POLYURETHANE FOAMS MADE FROM BIO-BASED POLYOLS

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In Partial Fulfillment of the Requirements for the Degree

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

POLYURETHANE FOAMS MADE FROM BIO-BASED POLYOLS

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ABSTRACT

Polyurethane (PU) foams have widespread applications and market demand for PU foams is still growing globally. The raw materials of PU, polyol and isocyanate, are conventionally derived from petroleum. Bio-based polyols are promising substitutes for petrochemical polyols due to their sustainability. This project studied water-blown polyurethane (PU) foams made from soy-polyols. The flexible bio-based PU foams were successfully produced by mixing petroleum polyol and commercial soy-polyols with different hydroxyl numbers and functionalities. The effect of hydroxyl number and functionality of soy-polyols, and the effect of tin catalyst, cross-linker levels and isocyanate index on foam properties were identified. PU foams had better compression force deflection (CFD) and tear resistance (TR) values than the control foams made from 100% petroleum polyol. Due to a lower equivalent weight and the triglyceride structure, bio-based PU foams displayed less flexibility than the control foams, and thus had a lower resilience and higher constant deflection compression (CDC).Disregard of the soy-polyol percentage and isocyanate index, the glass transition temperature (T_g) remained the same value. But the change in specific heat, Δc_p, decreased with increasing soy-polyol percentages. The transmittance in Fourier transform infrared spectroscopy (FTIR) showed the increase of hard segments when soy-polyol percentages increased.

Water-blown rigid polyurethane (PU) foams were made from 0-50% soy-phosphate polyol (SPP) and 2-4% water as the blowing agent. The effects of water content and isocyanate index on physical properties of SPP PU foams were investigated. Because higher amount of blowing agent generated more carbon dioxide to expand the foam, larger foam volume was obtained. Thereby, SPP PU foams with higher water content had lower density and compressive strength. The thermal conductivity of SPP PU foams decreased and then increased with increasing SPP percentage. Especially, at 3% water content and 20% SPP percentage, the lowest thermal conductivity was obtained. SPP PU foams containing higher isocyanate density performed higher compressive strength. Interestingly, the compressive strength of some 20% SPP foams was close or similar to the control foams at the same isocyanate density.

Low density soy-polyol based rigid PU foams were modified with different concentrations of glass microspheres and nanoclay. Since the filler surface provided nucleation sites for gas bubble formation, foams modified with fillers obtained larger volume and lower density. The overall compressive strength was determined by the positive effects of fillers on polymer network reinforcement and the negative effects resulting from decreasing foam density. For foams with microspheres, the compressive strength decreased slightly from 1 to 3% and then increased; while in foams with nanoclay, the compressive strength remained unchanged from 1 to 5%, and then significantly decreased at 7%.It was interesting that foams containing 5 to 7% microspheres or 3 to 7% nanoclay had comparable density-compressive strength to the control. The morphology observed with SEM displayed that foams containing fillers had more cells and smaller cell size than foams without fillers.

The effects of high viscosity soy-polyols (13,000 cP to 31,000 cP) on water-blown rigid polyurethane foams (SBO PU foams) containing 1-50% high viscosity soy-polyols were investigated. With increasing soy-polyol percentage, the density of SBO PU foams decreased because of a lower hydroxyl number in soy-polyols; the compressive strength decreased, decreased and then increased, or remained at the same level and then increased when soy-polyols had viscosity of 13,000 cP, 21,000 cP and 31,000 cP, respectively. With regard to density-compressive strength, foams made from high viscosity (21,000 to 31,000 cP) soy-polyols demonstrated comparable or superior value to the control foam. Most SBO PU foams performed better isocyanate density-compressive strength to the control foams. In addition, the foam cell size decreased and the cell number increased as the soy-polyol percentage increased.

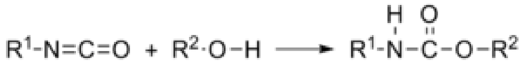
CHAPTER 1

INTRODUCTION

1.1 Polyurethane

Polyurethanes are versatile materials and have many applications in industry due to their wide range of stiffness, hardness, and densities. The polyurethane (PU) materials include: soft solid elastomers used for gel pads and print rollers, low density elastomers used in footwear, hard solid plastics used as electronic instrument bezels and structural parts, flexible foams used in upholstery and bedding, and rigid foams used for thermal insulation. Figure 1.1 outlines the characteristics of polyurethane materials (Woods 1990; Klempner and Frisch 1991) and Table 1.1 displays how polyurethanes are used in the United States (PURRC 2004). Globally over three quarters of the polyurethanes are consumed in the form of foams, either flexible foams or rigid foams. In 2007, the worldwide consumption of PUs was over 12 million metric tons, and is continuously increasing at an average annual growth rate of 5% (Avar 2008).

The two essential components to produce polyurethanes are the isocyanate containing isocyanate group (-N=C=O) and polyols containing the hydroxyl group (-OH). A urethane linkage is produced by reacting an isocyantee group with a hydroxyl group, and therefore, polyurethanes are manufactured by the reaction of isocyanate with polyol in the presence of catalysts and other additives. The generalized polyurethane reaction is shown as follows (Klempner and Senijarevic 2004):



$$R^1\text{-}N{=}C{=}O + R^2\cdot O\text{-}H \longrightarrow R^1\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$$

In the polyurethane industry, both isocyanate and polyols are usually made from feedstocks derived from petroleum. However, in recent decades, various factors spur researchers to explore alternative resources as feedstock of polyol, such as the continuously rising costs of petroleum, the increasing global consumption of polyurethanes, the unstable supply of petroleum market partially due to political factor, and the enhanced public desire for environmentally friendly green products. Furthermore, the potential for polyols derived from vegetable oils to replace petrochemical-based polyols exists (Niemeyer and others, 2006).

Table 1.1 How PUs were used in the US in 2004 (PURRC 2004).

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

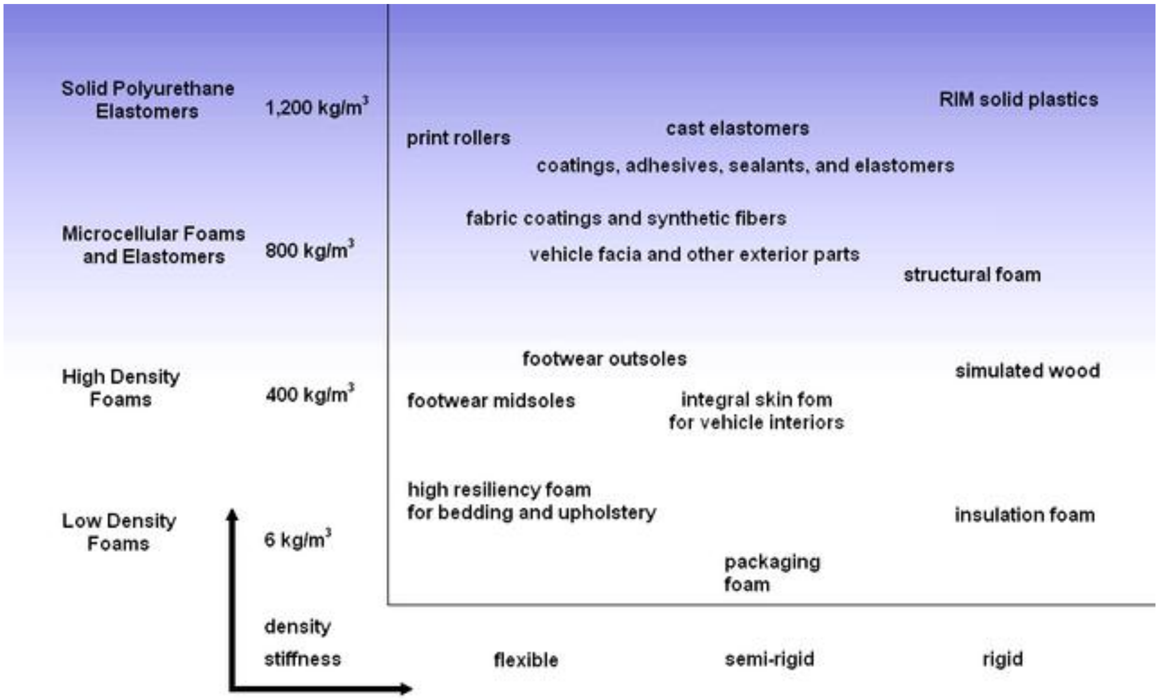


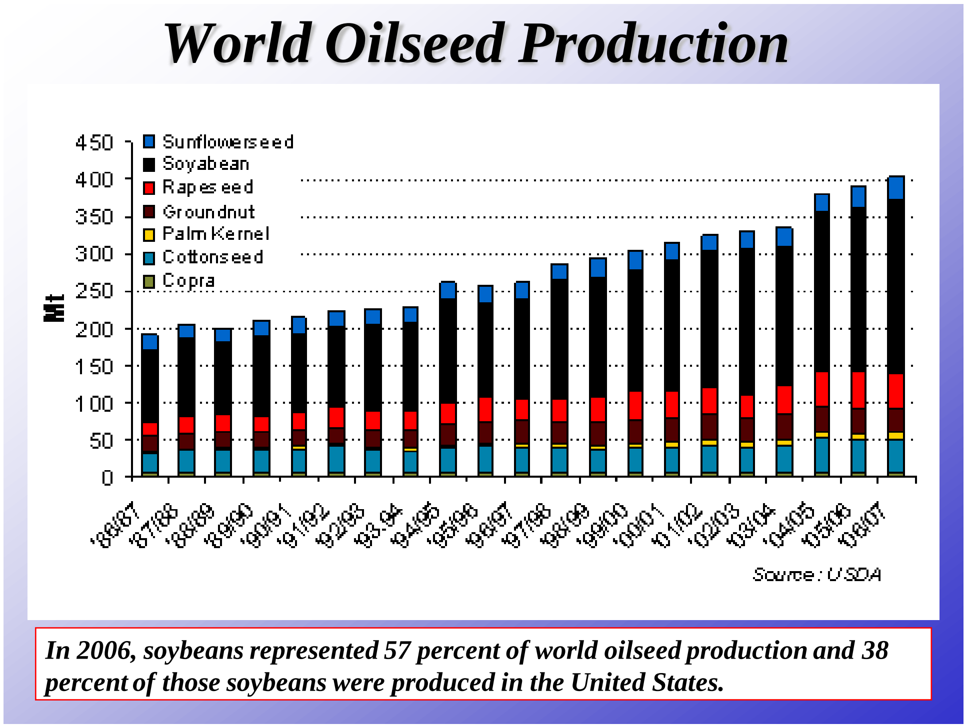
Figure 1.1 Characteristics of polyurethane materials.

1.2 Vegetable Oil-Based Polyols

Vegetable oils are renewable resources and are abundant in many countries. These oils are predominately composed of triglyceride molecules, which consist of three fatty acids connected to a glycerol juncture. These fatty acids usually contain fourteen and twenty-two carbons in length and 0-3 double bonds per fatty acid (Wool and Sun 2005). But most vegetable oils do not naturally bear hydroxyl groups that are essential to the polyurethane reactions. Therefore, except castor oil, most vegetable oils need physical treatment and chemical modification to introduce the hydroxyl groups. Due to the natural presence of the hydroxyl groups, castor oil has been studied in a variety of polyurethane products (Athawale and Kolekar 1998; Zhang and Ding 1998). However, the high cost and lack of productions in many industrialized countries limit the study and applications of castor oil. Aside from castor oil, some vegetable oils were studied to prepare polyols and to explore their applications in polyurethanes. Hu et al (2001) prepared repeseed oil based polyol by peroxy acid treatment of rape seed oil followed by alcoholysis. Zlatanic et al (2004) prepared a series of vegetable oil-based polyols using canola oil, sunflower oil, soybean oil, linseed oil and corn oil. These vegetable oil based polyols were synthesized by epoxidation of the oils and subsequent opening of the ring of the epoxy groups with methanol to obtain hydroxyl groups. Kiatsimkul et al (2008) successfully prepared high hydroxyl equivalent weight polyols by enzyme hydrolysis of castor oil, epoxidized soyben oil and alkoxyl hydroxyl soybean oil. Lozada et al (2009) reported the preparation of polymerized soybean oil and soy-based polyols using two different heat-polymerization approaches.

1.3 Soybean Oil-Based Polyols

The United States is a major producer of soybeans. In 2006, soybeans occupied 57% of the world's oilseed production and 38% of these soybeans were produced by the United States (Figure 1.2). In recent years, U.S. soybean yields increased average 0.4 bushels per year and the prices are forecasted to be relatively stable (Figure 1.3 and Figure 1.4). Within the U.S., soybeans are inexpensive and their production greatly exceeds edible demands. Additionally, refined soybean oils contain more than 99% triglycerides with active sites amenable to chemical reactions (Wool and Sun 2005). Therefore, soybean oil is one of the most promising bio-based resources for feedstock of polyols. In this study, we explored and improved the physical properties of PU foams made from a series of soybean oil-based polyols. These soybean oil based polyols are Soy- Polyols (SPs) with a series of different functionalities, soy-phosphate polyol made with the presence of phosphate acid as catalyst, and soy-based polyol made from oxirane-ring opening by alcoholysis reaction. Soy-Polyols were a series of commercial soybean oil-based polyols manufactured by BioBased Technology, and the last two soy based polyols were prepared by Dr. Suppes's lab at the University of Missouri.



World Oilseed Production

Source: USDA

In 2006, soybeans represented 57 percent of world oilseed production and 38 percent of those soybeans were produced in the United States.

Figure 1.2 World oilseed production.

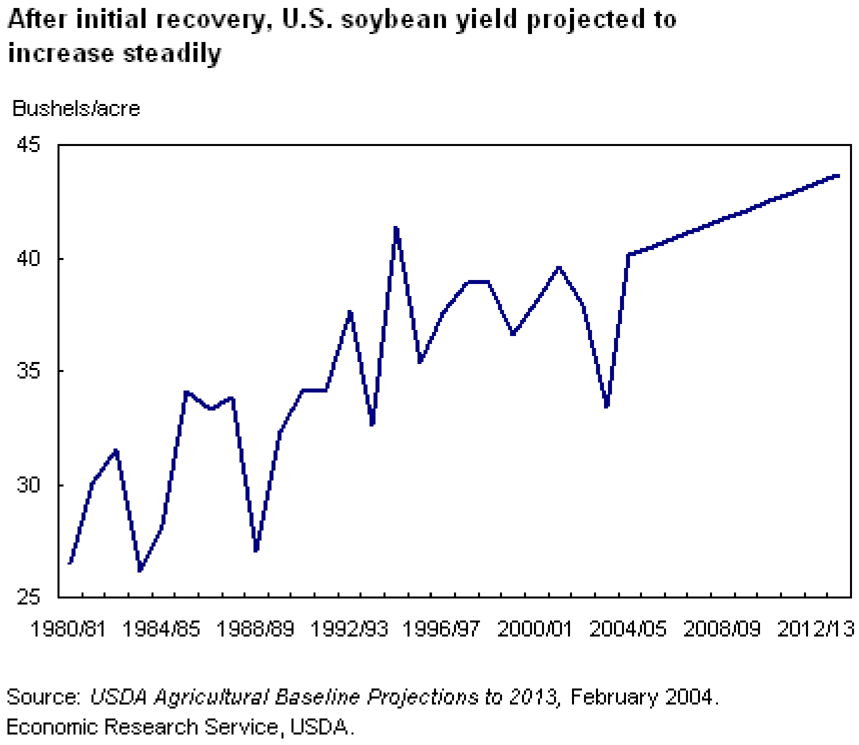


Figure 1.3 After initial recovery, U.S. soybean yield projected to increase steadily.

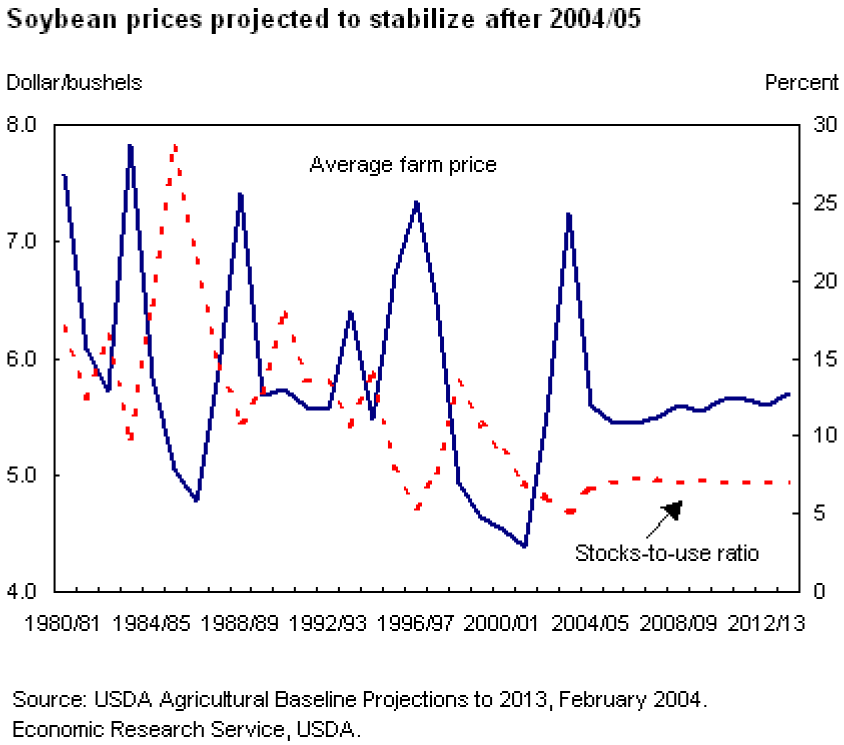


Figure 1.4 Soybean prices are projected to stabilize after 2004/2005.

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CHAPTER 2

LITERATURE REVIEW

2.1 Water-Blown Polyurethane (PU) Foams

2.1.1 Chemical Reactions of Water-Blown PU Foams

In PU chemistry, isocyanate and polyol containing active hydrogens are two major compounds in PU formation. The polymerization between isocyanate and polyols generates urethanes, which are the prime components in the PU. PU foams are produced by forming gas bubbles in the polymerizing mixture, which determines their microcellular structures. During the foaming process, the process of the bubble formation is called "forming" and the gas is produced by the reaction of isocyanate with water, which is the blowing agent (called blowing agent). Generally, the chemical principle governing the production of PU foams is based on those two synchronous reactions: PU formation and gas generation with the presence of catalysts.

(1) Reaction of isocyante with polyol to form urethane:

$R\text{-}OH + R'\text{-}N{=}C{=}O \rightarrow R'NHCOOR$

Polyol Isocyanate   Urethane

The rate of reaction depends on the chemical structure of polyol and isocyanate. This reaction results in the formation of urethane groups and this reaction is exothermic.

(2) Reaction of isocyanate with water (blowing agent) to generate carbon dioxide (gas) and a urea:

$$\text{R-N=C=O} + H_2O \rightarrow (\text{R-NH-CO-OH}) \rightarrow \text{R-}NH_2 + CO_2$$

Isocyanate Water Carbamic acid Urea Carbon dioxide

The reaction ejects carbon dioxide, which is a predominant source of gas for "blowing".

(3) Reaction of isocyanate with amine to form a urea linkage:

$$\text{R-}NH_2 + \text{R'-N=C=O} \rightarrow \text{R-NH-CO-NH-R'}$$

Amine Isocyanate Diisocyanate urea

The reaction between isocyanate and amine yields substituted urea (Klempner and Frisch 1991; Woods 1990).

2.1.2 Chemicals Used in the Preparation of PU Foams

The major chemicals applied in the manufacture of PU foams include polyols, isocyanate, blowing agents, catalysts, surfactants, and crosslinkers. The functions of these chemicals are described briefly in the following paragraphs.

2.1.2.1 Polyols

2.1.2.1.1 Introduction of Polyols

In PU manufacturing, polyols are defined as the polymeric compounds containing at least two hydroxyl groups (isocyanate-reacting groups). There are several types of polyols that can be used for PU foams, such as polyether polyols, polyester polyols, and hydroxyl-terminated polyolefins. Polyether polyols with terminal hydroxyl groups are predominantly used and representative polyols for PU foams, occupying approximately 90% of the polyols used in making PU foams. They are produced by the polymeric reaction between organic oxides, such as ethylene oxide and propylene oxide, and initiator compounds containing two or more active hydrogen atoms. In the presence of a base catalyst, the initiator initiates the ring opening and adds the oxides. The addition reaction continues until the desired molecular weight is obtained. When the initiator contains two or three active hydrogens, a diol or triol can be formed. Figure 2.1 shows the reactions that represent the basic production of a diol and a trio (Herrington and Hock 1997).

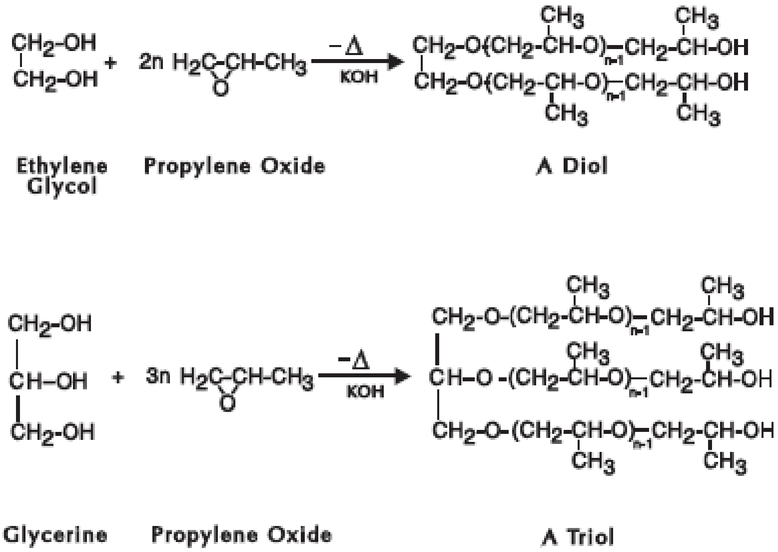


Figure 2.1 Reactions of propylene oxide to produce a diol and a triol **(**Herrington and Hock 1997**)**

The properties of polyols, such as chemical structure, functionality, and molecular weight, play a significant role in determining the final properties of foams. To a large extent, the selection of polyol controls the degree of cross-linking in the polymer network formed in the reaction with iscoyanate (Molero et al 2008). Furthermore, the degree of cross-linking has a significant effect on the polymer stiffness. For example, in rigid foams specialized for load bearing, there is a high degree of cross-linking, which creates a stiff polymer network (Seo et al 2004); while flexible foams with good recovery and resiliency properties have a proportionally less degree of cross-linking (Kaushiva et al 2000).

2.1.2.1.2 Polyol Characterizations

The basic major criteria for characterizing a polyol are functionality, hydroxyl number, and equivalent weight.

Functionality – It originates from the initiator of the polyol. Simply, it is the average number of isocyanate reactive sites per molecule.

Hydroxyl Number – It is the amount of hydroxyl groups available for polyol and isocyanate reaction. The hydroxyl number (mg KOH/g sample) is defined as the mili-grams of potassium hydroxide equivalent to the hydroxyl content per gram of sample according to ASTM Designation: E222-10 (2010). For epoxidized oils, the hydroxyl number is determined according to the AOCS official method Tx 1a-66 (2009).

Equivalent Weight – It is defined as the molecular weight of a polyol divided by its functionality. In practice, the equivalent weight is calculated from the analyzed hydroxyl (OH) number from the following expression. The equivalent weight is necessary for the isocyanate requirement calculations.

Equivalent Weight = 56.1x 1000 / OH number (Herrington and Hock 1997)

2.1.2.1.3 Bio-Based Polyols

2.1.3.2.3.1 Introduction of Bio-Based Polyols

Natural oils, which can be derived from plant sources, are abundant in most parts of the world, making them an ideal alternative to petroleum-based chemical feedstocks. Although many types of vegetable oils have been tested and reported for polyol and PU applications, soybean oil is the most promising one to partially replace petroleum to make polyols due to its great production and price stability. The United States has a great potential to produce soybeans and its price is forecasted to be relatively stable in the next decade (Economic Research Service, USDA 2010a, 2010b). Also, refined soybean oil contains more than 99% triglycerides (Figure 2.2) and about eight major fatty acids. Using chemical or physical methods, these triglycerides can be used in polymerization by introducing critical groups on the active sites including the double bonds, the allylic carbons, the ester groups and the carbons alpha to the ester groups (Zlatanic et al 2004). During this process, the key step is to reach a high molecular weight and to incorporate chemical functional groups, such as hydroxyl groups, that can impart stiffness to a polymer network (Babb et al 2007; Wool and Sun 2005). So far, several methods are known to introduce hydroxyl groups at the unsaturated sites of triglycerides in soybean oil: hydroformylation followed by hydrogenation (Lysenko et al 2004); epoxidation followed by oxirane opening (Petrovic et al 2002; Lozada et al 2008; Lubguban et al 2009); ozonolysis followed by hydrogenation (Petrovic et al 2005); and microbial conversion (Hou 1995). Figure 2.3 schematically shows how the polyols can be derived from a single vegetable oil triglyceride assuming no coupling or side reactions (Zhang et al 2007).

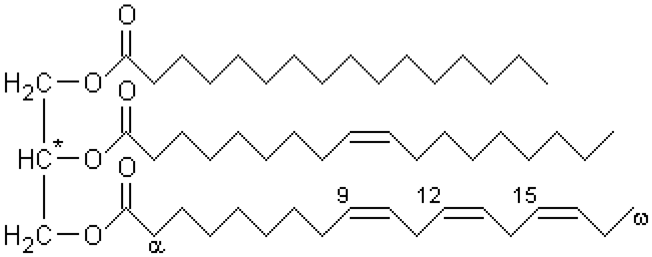


Figure 2.2 A triglyceride molecule, the major component of natural oils (http://en.wikipedia.org/wiki/Triglyceride).

