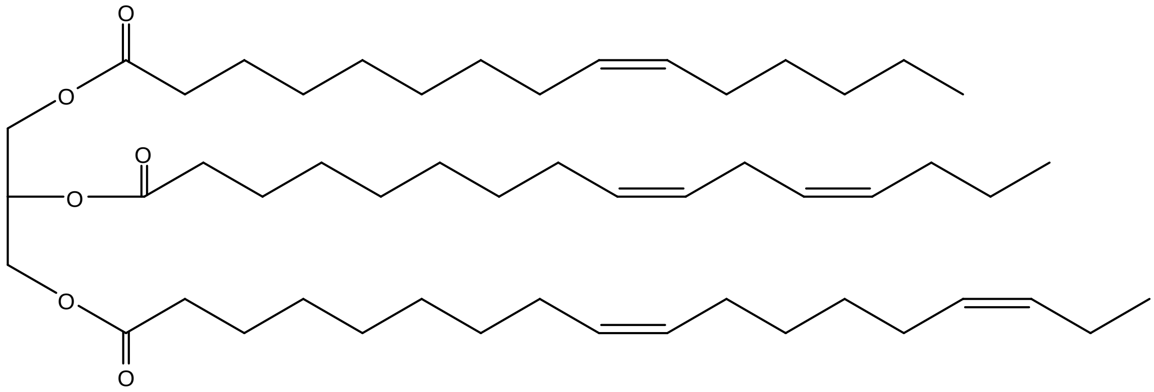


Figure 3.1. The chemical structure of soybean oil triglyceride.

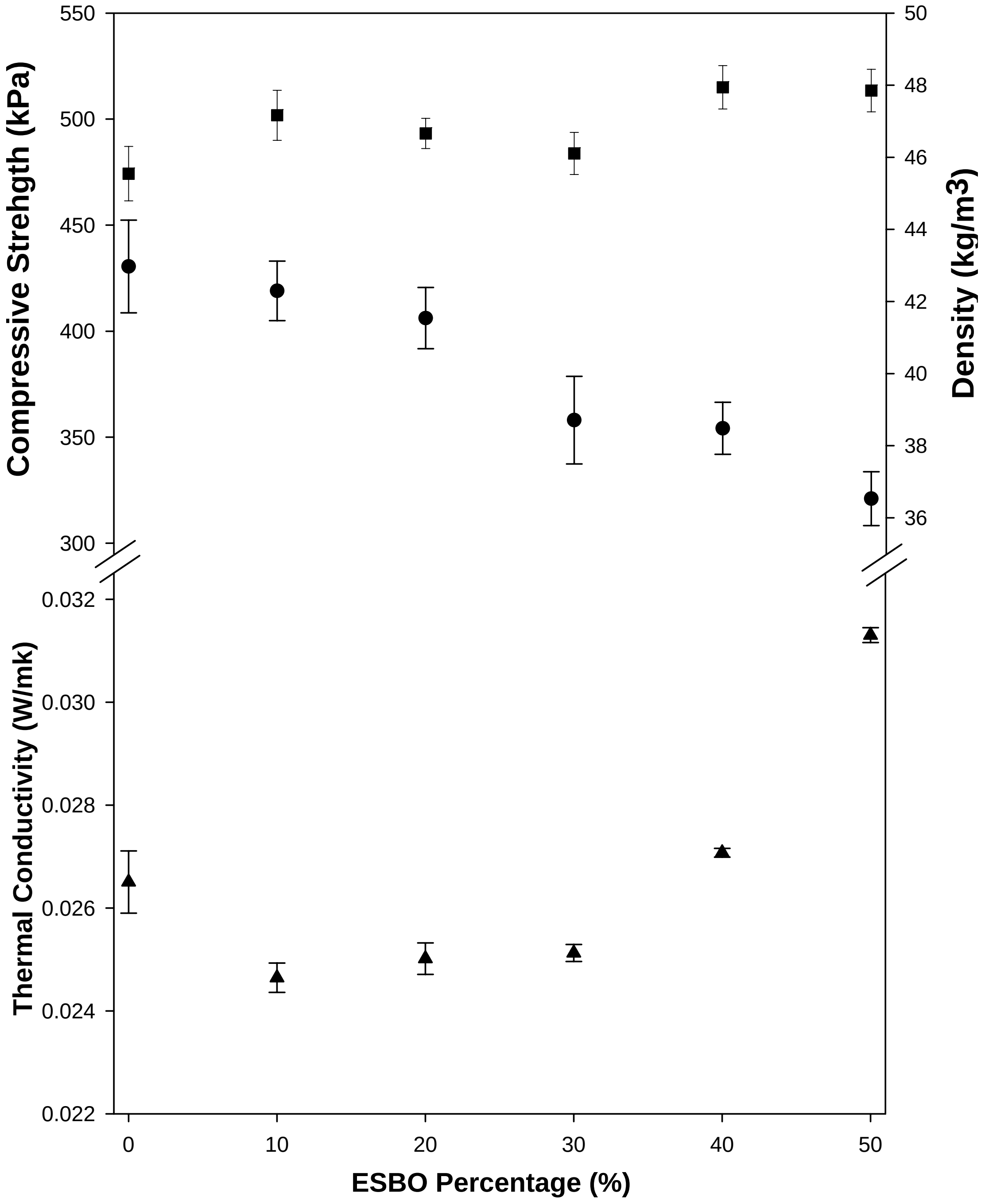
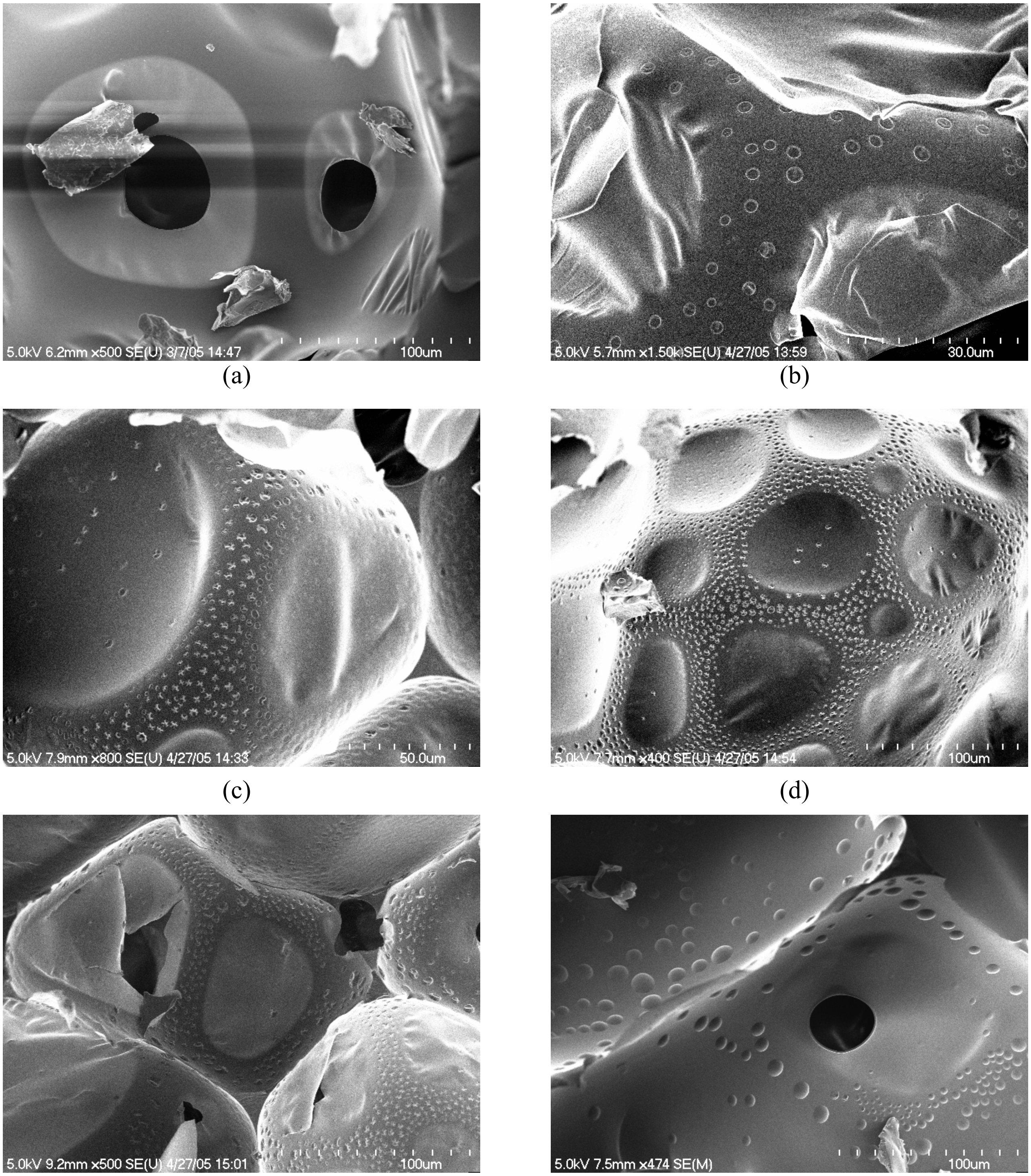


Figure 3.2. Compressive strength (●), density (■) and thermal conductivity (▲) of water-blown rigid polyurethane foams in different epoxidized soybean oil percentage.

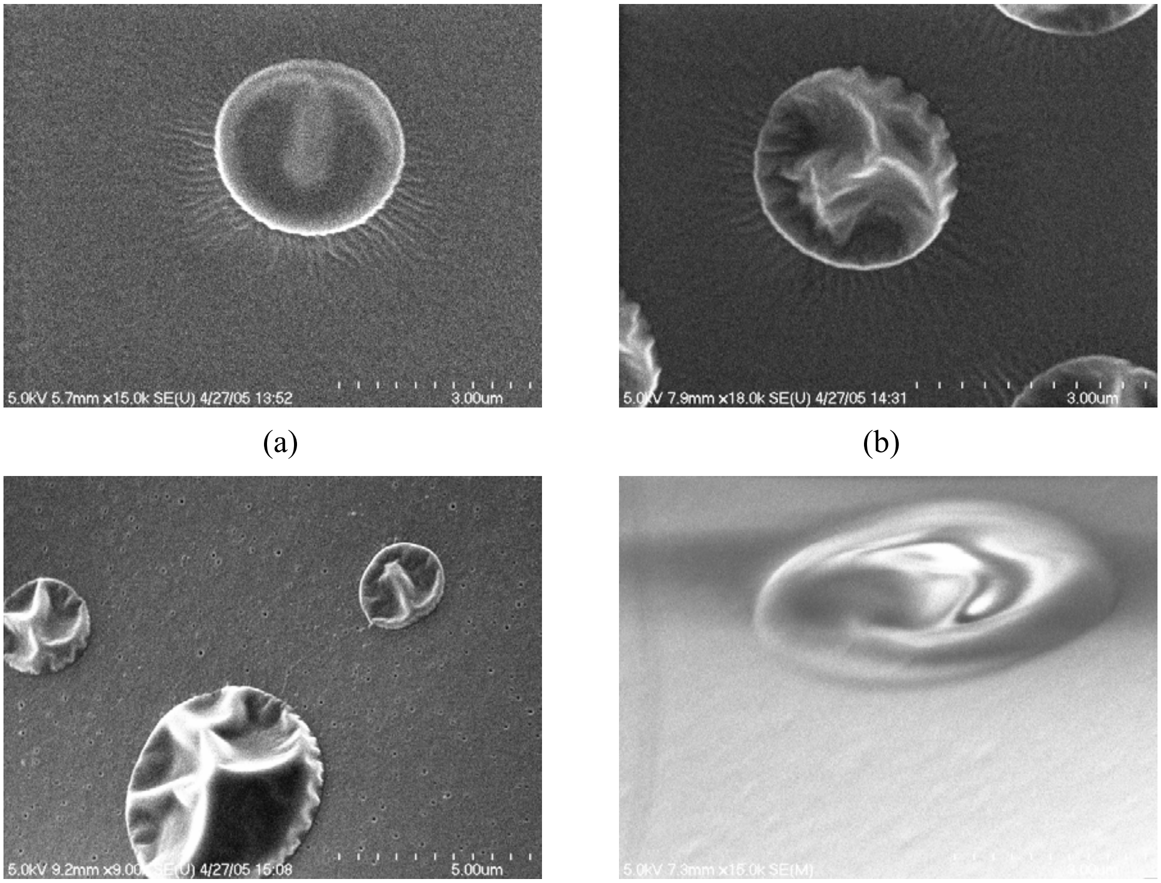


(a) (b)

(c) (d)

(e) (f)

Figure 3.3. SEM images of water-blown rigid polyurethane foams with (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, and (f) 50% of epoxidized soybean oil.



(a) (b)

(c) (d)

Figure 3.4. SEM images of water-blown rigid polyurethane foams with (a) 10%, (b) 20%, (c) 40%, and (d) 50% of epoxidized soybean oil.