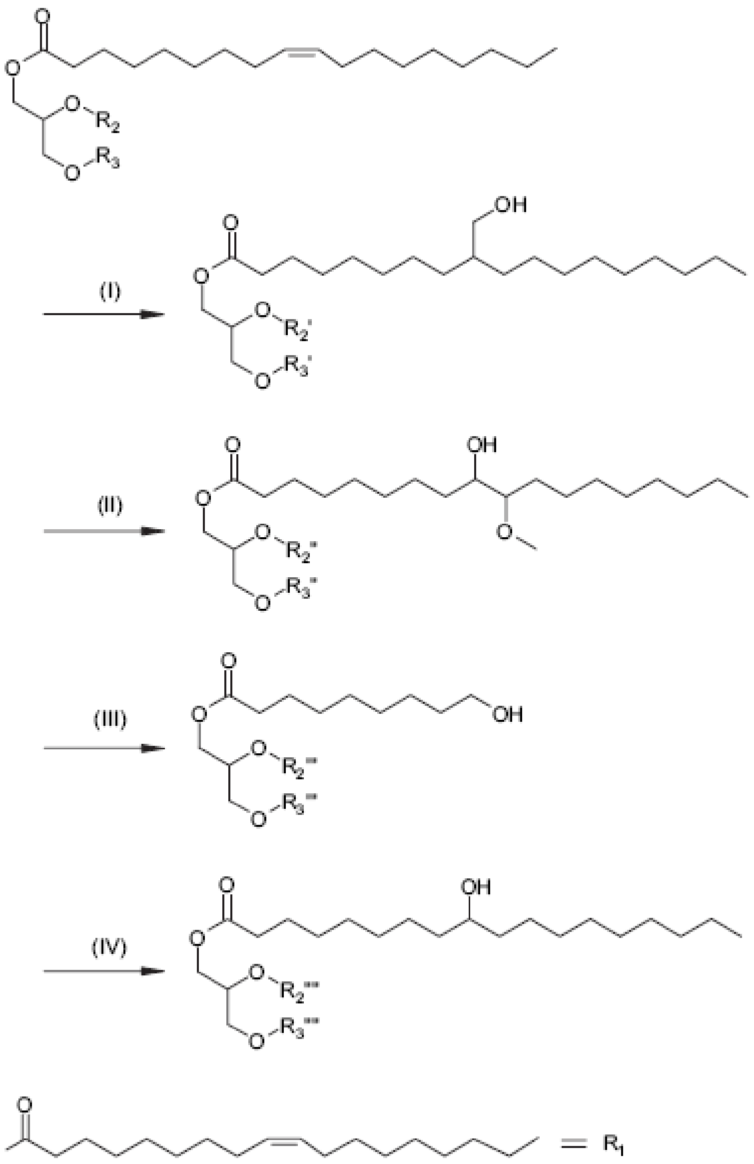


Figure 2.3 A schematic representation of reactions to derive polyols from vegetable oil: (I) hydroformylation followed by hydrogenation; (II) epoxidation followed by oxirane ring-openingm; (III) ozonolysis followed by hydrogenation; (IV) microbial conversion.

2.1.2.1.3.2 Commerical soy-polyols

Commercially, Soy- Polyols are a series of high quality soybean oil-based polyols. They bear an array of hydroxyl groups in their structures and can replace the conventional pertroleum-based polyols in commercial and industrial PU applications for flexible foams, coatings, adhesives, sealants, and so on. At room temperature, Soy-Polyols are viscous liquid, pale yellow to amber in appearance (BioBased Technology Website). They are derived by converting the alkene groups of the unsaturated molecules that make up vegetable oils, into hydroxyl groups. Figure 2.4 is the schematic of the proposed reactions to prepare Soy-Polyols.

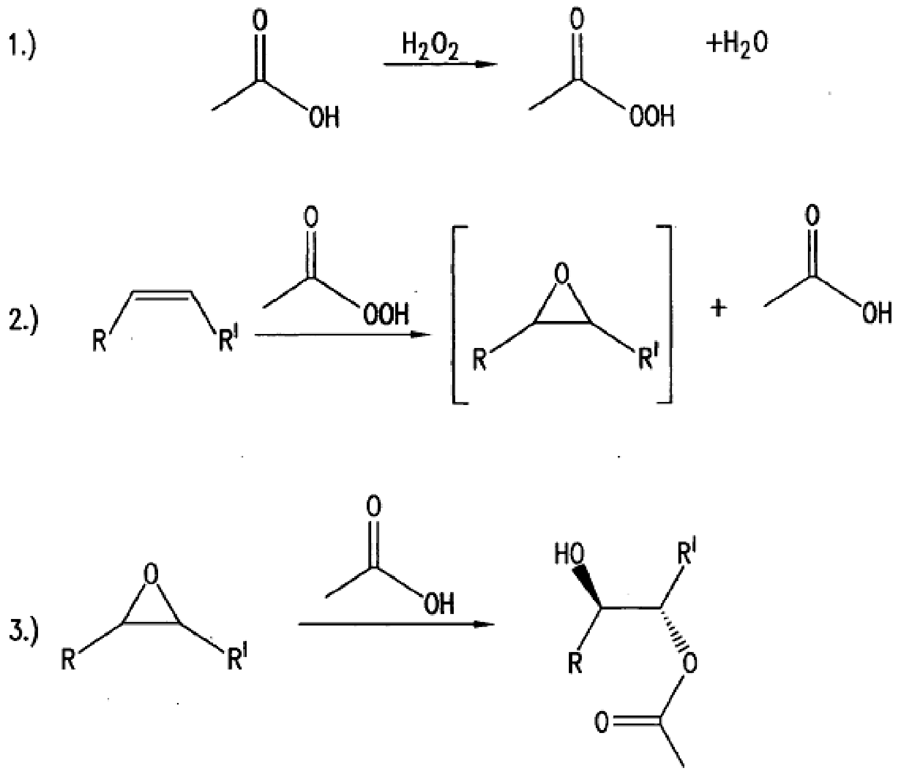


Figure 2.4 The schematic of the proposed reactions to prepare soy-polyols (Casper and Newbold 2006)

2.1.2.1.3.3 Soy-Phosphate Polyol

Soy-phosphate polyol (SPP) is a new kind of soybean oil-based polyol prepared by Dr. Galen Suppes's lab in the Department of Chemical Engineering at the University of Missouri. The basic process of soy-phosphate polyol preparation is simply listed as:

1) Place approximately 300 grams of full epoxidized soybean oil-Vikoflex 7170 (Arkema Inc, Philadelphia, PA) in a 400-mL capacity beaker.
2) Use a mechanical stirrer (with impeller) for thorough mixing.
3) Add by dropping the desired amount of o-phosphoric acid (% by wt) into the ESBO.
4) After adding the acid, mix for another 5 minutes until uniform homogeneous polyol is obtained (Lubguban, 2009).

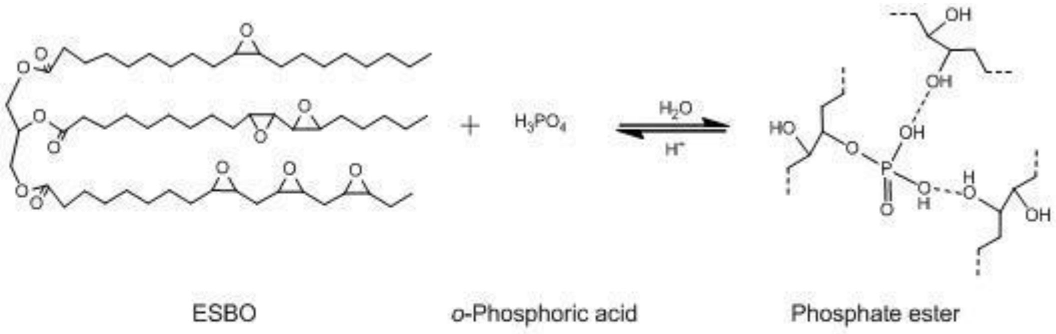


Figure 2.5 Schematic representation of phosphate ester formation (Lubguban, 2009; Lubguban et al, 2009)

2.1.2.2 Isocyanates

The isocyante is another important component in PU manufacturing. It is the source of N=C=O (NCO) groups which can react with the hydroxyl groups in polyol, water and cross-linkers in the foaming formulations. All isocyanates used usually contain at least two NCO groups per molecule. The major isocyanates produced are diisocyanate (TDI), diisocyanate-diphenylmethane (MDI) and their derivatives, and almost 95% of all polyurethanes are based on them. The chemical structures of TDI and MDI are shown in Figures 2.6 and 2.7, respectively. Especially, the various kinds of MDI are applied in high resiliency, semi-flexible and microcellular PU foams (Herrington and Hock 1997).

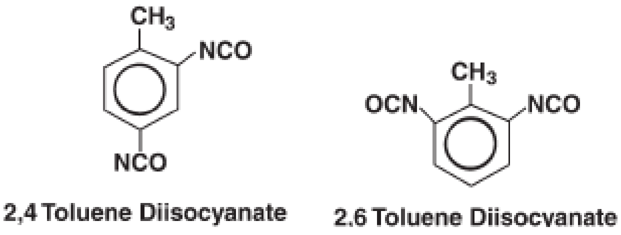


Figure 2.6 Isomers of TDI (Herrington and Hock 1997)

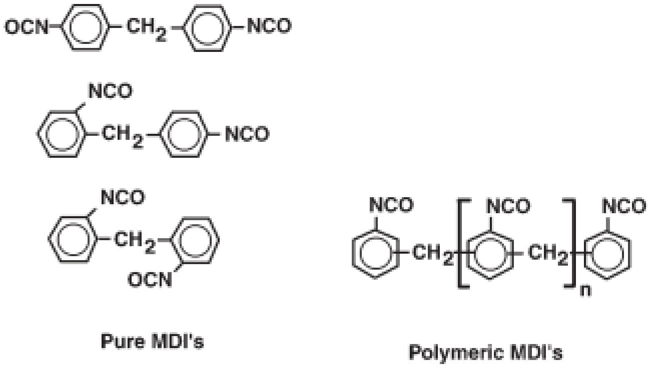
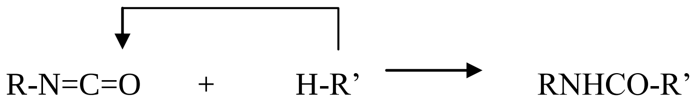


Figure 2.7 Chemical structures of MDI (Herrington and Hock 1997)

At ambient temperature, pure two-isomers of MDI exist as solids. In addition, the sterically free isocyanate groups of the 4, 4’ and 2, 4’ isomers are very reactive in polymerization. So in industry, polymeric MDI are commonly applied in PU foams. Two polymeric MDI-based isocyanates are being marketed: PAPI and Mondur MR. These polymeric isocyanates have lower vapor pressures which minimize toxicity problems which happen with isocyanates. Furthermore, foams produced from PAPI isocyanate tend to have good dimensional stability and structure strength at temperatures as high as 300 to 400 ^{o}F (Herrington and Hock 1997).

The isocyanate functionality in the structure of isocyanates [-N=C=O] is quite reactive toward proton-bearing nucleophiles. The chemical reaction can occur with a nucleophilic addition across the carbon-nitrogen double bond. When isocyanate reacts with a compound with “active hydrogens”, the hydrogen attaches to the isocyanate nitrogen, and the remainder of the compound (R’) covalently attaches to the carbonyl carbon (Woods 1990). The reaction is shown in Figure 2.8.



$$R\text{-}N{=}C{=}O \quad + \quad H\text{-}R' \longrightarrow \quad RNHCO\text{-}R'$$

Figure 2.8 Reaction of isocyanate with active hydrogen compounds (Woods 1990)

Isocyanate Index

The amount of isocyanate used relative to the theoretical equivalent amount is known as the Isocyanate Index:

Isocyanate Index = Actual amount of isocyanate used x 100 / Theoretical amount of isocyanate required

The isocyanate index has a pronounced effect on the stiffness or hardness of the final foam. In principle, a higher isocyanate index raises the actual amount of reacting isocyanate, increasing the cross-links in the polymer network (Dounis and Wilkes 1997) which in turn increases the hardness or stiffness of molded foams (Sonnenschein et al 2007). However, increasing the hardness of the foams by increasing the isocyanate index has its limit. There is a point beyond which the hardness does not increase any more and other physical properties begin to deteriorate. In the PU industry, isocyanate indices commonly range from 80 to 100 for flexible PU foams (Klempner and Senijarevic 2004).

2.1.2.3 Blowing Agents

In the manufacture of PU foams, the blowing agent produces gas bubbles in the polymerizing mixture and the mixture is blown to form foams. The conventional blowing agent is water, which is a source of active hydrogens, and the water-isocyanate reaction is section in 2.1.1. For better control of the foaming process, distilled or deionized water is used as the blowing agent by most foam manufacturers.

The amount of water used in the foam formulation has a significant effect in determining the foam density. As the amount of water increases, the foam volume also increases and therefore the density decreases. Conversely, too little water will result in a higher density because low foam volume is obtained. If there is a high water content in foam formulation of flexible foams, coarse cells and harsh textures may be formed. If the water content is high in rigid foams, the percentage of open cells will increase, and the property of thermal conductivity will suffer (Youn et al 2007).

2.1.2.4 Catalysts

Virtually all commercial PU foams are produced with the aid of at least one catalyst. Generally, catalysts used for the gelling reaction of isocyanate with polyols are called “gelling catalysts”; while catalysts applied for the blowing reaction of isocyanate with water are named “blowing catalysts”. Organo-metallic catalysts, such as the tin catalyst, are gelling catalysts to accelerate the urethane reaction. Aliphatic and aromatic tertiary amines are blowing catalysts for the blowing reaction (Herrington and Hock 1997). In the foaming process, it is critical to obtain a proper balance of catalysts between the gelling reaction and the blowing reaction for successful PU foam production. In order to establish an optimum, various combinations of catalysts are used. If the amount of the amine catalyst or the blowing catalyst is too high, the foams collapse because of the stronger blowing reaction. If the tin catalyst or gelling catalyst is too high, the foams will most likely split because of the faster gelling reaction. This may also lead to foam shrinkage due to a high content of closed cells (Szycher 1999).

2.1.2.5 Surfactants

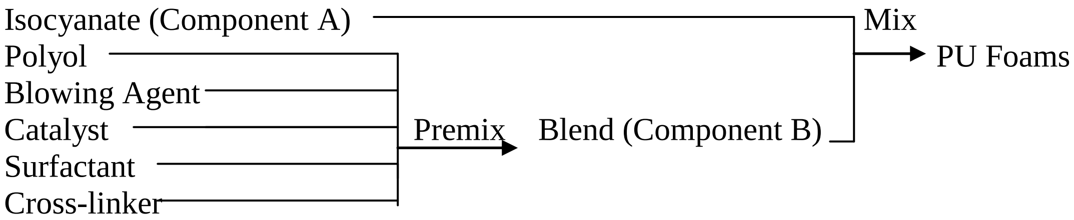
A surfactant is literally a combination of “surface active agents”. A surfactant plays an important role in mixing incompatible components of the polymerizing mixture. By stabilizing the gas bubbles formed during nucleation, surfactants help to control the foam cells. They prevent the coalescence of growing cells until those cells have attained sufficient strength to become self-supporting during polymerization. Without this effect of the surfactant, the rising foams probably have a risk of collapse (Ashida 2006).

2.1.2.6 Cross-linkers or Chain Extenders

Cross-linkers and chain extenders are usually compounds with active hydrogens and low molecular weight. Chain extenders are usually diols with a functionality of 2, such as ethylene glycol; while cross-linkers are usually compounds with the functionality of three or more, such as diamines and glycerol. These compounds react with isocyanate and generate hard segments (HS) of polyurea, which are believed to be the result of an increased intermolecular association or bonding, formed by covalent hydrogen bonds in the polymer. In the manufacture of PU, the selection of type and amount of crosslinker is based on the hardness and other specific properties of the desired foams (Ashida 2006).

2.1.3 Manufacture of PU Foams

There are three kinds of foaming systems for PU foam production. They are the one-shot one-step system, the quasi-prepolymer system, and the full-prepolymer system (Ashida 2006). Currently, the one-shot system is the major process for both flexible and rigid foam production in the foam industry. The schematic diagram of the one-shot system is shown below. In the one-shot process, polyol, water and other foam formulation ingredients are rapidly and intensively mixed and then added to the isocyanate for mixing and pouring for foaming.



2.1.4 Laboratory Production of PU Foams

In the laboratory scale, the key to making foams is to find a method for rapid intensive mixing of the ingredients and then pouring the rapidly reacting mixture into a box, usually a disposable papberboard container in which the expanding foam can rise. Usually, a standard laboratory mixing and pouring procedure includes the use of a commercial drill press fitted with a shaft. An impeller that can turn at 2,000 to 4,000 rpm is fixed at the end of shaft. The lower impeller speed is used to mix lower viscosity (lower molecular weight) polyols. In this procedure, polyol, catalyst, water, and surfactant are weighed and poured in the container and mixed for 10 to 30 s. Stirring is stopped for 15 seconds, allowing the mixture to de-gas. Then the isocyanate is rapidly added and stirring continues for another 15 seconds. Throughout this process an electric timer can be used to record the mixing times. When the mixing is finished, the mixture is rapidly poured into an open-top container to form foams to a desired shape (Klempner and Frisch 1991).

2.2 Properties and the Relationship to the Foam Structure of Flexible PU Foams

By knowing the chemistry of PU foams it can be concluded that the PU polymers are cross-linked, segmented block copolymers. Generally, relatively high equivalent weight active hydrogen compounds (usually long flexible chain polyether polyols) react with isocyanate to produce polyether segments (urethane linkage) of soft segments (SS). Relatively low equivalent weight active hydrogen compounds (such as water, crosslinkers) produce polyurea segments of hard segments (HS) (Ashida 2006). Therefore, the flexible foams can have a cross-linked polymer network consisting of elastomeric segments of polyether SS and glassy segments of polyurea HS. In the structure of flexible PU foams, SS contribute to the flexibility of the foams, while the HS contribute to the hardness. Therefore, an increase of HS in the polymer network can increase the stiffness of the final flexible foam (Sheth et al 2005; Chung et al 2009).

The polyol molecular weight has a strong relationship with the properties of the polymer. Usually, a higher polyol molecular weight or equivalent weight (EW) indicates a greater chain length between urethane linkages and between cross-links in the polymer network, and therefore makes more flexible foams. While polyols with lower EW tend to produce shorter chain length between cross-links and consequently decrease flexibility of the foam.

2.3 Properties of Rigid PU Foams

Rigid PU foams are not homogeneous solid but solid-gas composites. The solid parts provide the strength of the foam and guarantee the restriction of gas movement, thereby offering a good thermal insulation (Klempner and Frisch 1991). Other properties, such as thermal conductivity, depend on the combined effect of the solid phase and gas phase. However, the mechanical properties of rigid foams may widely differ from those of the corresponding solid (Jin et al 2005). It is necessary to develop sufficient strength to maintain their structure while cooling when preparing rigid foams. Otherwise a collapse or shrinkage will occur probably because of gas expansion or contraction. Therefore, a cross-linked structure is highly desirable to provide the necessary strength in the foam structure at an early stage of cure (Biedermann et al, 2001; Merline et al 2008).

2.4 Limitations of Existing Literature

The hydroxyl number and functionality were two critical characteristics of polyols and greatly influence the final properties of PU foams. However, a few papers intentionally investigated the properties of PU foams made of soybean oil-based polyols (SBOP) with a series of different hydroxyl numbers and functionalities, and there are usually no more than two types of commercial SBOP studied (Banik and Sain 2007). Although some SBOP were successfully synthesized in chemical companies and are already sold as a commodity, most SBOP that were reported to make PU foams are usually prepared in laboratories or research institutes by the authors and their groups. In addition, the replacements of those substituting commercial SBOP for petroleum based polyols are usually up to 30% (Das et al 2009). Due to their different original resources, SBOP and petroleum based polyols basically differ in chemical structures, and have distinct performances in the polymerization. Despite some papers studying the influence of various factors, such as catalyst, crosslinker and surfactant on the properties of soybean oil based PU foams, few papers attempted to improve the traditional foaming formulations used for petroleum based PU foams, and explore new formulations particularly for soybean oil based PU foams according to the distinctive characteristics of SBOP.

2.5 Commercialized Soy-Based Plastics in Market

With the increasing price of crude oil and strong public desire for environmentally -friendly products, companies are looking to get “greener” and use renewable materials to replace petrochemical products. In the United States, soy-based materials provide advanced, renewable and green technologies to industries. By offering environmental benefits and performing comparable and sometimes superior properties to the petrochemical products, soy-polyols are a popular ingredient in product formulations. Manufacturers mainly apply soy-polyols in diverse products, such as polyurethane foams, urethane coatings, elastomers, adhesives, thermosets, sealants and specialty products.

Ford Motor Company (Dearborn, MI) has collaborated with the United Soybean Board (USB) and pioneered the use of soy oil in foams for seat cushions, seatbacks, and vehicle headliners. In addition, Ford researchers can use soybean oil to replace 25% of the petrochemicals in automotive rubber applications, such as radiator deflector shields, air baffles, cup-holder inserts and floor mats.

Cargill (Chicago, IL) constructed a world-scale biobased polyol manufacturing facility in Chicago, IL. They were the first to launch biobased polyols, BiOH® polyols, into the flexible foam market in 2005. The products of BiOH® polyols are Polyol x-500 Family and Polyol x-0210 Family with hydroxyl number of 56 and 235, functionality of 2.0 and 4.4, respectively. They are made from soybean oil and can replace a portion of the petroleum-based polyols in flexible foam, such as upholstered furniture, mattresses, pillows, carpet cushion and automotive seats. Beyond flexible foam products, Cargill continues to explore their polyol products in a broader application including rigid foams such as insulation, coatings, adhesives and sealants (http://www.bioh.com/).

The DOW Chemical Company (Midland, MI) developed RENUVA™ Renewable Resource Technology to produce polyurethanes. In RENUVA technology, Dow utilizes a distinct, multi-step process to break down and functionalize the vegetable oil molecules, and then reconstructs them in combination with traditional polyurethane molecules to achieve quality and consistency. These polyurethanes have excellent performance in a wide breadth of applications. For example, coatings, adhesives, sealants, and elastomers made using RENUVA technology have improved chemical and water resistance. Memory foams made using RENUVA technology are viscoelastic over a wide temperature range. Generally, RENUVA soy-polyols can be used to manufacture furniture and bedding, carpets, footwear, coatings, adhesives, sealants, car seats and other everyday products (http://www.dow.com/renuva/).

Established in 2003, BioBased Technologies (Fayetteville, AR) have two product lines: Agrol® soy-based polyol and BioBased Insulation®. Agrol® is a family of soy-polyols that have a broad range of functionality from 2.0 to 7.0, and a hydroxyl number from 70 to 185. They are mainly used in flexible seat foam, carpet backing and carpet padding. BioBased Insulation® products, spray polyurethane foam insulation, are manufactured from renewable ingredients, such as Agrol polyols, as a portion of the petroleum (http://agrolinside.com/index.html).

Urethane Soy Systems (Volga, SD) produces soy based, high bio-content polyols under the trade name of Soyol® and rigid polyurethane insulation foam under the trade name of SoyTherm®. The Soyol® polyols usually have a hydroxyl number of 55-70 and 160-180, and can be used in the production of flexible and rigid foams. The SoyTherm® is spray insulation made from soy based polyols and is used in house construction (http://www.soyol.com/).

MCPU Polymer Engineering LLC (Corona, CA) developed novel soy polyols, Honey Bee™, which have 100% primary hydroxyl functionality, and consistent quality as well as low/no odor, low color. The products of Honey Bee™ are HB-150, HB-230, HB-230M, HB-530 with hydroxyl numbers of 150, 230, 238, 530, respectively. Due to their 100% primary hydroxyl functionality, Honey Bee™ can be used in high concentrations in rigid foams and elastomeric roof coatings (http://www.mcpurethanes.com/).

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CHAPTER 3

PHYSICAL PROPERTTIES OF SOY-POLYOL BASED FLEXIBLE POLYURETHANE FOAMS

3.1 Abstract

The effect of the cross-linker, tin catalyst and isocyanate index on the properties of water-blown flexible polyurethane foams made with a combination of soy-polyols (SP) and a petroleum based polyether polyol were investigated. Most PU foams containing SP had a lower density than control foams. Due to a higher cross-linking density, all PU foams containing SP had better compression force deflection (CFD) and tear resistance (TR) values than the control foams. In addition, most PU foams containing SP were less flexible than control foams, thereby resulting in a lower resilience and higher constant deflection compression (CDC). The glass transition temperature, T_g, of PU foams containing SP was constant at approximately -54^{o}C, independent of the foaming formulation, isocyanate index and SP percentages. The specific heat change, Δc_p, however, was influenced by the percentage of SP. The transmittance in Fourier transform infrared spectroscopy (FTIR) showed the increase of hard segments when increasing SP percentages in the foaming formulation. Both DSC and FTIR results confirmed that the foams made from SP were firmer than the control foams.

Key words: soy-polyol; polyurethane flexible foam; commercial soybean oil; DSC; glass transition; soft segments; FTIR

3.2 Introduction

Polyurethanes (PU) are versatile materials and have many applications in industry. Globally, over three quarters of the PU are consumed in the form of either flexible or rigid foams (Avar 2008). The two essential components of PU are isocyanate and polyols. Both isocyanate and polyols are usually made by feedstocks derived from petroleum. In recent decades, various factors spurred researchers to explore alternative resources as the feedstock of polyol (Niemeyer et al 2006). The United States is the world’s leading producer of soybeans and about 90 percent of the U.S. total oilseed production is soybean. In the past several years, the price of soybean varied from \$8.5to \$10 per bushel and its price is forecasted to be relatively stable, staying at \$9.20-\$9.25 per bushel in the next decade (Economic Research Service, USDA 2010a, 2010b). Refined soybean oils contain more than 99% triglycerides with active sites amenable to chemical reactions (Wool and Sun 2005). Therefore, researchers have been looking into the potential of synthesizing various soybean oil based polyols (SPs) for polyurethane foam applications (Lozada et al 2009; Lubguban et al 2009).

Zhang et al (2007) synthesized an SP by epoxidization followed by oxirane ring opening reactions, and studied the properties of a series of flexible foams prepared by replacing up to 30% of petroleum based polyol (PP) with this SP. Das et al (2009) studied the properties of flexible foams made with up to 30% replacement of PP with two commercial SPs from BioBased Technology (Rogers, AR). Campanella et al (2009) made PU foams with three different SPs prepared in the laboratory, and analyzed the effect of water content, catalyst, isocyanate, and surfactant on foam structure and properties. Banik and Sain (2008a) reported the influence of various factors like the catalyst, blowing agent, functionality and viscosity of polyols, on the structures of rigid PU foams made with two commercial SPs supplied by Urethane Soy Systems Inc. (Volga, SD). It is interesting to note that the percentage of PP replacement and the SP used in these studies were limited to 30% and two or three types, respectively.

In the manufacture of PU foams, the characteristics of polyol, such as the hydroxyl number and functionality as well as whether the hydroxyl group in the polyol is primary or secondary, play a significant role in the final properties of foams. When the hydroxyl group in the polyol is primary, it has been shown that polyols with a higher hydroxyl number or functionality would produce harder PU foams, whereas flexible foams are usually made from polyols with a lower hydroxyl number and functionality (Maslov et al 2006; Klempner and Senijarevic 2004). Because the hydroxyl group in SPs is usually secondary which has a lower reactivity toward isocyanates than the primary hydroxyl group in petroleum based polyols (PP), it would be interesting to investigate the effect of the hydroxyl number and functionality of SPs on the final properties of foams. In addition, literature is limited regarding the effect of tin catalyst and cross-linker in the foam formulation (Das et al 2009; Guo et al 2002; Narine et al 2007). The objective of this study was to investigate the effect of the hydroxyl number and functionality of soy-polyols (SPs) and the effect of tin catalyst and cross-linker levels on the properties of flexible PU foams.

3.3 Materials and methods

3.3.1 Materials

The petroleum-based polyether polyol and isocyanate used in this study were VORANOL® 4701 and PAPI® 27, respectively. They were obtained from Dow Chemical Co. (Midland, MI). Soy-polyols were made following the methods and chemical reaction schemes reported by Casper and Newbold (2006). Their specifications are shown in Tables 3.1-3.3. Dabco® 33-LV, Dabco® BL-17 and stannous octoate were used as catalysts. Stannous octoate (tin catalyst) and Dabco 33-LV® (organo catalyst) are catalysts for gelling reactions. Dabco® BL-17 is a delayed-action blowing catalyst. Dabco® DC 2585 is a silicone type non-ionic surfactant. Dabco® 33-LV, Dabco® BL-17, and Dabco® DC 2585 were from Air Products & Chemicals (Allentown, PA). Stannous octoate was obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). Diethanolamine is a cross-linker and was obtained from Fisher Scientific (Hanover Park, IL). Distilled water was used as a blowing agent.

3.3.2 Experimental Design and Formulations

A standard laboratory mixing and pouring method was applied to make PU foams. Polyol or polyol blend and other additives (B-side materials) including water, catalysts, cross-linker and surfactant were successively weighed and added into a disposable plastic cup. The mixture was mixed at 3450 rpm for 10-15 s with an impeller and was allowed to de-gas for 120 s. PAPI® 27 (A-side material) was then rapidly added into the cup and stirred at the same speed for another 10-15 s. The mixture was immediately poured into a wooden mold (11.4 × 11.4 × 21.6 cm) with an aluminum foil lining and was allowed to rise and set in the mold at ambient temperature. The experimental design and formulations are shown in Table 3.4.

3.3.3 Foam Property Measurements

All physical properties of flexible PU foams were measured according to the American Society of Testing Materials (ASTM) D 3574-08 (2008). The dimension of the foam samples was 5.08 × 5.08 × 2.54 cm. The apparent density was calculated by sample weight divided by its volume. Compression force deflection (CFD) is a measurement of load bearing properties and was determined by a TA.HDi Texture Analyzer (Texture Technologies, Scarsdale, NY). Constant deflection compression set (CDC) is a measurement of the deformation of the foam after it is compressed under controlled time and temperature conditions. It was calculated by Eq. (1). The equipment used for testing CDC was a Versa Tenn III Temperature-Humidity Chamber (Tenney Engineering, Williamsport, PA).

$$C_t = \left(\frac{t_o - t_f}{t_o} \right) \times 100\% \qquad \text{Eq. (1)}$$

where:

C_t = constant deflection compression set as a percentage of original thickness

t_o = thickness of the original, uncompressed sample

t_f = thickness of the test specimen after recovery

Resilience is a measurement of the elasticity of the flexible foams. A small steel ball was dropped from a set height onto the foam, and the rebound height was recorded. Tear resistance (TR) is a measurement of the force required to tear the foam after a split is cut at one end and was determined by a TA.HDi Texture Analyzer (Texture Technologies, Scarsdale, NY). A differential scanning calorimeter (DSC, Perkin-Elmer, Waltham, MA) was used to measure the glass transition temperature (T_g) and specific heat change (Δc_p). The sample was cooled to -140°C first and then heated to 160°C at 10°C/min. The functional groups of polyurethane foams were characterized by a Thermo Scientific Nicolet® 380 FTIR equipped with a smart orbit diamond ATR attachment (FTIR, Thermo Electron Corp., Madison, WI).

3.4 Results and Discussion

3.4.1 Density

Figure 3.1 shows the effect of the tin catalyst and cross-linker on the density of control (VORANOL® 4701 PU foam) and SP1 PU foams with different isocyanate indices. At the same catalyst and cross-linker levels, the density of control and SP1 PU foams decreased when the isocyanate index increased. The primary hydroxyl groups in water and petroleum polyol have the same reactivity to isocyanate (Herrington and Hock 1997). However, in the foaming formulation, Dabco® BL-17 was employed as a delayed blowing catalyst for isocyanate and water, which was chemically blocked to reduce its catalytic effect in the early stage of the polyurethane reaction (Air Products 2003). When the isocyanate index was less than 100, the amount of isocyanate needed to react with water and polyol was insufficient. The reaction of isocyanate with water produced carbon dioxide which acted as a blowing agent. As the isocyanate index increased, the actual amount of isocyanate reacting with water also increased, and therefore the foam volume increased. Although the weight of the polymer matrix also increased slightly at a higher isocyanate index, the weight increase was less than the volume increase. Therefore, the foam density decreased when the isocyanate index increased.

Figure 3.1 also shows that at the same isocyanate index, the density of foam without the cross-linker was the lowest, followed by foam without the tin catalyst and cross-linker and foam with both catalyst and cross-linker (control). The tin catalyst, stannous octoate, is known to accelerate the reaction between the isocyanate and polyol. In the presence of this catalyst, polyurethane network was generated faster capturing more carbon dioxide during the foaming process (Syzcher 1999). Thus, in the absence of a cross-linker, foams made with this catalyst would have a larger volume and lower density than foams made without it. The cross-linker, diethanolamine ($HOCH_2CH_2$-NH-CH_2CH_2OH), contains a highly reactive secondary aliphatic amine and two primary hydroxyl groups. Compared with water, its reaction rate with isocyanate is approximately 20,000-50,000 versus 100 (Herrington and Hock 1997). In the presence of this cross-linker during the foaming process, less isocyanate was available for reacting with water to produce carbon dioxide. Therefore, PU foams with the cross-linker had the lowest volume and the highest density.

SP1 foams showed a higher density than the control foams (Figure 3.1). This was caused by the differences in 1) the polyol functionality and 2) the nature of the polyol's hydroxyl groups. SP1 has a functionality of 2 while VORANOL® 4701 has a functionality of 2.6. In addition, the hydroxyl groups in SP1 are secondary while they are primary in VORANOL® 4701. Primary hydroxyl groups are approximately three times faster than secondary hydroxyl groups when they react with isocyanate (Campanella et al 2009; Banik and Sain 2008b; Narine et al 2007). Because of a lower reactivity resulting from the lower functionality and less hydroxyl groups, less polymer network was generated to capture carbon dioxide for SP1 foams leading to a lower volume and higher density.

Figure 3.2 displays the effect of the tin catalyst on density of SP PU foams (SP1, SP2, SP3 and SP4) with different isocyanate indices. Similar to the results shown in Figure 3.1, the density of SP PU foams decreased with the increase of the isocyanate index. In addition, foams with the tin catalyst also displayed a lower density than foams without it. Figure 3.2 also shows that PU foams made from soy-polyols with a higher functionality had a slightly lower density. Soy-polyols with a higher functionality had a higher hydroxyl number, indicating a greater demand for isocyanate and more PU polymer network was generated to capture carbon dioxide during the foaming process (Lim et al 2008). Therefore, foams with a higher functionality had larger volumes and lower densities. It is interesting to note most SP PU foams had a remarkably lower density than petroleum-based VORANOL® 4701 foams shown in Figure 3.1.

3.4.2 Compression Force Deflection (CFD)

Figure 3.3 shows the effect of the tin catalyst and cross-linker on compression force deflection (CFD) of control and SP PU foams with different isocyanate indices. Within PU foams, the CFD is mainly determined by two factors: the density and the number of cross-links produced by the reaction of isocyanate and polyol in the polymer network. Higher density and/or higher number of cross-links result in foams with a higher CFD (Cassel and Wadud 2005; Chung et al 2009; Merline et al 2008; Banik and Sain

2008b). Thus, Figure 3.3 shows the CFD of SP PU foams were higher than the control foams because SP PU foams had a higher density (Figure 3.2).

The CFD of foams slightly increased with the increasing isocyanate index (Figure 3.3). This was because increasing the isocyanate index raised the number of network cross-links due to more isocyanate present to react with polyol. Though the foam density decreased while the isocyanate index increased, the effect of increasing cross-links exceeded the effect of decreasing density leading to increased CFD. Figure 3.3 also shows foams with the tin catalyst had a higher CFD than foams without it. This was because the catalyst accelerated the isocyanate-polyol reaction and also generated more cross-links strengthening the foam cell wall structure. Also, when the cross-linker was employed in the foaming formulation, foams displayed a higher CFD (Figure 3.3). As discussed earlier, the cross-linker contained highly active hydrogens and produced hard segments of polyurea when reacted with isocyanate. This dispersion of hard segments of polyurea in the PU polymer increased the stiffness of the foam and consequently led to a higher CFD. Figure 3.4 presents the effect of the tin catalyst on CFD of SP PU foams (SP2, SP3, SP4 and SP5) with different isocyanate indices. As expected, at the same isocyanate index, the CFD of foams with the tin catalyst was slightly higher than foams without it. In addition, foams with a higher functionality and hydroxyl number showed a higher CFD because more cross-links were generated by the reaction of isocyanate and polyol. It was promising that all SP PU foams had comparable or superior CFD values than the control foams under the same foaming formulations.

3.4.3 Tear Resistance (TR)

Figure 3.5 shows the effect of the tin catalyst and cross-linker on tear resistance (TR) of control and SP 2.0 PU foams with different isocyanate indices. TR increased with the isocyanate index. In accordance with the standard test methods for flexible foams, TR is a measure of the force required to tear a foam in a constant rate after a split has been made at one end of the sample. As discussed previously, increasing the isocyanate index raised the number of cross-links of the polymer network and therefore a higher force was required to tear the foam. Also, at the same isocyanate index, TR decreased in the same order as CFD − foams with the tin catalyst and cross-linker (control), foams with a catalyst only (or without cross-linker), and foams without catalyst and cross-linker. These results were also due to the effects of the cross-linker and catalyst as discussed earlier.

Figure 3.6 displays the effect of the tin catalyst on TR of SP PU foams (SP2, SP3, SP4 and SP5) with different isocyanate indices. As expected, TR increased with the increasing isocyanate index as shown in Figure 3.5 for petroleum-based foams. Also, foams with a higher functionality/higher hydroxyl number had a higher TR, because soy-polyols with a higher functionality had more isocyanate to react with and produced more cross-links in the polymer network.

Also in Figure 3.6, when Soy-polyol percentage (SP2, SP3) was less than 50%, TR slightly increased with increasing Soy-Polyol replacements (from 20% to 40%). But when the replacement was over 50% (60% of SP2), the TR decreased slightly. In flexible PU foams, TR was influenced by many factors including cross-linking density, molecular weight of polyols, and the structure of polymer chains of polyols (Ashida 2006; Kabir et al 2006). Foams with a higher cross-linking density, or higher molecular weight, or more linear and longer polymer chains would have a higher TR. The petroleum-based polyol, VORANOL® 4701, had an average molecular weight of 4290, and was linear in chemical structure (Dow, 2001); while SP2 had a molecular weight of 1650 and was derived from soybean oil, which was a triglyceride in the chemical structure. SP2 had a lower molecular weight and much shorter polymer chains than VORANOL® 4701. The final TR of SP PU foams was the combination of properties of VORANOL® 4701 and SP2. When the percentage of SP2 reached 60%, the property of soybean-oil based polyol became dominant and the foams showed slightly lower TR than those in which SP2 replacements were 20% and 40%. Also, it is interesting to note that most SP PU foams shown in Figure 3.6 displayed superior TR than control foams shown in Figure 3.5.

3.4.4 Resilience

Figure 3.7 shows the effect of the tin catalyst and cross-linker on resilience of control and SP1 PU foams with different isocyanate indices. In flexible PU foams, resilience is correlated to overall cushion comfort, and foams with a higher resilience are softer and more flexible. As shown, resilience decreased when the isocyanate index increased. Increasing the isocyanate index raised the number of polymer network cross-links and therefore produced harder foams with a lower resilience. In addition, at the same isocyanate index, the resilience decreased in all circumstances tested. This was because the addition of the cross-linker and/or the tin catalyst increased the hardness of the foam and consequently sacrificed some resilience (Ashida 2006; Klempner and Senijarevic 2004).

SP1 PU foams had a lower resilience than the control foams at the same isocyanate index (Figure 3.7). This was because the foam resilience is largely affected by the properties of the polyols, such as equivalent weight (EW) and molecular structure. Foams made from polyols with a higher EW and linear chemical structure would show more flexibility and higher resilience (Ashida 2006; Molero et al 2008). The EW of SP1 was 825 while it was 1650 for VORANOL® 4701. Besides, VORANOL® 4701 was a petroleum-based polyether polyol with a linear chemical structure, while SP1 was a soybean oil-based polyol with a triglyceride structure (Tu et al 2008).

Figure 3.8 presents the effect of the tin catalyst on the resilience of SP PU foams (SP2, SP3, SP4 and SP5) with different isocyanate indices. The resilience decreased with increasing isocyanate index, similar to the control foams shown in Figure 3.7. Also, SP PU foams with the tin catalyst showed lower resilience than those without it. Additionally, SP PU foams with a higher functionality had a lower resilience. This was caused by the difference in EW of soy-polyols. Because of the differences in EW and chemical structure between soy-polyols and VORANOL® 4701, SP PU foams shown in Figure 3.8 had a lower resilience than the control foams (Figure 3.7). However, the resilience of the SP2 and SP3 foams in 20% and 40% replacements was close to those control foams at the isocyanate index 90 and 100.

3.4.5 Constant Deflection Compression (CDC)

Figure 3.9 shows the effect of the tin catalyst and cross-linker on a 50% constant deflection compression set (CDC) of control and SP1 PU foams with different isocyanate indices. A lower CDC value indicates that the foam is more flexible and recovers easily after compression. Conversely, harder foams usually have higher CDC and less flexibility. Figure 3.9 shows the CDC of SP1 PU foams is higher than the control foams. This was due to differences in their EW and chemical structure as discussed earlier. In addition the CDC increased slightly with the isocyanate index. This was because increasing the isocyanate index increased the hardness of the foams and meanwhile diminished the foam flexibility. Also, the CDC increased in the following order: foams without the tin catalyst and cross-linker, foams with the tin catalyst only, foams with a catalyst and cross-linker (control). This result was expected because the addition of a cross-linker and/or catalyst also increased the foam stiffness and diminished the foam flexibility. Figure 3.10 presents the effect of the tin catalyst on 50% CDC of SP PU foams (SP2, SP3, SP4 and SP5) with different isocyanate indices. As shown, the CDC increased when the isocyanate index increased similar to the control foams. Compared to the control foams, SP PU foams usually had higher CDC values under the same conditions. Again, this was caused by differences in EW and the molecular structure of VORANOL® 4701 and soy-polyols. VORANOL® 4701 had an EW of 1650 and was a linear polyether polyol while soy-polyols had lower EWs (Table 3.3) and were triglyceride in chemical structure. Therefore, the SP PU foams were more easily crushed and difficult to recover after compression leading to a higher CDC. Also, Figure 3.10 shows that SP PU foams with the tin catalyst had a higher CDC than foams without it. This was because addition of the catalyst increased the foam hardness as mentioned earlier. In addition, SP PU foams with a higher functionality had a higher CDC, because they produced harder foams. However, there were still some SP PU foams showing comparable CDC values to the control foams at the isocyanate index 100, such as SP2 foams and SP3 foams in 20% replacement; and SP2 foams and SP3 foams in 40% replacement at isocyanate index 80.

3.4.6 Differential Scanning Calorimetry (DSC)

The polymer chains in flexible PU foams consist of polyether soft segments (SS), produced from long-chain polyether polyol with isocyanate, and polyurea hard segments (HS), produced from water and a cross-linker with isocyanate. The polyurea HS are not inherently compatible with the polyether SS and tend to form a separate phase in the elastomer network (Kaushiva et al 2000; Klempner and Frisch 1991; Sheth et al 2005). Basically, both the SS and HS domains in polymers have distinct glass transition temperatures (T_g), which can be tested by the differential scanning calorimetry **(**DSC) instrumentation (Bershtein and Egorov 1994).

Tables 3.5 and 3.6 show the glass transition temperatures (T_g) and changes in specific heat (Δc_p) during the glass transition in control and SP PU foams. It was found that all foams, including control foams and SP foams, shared the same T_g of approximately -54ºC (the instrumentation error was within ±1ºC.), similar to that reported in the literature (Tu et al 2009). This was reasonable, because the soft phases in all flexible foams were long and linear polyether polyol-based SS with a T_g approximately -54ºC independent of the isocyanate index and foaming formulation (Zhang et al 2007; Tu et al 2009).

As shown in Table 3.5, the change in specific heat, Δc_p, of control foams decreased with the decreasing isocyanate index. And at the same isocyanate index, Δc_p decreased in the order as follows: foams with the tin cross-linker and catalyst, foams with the tin catalyst only, foams without the cross-linker and catalyst. Δc_p was an indication of the energy consumed for the phase change of the SS during thermal transition (Bukhina and Kurlyand 2007). As discussed previously, decreasing the isocyanate index, removing the cross-linker and/or catalyst diminished the amount of polyether polyol-based SS. Therefore, with decreasing mass fraction SS, Δc_p decreased.

Table 3.6 shows the effect of the isocyanate index and tin catalyst on Δc_p of the SP PU foams was similar to the control foams, i.e., decreasing the isocyanate index and/or removing the tin catalyst diminished Δc_p. Additionally, in SP2 and SP3 PU foams, Δc_p showed a decrease when increasing soy-polyol replacement level. This was because the soy-polyols had a lower EW and nonlinear triglyceride chemical structure; their reactions with isocyanate were expected to generate more HS. Therefore, as more and more VORANOL® 4701 was replaced by the soy-polyol, the number of SS diminished, resulting in a decrease in Δc_p. In addition, the EW and functionality of soy-polyols did not influence Δc_p of SP PU foams.

3.4.7 Fourier Transform Infrared Spectroscopy (FTIR Spectroscopy)

Because of the similar chemical structures of soy-polyols, SP2 PU foams containing 0 to 60% SP2 as representatives for Fourier transform infrared spectroscopy (FTIR) measurements and the results are shown in Figure 3.11. The details of spectra interpretation and band assignments are showed in Table 3.7 (Bion et al 2001; Dillon 1989; Kimura and Nagao, 2003; Wang et al 2008). The transmittance at wave number 1097 cm^{-1} represents aliphatic ether in VORANOL® 4701. Thus, the transmittance at this wave number gradually decreased when SP2 percentages increased in the SP2 PU foams.

Also, with increasing percentages of SP2, the transmittance at wave numbers 1508 cm^{-1} and 1592 cm^{-1} (resulting from presence of aromatic ring in isocyanate) and at wave number 2281 cm^{-1} (resulting from presence of cyanate group in isocyanate) became intensified. This was because SP2 had a higher hydroxyl number and required more isocyanate than VORANOL® 4701 in polymerization. Additionally, with increasing SP2 percentages, the transmittance at wave number 2923cm^{-1} (stretching mode (C-H) in CH_2) also became more pronounced because CH_2 was abundant in the chemical structure of SP2 but not in VORANOL® 4701. The transmittance at wave numbers 1716 cm^{-1} and 3351 cm^{-1} indicated the appearance of hydrogen-bonded urethane amide (C=O) and (N-H), which were parts of components of hard segments in PU foams. As SP2 percentages increased, the transmittance at these areas became slightly intensified, revealing an increase of hardness of flexible PU foams.

3.5 Summary and conclusion

In this study, water-blown flexible PU foams (SP PU foams) were successfully produced by combining petroleum polyol (VORANOL® 4701) and a series of soybean oil-based polyols (soy-polyols) with different functionalities. By changing foaming formulations, such as the catalyst, cross-linker, and isocyanate index in traditional petroleum polyol based PU foams, their effects on different foam properties were elucidated. The results from this study have useful and practical implications. For example, the cross-linker generates hard segments and increases the foam stiffness. So when the functionality of soy-polyols is higher than VORANOL® 4701, the cross-linker in the foaming formulation could be removed to increase SP PU foam flexibility.

It was interesting that some SP PU foams displayed better or comparable properties to control foams in certain areas. In density, because a larger volume was obtained, except SP1 PU foams, most SP PU foams had a lower density than control foams. In compression force deflection (CFD) and tear resistance (TR), due to a higher cross-linking density, all SP PU foams had better CFD and TR values than the control foams. In resilience and 50% constant deflection compression set (CDC), because soy-polyols had a lower equivalent weight and triglyceride chemical structure, SP PU foams were less flexible than control foams, thereby resulting in a lower resilience and higher CDC. However, some SP PU foams still displayed resilience and CDC values similar to the control foams in different isocyanate indices. In differential scanning calorimetry (DSC), the glass transition, $T_{g,}$ was constant at approximately -54°C, independent of foaming formulation, isocyanate index and soy-polyol percentages. This was because the soft phases in PU foams were polyether polyol-based soft segments, which were produced from VORANOL® 4701 with isocyanate. In addition, the change in specific heat, $\Delta c_{p,}$ was influenced by the soy-polyol percentage because the fraction of soft segments decreased when more VORANOL® 4701 was replaced by soy-polyols. In Fourier transform infrared spectroscopy (FTIR), the transmittance showed the increase of hard segments when increasing soy-polyol percentage in the foaming polymerization. Both the results of DSC and FTIR explained that the SP PU foams were firmer than the control foams.

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Table 3.1 Specifications of polymeric isocyanate PAPI® 27 (Dow 2001a).

Properties	Values
Density, g/ml @ 25°C	1.23
Average Molecular Weight	340
Functionality	2.7
NCO Content by Weight, %	31.4
Viscosity, cP@ 25°C	150-220
Acidity, %	0.017
Vapor Pressure, mm Hg@ 25°C	$<10^{-5}$
Decomposition Point °C	230

Table 3.2 Specifications of VORANOL® 4701 (Dow 2001b).

Properties	Values
Density, gm/cc @25°C	1.018
Average Molecular Weight	4290
Hydroxyl Number, mg KOH/g	34
Functionality	2.6
Equivalent Weight[a]	1650
Flash point, PMCC (°C)	185
Water, max. %	0.05
Viscosity, cst @ 25°C	860

[a] Equivalent Weight (E.W.) = Molecular Weight / Functionality = 56.1 × 1000 / OH Number

Table 3.3 Specifications of soy-Polyols.

Properties	SP1	SP2	SP3	SP4	SP5
Density (lbs/gal)	7.5	7.9	8.4	8.3	8
Average Molecular Weight	1650	1650	1800	1950	2100
Hydroxyl Number, mg KOH/g (AOCS)	70	112	128	164	185
Functionality	2.0	3.6	4.3	5.6	7.0
Equivalent Weight[a]	825	458.3	418.3	348.2	300
Water Content, %	0.01	0.02	0.02	0.02	0.06
Viscosity, cP@ 25°C	201	610	1150	4580	23,300
Acid Value (AOCS)	0.3	0.2	0.4	0.1	0.3

[a] Equivalent Weight (E.W.) = Molecular Weight / Functionality = 56.1 × 1000 / OH Number

Table 3.4 Formulations for water-blown flexible polyurethane foams with soy-polyols.

Ingredients	Parts by Weight[a]	
B-side Materials	**Control PU foams**	**SP PU foams**
VORANOL® 4701 (Petroleum-based Polyether Polyol)	100	80 (SP1, SP2,SP3, SP4, SP5), 60 (SP2, SP3), 40 (SP2)
Soy- Poyols (Commercial Soybean Oil-based Polyols)	0	20 (SP1, SP2,SP3, SP4, SP5), 40 (SP2, SP3), 60 (SP2)
Dabco 33-LV® (Gelling Catalyst)	0.6	0.6
Dabco® BL-17 (Delayed Blowing Catalyst)	0.2	0.2
Stannous Octoate (Tin Catalyst)	0.3	0.3/0
Diethanolamine (Cross-linker)	2.2	0
Dabco® DC 2585 (Surfactant)	1.0	1.0
Distilled Water (Blowing Agent)	3.0	3.0
A-side Material		
Isocyanate Index[b] of PAPI 27	80, 90, 100	80, 90, 100

[a] All recipes and calculations are based on 100 total parts by weight of polyol, which conventionally dictates that the sum of all polyols adds up to 100 parts.

[b] The amount of isocyanate is based on the isocyanate index. The isocyanate index is the ratio of the actual amount of isocyanate used relative to the theoretical amount times 100.

Table 3.5 T_g and Δc_p of the petroleum-based PU foams.

	Iso Index	**with cross-linker and tin catalyst**		**with tin catalyst only**		**without cross-linker and tin catalyst**	
		T_g (℃)	**Δc_p (J/g℃)**	**T_g (℃)**	**Δc_p (J/g°C)**	**T_g (℃)**	**Δc_p (J/g°C)**
100% VORANOL® 4701	100	-54.27^{a}	0.337^{a}	-54.00^{b}	0.305^{a}	-54.18^{a}	0.290^{a}
	90	-53.80^{b}	0.311^{b}	-53.97^{b}	0.294^{b}	-54.50^{a}	0.281^{b}
	80	-54.45^{a}	0.296^{c}	-54.50^{a}	0.287^{c}	-54.43^{a}	0.259^{c}

Table 3.6 T_g and Δc_p of SP PU foams

Soy-Polyols	**Soy-Polyol Percentage**	**Iso Index**	**with Cross-linker and Catalyst**	
			T_g (°C)	**Δc_p (J/g°C)**
SP1	20%	100	-54.87^{a}	0.251^{a}
		90	-54.78^{a}	0.233^{b}
		80	-55.06^{a}	0.202^{c}

Soy-Polyols	**Soy-Polyol Percentage**	**Iso Index**	**with Catalyst**		**without Catalyst**	
			T_g (°C)	**Δc_p (J/g°C)**	**T_g (°C)**	**Δc_p (J/g°C)**
SP2	20%	100	-55.20^{a}	0.205^{a}	-54.46^{d}	0.187^{a}
		90	-54.52^{c}	0.186^{b}	-53.64^{e}	0.175^{b}
		80	-54.89^{b}	0.170^{c}	-55.34^{a}	0.152^{c}
	40%	100	-55.25^{a}	0.086^{d}	-55.12^{b}	0.078^{d}
		90	-55.40^{a}	0.070^{e}	-54.78^{c}	0.062^{e}
		80	-54.62^{c}	0.055^{f}	-55.35^{a}	0.045^{f}
	60%	100	-54.14^{d}	0.031^{g}	-55.34^{a}	0.030^{g}
		90	-54.69^{bc}	0.027^{h}	-54.94^{bc}	0.022^{h}
		80	-55.34^{a}	0.021^{i}	-54.99^{bc}	0.019^{i}
SP3	20%	100	-53.62^{c}	0.203^{a}	-53.73^{b}	0.190^{a}
		90	-55.22^{a}	0.188^{b}	-55.28^{a}	0.172^{b}
		80	-55.11^{a}	0.174^{c}	-55.29^{a}	0.148^{c}
	40%	100	-53.79^{c}	0.090^{d}	-53.73^{b}	0.082^{d}
		90	-54.02^{b}	0.071^{e}	-55.25^{a}	0.062^{e}
		80	-55.19^{a}	0.060^{f}	-55.39^{a}	0.048^{f}
SP4	20%	100	-54.23^{b}	0.203^{a}	-53.81^{a}	0.188^{a}
		90	-54.83^{a}	0.189^{b}	-53.59^{a}	0.170^{b}
		80	-53.82^{c}	0.174^{c}	-53.62^{a}	0.150^{c}
SP5	20%	100	-54.03^{a}	0.204^{a}	-54.31^{a}	0.189^{a}
		90	-54.22^{a}	0.187^{b}	-53.83^{b}	0.170^{b}
		80	-53.87^{b}	0.171^{c}	-53.77^{b}	0.148^{c}

The statistical analysis in Tables 3.5 and 3.6 was based on the Fisher's least significant difference. Values with the same superscript were not significantly different at 0.05 level in each column in PU foams made from the same kind of polyol (Gonzalez 2009).