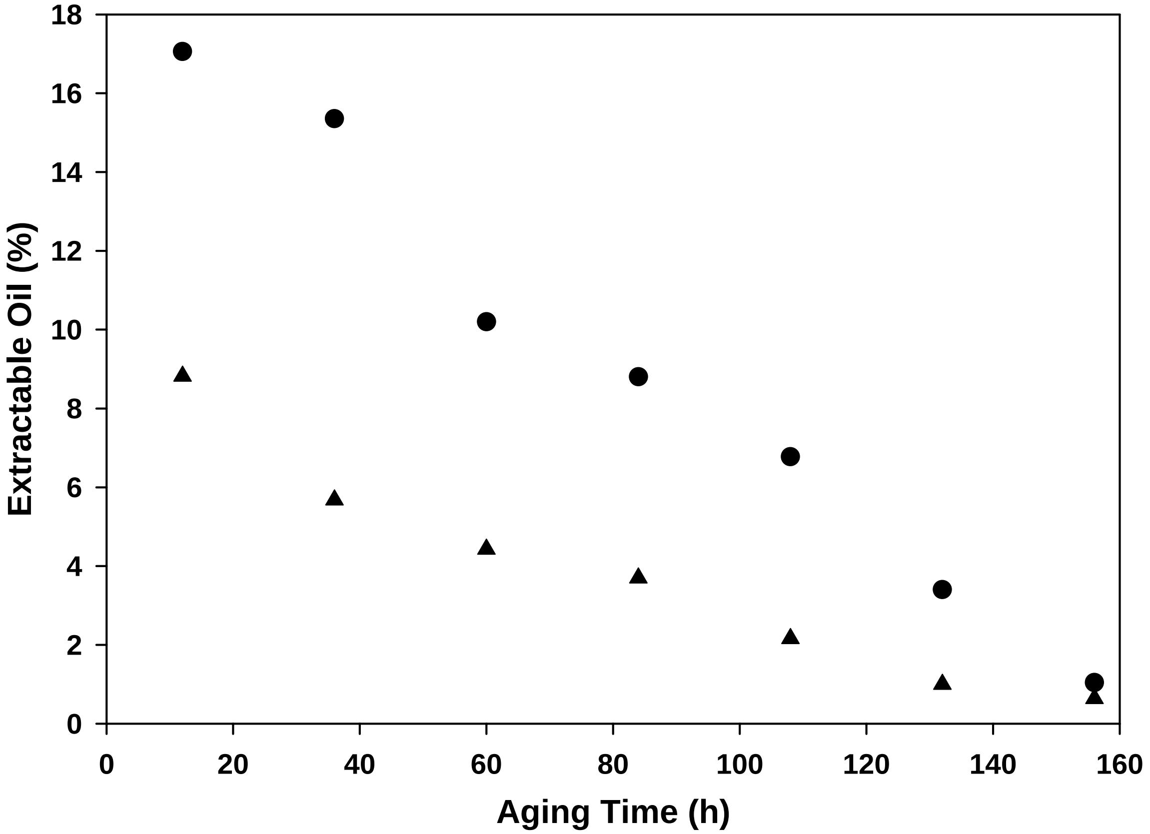


Figure 3.5. Oil extraction ratio of water-blown rigid polyurethane foams containing 50% of epoxidized soybean oil with different aging time.

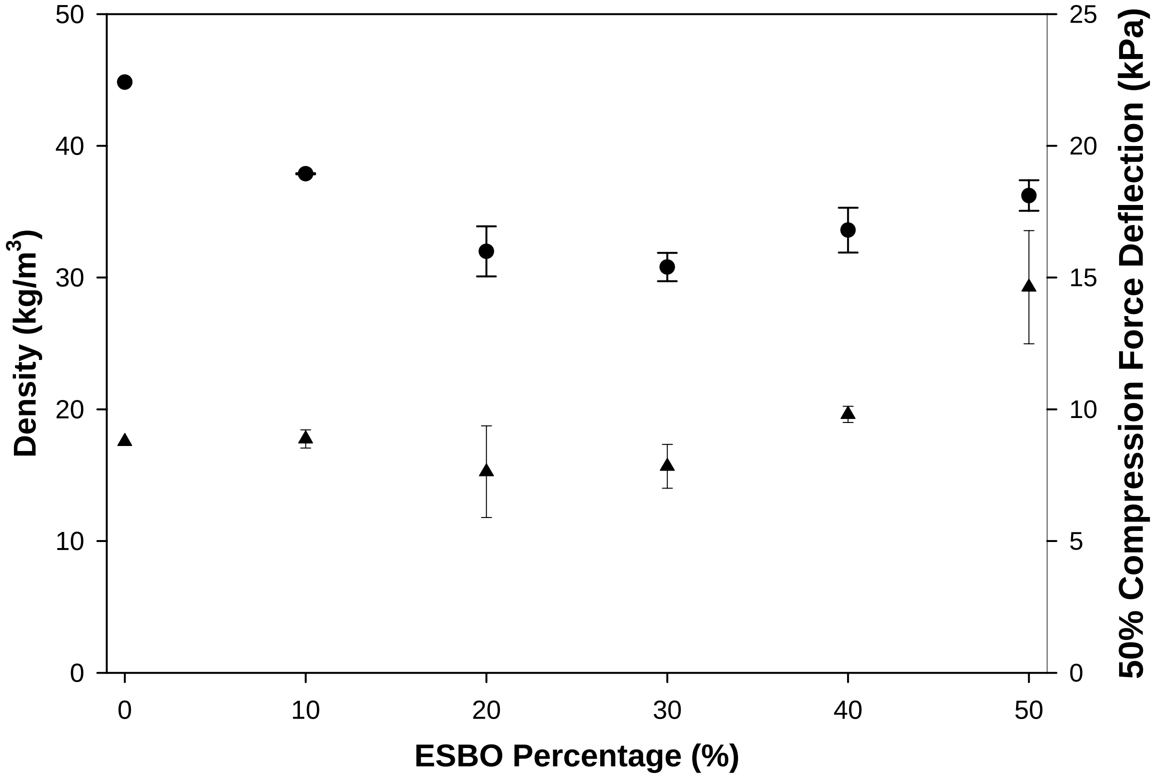


Figure 3.6. Density (●) and 50% compression force deflection (▲) of water-blown flexible polyurethane foams in different epoxidized soybean oil percentage.

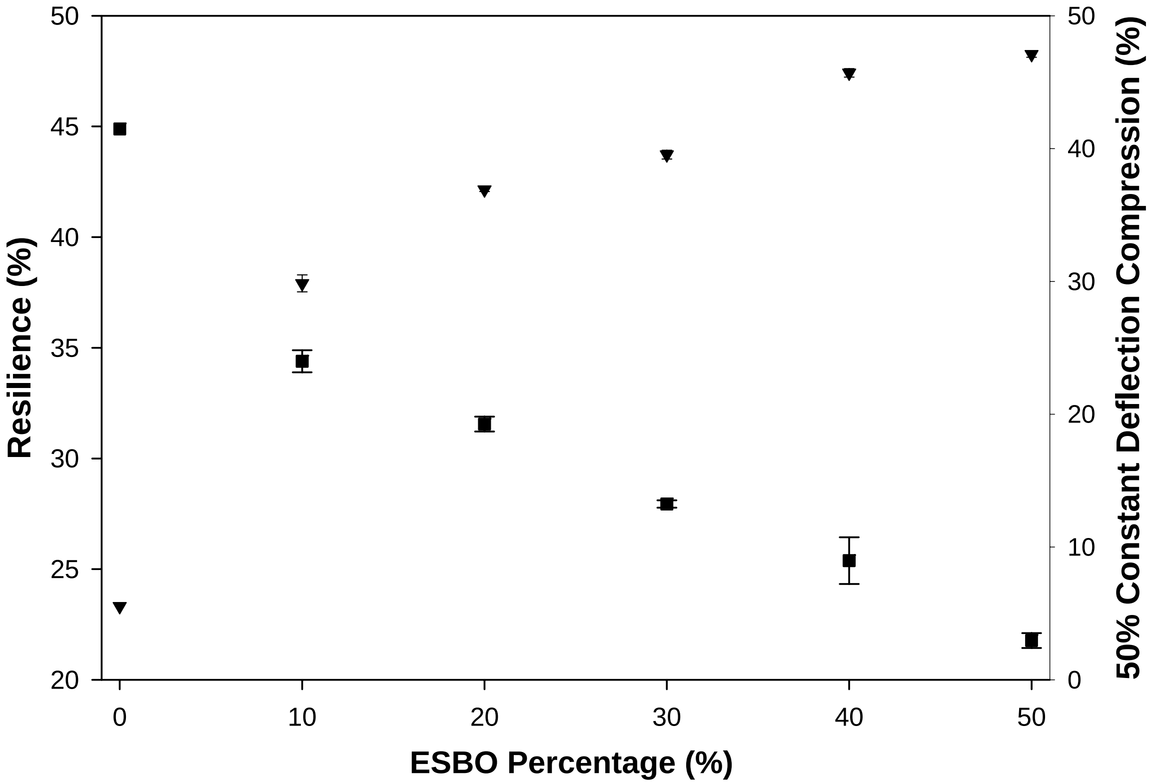


Figure 3.7. The resilience (■) and 50% constant deflection compression (▼) of water-blown flexible polyurethane foams in different epoxidized soybean oil percentage.

CHAPTER 4
THERMAL AND MECHANICAL BEHAVIOR OF FLEXIBLE POLYURETHANE MOLDED PLASTIC FILMS AND WATER-BLOWN FOAMS WITH EPOXIDIZED SOYBEAN OIL

4.1 Abstract

Water-blown flexible polyurethane foams and molded plastic films were made by replacing 0 to 50% of Voranol® 4701 in the B-side of the foam and plastic film formulation by epoxidized soybean oil (ESBO). Physical properties of foams including density, 50% compression force deflection (CFD), 50% constant deflection compression (CDC) and resilience were determined. A dynamic mechanical spectrometer (DMS) and a differential scanning calorimeter (DSC) were used to characterize the hard segment (HS) and soft segment (SS) ratio and thermal properties of plastic. Various functional groups in both flexible polyurethane foam and plastic film were characterized using Fourier transform-infrared spectroscopy with attenuated total reflectance (FTIR-ATR). When increasing the ESBO content, both density and 50% CFD of water-blown polyurethane foams decreased at first, then increased. On the other hand, the 50% CDC and resilience of foams showed a sharp increase and decrease, respectively. When increasing the ESBO content, the peak of tanδ in DMS analysis and Δc_p in DSC analysis of plastic films both decreased indicating that the hard segment increased and the soft

segment decreased in plastic films, respectively. The FTIR-ATR results also showed the hydrogen-bonded urethane group increased in plastic films with increasing ESBO content.

4.2 Introduction

For several years the derivatives from petroleum have been the major feedstock or raw materials for the polymer industry. Polyurethane polymer is one of the most versatile plastic materials derived from the petroleum resource. Depending on the reactants and process methods, polyurethane polymer can be an elastomer, viscoelastic gel, foam, or plastic with a wide range of applications such as construction materials, automotive seating, furniture, packing materials and medical devices.[1-4] The global consumption of polyurethane polymer shows more than 7% average growth rate annually in the past decade.[5,6] The petroleum price also shows a steady increase at the same time and a drastic increase within the last year. Additionally, the petroleum is a finite and not environmental friendly resource. Therefore, finding a new and renewable resource to fully or partially replace the petroleum resource is urgent for both environmental and economic considerations.[7]

Because of lower costs, more environmental friendly and bio-renewable polyols derived from vegetable oils have a great potential to partially replace the petroleum resource. In order for the triglycerides, the major component of vegetable oils, to react with isocyanate and synthesize polyurethane, it is believed that the hydroxyl functional groups would have to be attached to them first and one of the common methods is through alcoholysis of epoxidized vegetable oils.[8.9] In this method, the triglycerides of vegetable oils were epoxidized first. Methanol was then used to open the oxirane ring and attach the hydroxyl groups, a process called alcoholysis. We reported in our previous studies, that the epoxidized soybean oil (ESBO) can directly participate in the polyurethane foaming reaction without opening the oxirane ring first even though there is no hydroxyl functional group in ESBO.[10,11] The reaction mechanism between ESBO and isocyanate has yet to be elucidated and the effect of ESBO on the thermal, mechanical, and chemical properties of the resulting final products ─ polyurethane foams ─ has not been thoroughly studied and characterized. Therefore, a series of water-blown flexible polyurethane foams and molded plastic films were prepared in this study where 0-50% of a petroleum-based polyether polyol was replaced by ESBO. The objectives of this study were to investigate the effect of ESBO on the physical properties of water-blown polyurethane foams and on the thermal, mechanical, and chemical properties of water-blown polyurethane foams and molded plastic films.

4.3 Materials and Methods

4.3.1 Materials

The petroleum-based polyether polyol and isocyanate used in this study were Voranol® 4701 with a hydroxyl number of 34 and PAPI® 27, a polymeric diphenylmethane diisocyanate (MDI) with a functionality (the average number of reactive functional group which is NCO) of 2.7, an average molecular weight of 340, and 31.4% part by weight of NCO (isocyanate) content. Voranol® 4701 and PAPI® 27 were obtained from Dow Chemical Co. (Midland, MI). The epoxidized soybean oil, Vikoflex® 7170, with a hydroxyl number of 403.8,[10,11] was supplied by Arkema Chemicals Inc. (Philadelphia, PA). DABCO® 33-LV, DABCO® BL-17, stannous octoate, dibutyltin dilaurate were used as catalysts and DABCO® DC2585 and diethanolamine, as a surfactant and a cross-linker, respectively, for flexible polyurethane foaming. DABCO® 33-LV is a gelling catalyst containing 33% triethylenediamine (TEDA) and 67% dipropylene glycol. DABCO® BL-17 is an acid-blocked delayed-action blowing catalyst containing 70% bis (dimethylaminoethyl) ether diluted with 30% dipropylene glycol. DABCO® DC2585 is a silicone type non-ionic surfactant. DABCO® 33-LV, DABCO® BL-17, and DABCO® DC2585 were from Air Products & Chemicals (Allentown, PA). Both stannous octoate and dibutyltin dilaurate were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). Diethanolamine was from Fisher Scientific (Hanover Park, IL). Distilled water was used as the blowing agent.

4.3.2 Flexible Polyurethane Foam

Water-blown flexible polyurethane foams were made by replacing 0-50% of the B-side polyether polyols (Voranol® 4701) with ESBO in the foam formulation and the foaming procedure was the same as reported previously.[10] B-side materials contained a blend of polyols, chain extender, cross-linker, catalysts, surfactants, and blowing agent (water) while the A-side contained the isocyanate only. Other factors in the foam formulation such as water content, catalysts, surfactant, and isocyanate index were kept constant. Table 4.1 shows the foam formulations for water-blown flexible polyurethane foams and Figure 4.1 shows typical foam specimens with 10% to 50% ESBO replacement. The amount of isocyanate was based on the total hydroxyl content of Voranol® 4701, epoxidized soybean oil, and distilled water.

4.3.3 Flexible Polyurethane Mold Plastic Film

Flexible polyurethane plastic films were made by replacing 0-50% polyether polyol (Voranol® 4701) with ESBO. The isocyanate index was 100. Both polyol (Voranol® 4701 and ESBO) and PAPI® 27 were placed into a 500 mL plastic cup and mixed with a high speed mixer (3450 rpm) for 10 s. The mixture was then placed into a vacuum chamber and degassed for 15 min. The mixture was then poured into a mold and placed into a vacuum chamber to degas for 15 min. The mold was made of PTFE (Polytetrafluoroethylene) and it has 6 rectangular cells of 1 mm in depth, 15 mm in width, and 50 mm in length. Excess mixture with small bubbles was then scraped off from the PTFE mold. The plastic films, free from bubbles, were cured at 105ºC overnight by placing the mold into a vacuum oven. After cooling at 23ºC and 50% RH, the films were peeled off from the mold. Typical flexible polyurethane plastic film specimens made by replacing 0-50% polyether polyol with ESBO are shown in Figure 4.1.