Table 3.7 Assignments of functional groups in FTIR spectra (Bion et al 2001; Dillon 1989; Kimura and Nagao 2003; Wang et al 2008).

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

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.

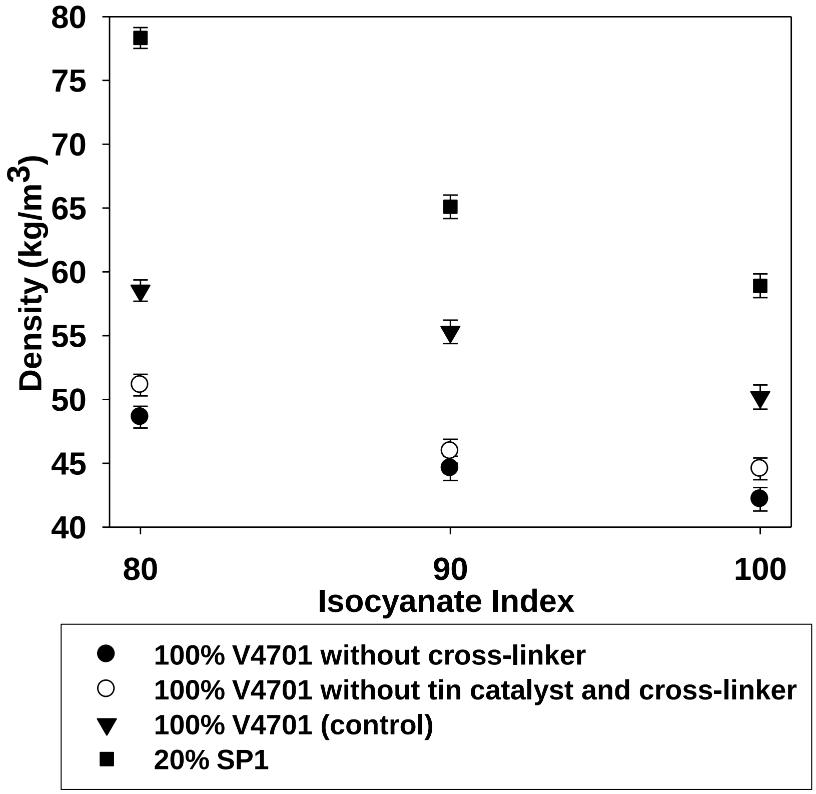

Figure 3.1 Effect of tin catalyst and cross-linker on density of control and SP1 PU foams with different indices.

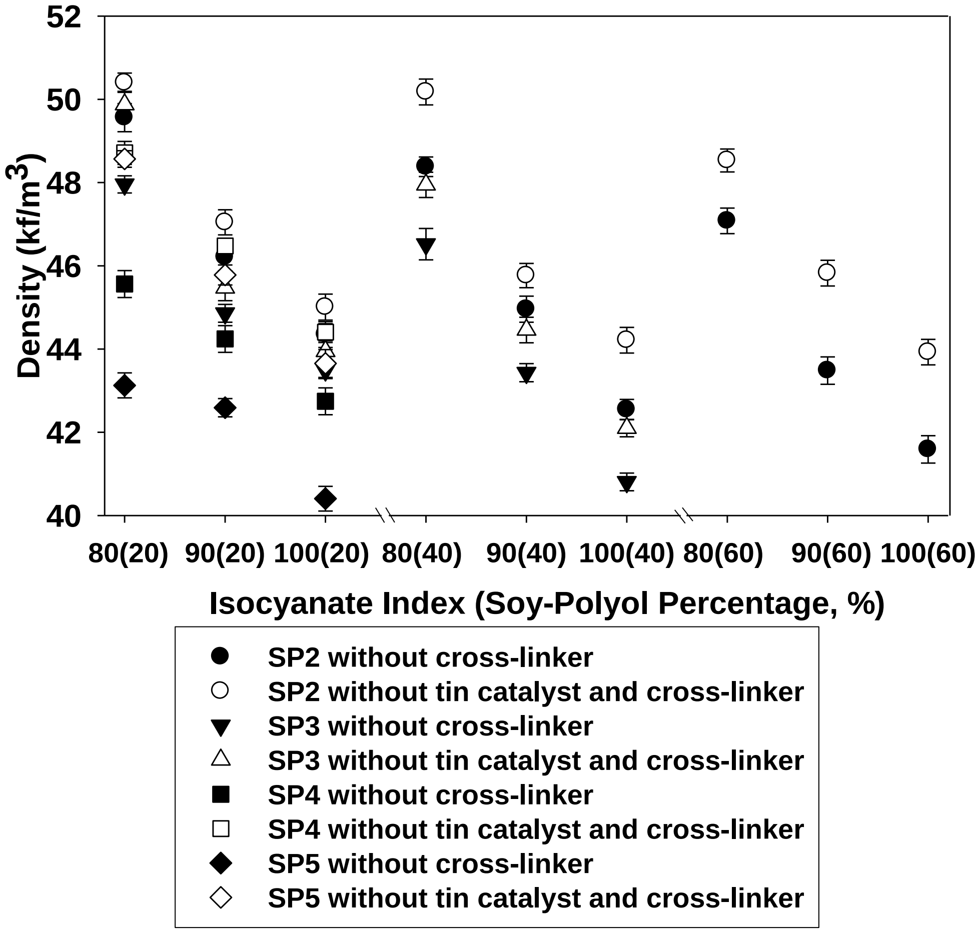

Figure 3.2 Effect of tin catalsyt on density of SP PU foams with different isocyanate indices.

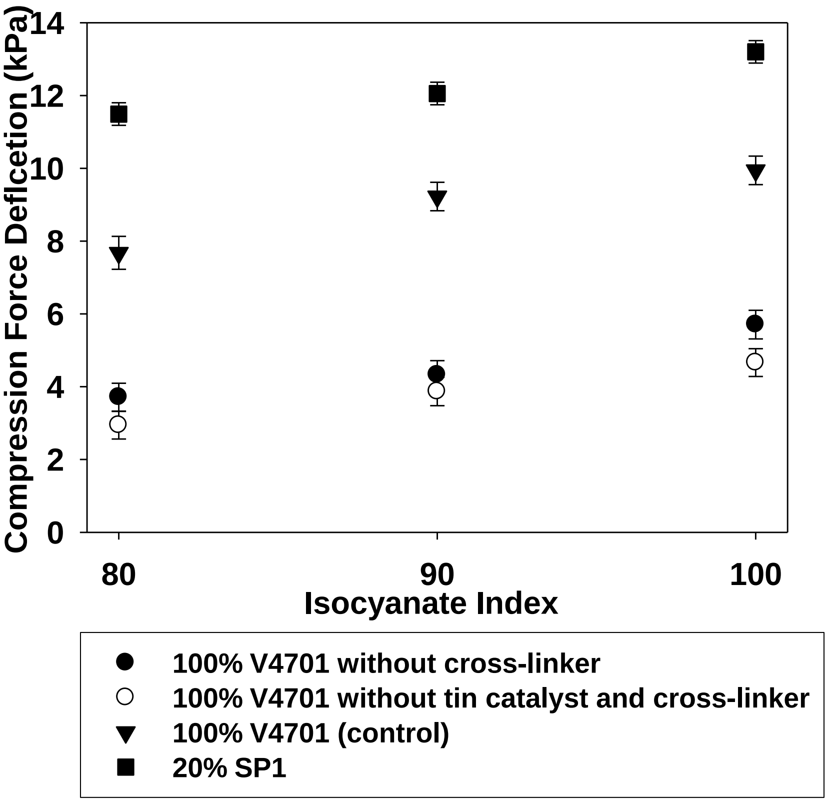

Figure 3.3 Effect of tin catalyst and cross-linker on compression force deflection of control and SP1 PU foams with different isocyanate indies.

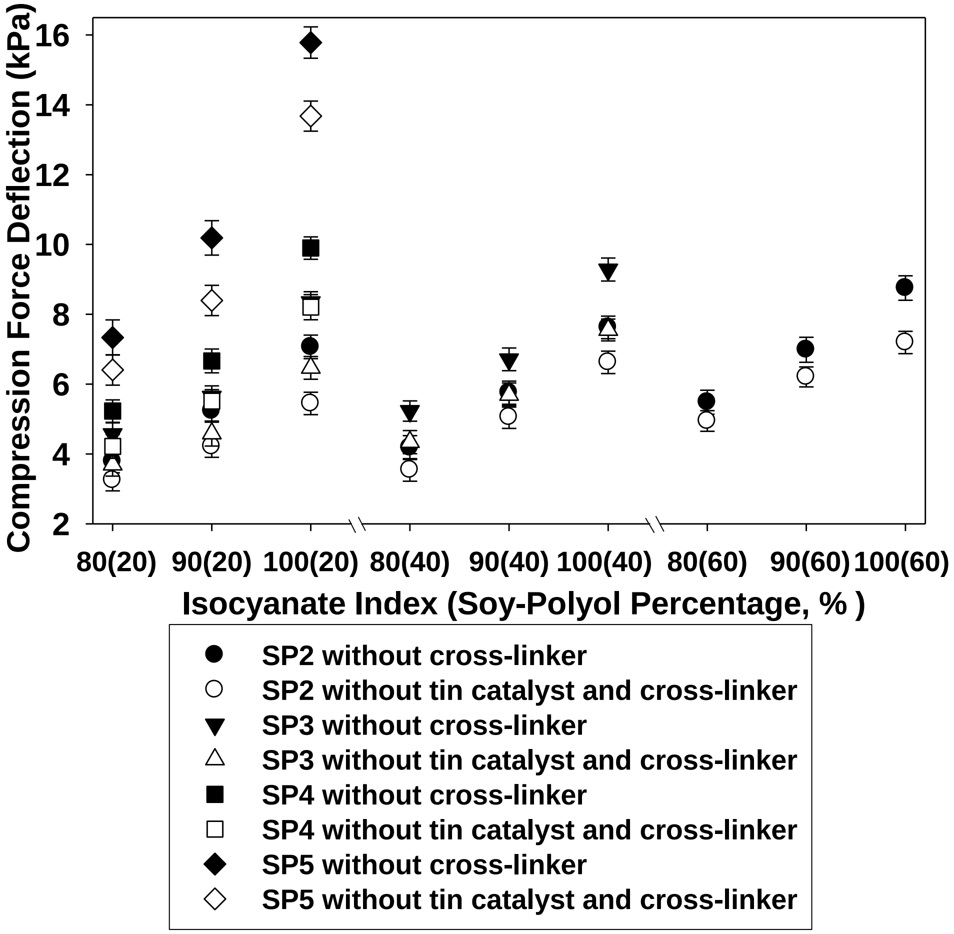

Figure 3.4 Effect of tin catalyst on compression force deflection of SP PU foams with different isocyanate indices.

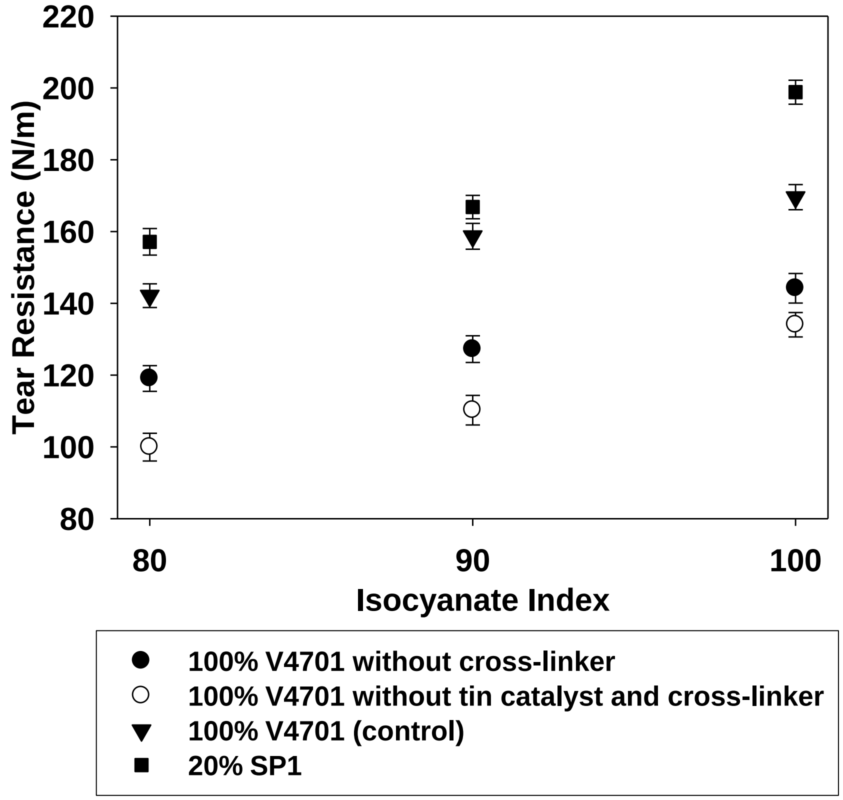

Figure 3.5 Effect of tin catalyst and cross-linker on tear resistance of control and SP1 PU foams with different isocyanate indices

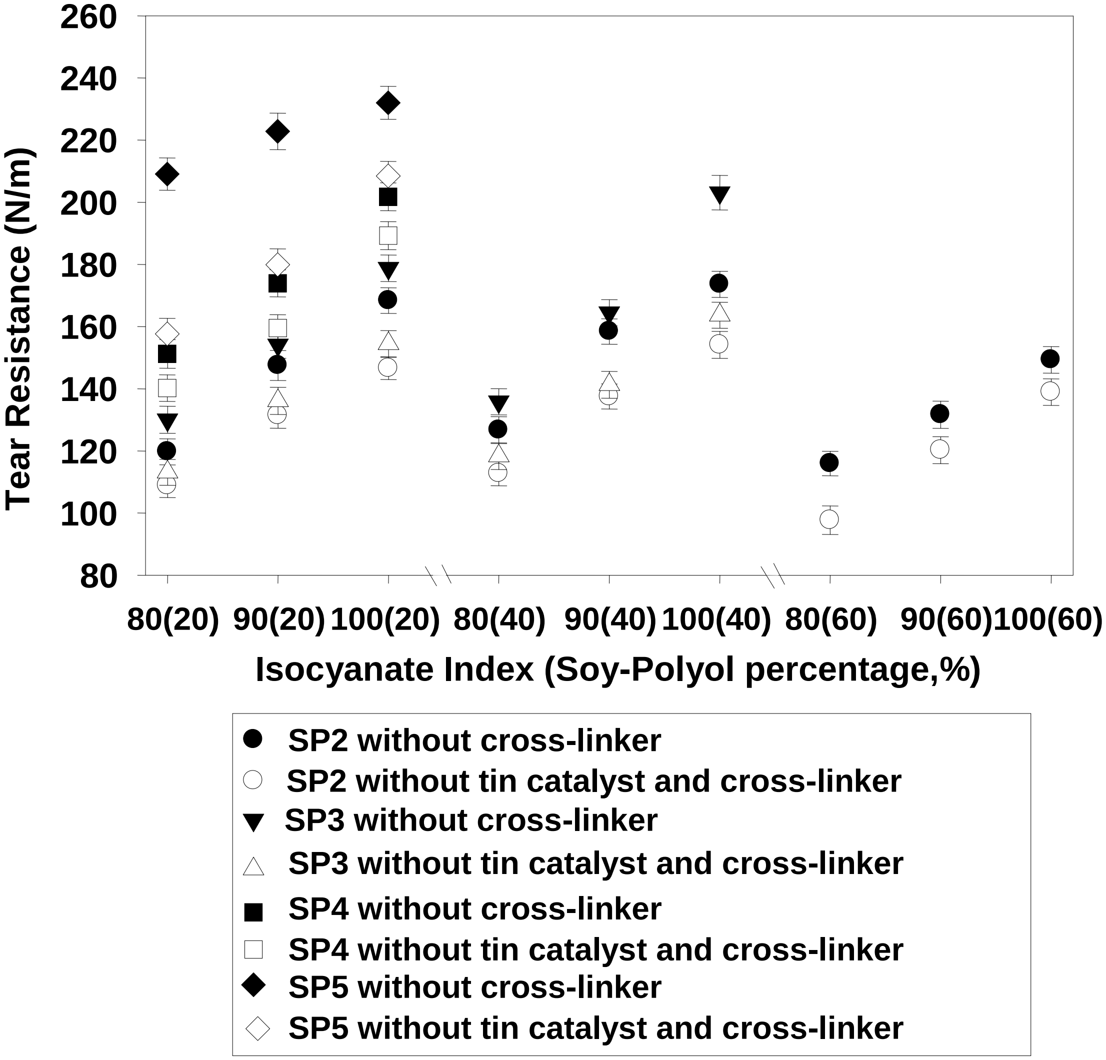

Figure 3.6 Effect of tin catalyst on tear resistance of SP PU foams with different isocyanate indices.

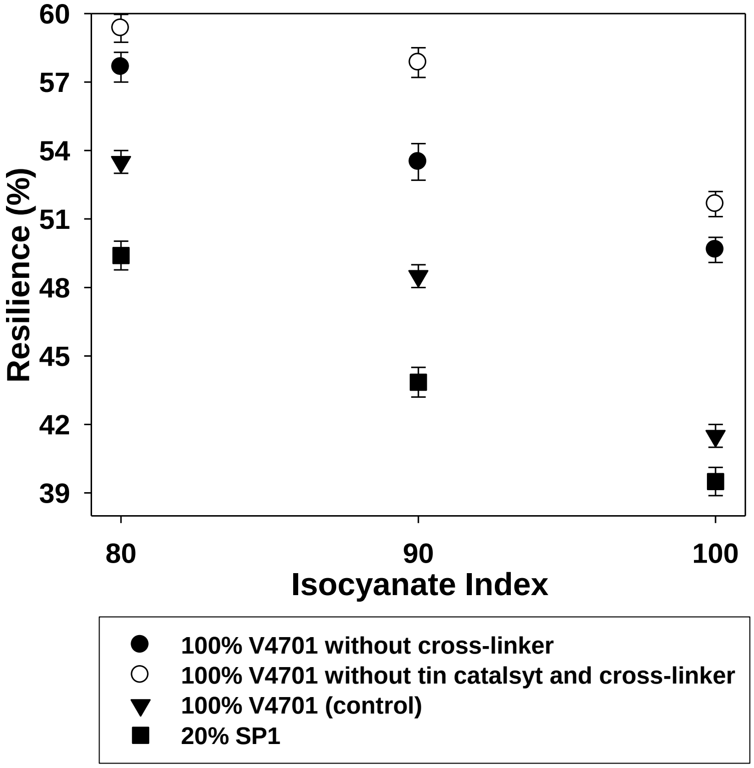

Figure 3.7 Effect of tin catalyst and cross-linker on resilience of control and SP1 PU foams with different isocyanate indices.

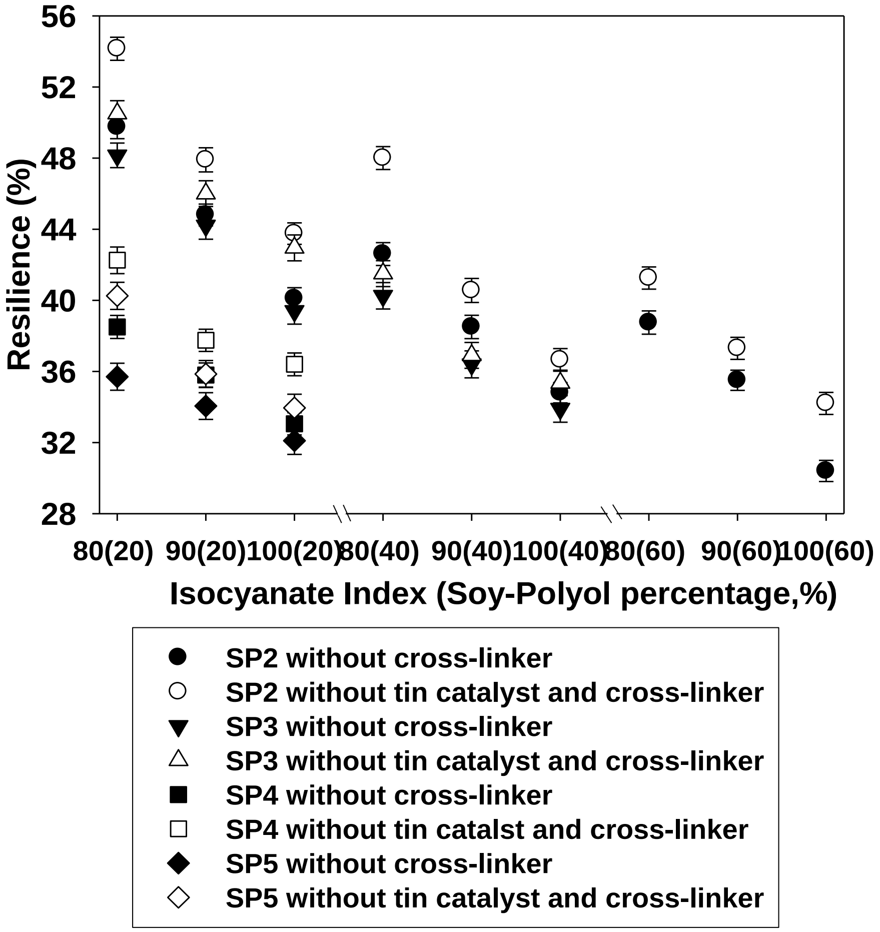

Figure 3.8 Effect of tin catalyst on resilience of SP PU foams with different isocyanate indices.

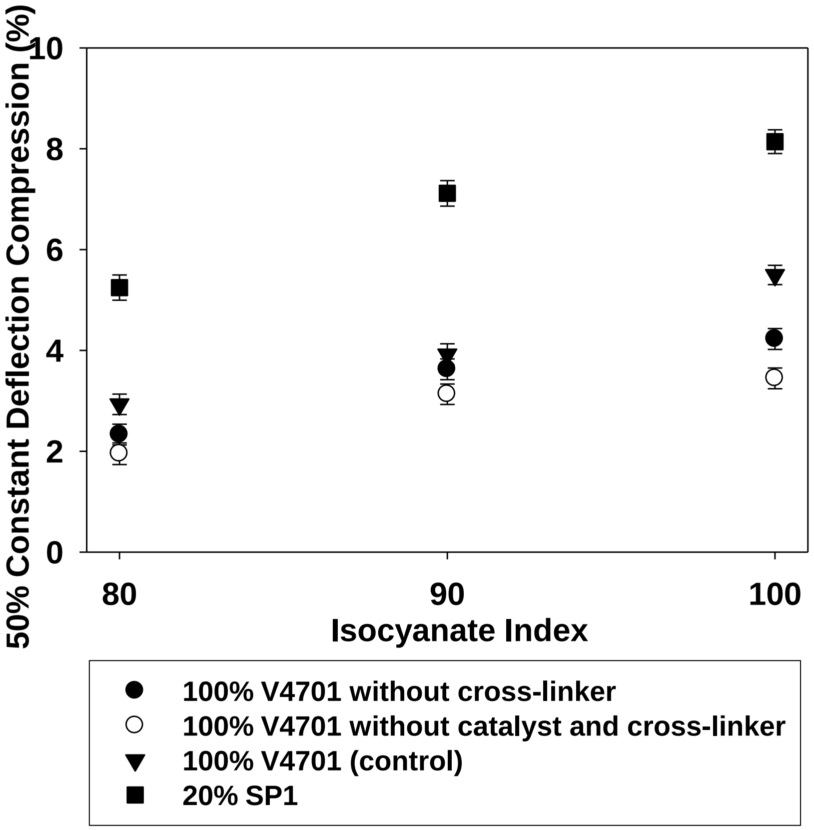

Figure 3.9 Effect of tin catalyst and cross-linker on 50% constant deflection compression of control and SP1 PU foams with different isocyanate indices.