4.3.4 Flexible Polyurethane Foam Properties

Based on the ASTM procedure D 3574-05, the density, 50% compression force deflection (CFD), 50% constant force deflection (CDC) or compression set, and resilience (ball rebound test) of flexible polyurethane foams were measured. The ASTM procedure D 3574-05 describes the standard test methods for flexible cellular materials including slab, bonded, and molded urethane foams. Fifty percent CFD was determined by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). For 50% CDC or compression set, the initial foam sample thickness was measured first. The sample was then clamped between two flat plates and compressed to 50% of its initial thickness and placed into a VersaTenn III Temperature-Humidity Chamber (Tenney Engineering Inc., Williamsport, PA) set at 70ºC and 6% RH for 22 h. The final thickness was measured after the sample was removed from the constant temperature-humidity chamber and flat plates and placed in an ambient environment (23°C and 50% RH) for 30 to 40 min. The compression set was calculated by the following equation:

$$C_t = \left(\frac{t_o - t_f}{t_o} \right) \times 100\%$$

where:

C_t = compression set expressed as a percentage of the original specimen thickness,

t_o = original thickness of test specimen, and

t_f = final thickness of test specimen.

4.3.5 Dynamic Mechanical Analysis

The dynamic mechanical properties of flexible polyurethane films were determined under a sinusoidal oscillation tension mode by a dynamic mechanical spectrometer (DMS 6100, Seiko Instruments, Kotoku, Japan). The dimensions of film samples were 20 mm × 5 mm × 1 mm. The strain amplitude, initial force, and minimum tension force were 10 μm, 400 g, and 20 g, respectively. The storage modulus (*E'*), loss modulus (*E"*) and tanδ were recorded at a frequency of 1 Hz from -140 to 300°C at a ramp rate of 2°C/min.

4.3.6 Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter (DSC 7, Perkin-Elmer, Waltham, MA) was used to determine the glass transition temperatures (T_g) and specific heat change (Δc_p) of polyurethane films. Approximately 6 to 7 mg of polyurethane film was loaded into an aluminum sample holder and sealed. The sample was cooled to -140°C and equilibrated for 5 min first and then heated to 300°C at 10°C/min.

4.3.7 Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR)

A Thermo Scientific Nicolet^{TM} 380 FT-IR equipped with Smart Orbit diamond ATR attachment (Thermo Electron Corp., Madison, WI) was used to characterize the functional groups in both the flexible polyurethane films and foams. The flexible polyurethane foams were ground first and then placed into a 105°C oven for 4 h to remove water that might have been absorbed. Both flexible foam powder and film samples were pressed against the ATR diamond to ensure complete contact between them. A total of 64 scans of each sample from 4000 to 400 cm^{-1} wavenumber were obtained at a resolution of 2 cm^{-1}.

4.4 Results and Discussion

4.4.1 Physical Properties of Flexible Polyurethane Foams

Table 4.2 shows the effect of epoxidized soybean oil on the density, 50% CFD, 50% CDC, and resilience of water-blown flexible polyurethane foams. The density decreased when increasing ESBO up to 30% and then increased. Due to the hydroxyl number difference between ESBO (403.8) and Voranol® 4701 (34), the quantity of isocyanate (PAPI® 27) used in the foam formulation increased with ESBO. At the same time, the foam volume would also increase due to more carbon dioxide generation from the reaction of isocyanate with the blowing agent (water). The foam volume increase exceeded the weight increase resulting in a decrease in density. Above 30% ESBO, the volume increase effect might have reached its limit because the blowing agent (water) was exhausted. In addition, the gas retention might have deteriorated in the foam matrix. Both could be caused by the slower reaction rate of ESBO with PAPI® 27 than Voranol® 4701.[11]

Table 4.2 also shows the effect of ESBO on 50% compression force deflection of water-blown flexible polyurethane foams. The 50% CFD was almost identical at 0% and 10% ESBO replacement, and then slightly decreased at 20%. At 30% ESBO replacement, the 50% CFD was almost identical to that at 20% replacement. A sharp increase in 50% CFD, however, was observed at 40% and 50% replacement. This could be explained by changes in foam density and hard segment. As ESBO increased from 0 to 30%, foam density decreased which would reduce the 50% CFD. However, the hard segment (HS) might have increased because ESBO had a higher hydroxyl number than Voranol® 4701 resulting in more isocyanate in the foam formulation, which would increase the 50% compression force deflection.[12] These two effects (density decrease and hard segment increase) might have counteracted and cancelled each other. Thus, there was no significant change in 50% compression force deflection. When ESBO in foam exceeded 30%, both foam density and cross-linking density increased resulting in firmer foams.

The constant deflection compression set (50% CDC) of foams increased sharply when increasing ESBO (Table 4.2). On the contrary, the resilience of foams decreased when increasing ESBO (Table 4.2). It appears that the foams became less flexible and less resilient when increasing ESBO. This might be due to the difference in equivalent weight between Voranol® 4701 and ESBO. The equivalent weight of a polyol relates to or gives an indication of the length or distance between two adjacent hydroxyl functional groups in a polyol molecule. The polyol with a higher equivalent weight is expected to have a greater length or distance between two adjacent hydroxyl groups resulting in a longer "soft segment" in the polyurethane foam. When ESBO was introduced into the foaming system, the HS increased and SS decreased because the equivalent weight of ESBO (139) is only about one-twelfths of Voranol® 4701 (1650). A lower equivalent weight of ESBO would result in shorter polymer chains causing stiffer foams. Moreover, the backbone of ESBO is a triglyceride while Voranol® 4701 is linear in chemical structure. Thus, foams containing more ESBO would contain polymers with shorter chains. They would be more easily crushed or damaged by compression and less resilient than foams with more Voranol® 4701 in the foam formulation.[11]

4.4.2 Dynamic Mechanical Analysis of Polyurethane Films

Dynamic mechanical analysis is often used to investigate the mechanical and thermal properties of polymers. Figure 4.2 shows both storage modulus and loss modulus and Figure 4.3 shows tanδ of flexible polyurethane films containing 0 to 50% of ESBO from -100 to 200°C. Although the experiments were carried out from -140 to 300°C, no significant change in tanδ was observed either in the temperature range lower than -100°C or higher than 200°C. This was also observed in the DSC results to be discussed later. The glass transition temperature was determined from the maximum or peak in tanδ or loss modulus. It is interesting to note that the glass transition temperatures for all films were about -48ºC and were not affected by the percentage of ESBO. This is not unexpected as the soft segment (SS) of these polyurethane films was essentially the same[13] forming from the reaction of Voranol® 4701, a long and linear polyether polyol, with isocyanate. At temperatures lower than the glass transit temperature (T_g), the storage moduli, *E',* were high ($\sim 10^9$) indicating these films behave like a solid material. For the film made with 100% Voranol® 4701 and isocyanate, the storage modulus decreased rapidly and reached a plateau when the temperature exceeded T_g. This decrease was due to the dramatic increase in molecular motion.[13] When ESBO was introduced replacing some Voranol® 4701 in the polyurethane film, the decay or decrease in the film's storage modulus was reduced and the reduction became more pronounced when increasing ESBO (Figure 4.2). Also, instead of a plateau the storage modulus decreased gradually with temperature. Moreover, the storage modulus increased with increasing ESBO at temperatures higher than T_g. All of these phenomena indicate that the films became stiffer with increasing ESBO.[14-16]

Similar conclusions can be drawn based on the results of loss modulus, *E"*, and tanδ. The magnitude of maximal loss modulus (Figure 4.2) and tanδ (Table 4.3) decreased with increasing ESBO indicating these films became less soft.[13-14] Because of the low equivalent weight and non-linear triglyceride backbone chemical structure of ESBO, its reaction with isocyanate is expected to form a harder segment (HS) than the reaction between Voranol® 4701 and isocyanate. Therefore, as ESBO increased and Voranol® 4701 decreased, HS would increase resulting in stiffer or firmer films.

4.4.3 Differential Scanning Calorimetry Analysis Polyurethane Films

Figure 4.4 shows the DSC heating curves of polyurethane films containing 0 to 50% ESBO from -100 to 200°C. All curves show a discontinuity in specific heat indicating a second-order transition. The glass transition temperature, T_g, of the polyurethane films were determined by taking the middle of the change in baseline which is the inflection point. They were about -54°C, independent of the percentage of ESBO in the film and slightly lower than that determined from the dynamic mechanical analysis method. This might be due to differences in heating rate (2ºC/min by DMS versus 10ºC/min by DSC) and/or due to using the peak tanδ value which is several degrees higher than peak *E"* in DMS.[17] The specific heat changes at T_g, Δc_p, of the polyurethane films are listed in Table 3. They decreased with increasing ESBO percentage. The specific heat change (Δc_p) is an indication of the energy consumed for the phase change of the soft segment in polyurethane films at T_g.[13] As discussed in the previous section, the soft segment in the polyurethane films was formed from the reaction between Voranol® 4701, a long and linear polyether polyol, with isocyanate. Therefore, as more and more Voranol® 4701 was replaced by ESBO in the polyurethane film, the soft segment fraction in the film would decrease leading to the decrease in $\Delta c_{p.}$[18-20]

4.4.4 FTIR-ATR Analysis of Polyurethane Foams and Films

The FTIR-ATR results of polyurethane films containing 0 to 50% of ESBO are shown in Figure 4.5 (wavenumber range 4000 to 500 cm^{-1}) and Figure 4.6 (wavenumber range 1900 to 800 cm^{-1}). The details of spectra interpretation and band assignments are provided in Table 4.4.[21-23] It is interesting to note that there are two peaks between 1000 and 800 cm^{-1}–one is 818 cm^{-1} indicating the in-plane bending or scissoring (C-H) aromatic ring and the other, 923 cm^{-1}, indicating the out-of-plane bending or wagging (C-H) aromatic ring.[22] No change in transmittance was found at wavenumber 863 and 916 cm^{-1}(Figure 4.6), the transmittances of the epoxy ring[22]. This seems to indicate all epoxy rings in ESBO were consumed when reacting with isocyanate in the presence of Voranol® 4701. The transmittance at wavenumber 1097 cm^{-1} represents the aliphatic ether which is present in Voranol® 4701, but not in ESBO. Therefore, the transmittance at wavenumber 1097 cm^{-1} became less pronounced with increasing ESBO. As shown by the transmittances at 1411, 1508, and 1592 cm^{-1} (due to aromatic ring from isocyanate) and at wavenumber 2281 cm^{-1} (due to the cyanate group from isocyanate), the residual or unreacted isocyanate in the polyurethane film increased with increasing ESBO. This was because the hydroxyl number of ESBO (403.8) is much greater than Voranol® 4701 (34). Thus, the amount of isocyanate used in the film formulation increased with increasing ESBO. In addition, the hydroxyl groups in Voranol® 4701 are primary and are much more reactive with isocyanate than ESBO. The transmittance at wavenumber 2923 cm^{-1} shows the stretching mode (C-H) in CH_2 became more pronounced with increasing ESBO. This is not unexpected since CH_2 was abundant in the chemical structure of ESBO, but not in Voranol® 4701 which is a polyether polyol. The transmittances at wavenumbers 1716 cm^{-1} and 3351 cm^{-1} represent hydrogen-bonded urethane amide (C=O) and (N-H), while that at wavenumber 1729 cm^{-1} represent non-bonded urethane amide (C=O) (Table 4.4). It is interesting to note that the hydrogen-bonded urethane amide was absent in the polyurethane film containing 100% Voranol® 4701 and appeared only after some of the Voranol® 4701 was replaced by ESBO. On the other hand, the non-bonded urethane amide remained the same with or without ESBO. It is expected that the presence of more hydrogen-bonded urethane amide would result in firmer or stiffer polyurethane film. Thus, the results were consistent with those obtained from DMS analysis.

The epoxy functional group in ESBO can react with isocyanate and produce oxazolidone[5]. This reaction, however, takes place at a much higher temperature (~250ºC)[24] and a longer reaction time than those of typical polyurethane foaming reactions. The infrared absorbance or transmittance of oxazolidone is at wavenumber 1750 cm^{-1}.[24,25] This was absent in the FTIR-ATR results (Figure 4.6). Thus, oxazolidone was not present in the polyurethane film.

The FTIR-ATR results of polyurethane foams containing 0 to 50% ESBO (Figure 4.7) were similar to those of polyurethane films containing 0 to 50% of ESBO. The transmittances at wavenumbers 2856 and 2923 cm^{-1} became more pronounced with increasing ESBO. These two wavenumbers are assigned to the symmetric and asymmetric stretching mode (C-H) in CH_2 which is present in the triglyceride structure of ESBO. In addition, increasing residual isocyanate in the polyurethane foam with increasing ESBO was evident as shown by the transmittances at wavenumbers 1411, 1508, 1592 and 2281 cm^{-1}. Similar to the FTIR-ATR results of polyurethane film, the transmittances at wavenumbers 863, 916 and 1750 cm^{-1} in all polyurethane foams indicate that these foams did not have any residual epoxy ring or contained any trace of oxazolidone. Further studies are needed to elucidate the reaction mechanism between ESBO and isocyanate.

4.5 Conclusions

The physical properties of water-blown flexible polyurethane foams containing 0 to 50% ESBO were studied. The density and 50% compression deflection properties were similar to or better than control flexible foams up to 30% ESBO, while the resilience and 50% constant deflection compression properties were inferior to control flexible foams. These were due to increase in hard segment with increasing ESBO resulting in firmer foams. In DMS analysis of plastic films, decreasing maximal tanδ and increasing E' indicates the hard segment in plastic film increased with increasing ESBO. In DSC analysis, decreasing Δc_p indicates the soft segment in plastic film decreased with increasing ESBO. In FTIR-ATR experiment, hydrogen-bonded urethane group (HS) was found once ESBO was introduced into the molded plastic films, the films became firmer or stiffer. In addition, the epoxy ring and oxazolidone were absent in both flexible mold plastic and foams.