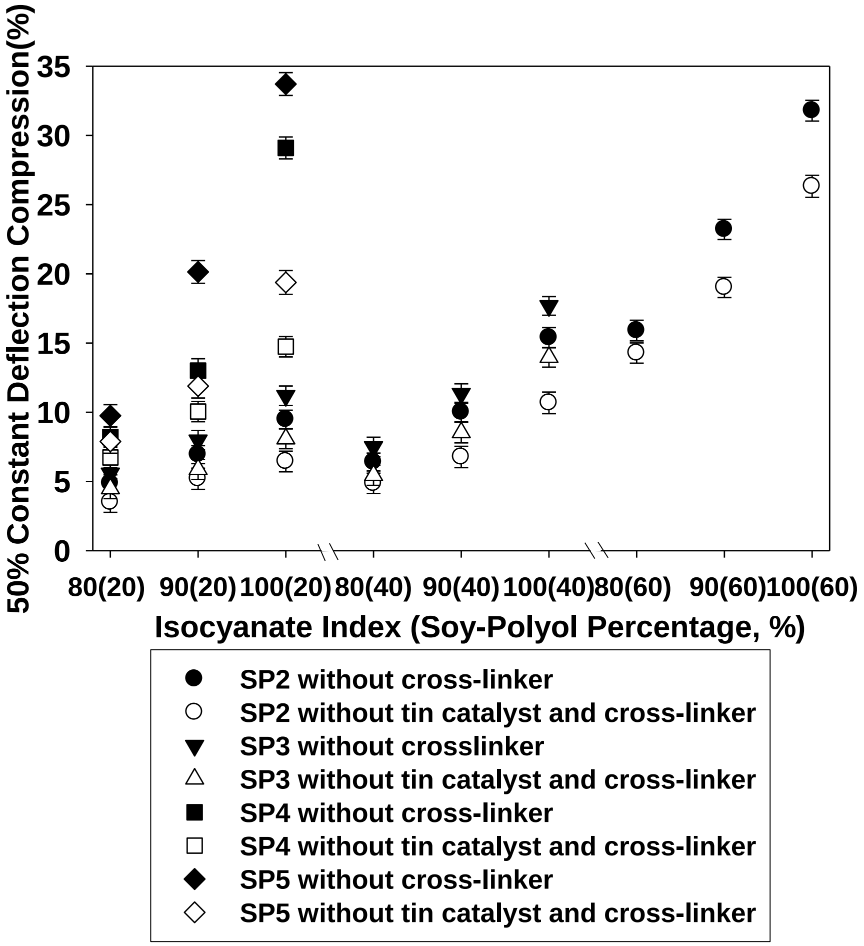

Figure 3.10 Effect of tin catalsyt on 50% constant deflection compression of SP PU foams with differen isocyanate indices.

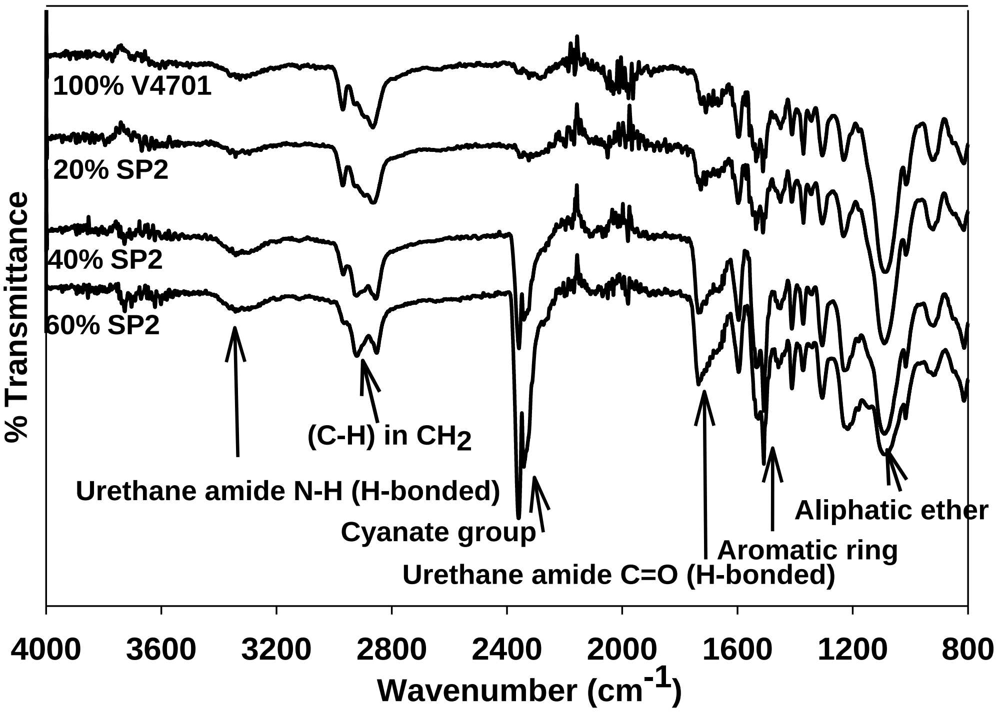

Figure 3.11 FTIR results of SP PU foams containing 0 to 60% SP2 (isocyanate index=80).

CHAPTER 4

PHYSICAL PROPERTIES OF SOY-PHOSPHATE POLYOL-BASED RIGID POLYURETHANE FOAMS

4.1 Abstract

Water-blown rigid polyurethane (PU) foams were made from 0-50% soy-phosphate polyol (SPP) and 2-4% water as the blowing agent. The mechanical and thermal properties of these SPP based PU foams (SPP PU foams) were investigated. SPP PU foams with a higher water content had greater volume, lower density and compressive strength. SPP PU foams with a 3% water content and 20% SPP had the lowest thermal conductivity. The thermal conductivity of SPP PU foams decreased and then increased with increasing SPP percentage, resulting from the combined effects of thermal properties of the gas and solid polymer phases. Higher isocyanate density led to higher compressive strength. At the same isocyanate density, the compressive strength of some 20% SPP foams were close or similar to the control foams made from VORANOL® 490.

Keywords: soy-phosphate polyol; rigid polyurethane foam; isocyanate index; thermal conductivity; compressive strength.

4.2 Introduction

Polyurethanes (PU) are important chemical products and over three quarters of the PU are consumed in the form of foams globally (Avar 2008). Isocyanates and polyols are two major components in polyurethane (PU) production, and they both rely on petroleum as feedstocks (Woods 1990; Szycher 1999; Ulrich 1982). In recent years, various factors motivate foam researchers to investigate potential and renewable resources as feedstocks of polyols. The United States is a major producer of soybean oils and the price of soybean oil is forecasted to be relatively stable, ranging near $9.20-9.25 per bushel in the next decade (Economic Research Service, USDA. 2010). Refined soybean oils contain more than 99% triglycerides with active sites amenable to chemical reactions (Wool and Sun 2005). Therefore, soybean oil (SBO) is one of the most promising bio-based resources as a feedstock of polyols for PU manufacture. Several synthetic approaches have been reported to introduce hydroxyl groups to the triglycerides: 1) hydroformylation followed by hydrogenation (Guo et al 2002; Lysenko et al 2004), 2) epoxidation followed by oxirane opening (Petrovic et al 2002; Lozada et al 2009; Lubguban et al 2009), 3) ozonolysis followed by hydrogenation (Petrovic et al 2005; Narine et al 2007a), and 4) microbial conversion (Hou 1995). It has been reported that flexible and rigid PU foams could be made with a mixture of petroleum polyol and soybean oil-based polyols (Petrovicet al 2007; Monteavaro et al 2005; John et al 2002).

Soy-phosphate polyol (SPP) is made from the SBO derived epoxides with the presence of phosphate acid as catalyst by acidolysis reaction. Normally, the acidolysis reaction is carried out by mixing SBO derived epoxides, o-phosphate acid (o-H_3PO_4), water and polar solvents, and the oligomerization occurs instantly to produce clear, viscous, homogeneous SPP with a low acid value and high average functionality. In this reaction, SBO derived epoxides is able to directly react with water to form diols because of their high reactivity through cleavage of the oxirane ring (Knothe and Derksen 1999). Phosphoric acid not only catalyzes ring-opening reaction but also is chemically involved to become part of the polyol (Lubguban 2009; Guo A et al 2006). Guo Y et al (2006;

2007) prepared SPP by using water and a significant amount of polar solvents to obtain high hydroxyl functionality while keeping the final acid value low.

The distilled water, acting as the blowing agent, reacts with isocyanate to generate carbon dioxide, which blows the reactant mixture to form a cellular structure. It is an important parameter that influences the properties and performance of rigid PU foams. By varying the amount of distilled water, Thirumal et al (2008) studied the effect of foam density on the properties of rigid PU foams made from a petroleum polyol. They found that the strength properties increase with the increase in density of the foams and their relationship can be roughly depicted by the Power law (Kurt and James 1973; Goods et al 1998). Campanella et al (2009) analyzed the effect of foaming variables, such as water content, polyol reactivity, catalyst, surfactant and isocyanate, on the structure and properties of soybean oil-based PU foams. Water was used as a reactive blowing agent to produce $CO_2$with isocyanate. They found that an increase in the water content produced more CO_2 and resulted in a larger foam volume as well as lower foam density. Also, the foam morphology was influenced by the water content. An increase in the water content produced rigid PU foams with thinner foam cell walls and larger foam cells, changing the density and morphology of the foams.

Isocyanate, which is derived from petroleum, is another critical component in PU production. Its amount (or the isocyanate index) and property greatly affected the performance of PU foams (Javni et al 2003; Pechar et al 2007). Guo et al (2000) investigated the effect of the isocyanate index (ranging from 110 to 130) on the compressive strength of rigid PU foams made from soybean oil-based polyol. They found that the compressive strength of soy-polyol based foams varied proportionally with the isocyanate index when the isocyanate index was over 100, indicating that the mechanical property of rigid foams could be modified by altering the amount of isocyanate used in the foaming formulation. They concluded that excess isocyanate used in the foam formulation gave rise to a more rigid structure in rigid PU foams because of the more complete conversion of OH groups in polyols and the reaction of isocyanate with moisture in the air. Tu et al (2009) studied the physical properties of water-blown rigid PU foams containing epoxidized soybean oil with an isocyanate index ranging from 50 to 110. They reported that the foam density decreased when the isocyanate index decreased to 60. But a sharp increase in density occurred at isocyanate index 50 due to foam shrinkage. Also, the compressive strength decreased with decreasing isocyanate index. Decreasing the isocyanate index would reduce isocyanate and meanwhile increase the bio-based content in PU formulations. In this study, the objective was to investigate the effect water (blowing agent) content and the isocyanate index on the physical properties of SPP PU foams.

4.3 Materials and methods

4.3.1 Materials

The petroleum-based polyol and isocyanate used in this study were VORANOL® 490 and PAPI® 27, respectively. Both were obtained from Dow Chemical Co. (Midland, MI). Their specifications are shown in Tables 4.1 and 4.2, respectively. Soy-phosphate polyol (SPP) was obtained from Dr. Galen Suppes’s lab in the Department of Chemical Engineering at the University of Missouri and its specification is shown in Table 4.3. It was made from the soybean oil derived epoxides with the presence of phosphate acid as a catalyst by acidolysis reaction as shown in Figure 4.1 (Lubguban 2009).

Dimethylcyclohexylamine and pentamethyldiethylentriamine were used as catalysts. They were from Sigma-Aldrich (St. Louis, MO). Dabco®DC 5357 (Air Products & Chemicals, Allentown, PA) was used as a surfactant.

4.3.2 Experimental Design and Foaming Formulations

This experiment consisted of two stages. In the first stage, the effect of water content (2, 3 and 4%) with different soy-phosphate polyol (SPP) percentages (0, 10, 20, 30, 40 and 50%) on the properties of rigid PU foams were studied. Table 4.4 shows the foaming formulations for rigid SPP based polyurethane foams (SPP PU foams). Based on the results obtained from the first stage, the water content was fixed at 3% at the second stage to study the effect of the isocyanate index and SPP percentage on the properties of SPP PU foams. The formulations are shown in Table 4.5.

4.3.3 Foam Preparation

The water-blown rigid polyurethane foams were made through one-shot and free-rising method. A total of 100g of VORANOL® 490 and soy-polyol mixture were weighed into a plastic container. Other B-side components such as water, catalysts and surfactant were added successively and all B-side materials were mixed with an electric mixer at 3450 rpm for 2 min. The mixture was allowed to degas for 2 min. Thereafter, pre-weighed isocyanate (A-side material) was added rapidly and mixed at the same speed for 10s. Then the reacting mixture was poured quickly into a wooden mold (11.4×11.4×21.6cm) with aluminum lining and the foam was allowed to free-rise and set at ambient conditions (23^{o}C) for 7 days before measurement except thermal conductivity which was conducted within 24-48 h.

4.3.4 Foam Property Measurements

The apparent density of foam samples were measured according to the American Society of Testing Materials (ASTM) Designation: D1622-08 (2008). The apparent thermal conductivity of rigid foams (20×20×2.5 cm) was determined according to ASTM Designation: C518-10 (2010a) and was tested by a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA), after foam curing at room temperature (25°C) for 24-48h. The compressive strength was determined according to ASTM Designation: D1621-10 (2010b) by a TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY). The compressive strength was also tested after foam is stored seven days at room temperature. The dimension of the specimen in both density and compressive strength was 6.35×6.35×3.81 cm. Five specimens per sample were measured and the average was reported.

4.4 Results and discussion

4.4.1 Effect of Water Content

4.4.1.1 Density

Figure 4.2 shows the effect of soy-phosphate polyol (SPP) percentage on the density of rigid PU foams with different water contents. With a 2% water content, the density of PU foams decreased slightly with increasing SPP percentage. Because SPP has a lower hydroxyl number (OH number of 240) than the petroleum based polyol, VORANOL® 490 (OH number of 490), a higher percentage of SPP would require less isocyanate in the foam formulation. Furthermore, when the water content was fixed at 2%, the same amount of carbon dioxide was generated in the PU foams. Thus, all foam volumes remained essentially the same and the density of foams decreased slightly with an increase in SPP percentage. However, at 3% water content, the density of foams did not change significantly with increasing SPP percentage. In principle, a higher water content in the foaming formulation process generated more volume or amount of carbon dioxide gas (Youn et al 2007). More carbon dioxide forced the cell walls of the foams to become thinner, causing a weaker three dimensional network, which led to a decreased closed cell percentage (Figure 4.3) (Narine et al 2007b; Thirumal et al 2009; Tu et al 2008). Even though less isocyanate was present to take part in foaming with an increasing SPP percentage, the foam volume still decreased due to an increase in the open cell percentage. The effects of both decreasing amounts of isocyanate and foam volume caused the density to remain more or less the same. At 4% water content, the density of foams did not change significantly except the foam with the 50% SPP replacement. This was caused by the same reason as the 3% water content, which was discussed above. When SPP replacement reached 50%, the closed cell content was only 60% (Figure 4.3) resulting in a much lower volume compared to other replacements. Therefore, the foam with 50% SPP replacement displayed a slightly higher density.

4.4.1.2 Closed Cell Percentage and Thermal Conductivity

The effect of SPP percentage on the closed cell percentage and thermal conductivity of rigid PU foams with different water contents is shown in Figures 4.3 and 4.4, respectively. In the foaming process, water reacted with isocyanate to produce carbon dioxide, which expanded the gelling polymer creating many small cells in the foam. At the same water content, the closed cell percentage of PU foams decreased with the increasing SPP percentage. The functional hydroxyl groups of SPP were secondary, while in VORANOL®490 they were primary (Tu et al 2007; Guo A et al 2006). It is known that the primary hydroxyl groups react three times faster than secondary groups with isocyanate (Herrington and Hock 1997; Tu et al 2008). The lower reactivity between the SPP and isocyanate might have diminished the foam cell strength and meanwhile given rise to a weaker three dimensional polymer network of cell walls to hold the pressure of carbon dioxide trapped in the cells. Therefore, with an increase of SPP percentage, the closed cell percentage in PU foams decreased.

The closed cell percentage decreased when the water content increased. This was because at a higher water content, more carbon dioxide was generated leading to a larger foam volume and thinner cell walls. Thinner cell walls and a higher gas volume might have weakened the foam cell walls resulting in a lower closed cell percentage.

In Figure 4.4, at 2 to 4% water content, the thermal conductivity decreased from 0 to 20 or 30% SPP percentage and then increased. The thermal conductivity was mainly affected by two factors: the conduction of the polymer phase and convection of the gas trapped in the cells (Biedermann et al 2001; Tu et al 2008). With an increasing SPP percentage in the foam formulation process, less isocyanate was present to participate in the polymerization leading to less polymer phase. Therefore, the thermal conductivity was reduced when increasing the SPP percentage from 0 to 20 or 30%. On the other hand, the amount of carbon dioxide trapped in the foams decreased with increasing SPP percentage due to lower closed cell percentage (Figure 4.3). Carbon dioxide has a lower thermal conductivity (~0.0146 W/mK) than air (~0.024 W/mK) at room temperature (En.wikipedica.org 2010). The thermal conductivity of SPP PU foams were contributed by both the polymer phase and gas phase. When the SPP was higher than 20 or 30%, the effect of decreasing closed cells (less carbon dioxide in the foam) might have exceeded the effect of decreasing the polymer phase. This led to a higher thermal conductivity.

It is interesting to note that the thermal conductivity of foams at 3% water content was lower than those at 2% and followed by those at 4% at the same SPP percentage. As mentioned above, thinner cell walls (also less polymer phase) or higher closed cell percentage contributes to a lower thermal conductivity. Higher water content produced more gas, larger foam volume and therefore thinner cell walls in the foam. At 4% water content, foams had the lowest closed cell percentage but more gas volume. At 2% water content, foams had the highest closed cell percentage but the lease amount of carbon dioxide trapped in the cells as well as the thickest cell wall. It appears foams at 3% water content had the lowest thermal conductivity. This was due to the balanced effects from the closed cell percentage and amount of gas trapped in the cells.

4.4.1.3 Compressive Strength

Figure 4.5 shows the effect of SPP percentage on the compressive strength of rigid PU foams with different water contents. At 2% water content, the compressive strength decreased when the SPP percentage increased. Density and the number of cross-links of the polymer network are two main factors that affect property of compressive strength of PU foams. Higher density and/or more cross-links give rise to a higher compressive strength (Hawkins and Jackovich 2005; Jin et al 2005). As the SPP percentage increased, less isocyanate was present in foaming. Therefore, fewer cross-links were generated by the reaction of the hydroxyl and isocyanate functional groups (Lim et al 2008; Monteavaro et al 2005). In addition, the foam density decreased slightly as the SPP percentage increased (Figure 4.2). Therefore, the SPP percentage increasing, the compressive strength increased, due to both cross-links and density in PU foams decreasing.

Increasing the water content from 2 to 4% reduced the compressive strength (Figure 4.5). This was mainly due to the effect of water content on the foam density − higher density would result in a higher compressive strength. As shown in Figure 4.2, the density of foams with a 2% water content was higher than with 3% and followed by 4%. Therefore, the compressive strength of foams followed the same order.

In summary, the water content had a significant effect on the physical properties of SPP PU foams. Higher water content generated more carbon dioxide. Therefore, foams had larger volume, lower density as well as lower compressive strength. Based on the previous results, SPP rigid PU foams with 3% water content had the best thermal conductivity, medium density and compressive strength. Therefore, the effect of the isocyanate index was investigated at 3% water content.

4.4.2 Effect of Isocyanate Index

4.4.2.1 Density

Figure 4.6 shows the effect of isocyanate index on the density of rigid PU foamsat20 and 50% SPP. As shown, with the exception of 50% SPPPU foam at index 70, foam density increased when the isocyanate index increased. Increasing the isocyanate index raised the actual amount of isocyanate in the polymerizing reaction, thereby increasing the total amount of the polymer network (Dounis and Wilkes 1997). On the other hand, the foam volume was dictated by the amount of carbon dioxide generated by the reaction of water and isocyanate. This reaction was independent of the isocyanate index since the isocyanate was not limited when reacting with water. Therefore, the foam volume did not change with the SPP percentage which was also observed in the experiment. With more isocyanate in the foam formulation (increasing isocyanate index), foam density increased.

4.4.2.2 Compressive Strength

Figure 4.7 shows the effect of different isocyanate indices on the compressive strength of rigid PU foams at 20 and 50% SPP. Raising the isocyanate index increased the compressive strength of foams. This was because the more the isocyanate used in the foam formulation, more cross-links were formed from the reaction of isocyanate and the hydroxyl groups in the polyols. In addition, foam density increased with the isocyanate index (Figure 4.6). Both increases in cross-links and density contributed to a higher compressive strength.

The compressive strength of 50% SPP foam was less than the 20% SPP foam and both SPP foams were less than the control (Figure 4.7). This might be due to the difference in the reactivity of isocyanate with the hydroxyl groups that were in the petroleum polyol in the control (primary) and those in the SPP (secondary). This might have resulted in less cross-links when increasing the SPP percentage from 0 to 50%. In addition, the density of the control foam was also greater than the SPP foam leading to a higher compressive strength.

4.4.2.3 Compressive Strength versus Isocyanate Density

Figure 4.8 displays the results of compressive strength versus isocyanate density of rigid PU foams. The isocyanate density was calculated by percent of isocyanate multiplying by the density of PU foams (Table 4.6). As shown, at the same SPP percentage, higher isocyanate density foams were harder or had a higher compressive strength. While the compressive strengths of 50% SPP PU foams were always inferior to those of 100% VORANOL® 490 PU foams, it is interesting to note that some 20% SPPPU foams were close or similar to control in compressive strength at the same isocyanate density.

4.5 Summary and conclusion

In summary, water-blown rigid polyurethane foams were produced by combining 0 to 50% soy-phosphate polyol (SPP) with petroleum based-polyol VORANOL® 490 using 2-4% water as the blowing agent. The results showed that the water content significantly affected the physical properties of the final SPP PU foams, such as density, compressive strength, and thermal conductivity−lowest water content produced foams with the least volume but highest density and compressive strength. The lowest thermal conductivity was observed in SPP foams with a 3% water content. Because the hydroxyl number of SPP was lower than VORANOL® 490, the compressive strength of SPP foams decreased when increasing the SPP percentage in the foaming formulation. Increasing the isocyanate index or isocyanate density raised the compressive strength of SPP foams. At the same isocyanate index, the compressive strength of some 20% SPP foams were close or similar to the control foams made from VORANOL® 490.

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Table 4.1 Specifications of polymeric isocyanate PAPI®27 (Dow, 2001a).

Properties	Values
Density, g/ml @ 25°C	1.23
Average Molecular Weight	340
Functionality	2.7
NCO Content by Weight, %	31.4
Viscosity, cps@ 25°C	150-220
Acidity, %	0.017
Vapor Pressure, mm Hg@ 25°C	$<10^{-5}$
Decomposition Point °C	230

Table 4.2 Specifications of VORANOL® 490 (Dow 2001b).

Properties	Values
Density, g/cm^3	1.11
Hydroxyl Number, mg KOH/g	484.8
Functionality	4.3
Average Molecular Weight, g	460
Flash point, 0°C	31.4
Water Content, %	0.007
Viscosity, mPa.s (at 25°C)	6180

Table 4.3 Specifications of soy-phosphate polyol (Lubguban2009).

Properties	Values
Hydroxyl Number, mg KOH/g	240
Viscosity, mPa.s (at 25°C)	3946.8
Acid No.	0.5

Table 4.4 Foaming formulation of rigid polyurethane foams with different soy-phosphate polyol percentages.

Ingredients	Parts by Weight[a]	
B-side Materials	Control PU foams	SPP PU foams
VORANOL 490 (Petroleum-based Polyol)	100	90, 80, 70, 60, 50
Soy-phosphate Poyol (Soybean Oil-based Polyol)	0	10, 20, 30, 40, 50
Dimethylcyclohexylamine (Gelling Catalyst)	0.84	0.84
Pentamethyldiethylentriamine (Blowing Catalyst)	1.26	1.26
Dabco® DC 5357 (Surfactant)	2.5	2.5
Distilled Water (Blowing Agent)	2.0, 3.0, 4.0	2.0, 3.0, 4.0
A-side Material		
IsocyanateIndex[b] of PAPI 27	110	110

Table 4.5 Foaming formulation of rigid polyurethane foams with different isocyanate indices.

Ingredients	Parts by Weight[a]	
B-side Materials	Control PU foams	SPP PU foams
VORANOL 490 (Petroleum-based Polyol)	100	80, 50
Soy-phosphate Poyol (Soybean Oil-based Polyol)	0	20, 50
Dimethylcyclohexylamine (Gelling Catalyst)	0.84	0.84
Pentamethyldiethylentriamin (Blowing Catalyst)	1.26	1.26
Dabco® DC 5357 (Surfactant)	2.5	2.5
Distilled Water (Blowing Agent)	3.0	3.0
A-side Material		
IsocyanateIndex[b] of PAPI 27	70, 80, 90, 100, 110	70, 80, 90, 100, 110

[a] All recipes and calculations are based on 100 total parts by weight of polyol, which conventionally dictates that the sum of all polyols adds up to 100 parts. [b] The amount of isocyanate is based on the isocyanate index. The isocyanate index is the ratio of the actual amount of isocyanate used relative to the theoretical amount times 100. The theoretical amount is an index of 100.

Table 4.6 Calculation of isocyanate density.

SPP Percen-tage	**Iso index**	**Foam density (kg/m^3)**	**Theoretical Iso amount (g)**	**Actual iso amount (g)**	**Iso mass fraction**	**Isocyanate density (kg/m^3) = Foam density × iso mass fraction**	**Compressive strength (kPa)**
0	110	48.29	176.62	176.62	1	48.29	461.99
	100	44.25	160.57	160.57	1	44.25	424.79
	90	41.97	144.50	144.50	1	41.97	376.59
	80	38.5	128.45	128.45	1	38.5	347.71
	70	35.77	112.40	112.40	1	35.77	324.48
20%	110	45.62	176.62	163.73	0.93	42.29	379.04
	100	43.40	160.57	148.85	0.93	40.23	346.97
	90	39.65	144.50	133.97	0.93	36.76	313.95
	80	36.88	128.45	119.08	0.93	34.19	253.47
	70	36.39	112.40	104.20	0.93	33.73	197.40
50%	110	45.40	176.62	144.40	0.82	37.12	264.28
	100	41.87	160.57	131.28	0.82	34.23	232.98
	90	39.36	144.50	118.15	0.82	32.18	167.07
	80	36.98	128.45	105.02	0.82	30.23	147.29
	70	47.18	112.40	91.88	0.82	38.56	84.15

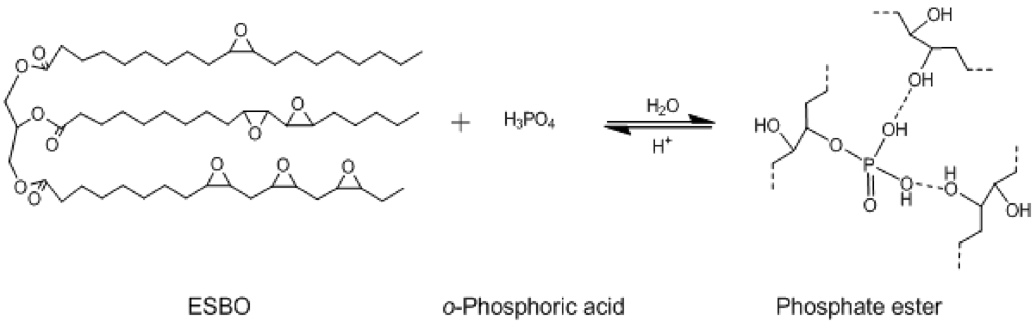

Figure 4.1 Schematic representation of soy-phosphate formation (Lubguban 2009; Lubguban et al 2009).