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Table 4.1 Formulations for water-blown flexible polyurethane foam with different percentages of epoxidized soybean oil.

Ingredients	Parts by weight
B-side materials	
Voranol® 4701	100, 90, 80, 70, 60, 50
Epoxidized Soybean Oil	0, 10, 20, 30, 40, 50
DABCO® 33-LV	0.6
DABCO® BL-17	0.2
Stannous octoate	0.3
Dibutyltin dilaurate	0.3
Diethanolamine	2.2
DABCO® DC 2585	1.0
Blowing Agent (distilled water)	5.0
A-side material	
PAPI® 27	Index 80[a]

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

Table 4.2 Physical properties of flexible polyurethane foams containing 0 to 50% epoxidized soybean oil.

	Control	10% ESBO	20% ESBO	30% ESBO	40% ESBO	50% ESBO
Density (kg/m^3)	44.83^a	37.88^b	31.98^d	30.88^d	33.60^{cd}	36.22^{bc}
50% CFD (kPa)	8.78^b	8.88^b	7.63^b	7.84^b	9.81^b	14.64^a
50% CDC (%)	5.54^f	29.85^e	36.91^d	39.54^c	45.70^b	47.10^a
Resilience (%)	44.89^a	34.39^b	31.39^c	27.95^d	25.39^e	21.78^f

^{abcdef}Values with the same superscript within the same row are not significantly different at 5% level.

Table 4.3. Tanδ maximum and Δc_p of flexible polyurethane molded plastic containing 0 to 50% epoxidized soybean oil.

	Control	10% ESBO	20% ESBO	30% ESBO	40% ESBO	50% ESBO
Tanδ maximum	1.771	0.962	0.584	0.314	0.191	0.143
Δc_p (J/°C·g)	0.332	0.323	0.286	0.230	0.181	0.109

Table 4.4. Assignments of functional groups in FTIR-ATR spectra.

Wavenumber (cm^{-1})	Possible interpretation
1097	υ(C-O-C) aliphatic ether [22]
1305	δ(N-H)[22]
1373	ω(C-H) in CH_2[22]
1411	υ(C=C) aromatic ring (1410)[22], υ(C-C) aromatic ring (1412-1414)[22] or deformed (C-H) epoxy (1414)?[21]
1457	δ(C-H) in CH_2[22]
1508	υ(C-C) aromatic ring[22]
1540	υ(C-N)+δ(N-H) Amide II[22]
1592	υ(C=C) aromatic ring [22]
1716	υ(C=O) urethane Amide I, H-bonded[22]
1729	υ(C=O) urethane Amide I, nonbonded[22]
2281	Cyanate group (2280)[23]
2856	υ_s(C-H) in CH_2[22]
2923	υ_a(C-H) in CH_2 (2925)[22], υ(C-H) epoxy (2929)?[21]
2969	υ(C-H) in CH_3 (2970)[22], υ_a(C-H) in CH_3 (2970)[22], υ_a(CH_3)+υ_a(OCH_2) (2968)?[21]
3351	υ(N-H) H-bonded[22]

Note: υ = stretching mode, υ_a = asymmetric stretching, υ_s = symmetric stretching, δ = in-plane bending or scissoring, ω = out-of-plane bending or wagging, τ = out-of-plane bending or twisting, ρ = in-plane bending or rocking

Figure 4.1. The picture of flexible polyurethane plastic films and water-blown foams. The upper image is the flexible water-blown polyurethane foams with 10% to 50% ESBO. The lower image is the polyurethane plastic films with 0% to 50% ESBO from left to right.

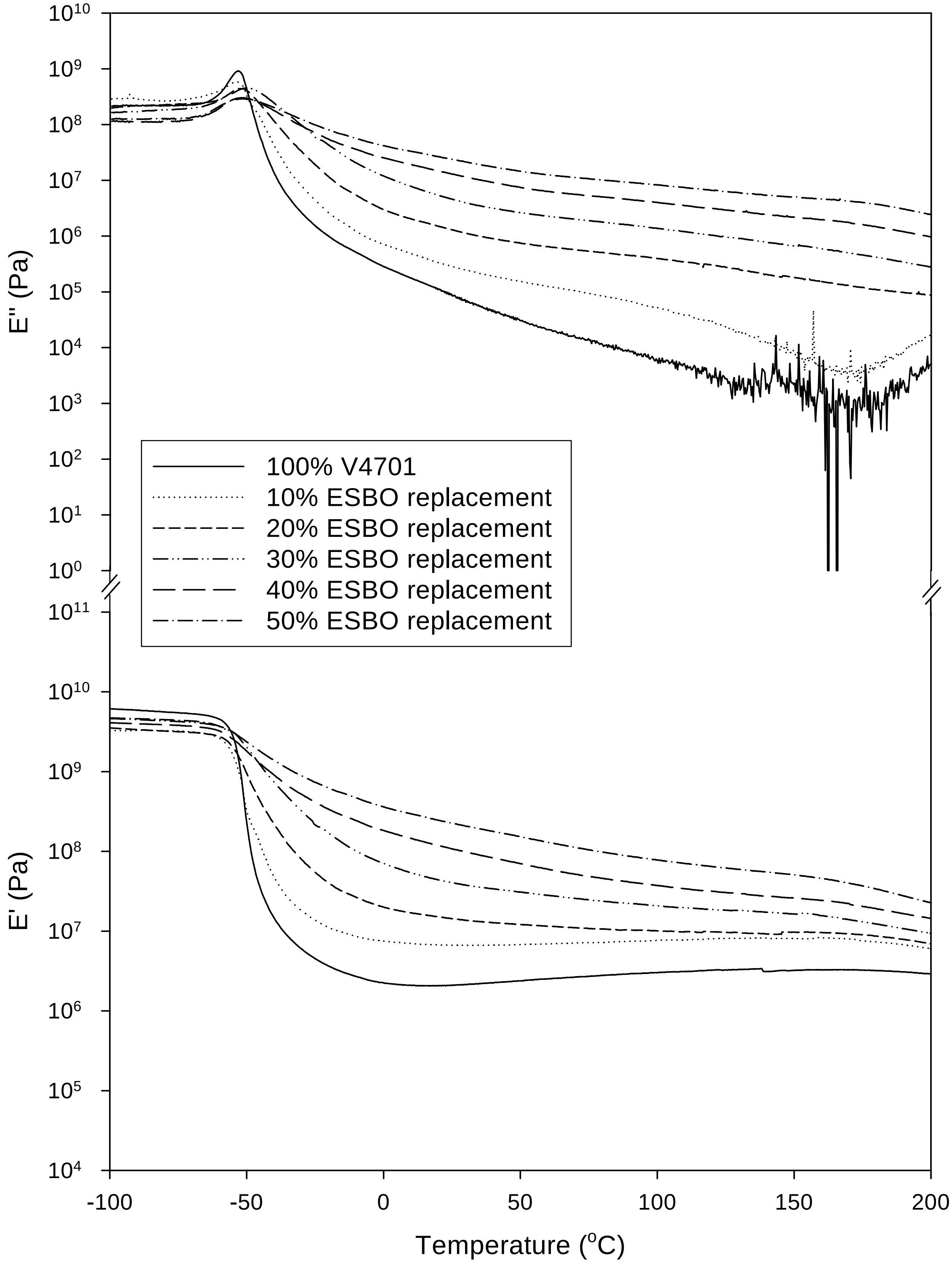

Figure 4.2. Storage modulus (E’) and loss modulus (E”) of flexible polyurethane films containing 0 to 50% ESBO.

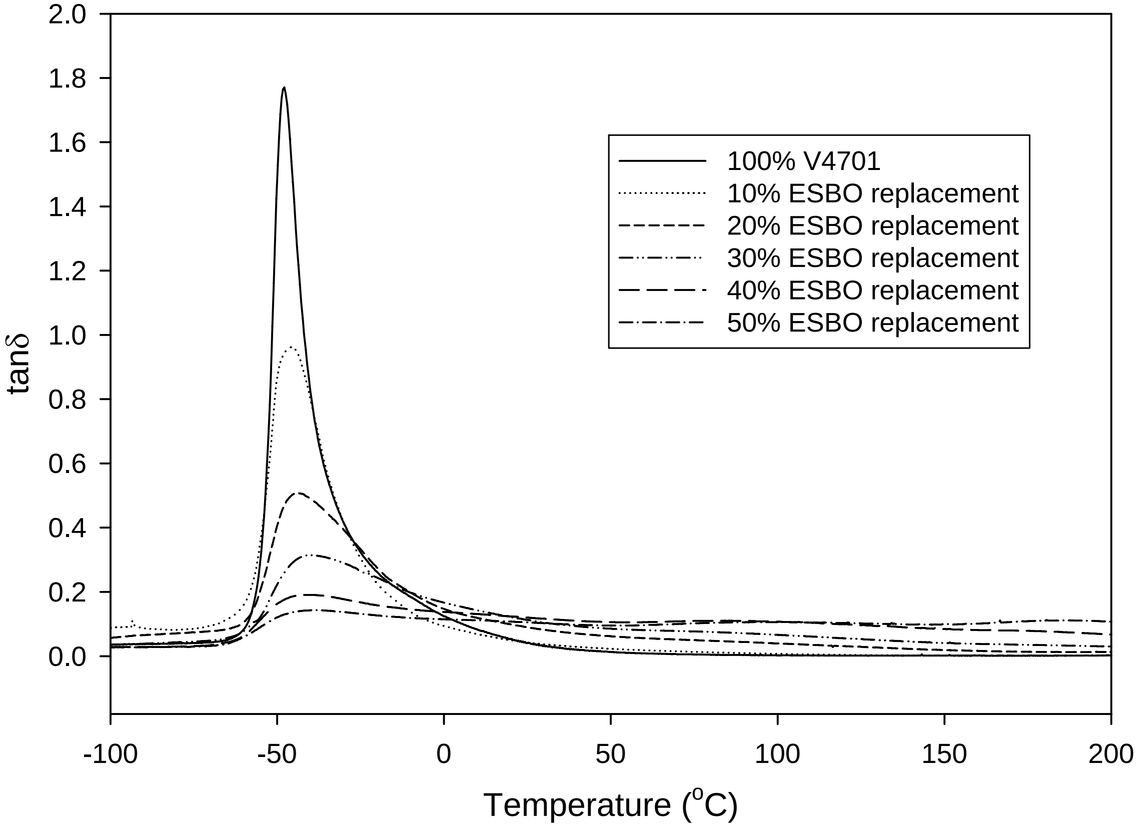

Figure 4.3. Tanδ versus temperature of flexible polyurethane films containing 0 to 50% ESBO.

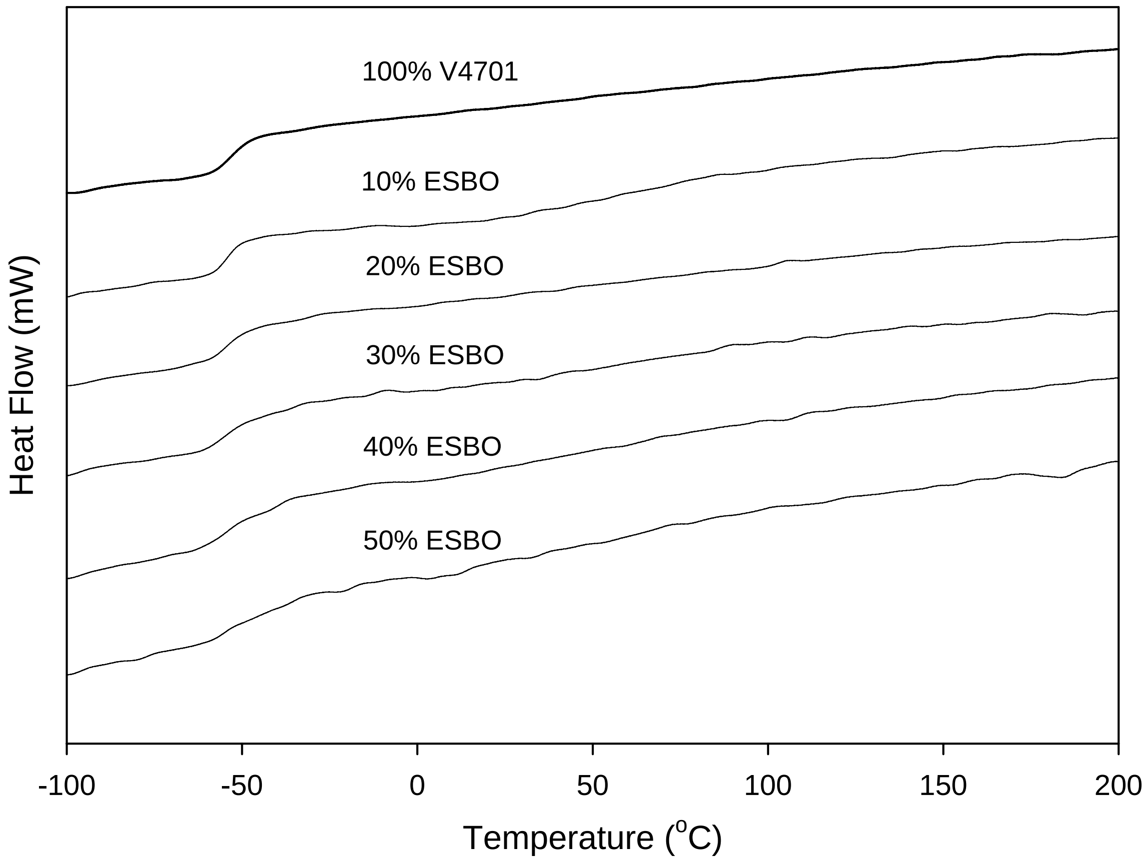

Figure 4.4. DSC analysis results of flexible polyurethane films containing 0 to 50% ESBO. The curves were vertical shift to simplify comparisons.