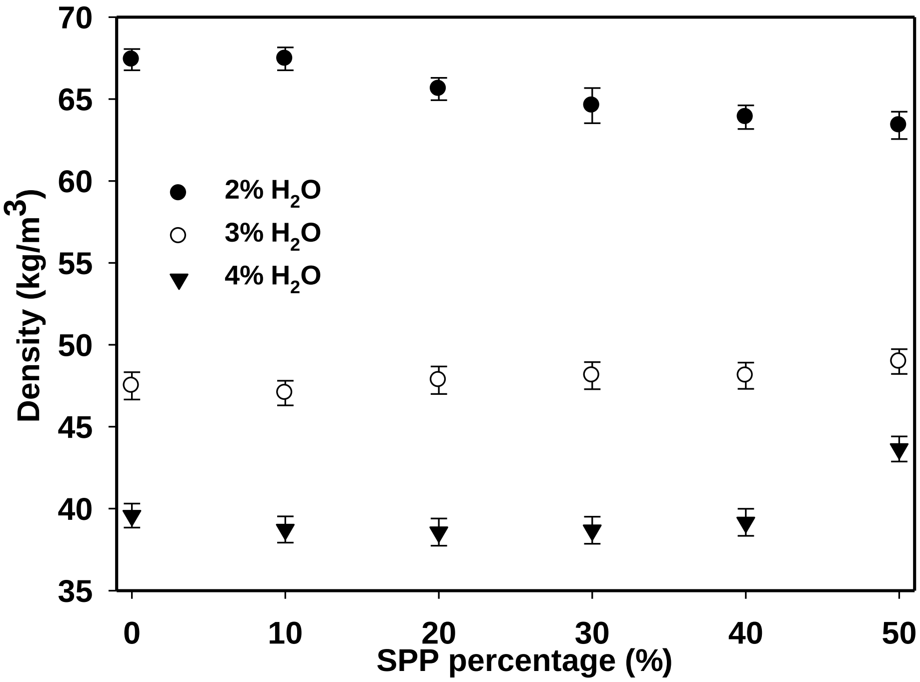

Figure 4.2 Effect of SPP percentage on density of rigid PU foams with different water contents.

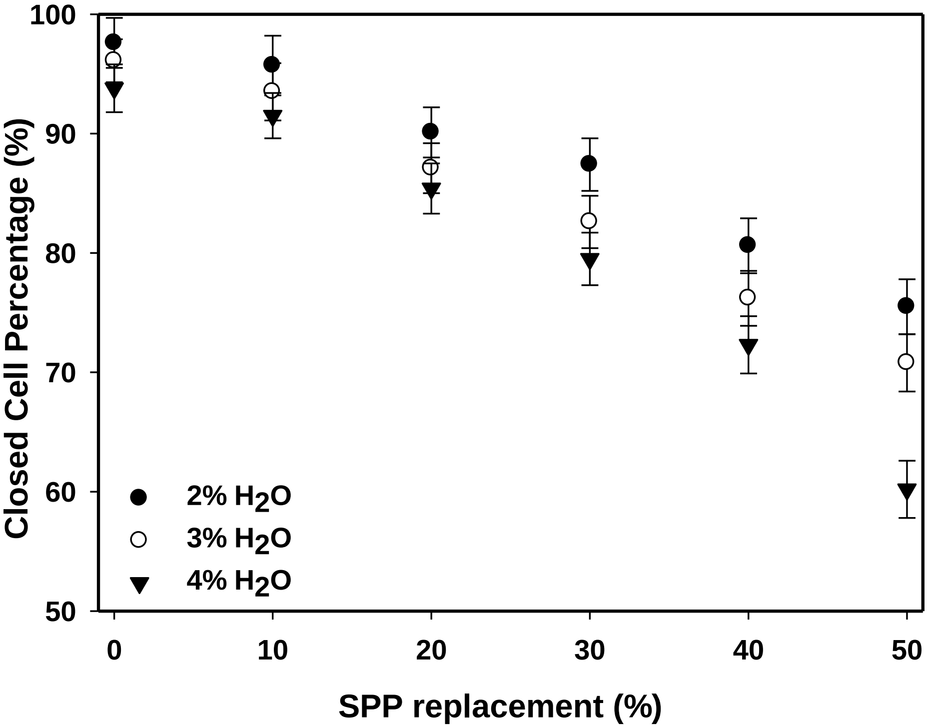

Figure 4.3 Effect of SPP percentage on closed cell percentage of rigid PU foams with different water contents.

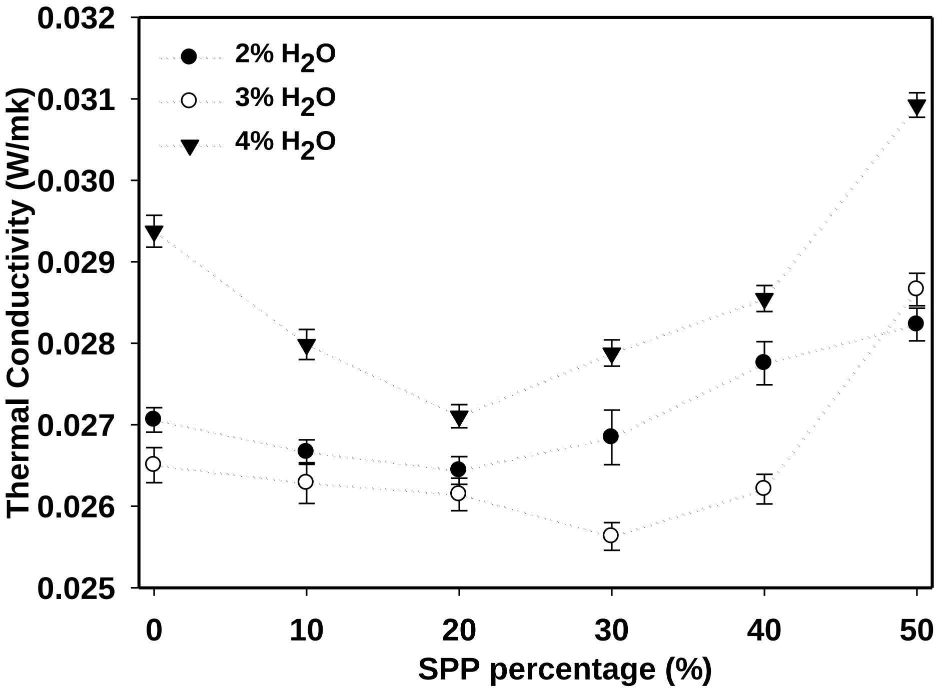

Figure 4.4 Effect of SPP percentage on thermal conductivity of rigid PU foams with different water contents.

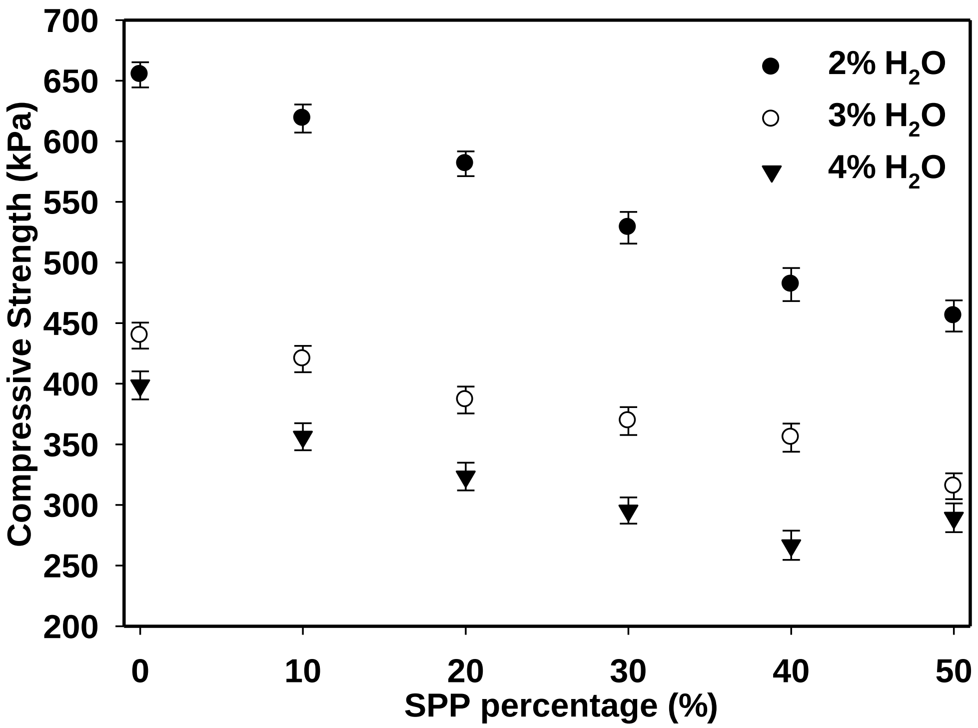

Figure 4.5 Effect of SPP percentage on compressive strength of rigid PU foams with different water contents.

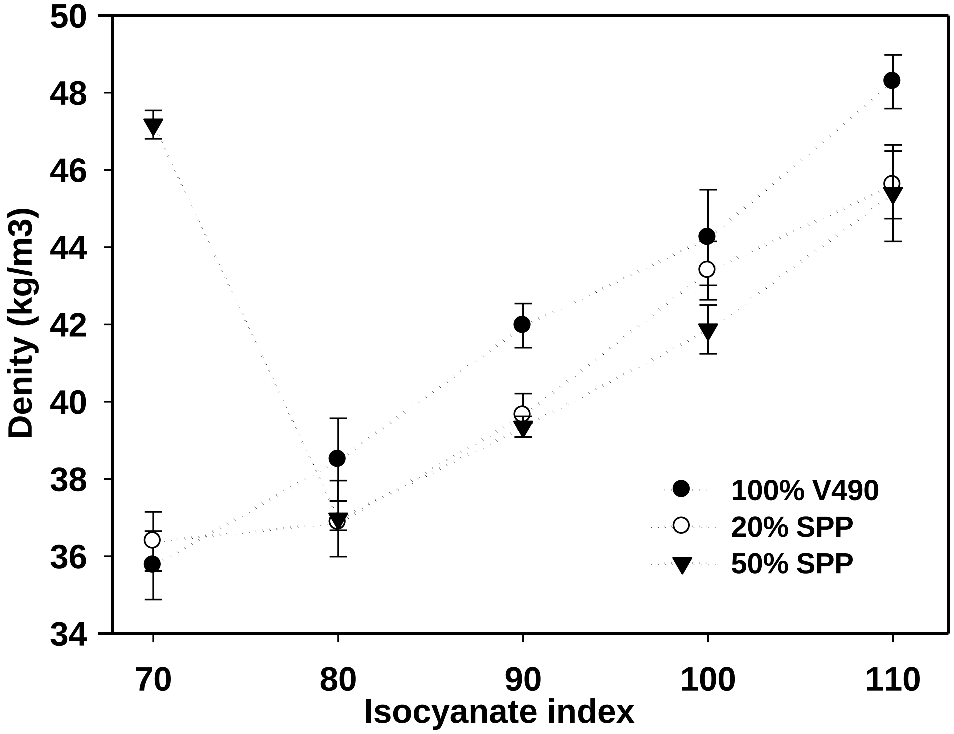

Figure 4.6 Effect of different isocyanate index on density of rigid PU foams with different SPP percentages.

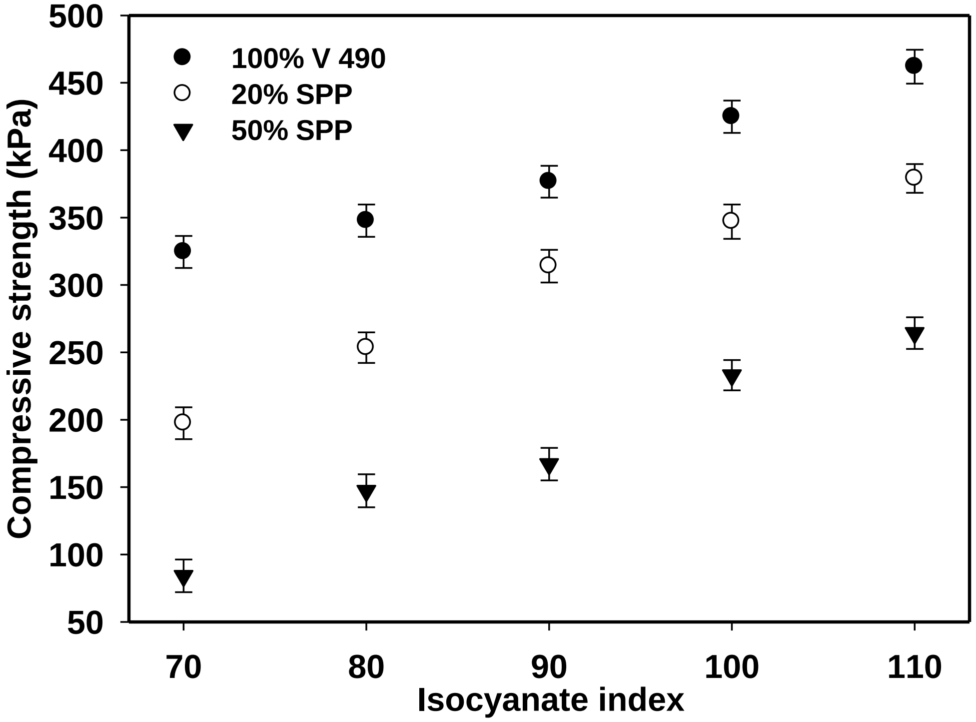

Figure 4.7 Effect of different isocyanate index on compressive strength of rigid PU foams with different SPP percentages.

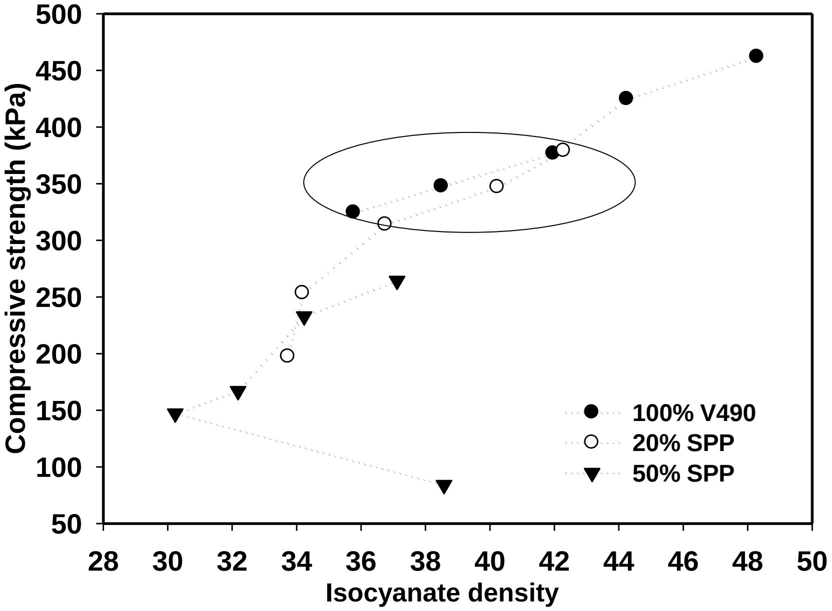

Figure 4.8 Results of compressive strength versus isocyanatye density.

CHAPTER 5

PROPERTIES OF BIO-BASED RIGID POLYURETHANE FOAMS REINFORCED WITH FILLERS: MICROSPHERES AND NANOCLAY

5.1 Abstract

This study investigated the effect of incorporating 1-7% microsphere and nanoclay fillers on the physical properties of polyurethane (PU) foams containing 15% soybean oil based polyol. With increasing filler percentage, the PU foam density was reduced because these fillers provided surfaces for nucleation and more gas bubbles were generated during the foaming process. The compressive strength of PU foams decreased slightly when increasing the microsphere content from 1 to 3% and then increased. At 7% microsphere content, the foams displayed the same compressive strength as the control foams made from 100% petroleum polyol. For PU foams reinforced with nanoclay, their compressive strength changed little from 1 to 5%, but decreased at 7% due to a lower density and weaker matrix structure. Foams containing 5 to 7% microspheres or 3 to 7% nanoclay had density-compressive strength comparable or superior to the control. SEM was used to observe the morphology of reinforced foams. Foams reinforced with fillers had more cells and smaller cell size than foams made from 15% soy-polyol but without fillers. During the foaming process, the maximal temperatures reached by PU foams were not affected by the presence of 1 to 7% of microspheres or nanoclay, but slightly lower than the control. In addition, foams with fillers displayed roughly the same thermal conductivity as soy-polyol based foams without fillers.

Keywords: soy-polyol; polyurethane foams; microsphere; nanoclay; physical properties; compressive strength; SEM; cell size; thermal conductivity

5.2 Introduction

Polyurethanes are very important polymers and have a surprising array of commercial applications. In recent years, polyurethane (PU) foams remain the largest demand sector, accounting for two-thirds of the total PU demand. In addition, this demand for PU foams, especially in construction and transportation, continues to strengthen across the globe. The main raw materials of PU foams are polyol and isocyanate and both are derived from petroleum (Ashida 2007). However, in recent years, high energy and feedstock costs have undercut margins, forcing producers to raise prices significantly for polyol and isocyanate. Also, the polyol supply is tight as demand increases greatly globally, especially in emerging regions such as China, the Middle East, and Africa (Hoffman 2004; Chemical Week 2006). Increasing costs of petrochemical feedstocks and public desire for environmentally friendly green products motivate many researchers to explore sustainable and renewable bio-based polyols to replace petrochemical polyols.

Soybeans are the dominant oilseed in the U.S. and account for about 90 percent of U.S. oilseed production. Soybeans were also the first bioengineered crops to achieve commercial success and the popularity of bioengineered soybeans among U.S. farmers improves the soybean production attributes, such as higher yields and lower price (Economic Research Service 2010a, b). Thus, soybean oil is promising and has great potential as the raw material of bio-based polyol to replace petrochemical polyol. In fact, rigid PU foams from a mixture of petrochemical polyol and soybean oil-based polyol have been reported in recent years (Guo et al 2002; Banik and Sain 2007).

Soybean oil-based polyols (SBOPs) used in making rigid PU foams in general have a hydroxyl number ranging from 150-250, lower than that of 400-500 in petrochemical polyols (Narine et al 2007). Derived from the triglycerides of soybean oil, SBOPs contain secondary hydroxyl groups, which are located in the middle of the triglyceride alkyl chains (Wool and Sun 2005). Upon cross-linking, a portion of these chains in the polyol is not included in the polymer network and is left dangling. These pendant chains can act as a plasticizer, and thereby reduce the polymer rigidity and meanwhile increase flexibility when the foam is under loading (Narine et al 2007). Also, when hydroxyl groups are located in the middle of the chains, steric hindrance to cross-linking would occur especially because of the bulky aromatic isocyanate (Javni et al 2003; Pechar et al 2007). Thus, rigid PU foams made from SBOPs tend to have inferior loading properties and lower compressive strength than petroleum based PU foams.

Chang et al (2001) studied the mechanical properties of water-blown rigid polyurethane foams with the addition of soy flour. In their results, both the density and compressive strength increased as the amount of soy flour increased. Lin and Hsieh (1998) incorporated soy protein isolate and soy fiber into water-blown flexible polyurethane foams. They found that the density of flexible foams also increased with the increasing amount of biomass materials. Banik and Sain (2009) enhanced the foam loading property by incorporation of cellulosic materials such as fibers, but the effect was limited due to the easy agglomeration of cellulosic materials. Nanotechnology is an advanced technology developed in recent years. Because of their extremely high surface area to volume ratio, nanoparticles can influence the physical properties of the material when they are brought into it (Wikipeida 2010). Widya and Macosko (2005) incorporated montmorillonite-based organoclay into rigid PU foams. They reported that the addition of 1 wt% clay reduced cell size and increased cell number density on 300-isocyanate index foams. Both smaller cell size and dispersed nanoclay decreased the permeability of the blowing agent. The compression strengths decreased with clay loading for the 250-isocyanate index foams, probably because the presence of clay interfered with the polymer formation. But there was no significant difference when compared with that of the 300-isocyanate index foams, because the reduction in compression strength caused by clay might have been offset by the decrease in cell size. Cao et al (2005) synthesized PU nanocomposite foams with modified layered silicates (organoclays). They found that the silicate layers of organoclay could be exfoliated in the PU matrix by adding hydroxyl and organotin functional groups on the clay surface. With addition of 5% organically treated clays, a significant increase in reduced compressive strength and modulus was observed. But opposite effects were observed in PU nanocomposite foams with a highly crosslinked structure probably due to the interference of the H-bond in the clay. They concluded that the overall mechanical property depended on the competition between the positive effects of clay on polymer reinforcement and foam morphology, and the negative effects on H-bond formation and network structure. Mondal and Khakhar (2007) studied the properties of high density (140-160 kg/m^3) rigid PU-clay nanocomposite foams made from polyether polyol. They found that the compressive modulus increased and the mean cell size decreased with the addition of clay. Liang and Shi (2011) researched the property of the compressive strength of high density (170-220 kg/m^3) soy-polyol based PU foams incorporated by modified nanoparticles, Cloisite 30B. They reported that the density increased as the nanoclay loading increased, due to a higher density of nanoclay than the

PU foam and a higher viscosity of the nanoclay polyol mixture than the polyol. The compressive strength and modulus increased first and then decreased as the nanoclay loading increased. The increase in the compressive strength and modulus of nanoclay soy-based PU foams resulted from the higher density and smaller cell size. But at high nanoclay loading, it was difficult to uniformly disperse the nanoparticles into the polyol mixture and this caused less uniform and some larger cell size, so the compressive strength and modulus decreased. The effect of microsphere and nanoclay on the properties of low density (45-50 kg/m^3) soybean oil-based rigid polyurethane foams has not been reported in the literature. The objective of this study was to investigate the properties of low density soybean oil based rigid polyurethane foams modified by different loadings of glass microspheres and nanoclay.

5.3 Materials and methods

5.3.1 Materials

The isocyanate, PAPI® 27, used in this study was a polymeric diphenylmethane diisocyanate (MDI), with functionality 2.7 and isocyanate equivalent weight 134. The petroleum-based polyol, VORANOL® 490, is a polyether polyol, with a hydroxyl number 490 and equivalent weight 114.5. Both PAPI® 27 and VORANOL® 490 were obtained from Dow Chemical Company (Midland, MI). Soybean oil-based polyol, with the hydroxyl number 250 and equivalent weight 224.4, was made from fully epoxidized soybean oil by alcoholysis reaction using p-toluenesulfonic acid as catalyst to promote the oxirane ring opening reaction (Lozada et al 2009). It was synthesized in Dr. Galen Suppes's lab in the Department of Chemical Engineering at the University of Missouri. Dimethylcyclohexylamine and pentamethyldiethylentriamine were used as catalysts. The fillers used in this study were glass microspheres and nanoclay. The glass spheres were hollow, spherical non-porous beads and the nanoclay was hydrophilic bentonite without surface modification. The dimethylcyclohexylamine, pentamethyldiethylentriamine, glass microspheres and nanoclay were bought from Sigma-Aldrich (St. Louis, MO). Dabco® DC 5357 from Air Products & Chemicals (Allentown, PA) was used as a surfactant. Distilled water was used as the blowing agent.

5.3.2 Foaming Formulation and Foam Preparation

Based on the results from a preliminary experiment, when reinforced with 1% glass microspheres, rigid PU foams made from 30% and 50% soybean oil-based polyol had a remarkably inferior density-compressive strength property compared to the control foams made from 100% VORANOL® 490. Therefore, a lower percentage (15%) of soybean oil-based polyol was used in the final foaming formulation. The PU foams modified with glass microspheres and nanoclay were prepared by one-shot and free-rising method, and the foaming formulation is shown in Table 5.1. Initially the glass microspheres (or nanoclay) were dispersed in the pre-weighed polyols in a plastic cup using an electric mixer operating at 3450 rpm for 15 s. Then the required amounts of water, catalysts, and surfactant were added and mixed for an additional 15 s. This polyol mixture (B-side materials) was then allowed to degas for 120 s. Thereafter, PAPI®27 (A-side material) was rapidly added to the cup and mixed at the same speed for another 10 s before dispensing into a wooden mold (11.4×11.4×21.6 cm) lined with aluminum foil to produce free-rise foams. All foams were cured at ambient temperature (23°C) for 24-48 h before thermal conductivity measurement and 7 days for other tests.

5.3.3 Foam Property Measurements

The optical density of B-side materials with varied filler percentages was tested by GENESYS^{TM} 20 Spectrophotometer (Thermo spectronic, Rochester, NY) at a wavelength of 600 nm. The apparent density of the foam samples was measured according to the American Society of Testing Materials (ASTM 2008). The compressive strength was measured according to ASTM C1621-10 by a TA.HDi Texture Analyzer with XTRA Dimension software (Texture Technologies Corp., Scarsdale NY). In both the density and the compressive strength, the size of the specimen was 6.35×6.35×3.81 cm. Five specimens were measured for each treatment and the average was reported. The apparent thermal conductivity was measured according to ASTM C518-10 using a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA). Two specimen were used for each treatment and the size of the specimen was 20×20×2.5 cm. The surface foaming temperature was monitored and recorded by an Omega Engineering OS 552A-MA-4 infrared thermometer equipped with a wireless transmitter and receiver (Omega Engineering Inc., Stamford, CT). The infrared thermometer was fixed at 40.64 cm above the wooden mold and focused on the center of the mold, an area of 2.54 cm in diameter. The response time of the temperature recording was 1 s (Tu et al 2009). The morphology of the foams was observed by a Hitachi S-4700 field emission scanning electron microscope (FESEM, Tokyo, Japan). The sample was cut into 3 mm cubes and attached to the substrate with silver glue. After being coated with gold by a plasma sputter, the sample was moved into the chamber and micrographs were taken at an accelerating voltage of 5000 V and emission current of 9700 nA (Tu et al 2008).

5.4 Results and discussion

5.4.1 Density

The effect of glass microspheres and nanoclay on the density of soybean oil based polyurethane foams (SBO PUF) is shown in Figure 5.1. SBO PUF without fillers showed a slightly lower density than the control foam. This was because while their volumes were similar due to using the same amount of blowing agent, SBO PUF had less weight than the control foam due to soybean oil-based polyols having a lower hydroxyl number than VORANOL® 490, thereby using less isocyanate in the formulation. Some researchers reported that the foam density increased after the filler addition (Chang et al 2001; Lin and Hsieh 1998; Liang and Shi 2011). However, in this study, when increasing the filler concentration from 1 to 7%, the density of SBO PUF with microspheres decreased from 47 to 43 kg/m^3; while the density of SBO PUF with nanoclay decreased from 46.5 to 35.5 kg/m^3. Both the polyol-isocyanate and water-isocyanate reactions were exothermic. During the foaming process, carbon dioxide was generated from the reaction of water and isocyanate. Due to the release of heat from the exothermic reactions, the carbon dioxide bubbles grew and expanded the polymerizing polymer to form a foam volume (Woods 1990). In control foams, rapid mixing of the polyol mixture and isocyanate brought many micro-bubbles of air into the liquid system, which served as sites for bubble growth. When microspheres or nanoclay was dispersed into the liquid mixture, their presence offered more nucleation sites for gas bubble formation. The increase of foam volume with an increase of filler concentration was also visually observed in the experiments. On the other hand, the dispersibility of glass microspheres and nanoclay in the polyol mixture is different. Table 5.2 shows, at the same filler percentage, the optical density (OD_{600}) of polyol with nanoclay, which is more hydrophilic, was always higher than that of polyol with glass microspheres. These results revealed that nanoclay had better dispersibility and was more easily dispersed in the polyol mixture than the glass microspheres. It appears nanoclay might have provided more nucleation sites than glass microspheres for bubble formation leading to a larger foam volume. Therefore, the foam with nanoclay had a lower density that with glass microspheres.

5.4.2 Compressive Strength

Figure 5.2 displays the effect of microspheres and nanoclay on compressive strength (CS) of SBO PUF. The mechanical properties of PUF are influenced by several parameters such as density, cross-linking density, and cell geometry (Thirumal et al 2008; Lim et al 2008; Smits 1994; Klempner and Sendijarevic 2004; Szycher 1999). In general, foams with higher density and/or cross-linking density are expected to be more rigid as well as higher in CS. The CS of SBO PUF without fillers was lower than that of the control. This was because soybean oil-based polyol had a lower hydroxyl number to react with isocyanate and thus, SBO PUF had a lower cross-linking density than control made from VORANOL® 490 (Lim et al 2008; Tu et al 2009). In SBO PUF with microspheres, the CS slightly decreased when increasing this filler concentration from 0 to 3% and then gradually increased. At 7% microsphere concentration, it was encouraging that CS of SBO PUF was similar to the control. In SBO PUF with nanoclay, CS remained at the same level around 380 kPa when increasing the filler concentration from 1 to 5%, but then decreased to 310 kPa at 7%.

SEM microphotographs show that introduction of fillers changed the morphology of rigid SBO PUF (Figures 5.3 and 5.4). As the filler concentration increased in SBO PUF, the foam cell size decreased and while the foam cell number increased. Both the cell size decrease and the cell number increase contributed to a higher CS because more cell walls and struts per unit area of PU foams were present to support the foam structure under loading. Furthermore, incorporation of fillers in the cell walls and struts strengthened the hardness of the foams. On the other hand, the density of SBO PUF in Figure 5.1 decreased with an increasing microsphere concentration, thereby decreasing CS in some degree. The overall CS of SBO PUF was dictated by the positive effects of fillers on polymer reinforcement and foam morphology and the negative effects from decreasing foam density (Cao et al 2005; Liang and Shi 2011). Consequently, CS in SBO PUF with microsphere decreased slightly at first (when the effect of foam density was more prominent) and then increased (when the effect of filler was more prominent). In SBO PUF with nanoclay, the CS remained at the same level from the nanoclay concentration of 1% to 5% (when the effects of foam density and filler were similar), but significantly decreased at the 7%. This was because the foam volume was large at 7% nanoclay concentration resulting in a sharp decrease in foam density and cross-linking density, which in turn diminished the CS.

5.4.3 Density-Compressive Strength

The density-compressive strength property of SBO PUF reinforced with fillers using 3% water content as the blowing agent is shown in Figure 5.5. The circle symbols represent the PUF made from 100% VORANOL$^{®}$490 with water content ranging from 2% to 4%. For rigid polyurethane foams with various levels of a blowing agent, there is a linear relationship between density and compressive strength (Oertel and Abele 1994; Tu et al 2007). In Figure 5.5, foams located on the left side of the regression line have inferior density-compressive strength property to the control (higher density foams at the same compressive strength or lower compressive strength foams at the same density), while foams on the right side of the regression line have superior density-compressive strength property. SBO PUF without fillers (the solid square symbol) was on the left side of the regression line, showing an inferior density-compressive strength property to the control foam. With the addition of fillers, it was interesting to note that some SBO PUF (those containing 5-7% glass microsphere or 3-7% nanoclay) displayed comparable or superior density-compressive strength property to the control foam.

5.4.4 Surface Temperature History during Foaming

The surface temperature history of SBO PUF modified with microspheres and nanoclay during foaming is shown in Figures 5.6 and 5.7, respectively. In general, the surface temperature rose sharply initially, reached its maximum, and then gradually dropped. This is expected because both polyol-isocyanate and water-isocyanate reactions are exothermic. The maximal foam surface temperature of the control was slightly higher and remained higher afterward than that of SBO PUF. This was caused by the lower reactivity of SBOP with isocyanate than petroleum polyol. Derived from vegetable oils, SBOP had a branched triglyceride structure, and contained secondary hydroxyl groups, which were located in the middle of the triglyceride alkyl chains (Lozada et al 2009; Lozada 2009). During the polymerizing process, steric hindrance to cross-linking would occur because of the bulky aromatic isocyanate in SBO PUF, while VORANOL® 490 was linear in the chemical structure and had primary hydroxyl groups (Herrington and

Hock 1997). The filler concentration did not seem to influence the surface temperature history of SBO PUF during foaming. This was because the fillers were not involved in the exothermic reactions.

5.4.5 Morphology

Figures 5.3 and 5.4 show the scanning electron micrographs (SEM) of SBO PUF modified with glass microspheres and nanoclay, respectively. As shown, SBO PUF without fillers had a large number of cells in the shape of irregular polyhedra. When fillers were introduced and with increasing filler concentration, it could be visually observed that the foam cell number increased and the foam cell size decreased. During the foaming process, the surface of the fillers provided many nucleation sites for bubble formation. Also, the addition of fillers increased the viscosity of the liquid system thus reducing coalescence among the bubbles (Mondal and Khakhar 2007). Both effects were enhanced with an increasing filler concentration leading to foams with more cells as well as smaller cell size.

5.4.6 Thermal Conductivity

The effect of fillers on thermal conductivity and closed cell percentage of SBO PUF is shown in Figure 5.8. The thermal conductivity of plastic foams is the sum of thermal conductivities of the solid phase and the gas phase. Derived from vegetable oils, the hydroxyl groups in SBOP are secondary, while they are primary in VORANOL® 490. Under the same conditions, the secondary hydroxyl groups are three times slower than the primary hydroxyl groups when they react with isocyanate functional groups (Herrington and Hock 1997; Tu et al 2007, 2008). The lower reactivity of SBOP with isocyanate might have decreased the strength of the cell walls and therefore the cells had a lower capacity to entrap the carbon dioxide. Also, from Figure 5.1, it was known that the volume of SBO PUF increased with an increasing filler concentration due to the formation of more nucleated bubbles. In foams with a larger volume, their cell walls became thinner and weaker, and these cells burst more easily in the foam rising phase. Thus, the closed cell percentage of SBO PUF slightly decreased with an increasing filler percentage (Figure 5.8), which in turn increased the thermal conductivity of the gas phase in plastic foams.

5.5 Conclusion

This work studied the physical properties of soybean oil-based rigid PU foams modified with glass microspheres and nanoclay, in concentrations ranging from 1% to 7%. Because the filler surface offered nucleation sites for bubble formation, the foam volume increased when the filler concentration increased. As the filler concentration increased, the density decreased. When incorporated with microspheres, the compressive strength of the SBO PUF decreased slightly from1 to 3%, and then increased up to 7%. At 7% microsphere concentration, SBO PUF displayed the same compressive strength as the control. When incorporated with nanoclay, the compressive strength of SBO PUF generally remained at the same level from 1 to 5%, and then decreased at 7% due to the decrease in density and weaker cell walls and struts. Considering the property of density-compressive strength, the filler did reinforce the cell walls and improved the mechanical properties of SBO PUF. It was encouraging that some SBO PUF (containing 5-7% microspheres or 3-7% nanoclay) displayed comparable or superior density-compressive strength properties to the control. Observation from SEM showed the increase of the cell number and the decrease of cell size in SBO PUF with the addition of fillers. In the foaming temperature, the SBO PUF, with the same filler, basically remained the same during the foaming process. In addition, the presence of fillers slightly increased the thermal conductivity of SBO PUF.

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Table 5.1 Foaming formulation of rigid soybean oil-based polyurethane foams (SBO PU foams) modified with fillers

Ingredients	Concentration, php[a]	
B-side Materials	Control PU foams	SBO PU foams
VORANOL$^{\circledR}$ 490 (Petroleum-based Polyol)	100	85
Soybean Oil-based Polyol	0	15
Dimethylcyclohexylamine (Gelling Catalyst)	0.84	0.84
Pentamethyldiethylentriamin (Blowing Catalyst)	1.26	1.26
Dabco$^{\circledR}$ DC 5357 (Surfactant)	2.5	2.5
Distilled Water (Blowing Agent)	3.0	3.0
Filler (glass microsphere or nanoclay)	0	1,3,5,7
A-side Material		
Isocyanate Index[b] of PAPI$^{\circledR}$ 27	110	110

[a] The concentration of all ingredients are expressed in parts per hundred part of polyol, which conventionally dictates that the sum of all polyols adds up to 100 parts.

[b] The amount of isocyanate is based on the ioscyanate index. The isocyanate index is the ratio of the actual amount of isocyanate used relative to the theoretical amount times 100. The theoretical amount is an index of 100.

Table 5.2 Optical density (OD) of B-side materials with varied filler percentages at 600 nm

Filler percentage (%)	0	1	3	5	7
Glass microspheres	0	0.439	0.795	1.236	1.668
Nanoclay	0	0.882	1.511	2.047	2.557

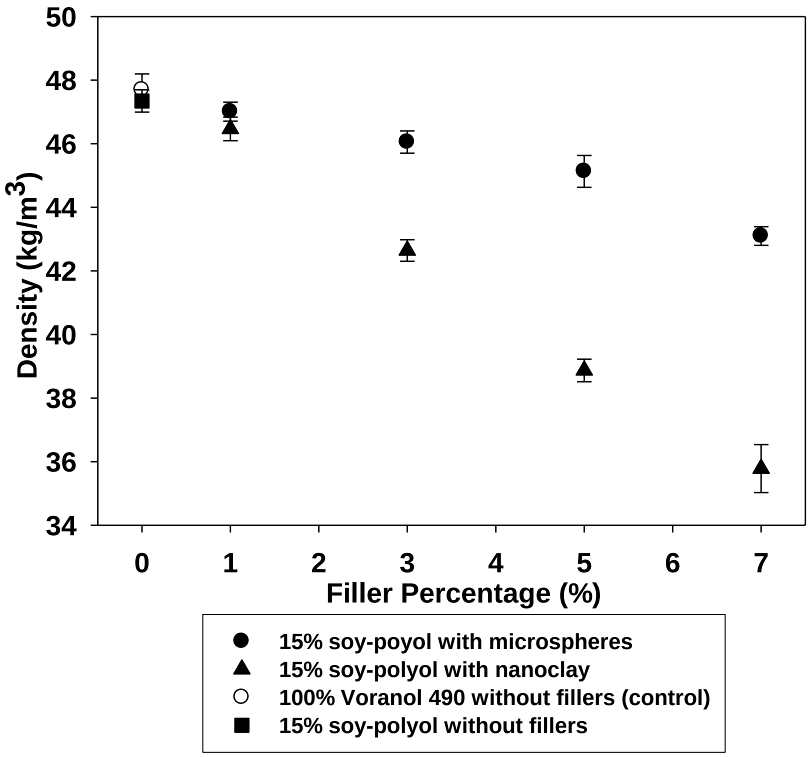

Figure 5.1 The effect of microspheres and nanocly on density of SBO PUF.

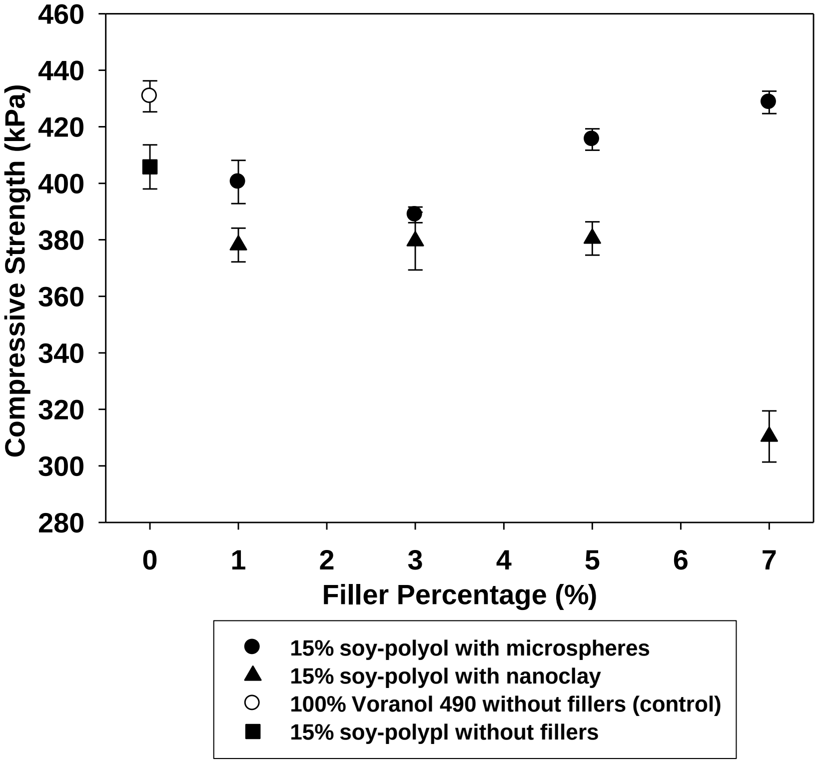

Figure 5.2 The effect of microspheres and nanoclay on compressive strength of SBO PUF.

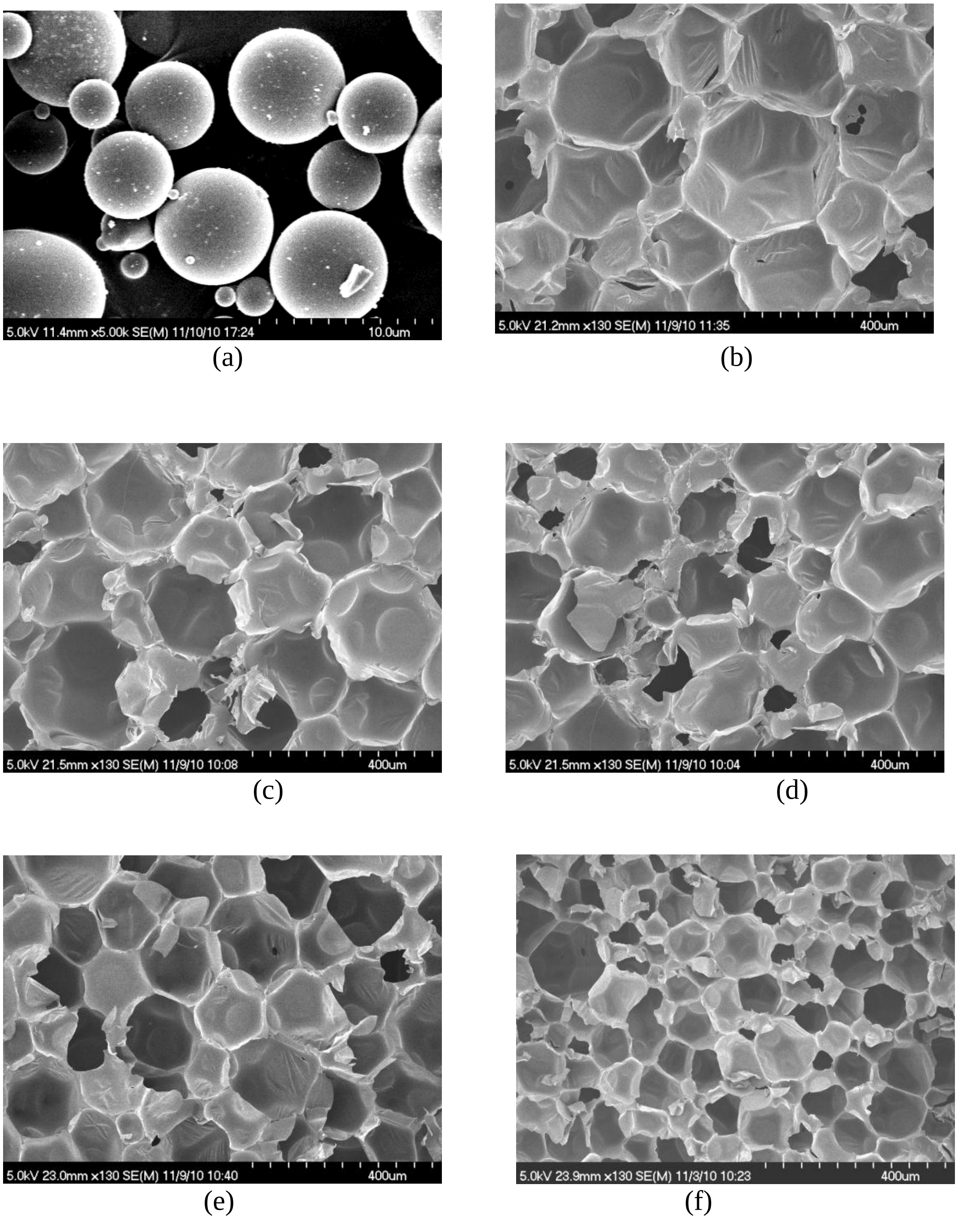

Figure 5.3 Scanning electron micrographs of SBO PU foams modified with microspheres

(a) microspheres	(b) 15% soy-polyol without fillers
(c) 15% soy-polyol with 1% microspheres	(d) 15% soy-polyol with 3% microspheres
(e) 15% soy-polyol with 5% microspheres	(f) 15% soy-polyol with 7% microspheres

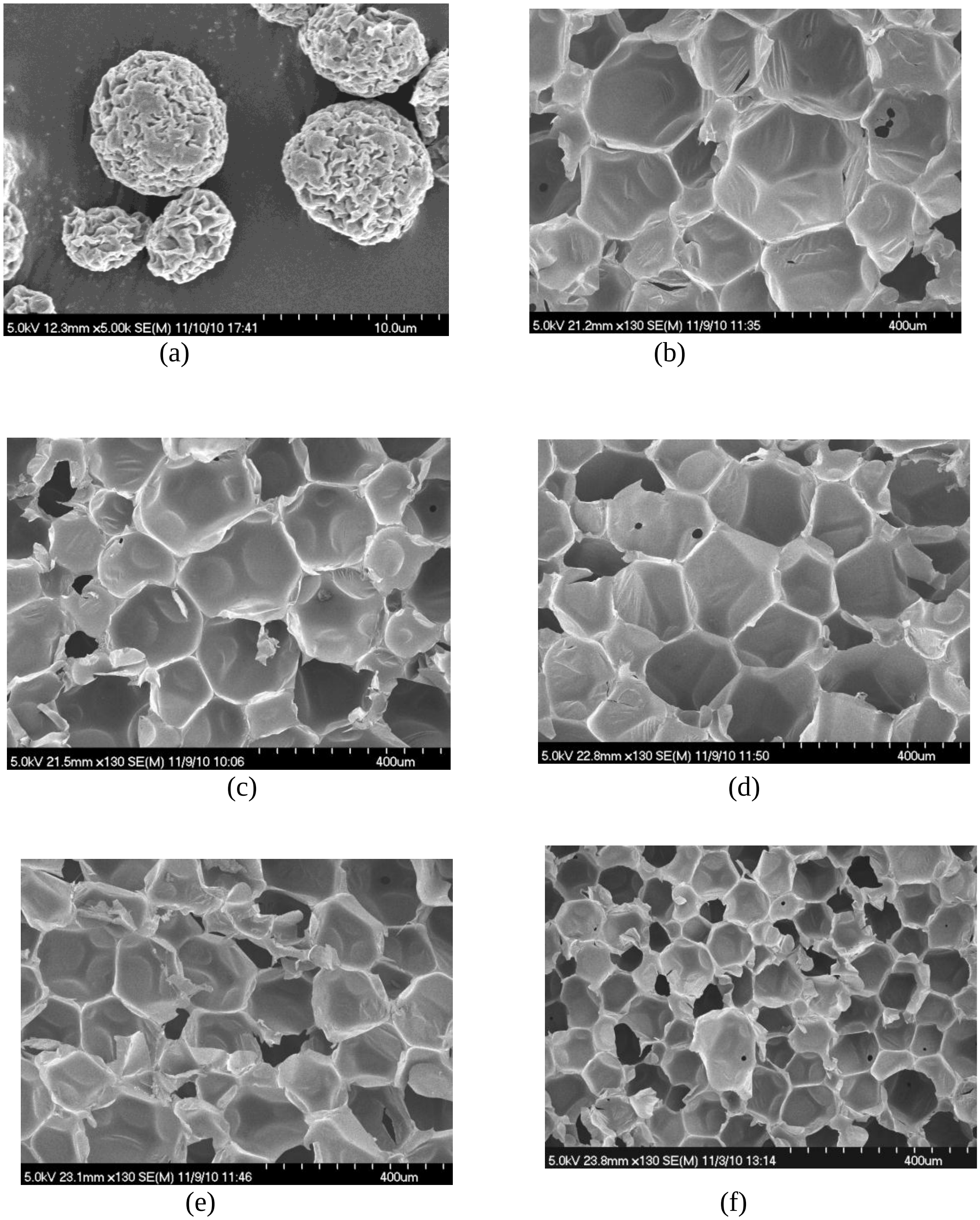

Figure 5.4 Scanning electron micrographs of SBO PU foams modified with nanoclay

(a) nanoclay (b) 15% soy-polyol without fillers

(c) 15% soy-polyol with 1% nanoclay (d) 15% soy-polyol with 3% nanoclay

(e) 15% soy-polyol with 5% nanoclay (f) 15% soy-polyol with 7% nanoclay

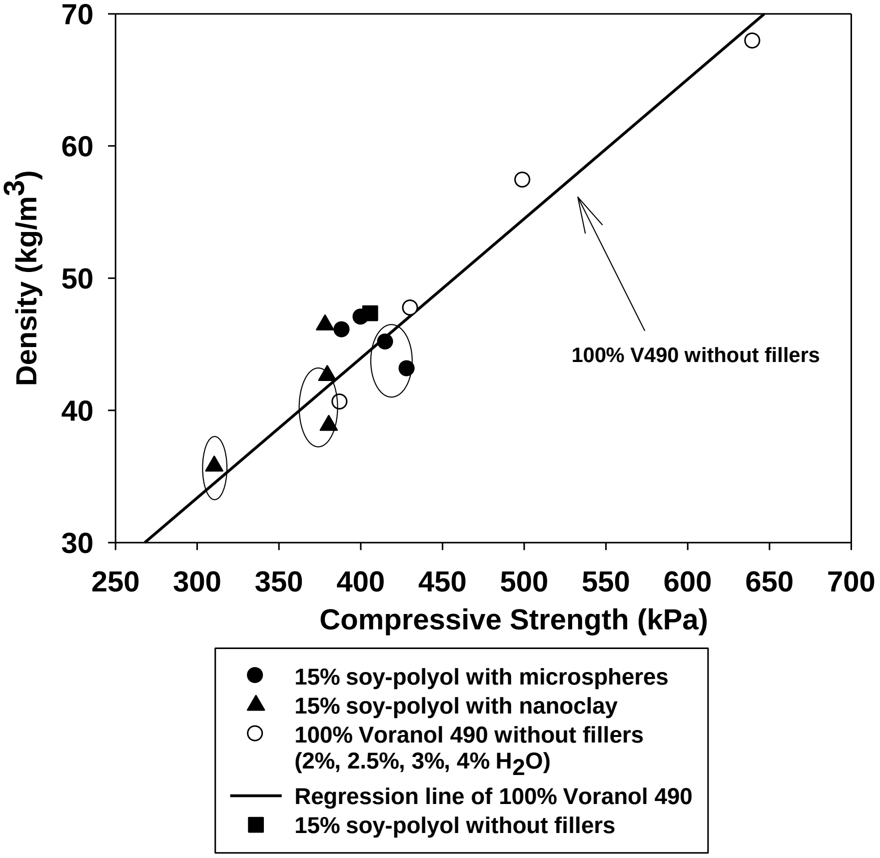

Figure 5.5 The effect of microspheres and nanoclay on density-compressive strength of SBO PUF.

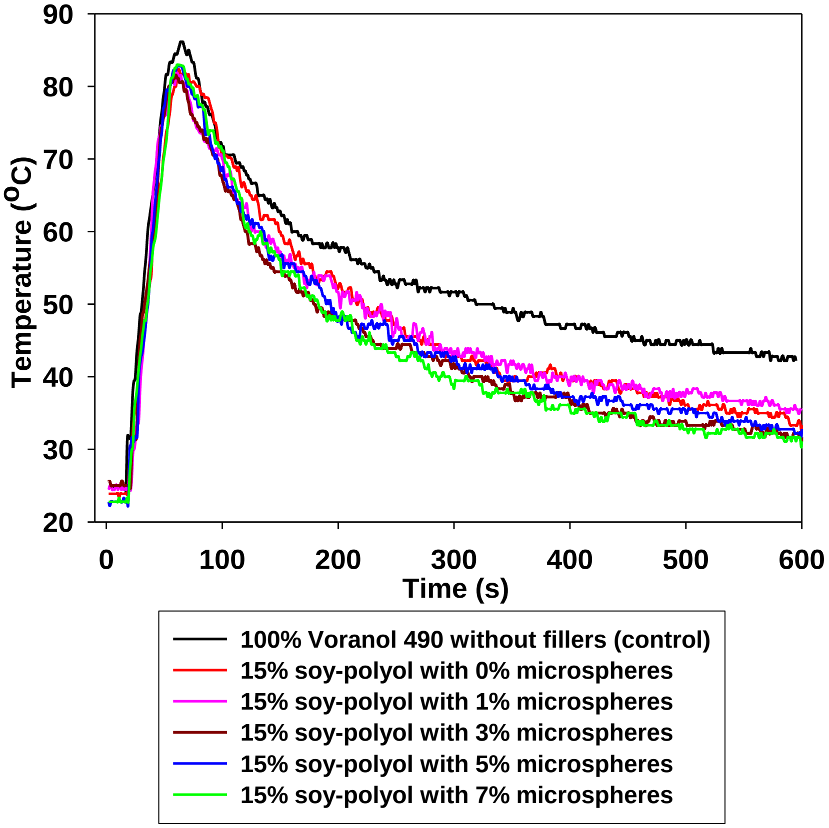

Figure 5.6 Foaming temperature of control and SBO PUF made from 15% soybean oil-based polyol and modified with microspheres.