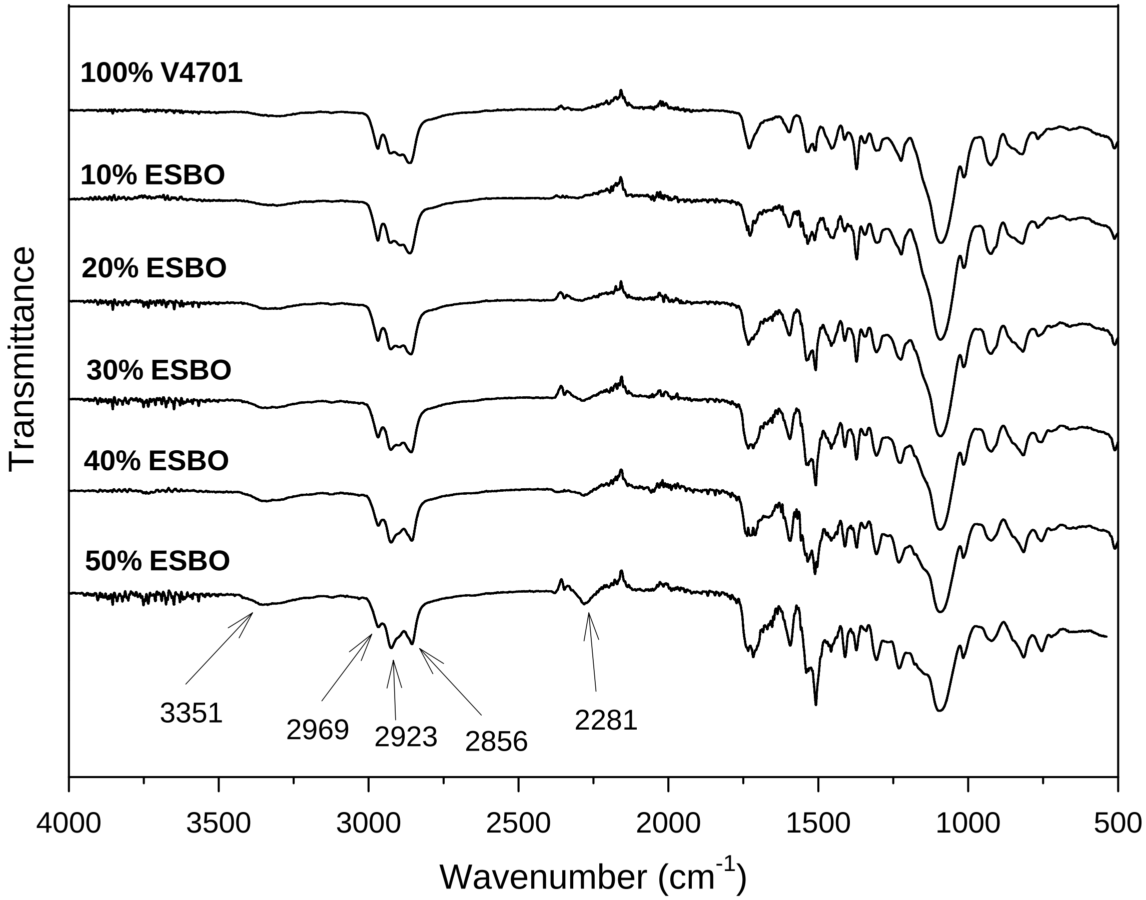

Figure 4.5. FTIR-ATR results of flexible polyurethane films containing 0 to 50% ESBO from wavenumber 4000 to 500 cm^{-1}.

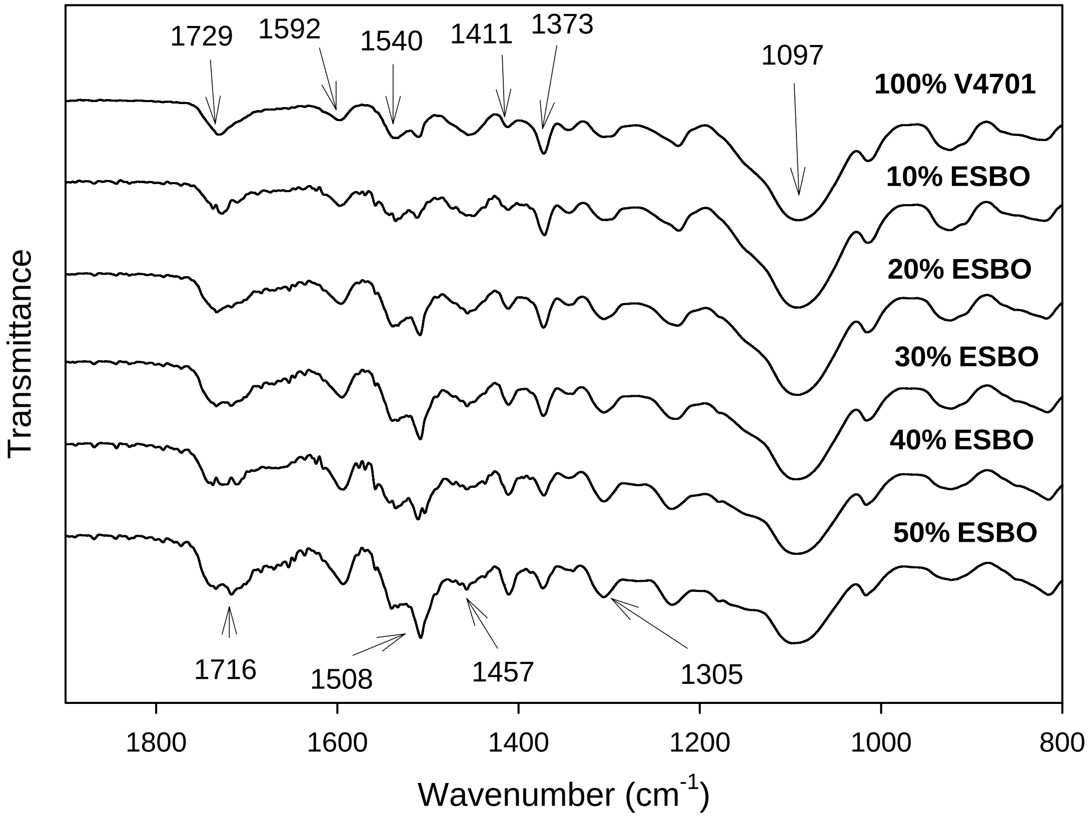

Figure 4.6. FTIR-ATR results of flexible polyurethane films containing 0 to 50% ESBO from wavenumber 1900 to 800 cm^{-1}.

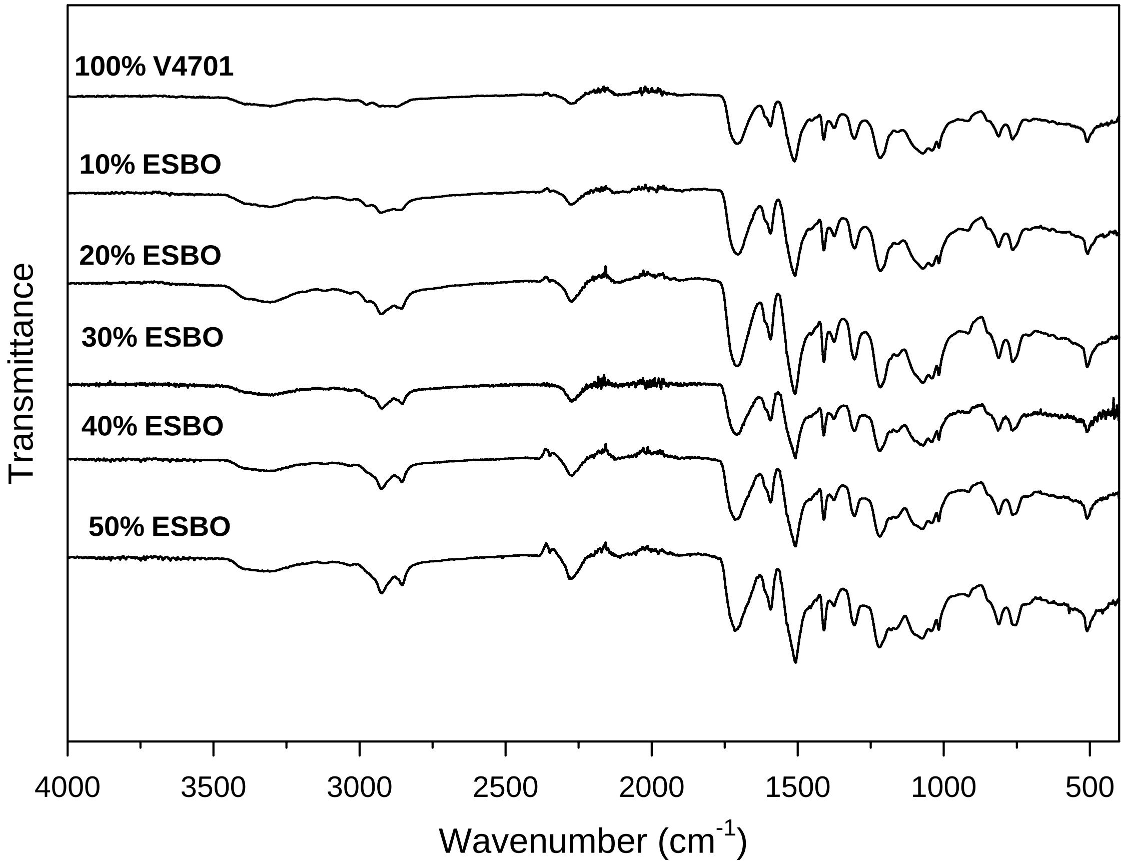

Figure 4.7. FTIR-ATR results of flexible polyurethane foams containing 0 to 50% ESBO from wavenumber 4000 to 400 cm^{-1}.

CHAPTER 5

PHYSICAL PROPERTIES OF WATER-BLOWN RIGID POLYURETHANE FOAMS CONTAINING EPOXIDIZED SOYBEAN OIL IN DIFFERENT ISOCYANATE INDICES

5.1 Abstract

To explore the potential of isocyanate usage reduction, water-blown rigid polyurethane foams were made by replacing 0%, 20% and 50% of Voranol® 490 in the B-side of the foam formulation by epoxidized soybean oil (ESBO) with an isocyanate index ranging from 50 to 110. The compressive strength, density, and thermal conductivity of foams were measured. The foam surface temperature was monitored before and throughout the foaming reaction as an indirect indication of the foaming temperature. Increasing ESBO replacement and/or decreasing isocyanate index decreased the foam's compressive strength. Foam's density decreased when decreasing the isocyanate index to 60. Further decrease in isocyanate index resulted in foam shrinkage causing a sharp increase in foam density. The thermal conductivity of foams increased when decreasing isocyanate index and increasing ESBO replacement. Mathematical models for predicting rigid polyurethane foam density, compressive strength, and thermal conductivity were established and validated. Similar to compressive strength, the foaming temperature decreased when decreasing isocyanate index and increasing ESBO replacement. Due to the lower reactivity of ESBO with isocyanate, the rate of foaming

temperature decrease with decreasing isocyanate index was in the order of 0%>20%>50% ESBO replacement.

5.2 Introduction

The crude oil price reached a historical high of 140 to 150 US dollars per barrel briefly in summer 2008.[1] This resulted in a significant price increase in petroleum-based raw materials needed to make many consumer plastic products. For example, polyols and isocyanates, the two major raw materials of polyurethane, derived from the petroleum feedstock, have become increasingly more expensive in the past few years.[2,3] Because of the wide range of properties and applications of polyurethane plastics[4], the global consumption of polyurethane polymer shows a steady increasing trend during the past decade.[5,6] As a result, there are more green house gases, resulting from the petroleum refining process when making polyols and isocyanate, which aggravate the global warming effect. Moreover, the petroleum is a finite resource and its supply will certainly be exhausted sooner or later. Because of these disadvantages, researchers have been looking for alternative resources that are cleaner, renewable, and lower in cost to replace the petroleum. One potential candidate that has received significant attention in recent years is vegetable oil.

The basic chemical structure of vegetable oil is unsaturated triglyceride. In order to make polyols from unsaturated triglyceride, one commonly used method is to epoxidize the double bonds in the triglyceride structure and then convert the epoxy groups to hydroxyl groups by methanolysis.[7-11] We have shown that the epoxidized soybean oil might be able to participate in the polyurethane foaming reaction without converting the epoxy groups to hydroxyl groups first.[12-14] Because of its lower reactivity with isocyanate than polyether polyols in polyurethane foaming, replacing polyether polyols partially with epoxidized soybean oil may reduce the foaming temperature and the isocyanate in the foam formulation. Therefore, the objectives of this study were to investigate the effect of epoxidized soybean oil replacement and isocyanate index on the foaming temperature and the physical properties, such as compressive strength, density, and thermal conductivity of water-blown rigid polyurethane foams.

5.3 Materials and Methods

5.3.1 Materials

Voranol® 490 (Dow Chemical Co., Midland, MI), a commercial petroleum-derived polyether polyols with 4.3 functionality, prepared using sucrose and glycerine initiator, having an equivalent weight about 115 and a hydroxyl number of 490, is used in this study. PAPI® 27 (Dow Chemical Co., Midland, MI), a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4% part by weight of NCO content. Vikoflex® 7170, an epoxidized soybean oil with a hydroxyl number of 403.8 was obtained from Arkema Chemicals Inc. (Philadelphia, PA). POLYCAT® 5 and POLYCAT® 8 were used as catalysts and DABCO® DC5357, the surfactant. POLYCAT® 5, POLYCAT® 8, and DABCO® DC5357 were from Air Products & Chemicals (Allentown, PA) gratis.

5.3.2 Experimental Design and Formulations

The experimental design included replacing the B-side polyether polyols (Voranol® 490) with 0, 20 and 50% of epoxidized soybean oil and using 7 isocyanate index levels ranging from 50-110 in the foam formulation. Other factors in the foam formulation such as water content, catalysts and surfactant were kept constant. Table 5.1 shows the foam formulations for water-blown rigid polyurethane foams. The amount of isocyanate was based on the total hydroxyl content of Voranol® 490, epoxidized soybean oil, and distilled water.

5.3.3 Rigid Polyurethane Foaming Temperature Measurement

An Omega Engineering OS552A-MA-4 (Omega Engineering Inc., Stamford, CT) infrared thermometer equipped with a wireless transmitter and receiver was used to measure the surface temperature of water-blown rigid polyurethane foams in different ESBO contents and isocyanate indices. The temperature measurement covered an area of 2.54 cm in diameter up to 76.2 cm between the subject and infrared thermometer. The infrared thermometer was held at 40.64 cm above the wooden mold and focused on the center of mold. The temperature recording started 10 s prior to the polyurethane mixture being poured into the wooden mold and stopped after 500 s. Figure 5.1 shows the foaming temperature profiles of rigid polyurethane foams containing 0% to 50% ESBO at isocyanate index 110. The response time of the temperature recording is 1 s.

5.3.4 Rigid polyurethane foam property measurement

Apparent thermal conductivity of samples was determined in duplicate, after curing at room temperature (23ºC) for 24 h by a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA) using the American Society for Testing and Materials (ASTM) Procedure C 518-04. The dimension of the foam samples was 20×20×2.5 cm. Density of foam samples was measured according to ASTM procedure D 1622-03. Compressive strength of foams was determined by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) following ASTM Procedure D 1621-04a. Both density and compressive strength were conducted after foams were stored for 7 days at room temperature (23°C and 50% RH) and the dimension of the foam sample was 6.35×6.35×3.81 cm. Five measurements were made for each treatment and the average reported.

5.3.5 Modeling of Compressive Strength, Density and Thermal Conductivity

Based on the data from a previous study[13] and this one, three mathematical models were established by regression to describe the effect of ESBO fraction and isocyanate ratio on compressive strength, density, and thermal conductivity of water-blown rigid polyurethane foams. The ESBO fraction is defined as the ESBO amount used in foaming divided by the total polyol amount and the isocyanate ratio is the actual amount of isocyanate used in foaming divided by the theoretical amount of isocyanate. Thus, the isocyanate index is equal to the isocyanate ratio multiplied by 100. These mathematical models were based on second order polynomial equations using the statistical software SAS 9.1 (SAS Institute, Cary, NC). The dependent variables were compressive strength, density, and thermal conductivity and the independent variables were the ESBO fraction from 0.1 to 0.5 and the isocyanate ratio from 0.5 to 1.1. The second degree order polynomial equation is as follows:

$$y_n = a_{n0} + a_{n1}e + a_{n2}i + a_{n3}ei + a_{n4}e^2 + a_{n5}i^2$$

where y_n = compressive strength (when n=1), density (when n=2), and thermal conductivity (when n=3)

e = ESBO fraction

i = isocyanate ratio

ei = interaction between ESBO fraction and isocyanate ratio

5.4 Results and Discussion

5.4.1 Density

Figure 5.2 shows the effect of ESBO replacement and isocyanate index on the density of polyurethane foams. The mathematical model is

$$y_2 = 57.149 - 48.725e - 39.541i + 37.689ei + 24.964e^2 + 27.316i^2$$

($R^2 = 0.8093$)

This model is depicted in Figure 5.3.

As shown in Figures 5.2 and 5.3, the density of polyurethane foams decreased with decreasing isocyanate index from 110 to 60. This was because, first of all, the isocyanate in the polyurethane formulation was less when deceasing the isocyanate index resulting in less polymer solid in the foam structure.[15] Secondly, the amount of blowing catalyst (POLYCAT® 5) in this experiment was higher than that of the gelling catalyst (POLYCAT® 8). Most of the water in the polyurethane formulation might have reacted with isocyanate producing carbon dioxide regardless of the isocyanate index. It was also likely that the effect of reducing isocyanate index has less effect on the reaction between water and isocyanate. Thus, the reduction in foam volume was less than the reduction in foam weight when reducing the isocyanate index from 110 to 60. Therefore, the density of foams was reduced when reducing the isocyanate index. When the isocyanate index was lower than 60, however, the structure of the polyurethane foam was probably too weak to hold its shape because of insufficient isocyanate in the foam formulation and the foam showed significant shrinkage within 24 h after the foam was made. As a result, the density of foam showed a sharp increase when reducing the isocyanate index from 60 to 50.

It is interesting to note that the density of foams increased with the percentage of ESBO replacement when the isocyanate index was 100 or higher, but decreased with the percentage of ESBO replacement when the isocyanate index was less than 80. We showed in a previous study that ESBO could react with isocyanate in the presence of a polyether polyol, but the reactivity between ESBO and isocyanate was lower than that between polyether polyol, which contains primary hydroxyl groups, and isocyanate.[14] When the isocyanate index was 100 or higher, the isocyanate in the foam formulation was sufficient to react with catalysts, water, polyether polyol, and ESBO. Due to the lower reactivity between ESBO and isocyanate, the polyurethane foam structure was weaker with more open cells at a higher percentage of ESBO replacement.[13] Therefore, the volume of foams was less, leading to higher foam density. When the isocyanate index was less than 80, catalysts, water, polyether polyol and ESBO would compete for a reaction with isocyanate. The higher the ESBO replacement percentage, the less the polyether polyol was in the foam formulation to compete with water for reacting with isocyanate. In addition, the hydroxyl number of ESBO is less than that of Voranol® 490. The foam with a higher ESBO replacement would weigh less at the same isocyanate index. Therefore, the higher the ESBO replacement percentage, the lower the foam density when the isocyanate index was less than 80.

When the isocyanate index was 50, the foam density at 0% ESBO replacement was much higher than at 20% and 50%. It was observed that the foam at 0% ESBO replacement had severe shrinkage within 24 h after foaming while the foams at 20 and 50% ESBO replacement had moderate shrinkage. This was because foam with a higher ESBO replacement would have a lower closed cell percentage.[13] When the isocyanate index was 50, the foam structure was too weak to hold its shape. Thus, all foams shrank within 24 h after foaming. Foams with a higher ESBO replacement containing more open cells, however, would shrink less due to less pressure difference between the inside and outside of foams.

5.4.2 Compressive Strength

Figure 5.4 shows the effect of epoxidized soybean oil (ESBO) replacement and isocyanate index on the compressive strength of water-blown rigid polyurethane foams. The second order mathematical model is

$$y_1 = -106.188 - 347.720e + 906.726i + 156.864ei - 198.899e^2 - 364.087i^2$$

($R^2 = 0.9715$)

This model is shown in Figure 5.5. As shown in Figures 5.4 and 5.5, the compressive strength of water-blown rigid polyurethane foams decreased not only with the decreasing isocyanate index but also with the increasing ESBO replacement. This was because both the decreasing isocyanate index and the increasing ESBO replacement would reduce the amount of isocyanate usage in the polyurethane foams. The latter was because the hydroxyl number of ESBO (403.8) is less than that of Voranol® 490 (490).

In polyurethane reaction, polyols react with isocyanate and generates polyurethane, which reacts with isocyanate further to generate allophanate. Water reacts with isocyanate generating carbon dioxide and amine; amine then reacts with isocyanate and generate disubstituted urea,[16] which may further react with isocyanate to generate biuret.[16] The more allophanate, disubstituted urea, and biuret are present in the polyurethane polymer, the higher the polymer's cross-linking density.[16] Therefore, the lower the isocyanate index or the less the isocyanate usage in the polyurethane foam, the lower the foam's cross-linking density which leads to a lower compressive strength.[12]

5.4.3 Thermal Conductivity

Figure 5.6 shows the effect of ESBO replacement and isocyanate index on the thermal conductivity of foams. The mathematical model is

$$y_3 = 0.04612 - 0.00943e - 0.03719i + 0.03750e^2 + 0.01718i^2 \qquad (R^2 = 0.8405)$$

and the model is shown in Figure 5.7. The thermal conductivity of foams with 0% and 20% ESBO replacement increased gradually with decreasing isocyanate index and most foams had a thermal conductivity lower than 0.028 W/mK. This might be due to a high percentage of closed cells in these foams.[13] When decreasing the isocyanate index, more polyols would remain unreacted which might cause a slight decrease in closed cell percentage leading to a slight increase in the thermal conductivity. When the isocyanate index was 50, the foams at 0% and 20% ESBO replacement showed shrinkage within 24 h after foaming. In fact, the thermal conductivity measurement of foam at 0% ESBO replacement was not possible due to severe shrinkage. The density of foam at 20% ESBO replacement was high due to foam shrinkage. Because foam solid conducts heat better than gases, a denser foam would result in higher thermal conductivity. The thermal conductivity change of foams at 50% ESBO replacement with decreasing isocyanate index followed the same trend as foams at 0 or 20% ESBO replacement and all foams had a thermal conductivity of 0.032 W/mK or slightly higher. This was because the closed cell percentage was lower or cells were more open than foams at 0 or 20% ESBO replacement. As a result, less carbon dioxide was trapped in the foam and foam had more convection heat transfer leading to a higher thermal conductivity.

5.4.4 Model Validation

In order to validate the reliability of the mathematic models of density, compressive strength, and thermal conductivity, four rigid polyurethane foams with different ESBO fractions and isocyanate ratios were made and foam properties were determined according to the methods mentioned previously. The results are shown in Table 5.2. It can be seen that the absolute errors between predicted and experimental value were less than 3.34, 2.44, and 3.56% for density, compressive strength, and thermal conductivity values, respectively. Thus, the mathematic models for these three physical properties appear to be adequate.

5.4.5 Foaming Temperature

Figure 5.8 shows the effect of ESBO replacement and isocyanate index on the foaming temperature of water-blown polyurethane foams. As shown, the foaming temperature decreased with both decreasing isocyanate index and increasing ESBO replacement percentage. In the water-blown polyurethane foaming reaction at isocyanate index 100, catalysts, water, and polyols reacted with isocyanate and released heat. At isocyanate index less than 100, less isocyanate was present to react with catalysts, water, and polyols and thus less heat was released leading to a lower foaming temperature. At isocyanate index 110, the 10% excess amount of isocyanate in the foaming system could react with amine, the byproduct from the reaction of water and isocyanate, and generate disubstituted urea. This chemical reaction is also exothermic raising the foaming temperature.

The foaming temperature decreased with increasing ESBO replacement percentage and could be explained by the fact that the reactivity of isocyanate with ESBO is lower than that with polyether polyol, which contains primary hydroxyl groups.[14] Regardless of the isocyanate index, a lower reactivity of isocyanate with ESBO would cause either a slower release of heat generated from this exothermic reaction, or partial release if insufficient isocyanate was present in the foaming system due to lower isocyanate index.

It is also interesting to note that the foaming temperature decreasing rate with decreasing isocyanate index at various ESBO replacement percentages differed. At 0% ESBO replacement, the decreasing rate was the highest, followed by at 20%, and then at 50% ESBO replacement. This could also be explained by the slower reaction rate between isocyanate and ESBO than that between isocyanate and polyether polyol. The presence of ESBO in the foaming system, due to its lower reaction rate with isocyanate, would lessen the impact of reducing isocyanate index causing the reduction in the foaming temperature.

5.5 Conclusions

In this work, the effect of epoxidized soybean oil (ESBO) replacement and isocyanate index on the foaming temperature and physical properties of water-blown rigid polyurethane foams was investigated. Changes in foaming temperature and physical properties essentially could be attributed to the lower reactivity between epoxidized soybean oil and isocyanate than between polyether polyol and isocyanate. It is worth noting that when 20% of the polyether polyol (Voranol® 490) was replaced by epoxidized soybean oil, the foam at isocyanate index 90 had slightly favorable (lower) density and thermal conductivity values than the control foam (containing 100% polyether polyol) at isocyanate index 110, although the compressive strength value was slightly less favorable.

Therefore, replacing 20% of the polyether polyol offers the possibility of reducing isocyanate in the foam formulation in applications that compressive strength is not as critical.

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Table 5.1 Formulations for Water-blown rigid Polyurethane Foam with different percentages of epoxidized soybean oil and isocyanate index.

Ingredients	Parts by weight
B-side materials	
Voranol® 490	100, 80, 50
Epoxidized Soybean Oil	0, 20, 50
POLYCAT® 5	1.26
POLYCAT® 8	0.84
DABCO® DC 5357	2.5
Blowing Agent (distilled water)	3.0
A-side material	
PAPI® 27	Index 110, 100, 90, 80, 70, 60, 50

Table 5.2. Experimental and predicted thermal conductivity, density and compressive strength.

ESBO Fraction	Isocyanate Ratio	Density (kg/m^3)		
		Regression	Experiment	|ε|, %
0.1	1.0	44.1	44.1	0.00
0.1	0.8	41.4	40.0	3.34
0.3	1.0	43.9	43.9	0.00
0.3	0.8	39.7	38.8	2.10

ESBO Fraction	Isocyanate Ratio	Compressive Strength (kPa)		
		Regression	Experiment	|ε|, %
0.1	1.0	415.4	410.7	1.12
0.1	0.8	362.0	366.0	1.11
0.3	1.0	361.3	354.0	2.02
0.3	0.8	301.6	294.2	2.44

ESBO Fraction	Isocyanate Ratio	Thermal Conductivity (W/mK)		
		Regression	Experiment	|ε|, %
0.1	1.0	0.02554	0.02589	1.36
0.1	0.8	0.02680	0.02584	3.56
0.3	1.0	0.02666	0.02664	0.06
0.3	0.8	0.02791	0.02717	2.65

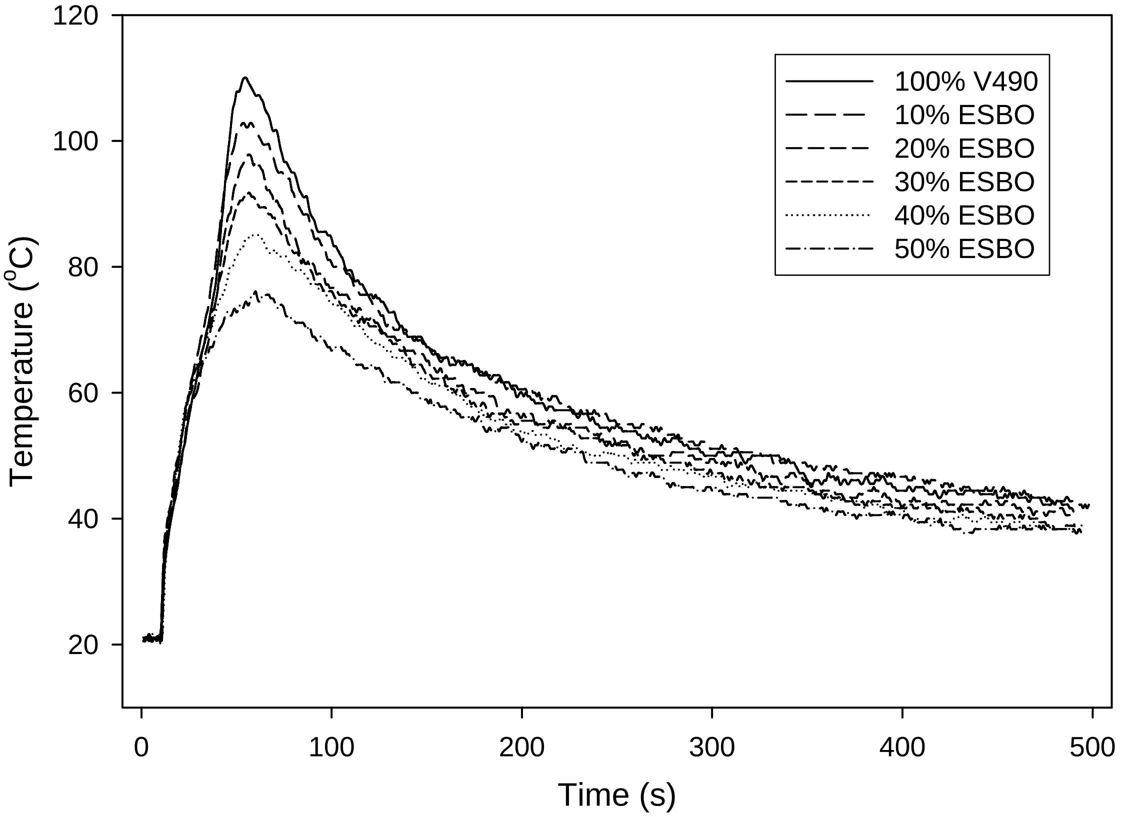

Figure 5.1. Temperature profiles of water-blown rigid polyurethane foams containing 0% to 50% ESBO at isocyanate index 110.

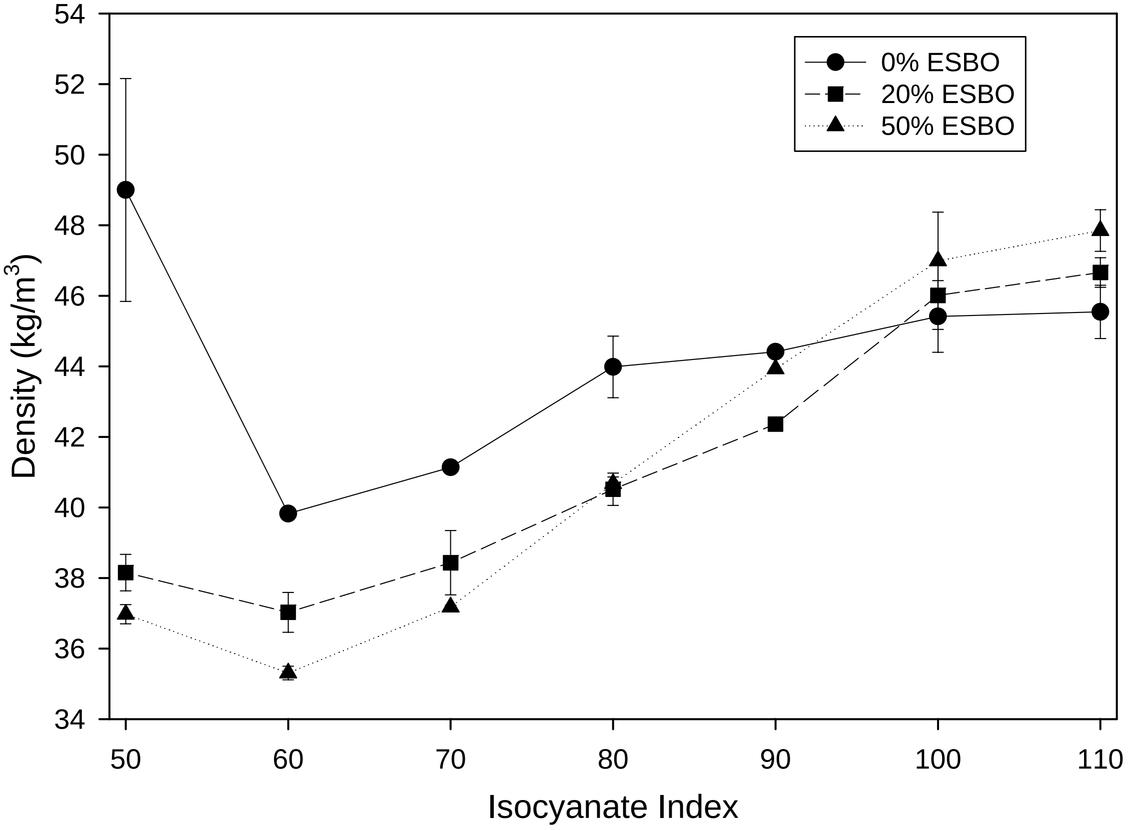

Figure 5.2. Effect of isocyanate index and ESBO replacement percentage on the density of water-blown rigid polyurethane foams.

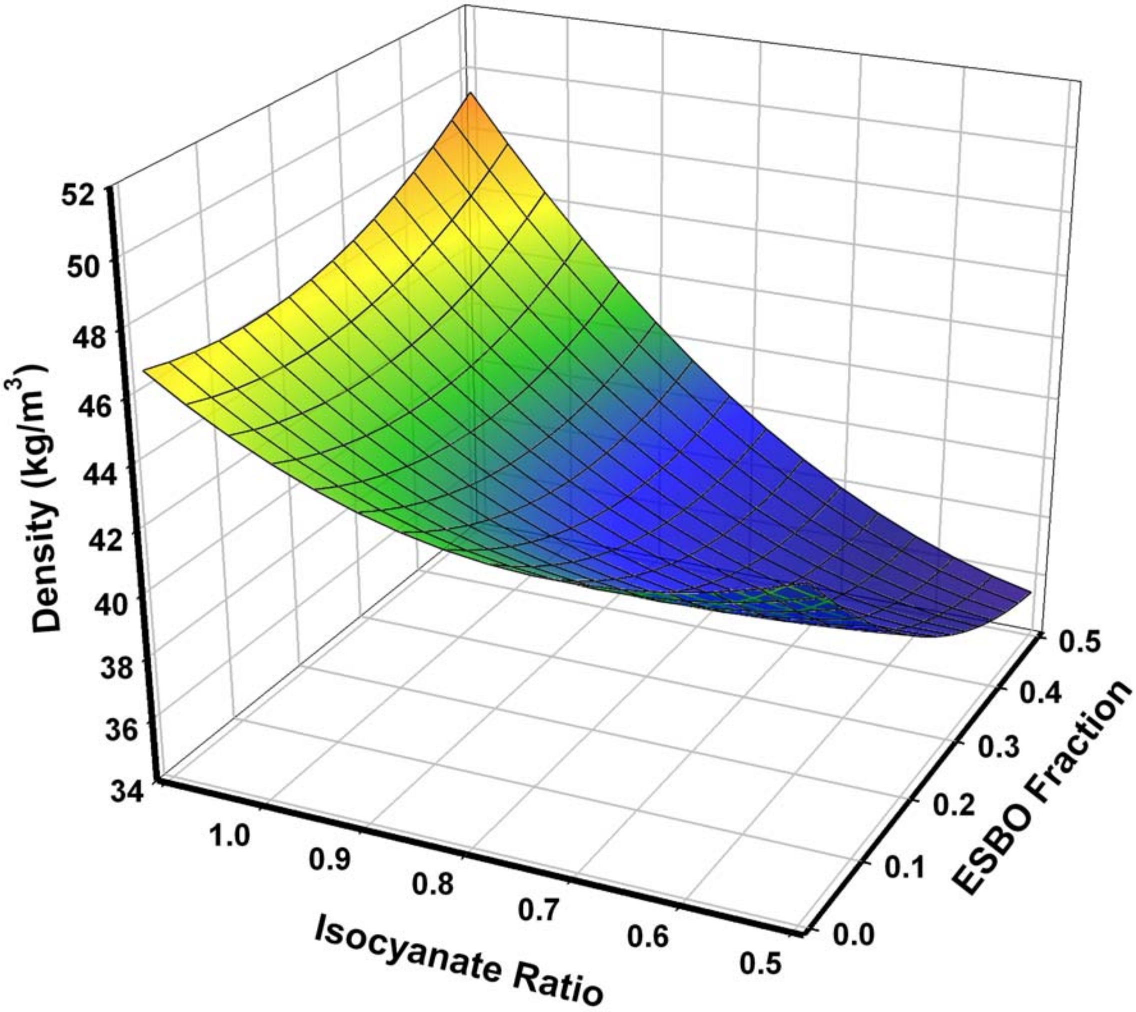

Figure 5.3. The regression plane ($R^2 = 0.8093$) of density of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios.

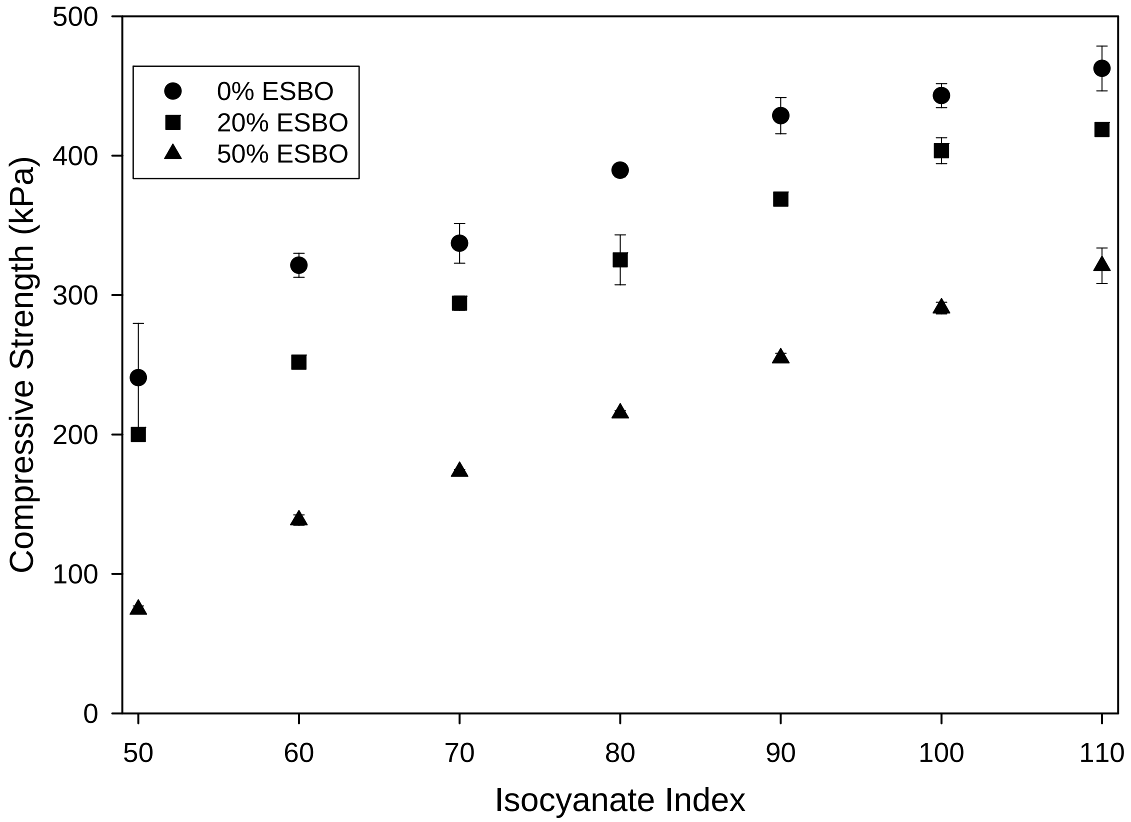

Figure 5.4. Effect of isocyanate index and ESBO replacement percentage on the compressive strength of water-blown rigid polyurethane foams.

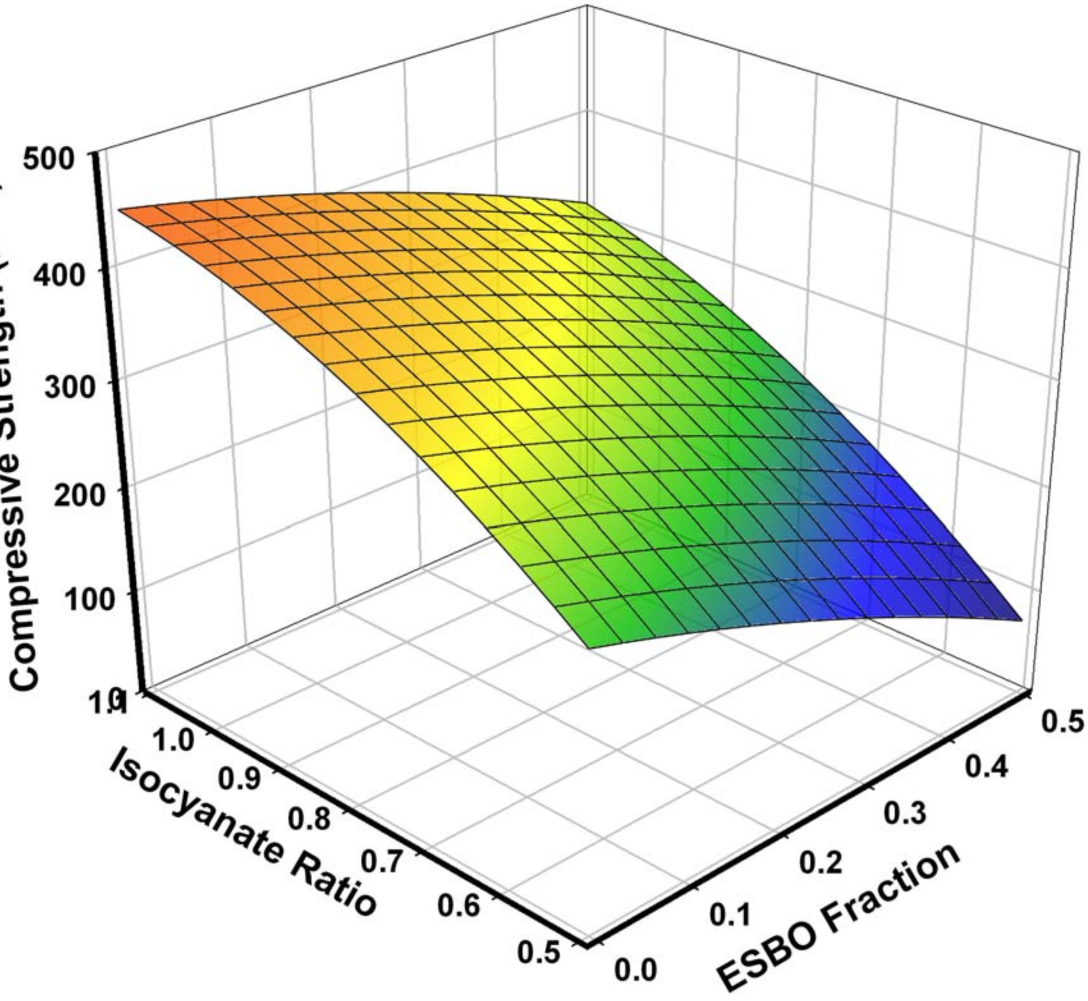

Figure 5.5. The regression plane ($R^2 = 0.9715$) of compressive strength of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios.

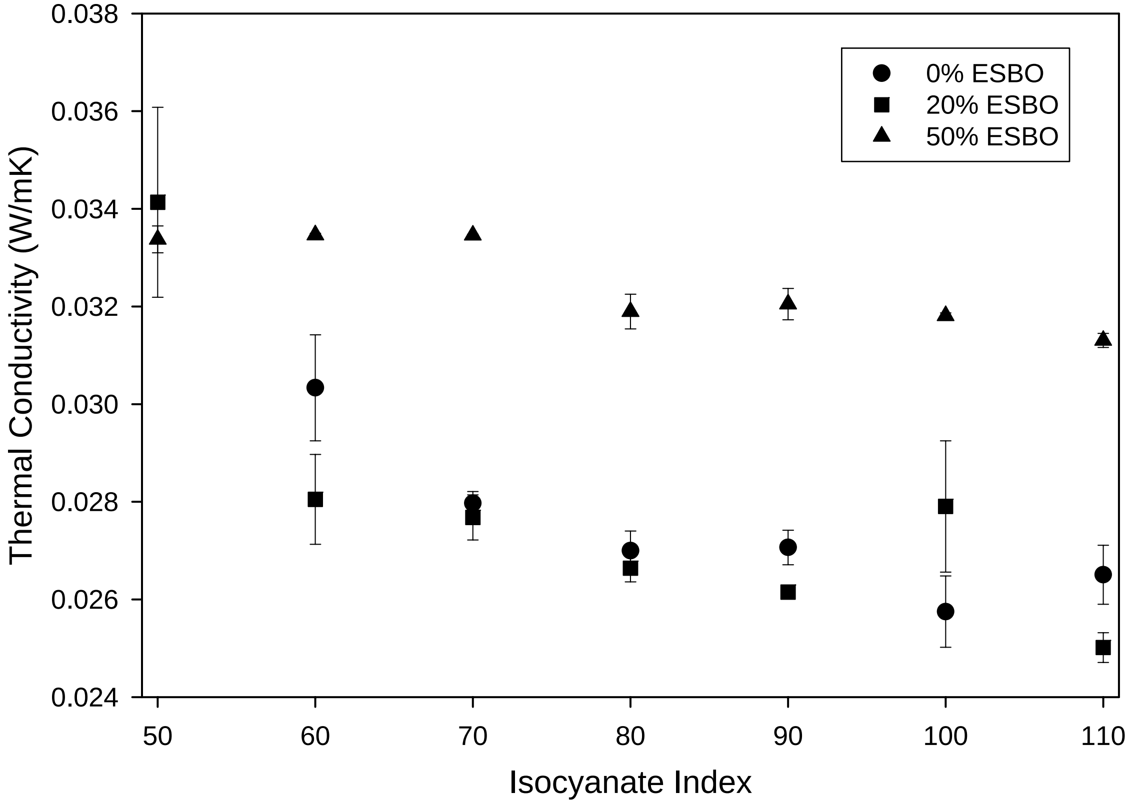

Figure 5.6. Effect of isocyanate index and ESBO replacement percentage on the thermal conductivity strength of water-blown rigid polyurethane foams.

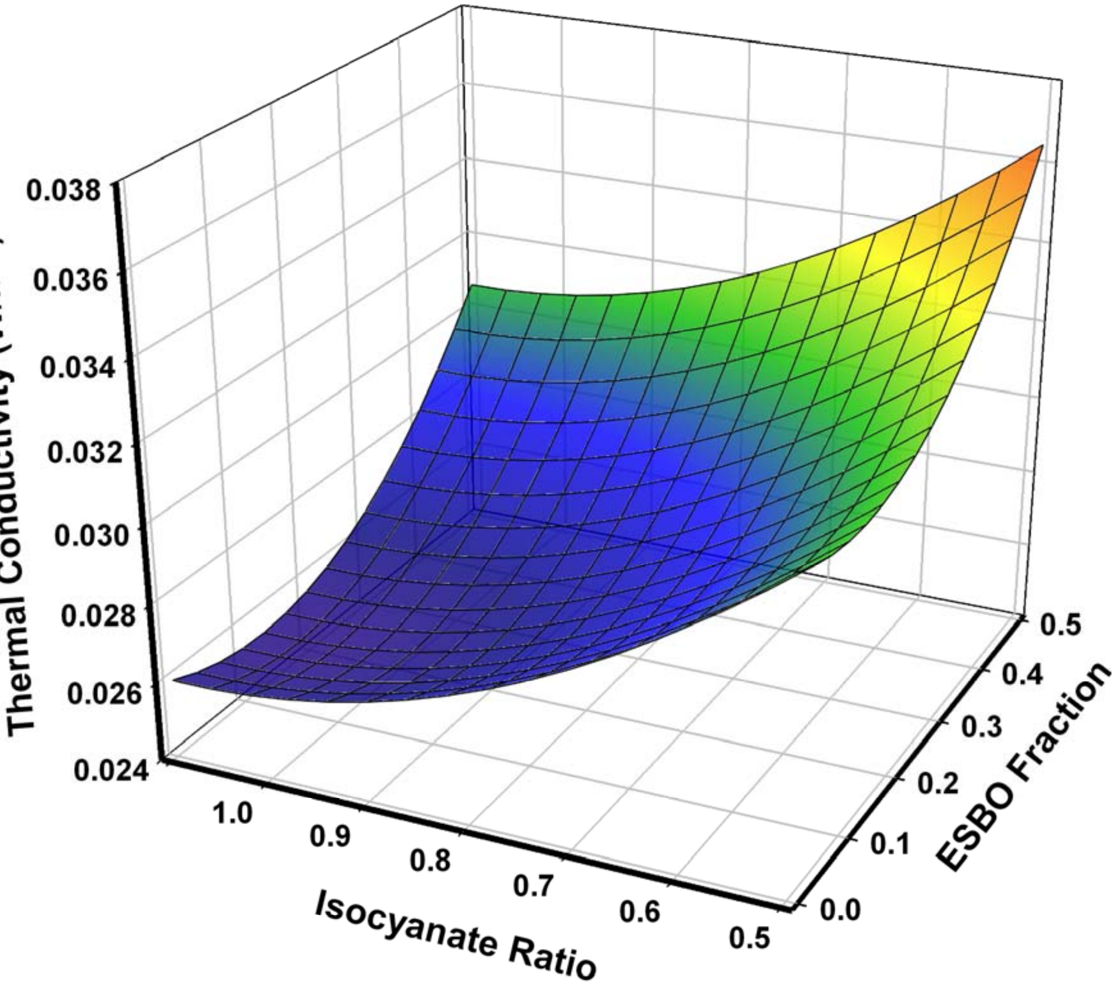

Figure 5.7. The regression plane ($R^2 = 0.8405$) of thermal conductivity of water-blown rigid polyurethane foams with different ESBO fractions and isocyanate ratios.

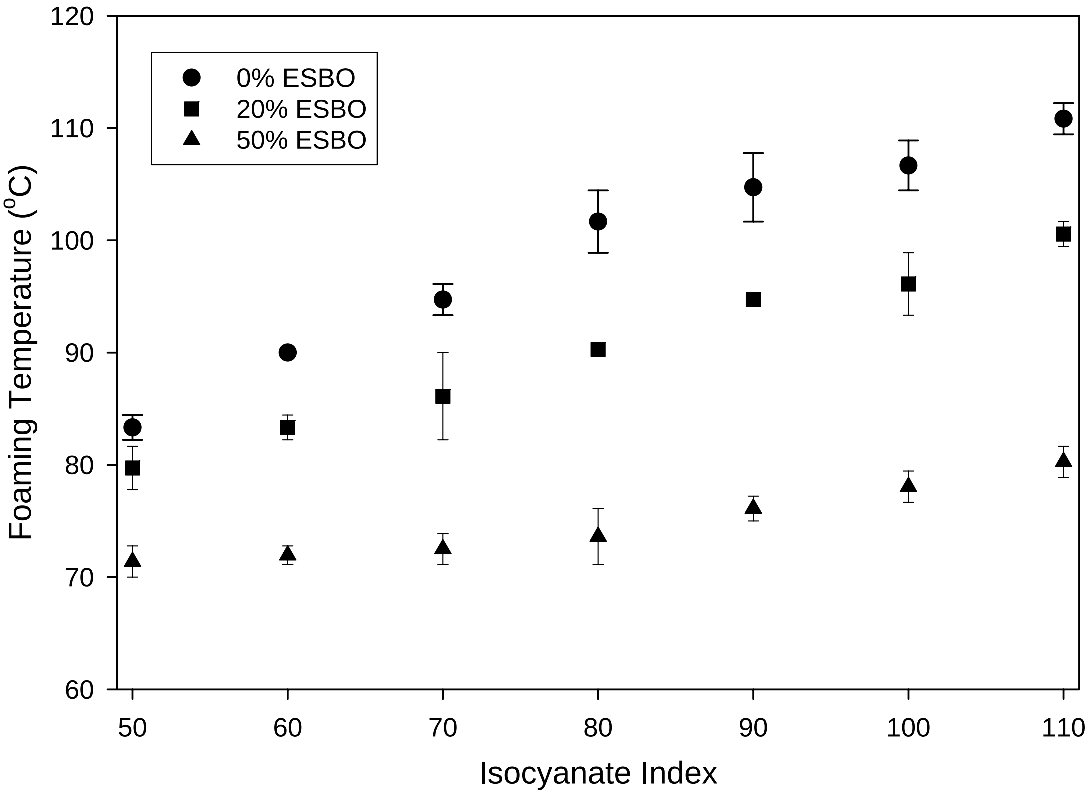

Figure 5.8. Effect of isocyanate index and ESBO replacement percentage on the foaming temperature of water-blown rigid polyurethane foams.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Novel water-blown rigid polyurethane foams were successfully prepared by blending petroleum polyol and vegetable oil based polyol together as the B-side component. Some polyols that derived from soybean oil had a lower thermal conductivity than petroleum polyol, such as epoxidized SBO series polyols, DG (ENOVA) series polyols, commercial soyols, and polyols made by reacting ESBO with acetol. Foams made from other soybean oil polyols had a higher thermal conductivity because the hydroxyl group in their chemical structure is secondary. The hydroxyl number of polyols affected the density and compressive strength of foams but not the thermal conductivity. Foams made with hydroxy SBO, ESBO/Acetol, and oxidized epoxidized DG SBO not only had superior thermal conductivity, but also better density and compressive strength properties than the petroleum polyol. These three vegetable oil based polyols appear to have the potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications.

Water-blown rigid polyurethane foams were successfully prepared by introducing epoxidized soybean oil in the foaming system. Although epoxidized soybean oil does not having any hydroxyl groups in its chemical structure, it appears that up to 20% of Voranol® 490 could be replaced by epoxidized soybean oil in rigid polyurethane foams without compromising the properties of rigid foams. Changes in foaming temperature and physical properties essentially could be attributed to the lower reactivity between epoxidized soybean oil and isocyanate than between polyether polyol and isocyanate. It is worth noting that when 20% of the polyether polyol (Voranol® 490) was replaced by epoxidized soybean oil, the foam at isocyanate index 90 had slightly favorable (lower) density and thermal conductivity values than the control foam (containing 100% polyether polyol) at isocyanate index 110, although the compressive strength value was slightly less favorable. Therefore, replacing 20% of the polyether polyol offers the possibility of reducing isocyanate in the foam formulation in applications that compressive strength is not as critical.

The physical properties of water-blown flexible polyurethane foams containing 0 to 50% ESBO were studied. The density and 50% compression deflection properties were similar to or better than control flexible foams up to 30% ESBO, while the resilience and 50% constant deflection compression properties were inferior to control flexible foams. These were due to an increase in the hard segment with increasing ESBO resulting in firmer foams. In the DMS analysis of plastic films, decreasing maximal tanδ and increasing *E'* indicates the hard segment in plastic film increased with increasing ESBO. In DSC analysis, decreasing Δc_p indicates the soft segment in plastic film decreased with increasing ESBO. In the FTIR-ATR experiment, the hydrogen-bonded urethane group (HS) was found. Once ESBO was introduced into the molded plastic films, the films became firmer or stiffer. In addition, the epoxy ring and oxazolidone were absent in both flexible mold plastic and foams.

As shown in this study, polyols derived from soybean oil have a great potential to replace petroleum-based polyols. Many other vegetable-based oils other than soybean oil have yet to be explored for polyol applications, in particular, non-edible vegetable oils. For example, the oil from *Jatropha curcas* seeds, which was cited as one of the best candidates for future biodiesel production by Goldman Sachs lately. *Jatropha* is resistant to drought and pests and produces seeds containing up to 40% oil while soybeans contain only 18-20% oil.

According to the FTIR-ATR results of polyurethane foams containing up to 50% epoxidized soybean oil (ESBO), no trace of epoxy ring was found. This indicated that ESBO participated in the polyurethane foaming reaction. Additional studies are needed to explore the uses of ESBO in polyurethane systems other than rigid and flexible foams such as elastomers, adhesives, and coatings, etc. In addition, the reaction mechanism between ESBO and isocyanate needs to be elucidated in these polyurethane systems and the resulting end products identified.

The overall economics of polyols derived from soybean oil or other vegetable oils need to be addressed taking into consideration the scale of production. Also, the carbon footprint of polyols derived from soybean oil or other vegetable oils against that from petroleum-based polyols should be studied.

VITA

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