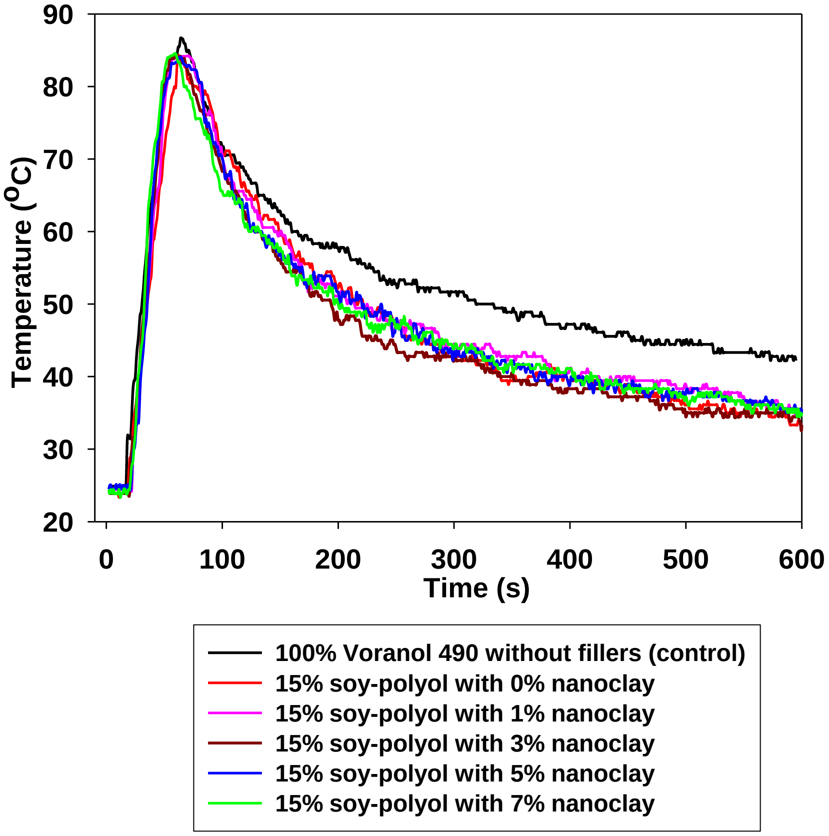

Figure 5.7 Foaming temperature of control and SBO PUF made from 15%soybean oil-based polyol and modified with nanoclay.

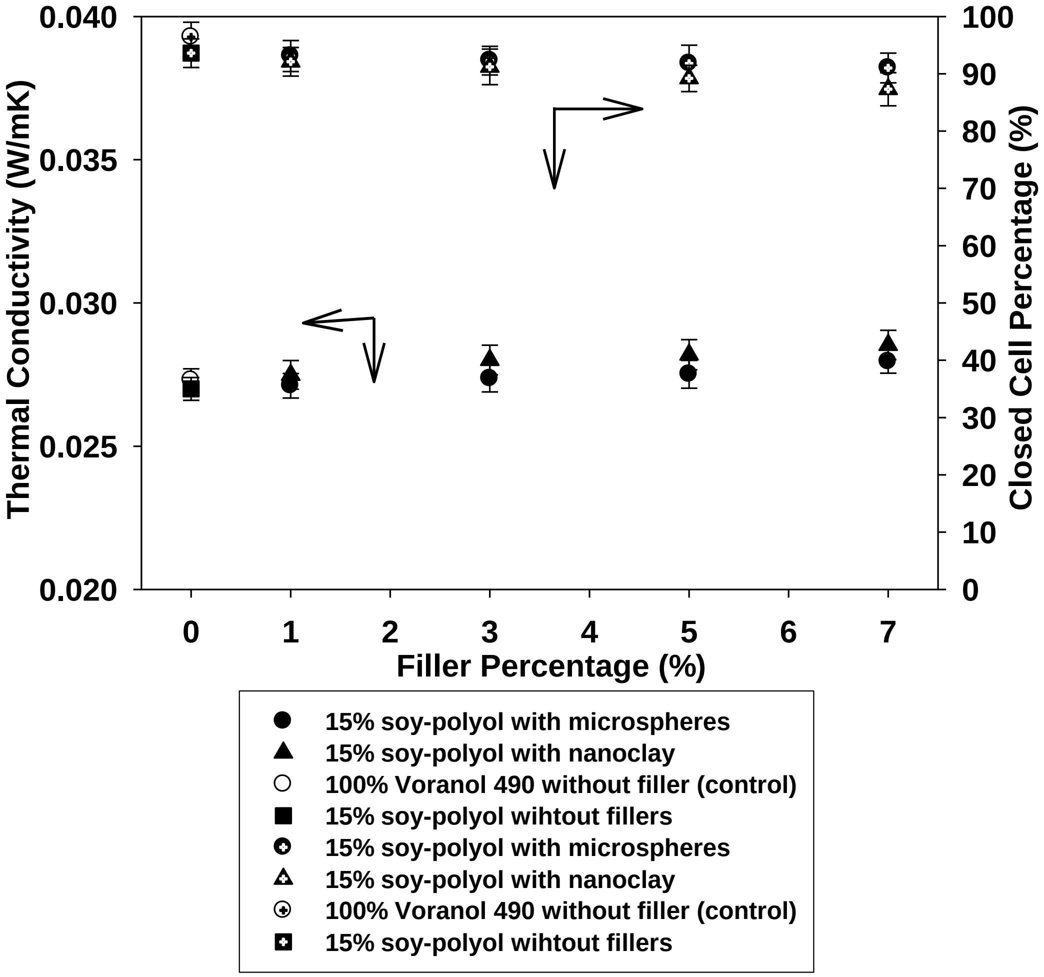

Figure 5.8 The effect of microspheres and nanoclay on thermal conductivity and closed cell percentage of SBO PUF.

CHAPTER 6

RIGID POLYURETHANE FOAMS MADE FROM HIGH VISCOSITY SOY-POLYOLS

6.1 Abstract

This study investigated the physical properties of water-blown rigid polyurethane (PU) foams made fromVORANOL® 490 (petroleum-based polyether polyol) mixed with 0-50% high viscosity (13,000 to 31,000 cP at 22°C) soy-polyols. The density of these foams decreased as the soy-polyol percentage increased. The compressive strength decreased, decreased and then increased, or remained unchanged and then increased with increasing soy-polyol percentage depending on the viscosity of the soy-polyol. Foams made from high viscosity (21,000 to 31,000 cP) soy-polyols exhibited similar or superior density-compressive strength properties to the control foam made from 100% VORNAOL® 490.The thermal conductivity of foams containing soy-polyols was slightly higher than the control foam. Micrographs of foams showed that they had many cells in the shape of sphere or polyhedra. With the increasing soy-polyol percentage, the cell size decreased and the cell number increased.

Key words: rigid polyurethane foams; soybean oil-based polyol; high viscosity; compressive strength; foaming temperature; thermal conductivity; SEM.

6.2 Introduction

Rigid polyurethane (PU) foams have excellent attributes such as low thermal conductivity, low density, high strength-to-weight ratio, and low moisture permeability.

They play an important role in industries and are widely used in transportation, refrigeration, packaging, the automotive industry and building construction. Therefore, demand of rigid PU foams has been growing at a rapid rate throughout the world. Polyol and isocyanate are two main raw materials of rigid polyurethane foams, both of which are derived from petroleum (Szycher 1999; Woods 1990). In recent years, increasing costs of petroleum and growing environmental concerns encourage researchers to explore renewable and bio-based resources as feedstocks in manufacture of PU foams (Wool and Sun 2005).

Because of the great yield of soybeans and stable price of soybean oils in the U.S., soybean oil-based polyols (SBOPs) have attracted considerable attention to replace petroleum-based polyols in the production of PU foams (Economic Research Service 2010). PU foams made from SBOPs have been reported in the literature. John et al (2002) studied the reaction kinetics of PU foams made from modified SBOPs. They concluded that PU foams could be successfully made from SBOPs and their properties could be changed by controlling variables like water content, isocyanate index, and catalysts. Narine et al (2007) compared the mechanical and thermal properties of PU foams made from castor oil, canola oil-based polyol, and SBOP. Their results indicated that the differences in foam performance were related to the differences in the number and position of OH-groups, dangling chains in the starting materials, and their cellular structure. Campanella et al (2009) made flexible PU foams from three SBOPs with different functionalities and positions of OH-groups (primary or secondary OH-groups). They found that SBOP containing primary OH-groups was the most reactive and produced foams with smaller and more uniform cells. When only the secondary OH-groups were present, SBOP with higher functionality was more reactive and produced smaller and more uniform cells. Veronese et al (2011) studied the properties of rigid PU foams made from soybean oil-based polyol and castor oil-based polyol. These bio-based polyols had an OH number between 393 and 477, and a viscosity ranging from 51 to 2,187 cP at 25°C, lower than 7,050 cP of the petroleum-based polyol Voranol 466N (Bayer SA, Brazil). They reported that foams made from SBOP with a higher OH number had higher T_g because of higher crosslinking density. In addition, bio-based PU foams showed slightly inferior mechanical properties than the control. Banik and Sain (2007) investigated the effects of various factors like catalyst, blowing agent, functionality and viscosity of soy-polyols on the structures and rigidity of rigid PU foams. Their results showed that a higher dosage of catalyst or higher functionality soy-polyols gave rise to a more rigid foam structure. Also, when soy-polyols with the same OH number, foams made from soy-polyol with a higher viscosity of 4,500 cP had a higher compressive strength and were more rigid than those made from a lower viscosity (1,250 cP) soy-polyol. While the effect of hydroxyl number, the position of hydroxyl groups (primary or secondary) and functionality of polyols on the properties of rigid polyurethane foams is well known, the effect of the viscosity of polyols is not. The objective of this study was to investigate the effect of high viscosity SBOPs with a viscosity up to31,351 cP on various physical properties of rigid polyurethane foams such as density, compressive strength, thermal conductivity, foaming temperature, and microstructure.

6.3 Materials and methods

6.3.1 Materials

The isocyanate used in this study was PAPI®27 with functionality 2.7. The petroleum-based polyether polyol was VORANOL® 490. Both PAPI® 27 and VORANOL® 490 were bought from Dow Chemical Company (Midland, MI). The high viscosity soy-polyols, A124, A125 and A73, were made from fully epoxidized soybean oil (ESBO) by alcoholysis reaction in Dr. Galen Suppes's lab in the Department of Chemical Engineering at the University of Missouri. In the alcoholysis reaction, ESBO was combined with ethylene glycol using p-toluenesulfonic acid as catalyst to promote the oxirane ring opening and form a hydroxyl group molecule (Lozada et al 2009b). Soy-polyol 1 (SP1) was a commercial soybean oil-based polyol, obtained from BioBased Technologies, LLC (Rogers, AR). Detailed specifications of these polyols are shown in Table 6.1 and Table 6.2. Dimethylcyclohexylamine and pentamethyldiethylenetriamine were obtained from Sigma-Aldrich (St. Louis, MO), and used as catalysts. Dabco® DC 5357 was used as surfactant and was bought from Air Products & Chemicals (Allentown, PA). Distilled water was used as the blowing agent.

6.3.2 Foaming Formulation

The foaming formulation of rigid polyurethane foams made with different high viscosity soy-polyol percentages was shown in Table 4.3.

6.3.3 Foam Preparation

The rigid polyurethane foams were made through one-shot and free-rising method. A total of 100g of VORANOL® 490 and soy-polyol mixture were weighed in a plastic container and preheated in the oven (65^{o}C) until the center temperature of the polyols reached 40-45°C for A124 and A125, and 55-65°C for A73. The polyols were then taken out of the oven and mixed with an electric stirrer at 3450 rpm for 15s. Other B-side components such as water, catalysts and surfactant were added and mixed for 10-15s. The mixture was allowed to degas for 2 min. Thereafter, pre-weighed isocyanate (A-side material) was added and mixed at the same speed for 10s. The reacting mixture was then poured quickly into a wooden mold (11.4×11.4×21.6cm) with aluminum lining and the foam was allowed to rise and set at ambient conditions (23°C) for curing. The thermal conductivity testing was conducted in 24-48 hours and other physical properties are tested after 7 days.

6.3.4 Foam Property Measurements

The apparent density was measured in accordance with the American Society of Testing Materials Designation: D1622-08 (2008). The compressive strength was measured in accordance with the ASTM Designation (2010b): C1621-10 by a TA.HDi Texture Analyzer with XTRA Dimension software (Texture Technologies Corp., Scarsdale, NY). The dimension of the specimens was 6.35×6.35×3.81 cm in both density and compressive strength. Five specimens per sample were measured and the averaged result was reported. The surface foaming temperature was detected and recorded by an Omega Engineering OS 552A-MA-4 infrared thermometer equipped with a wireless transmitter and receiver (Omega Engineering Inc., Stamford, CT). The infrared thermometer focused on the center of the wooden mold (a circle of 2.54cm in diameter) and was fixed at 40.64 cm above the mold. The interval of recording time was 1s (Tu et al 2009). The apparent thermal conductivity was measured in accordance with ASTM

(2010a) Designation: C518-10. After curing at ambient temperature for 24-48 hours, the sample (20×20 ×2.5 cm) was tested by a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA). The foam morphology was observed by a Hitachi S-4700 field emission scanning electron microscope (FESEM, Tokyo, Japan). A 3mm cube foam sample was adhered to a substrate with silver glue and coated with gold powder by a plasma sputter. The sample was observed with an accelerating voltage of 5000 V and emission current of 9700 nA in FESEM (Tu et al 2008).

6.4 Results and discussion

6.4.1 Density

Figure 6.3 shows the density of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL® 490 in different percentages. As shown, the density of soybean oil-based PU foams (SBO PU foams) decreased when increasing soy-polyol percentage from 0 to 50%. Soy-polyols have a hydroxyl number in the range of 243 to 265, lower than the hydroxyl number of 490 in VORANOL® 490. Thus, foams made from soy-polyols required less isocyanate than foams made from 100% VORANOL® 490. So were foams made from soy-polyols with a lower hydroxyl number than foams from soy-polyols with a higher hydroxyl number. In addition, the water content (blowing agent) in the foam formulation was fixed at 3% which generated the same amount of gas (CO_2) in the final foams. Therefore, the density decreased with increasing soy-polyol percentages in soybean oil-based rigid PU foams (Lim et al 2008; Singh et al 2007). Also, at the same soy-polyol percentage, SBO PU foams made from soy-polyol with a lower hydroxyl number had a lower density.

6.4.2 Compressive Strength (CS)

The soy-polyols, A73 and A125, were made from opening oxirane rings of fully epoxidized soybean oil (ESBO) by alcoholysis reaction. In the alcoholysis and addition polymerization reaction, ESBO was combined with ethylene glycol using p-toluenesulfornic acid as catalyst to promote the opening of epoxy rings and form hydroxyl groups in the molecule (Figure 6.1).High viscosity soy-polyols contain a large amount of ether chains in the molecules due to the formation of oligomeric ethers. During the polymerization between the hydroxyl and isocyanate groups, these soy-polyol ether bonds are also embedded in the cross-linking structure of PU polymers (Figure 6.3), which may replace the urethane linkage and support the structure when foams are under loading. The compressive strength (CS) of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL® 490 in different percentages is shown in Figure 6.4. Polyols with a higher hydroxyl number need more isocyanate for foaming and therefore produce PU foams with a higher cross-linking density. In general, higher density and/or higher cross-linking density result in foams with a higher compressive strength (Tu et al 2008; Thirumal et al 2008; Klempner and Sendijarevic 2004). Although A73 (31,351 cP viscosity) had a lower hydroxyl number than VORANOL® 490 and the density of foams made from A73 decreased with increasing soy-polyol percentages, the CS remained roughly the same level from 0 to 30% and then increased gradually with further increases in soy-polyol percentages. In fact, the CS of foams made from 50% A73 was similar to the control foam made from 100% VORANOL® 490. Also in Figure 6.4, the CS of foams made from A125 (21,514 cP viscosity) decreased to 30% and then increased up to 50%. These CS results of foams made from A73 and A125 revealed that the soy-polyol ether bonds could replace the urethane linkage to support the structure to a certain extent when foams are under loading. For foams made from A124 and SP1, the CS decreased with the increasing soy-polyol percentages, due to the decrease in both density and cross-linking density in those foams. Among those soy-polyols, SP1 had the lowest hydroxyl number and therefore the corresponding rigid PU foams had the lowest cross-linking density and the weakest basic polymer network matrix established by the reaction between the hydroxyl groups and isocyanate. Despite having a high viscosity, the CS of foams made from SP1 decreased with increasing soy-polyol percentages due to the decrease in density and the inferior polymer network structure. These results reveal that the hydroxyl number of polyols is important to the foam structure in addition to their viscosity.

6.4.3 Density-Compressive Strength and Isocyanate Density-Compressive Strength

Figure 6.5 presents the density-compressive strength property in rigid PU foams made from high viscosity soy-polyols mixed with VORANOL® 490 in different percentages using 3% water content as blowing agent. The square symbols are rigid PU foams made from 100% VORANOL® 490 using water content from 2 to 4% as the blowing agent. As shown, there was a linear relationship between the density and compressive strength in rigid PU foams made from 100% VORANOL® 490.This phenomenon was commonly observed in rigid PU foams (Oertel and Abele 1994; Tu et al 2007). Foams located on the left-hand side of the regression line indicated that their density-compressive strength property was inferior to the control foam. Conversely, foams on the right-hand side of the line were superior to the control. As seen in Figure 6.5, it was encouraging that foams made from mixing 40-50% A125 or 30-50% A73 with VORANOL® 490 were similar or superior to the control foam in terms of density-compressive strength property. A review of polyol properties (Table 6.1) indicates that this comparable performance of soy-based foams might depend on soy-polyols having a minimum viscosity of about 22,000 cP. Performance increased when the soy-polyol viscosity increased to 31,000 cP.

The property of isocyanate density-compressive strength of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL$^{®}$490 in different percentages is shown in Figure 6.6. Similar to Figure 6.5, there was a linear relationship between the isocyanate density and the compressive strength in rigid PU foams made from 100% VORANOL$^{®}$490. Foams on the right-hand side of the regression line were superior to the control foams in the isocyanate density-compressive strength property (i.e., having higher compressive strength at the same isocyanate density or lower isocyanate density at the same compressive strength). It was interesting that most SBO PU foams displayed comparable or superior isocyanate density-compressive strength property to the control.

Due to a hydroxyl number of about 240, soy-polyols produced foams having reduced isocyanate contents (VORANOL$^{®}$490 has a hydroxyl number of 490). Figure 6.6 actually summarizes the impact of isocyanate content in the foams on compressive strength. At lower isocyanate densities, most soy-polyols provided the advantage of reducing isocyanate content. The greatest reductions were obtained by A73 soy-polyol with a viscosity of 31,000 cP, and about 30% reduction in isocyanate content was achievable. These results indicated that rigid PU foams could be made by replacing 50% petroleum-based polyol with a high viscosity soy-polyol resulting in a 30% reduction in the isocyanate content.

6.4.4 Thermal Conductivity

The effect of high viscosity soy-polyols mixed with VORANOL® 490 on the thermal conductivity and closed cell percentage of rigid PU foams is shown in Figures 6.7 and 6.8, respectively. In general, the thermal conductivity of SBO PU foams increased as soy-polyol percentages increased. Also, all foams made from soy-polyols had a slightly higher thermal conductivity than the control foams made from 100% VORANOL® 490. VORANOL® 490 is a petroleum-based polyether polyol with a linear chemical structure and had primary hydroxyl groups; while soy-polyols were derived from vegetable oil and had secondary hydroxyl groups located in the middle of the triglyceride alkyl chains (Herrington and Hock 1997; Lozada et al 2009a). During polymerization between the secondary hydroxyl groups and isocyanate, steric hindrance to crosslinking would occur because of the bulky aromatic isocyanate (Javni et al 2003; Pechar et al 2007). Thus, soy-polyols had a lower reaction rate with isocyanate than VORANOL® 490. In the control foams, the polymer-forming reaction rate and blowing reaction rate was balanced. In SBO PUF, the polymer-forming reaction rate was actually slower than the blowing rate, so the cell walls were not sufficiently strong as in the control foams, and became easier to burst during the expansion of bubbles (Tu et al 2008). Figure 6.8 showed that the closed cell percentage of SBO PUF gradually decreased with increasing soy-polyol percentage, which in turn increased the foam thermal conductivity.

6.4.5 Foaming Temperature

The foaming temperatures of rigid PU foams made from soy-polyols A124, A125 A73 and SP1 are shown in Figures 6.9, 6.10, 6.11 and 6.12, respectively. The foaming temperature was taken on the center of the foam surface during foaming using an infrared temperature sensor. As shown in Figures 6.9 and 6.10, the maximal foaming temperatures of foams made from A124 and A125 slightly decreased with increasing soy-polyol percentages. These results were not unexpected. Both the polyol-isocyanate and water-isocyanate reactions are exothermic. In SBO PUF, the secondary hydroxyl groups and a lower hydroxyl number in soy-polyols resulted in a lower reactivity as well as less exothermic when they reacted with isocyanate than VORANOL® 490, which contained primary hydroxyl groups and a higher hydroxyl number. However, the maximal foaming temperatures of foams made from A73 and SP1 slightly increased with increasing soy-polyol percentages, as shown in Figures 6.11 and 6.12. Since A73 and SP1 had an ultra high viscosity (Table 6.1), a longer heating time was needed and a higher temperature was actually achieved after preheating for polyol mixture with a higher soy-polyol percentage. The chemical reactivity of polyols and catalysts varied with temperatures. Higher temperature of polyols not only resulted in a higher reactivity and a faster release of heat in polymerization, but also increased the efficiency of catalysts in the foaming process.

6.4.6 Microstructure

Figures 6.13 and 6.14 displays the scanning electron micrographs (SEM) of rigid PU foams made from high viscosity soy-polyols, A73 and SP1, mixing with VORANOL® 490 in different percentages. The micrograph of the control foam made from 100% VORANOL® 490 is shown in Figure 6.13 (a). It was observed that the rigid PU foams were composed of many cells in the shape of sphere or polyhedra. When the soy-polyol percentages increased from 0 to 50%, the foam cell size gradually decreased while the foam cell number increased. This change in the foam microstructure might be partially due to the difference of the chemical structure between the soy-polyols and petroleum-based polyether polyol. Soy-polyols were triglycerides with three pendant chains while petroleum-based polyether polyol was linear in its chemical structure. During polymerization, the branched and pendant chains of triglycerides in soy-polyols were able to offer more nucleation sites for bubble formation and growth than VORANOL ® 490. In addition, because soy-polyols had a significantly higher viscosity than VORANOL ® 490, the viscosity of the reacting polyol-isocyanate liquid mixture would increase with increasing soy-polyol percentage. The viscosity increase of the reacting liquid system would reduce the coalescence among bubbles, therefore decreasing foam cell size and increasing foam cell number (Mondal and Khakhar 2007).

6.5 Conclusion

Rigid PU foams were made with high viscosity soy-polyols mixed with VORANOL ® 490 in different percentages. Because soy-polyols had a lower hydroxyl number than VORANOL® 490 and the water content (blowing agent) was fixed, the density of SBO PU foams decreased with increasing soy-polyol percentages. The CS of SBO PU foams made from A125 (21,514, cP viscosity) decreased to 30% and then gradually increased up to 50%. For foams made from A73 (31,351 cP viscosity), the CS remained roughly at the same level from 0 to 30% and then gradually increased up to 50%. SBO PU foams made from 50% A73 and 50% VORANOL ® 490 displayed comparable property to the control foam in CS. In terms of density-compressive strength, SBO PU foams made from A125 and A73 showed comparable or superior property to the control foams when A125 percentage was at 50%, and A73 percentage was at 30% to

50%. Additionally, most SBO PU foams displayed comparable or superior isocyanate density-compressive strength property to the control foams. The results revealed that rigid PU foams can be made from a 50% replacement of petroleum-based polyol and a 30% reduction in isocyanate content. In thermal conductivity, SBO PU foams had slightly higher values than the control foams. This was caused by a lower closed cell content of PU foams made from soy-polyols than that in the control foams. Due to a higher temperature of the polyol mixture with a higher soy-polyol percentage after preheating, the foaming temperature of SBO PU foams made from A73 and SP1 rose faster and reached a higher maximal temperature as the percentage of A73 and SP1 increased from 0 to 50%. The micrographs presented that with increasing soy-polyol percentages the foam cell size decreased and cell number increased. This change was attributed to the difference in the chemical structure between soy-polyols and VORANOL® 490. In addition, with increasing soy-polyol percentages, the viscosity increase of the reacting liquid system reduced the coalescence among bubbles, consequently decreasing cell size and increasing cell numbers.

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Table 6.1 Properties of petroleum-based polyol and high viscosity soybean oil-based polyols

Polyol	Viscosity (cP)@22°C	ASTM hydroxyl number	Acid number
A124 (soy-polyol)	12,682	265	3.25
A125 (soy-polyol)	21,514	255	3.15
A73 (soy-polyol)	31,351	243	2.80
Soy-polyol 1 (commercial soy-polyol, SP1)	28,115	185	0.3
VORNAOL® 490 (commercial petroleum-based polyether polyol)	9,000	490	0

Table 6.2 Viscosity (cP) of soybean oil-based polyols at different temperatures

	35°C	45°C	55°C	65°C
A124	4759.5	2321.3	1293.5	752.8
A125	6848.3	3477.1	1980	1076.1
A73	7817.7	4534	2416.8	1425.9
SP1	6642	2957.2	1442.8	759.5

Table 6.3 Foaming formulation of rigid polyurethane foams with high viscosity soybean oil-based polyols

Ingredients	Concentration, php[a]	
B-side Materials	Control PU foams	Soybean Oil-based PU foams (SBO PU foams)
VORANOL® 490 (Petroleum-based Polyol)	100	90, 80, 70, 60, 50
High ViscositySoy-Polyol	0	10, 20, 30, 40, 50
Dimethylcyclohexylamine (Gelling Catalyst)	0.84	0.84
Pentamethyldiethylenetriamine (Blowing Catalyst)	1.26	1.26
Dabco® DC 5357 (Surfactant)	2.5	2.5
Distilled Water (Blowing Agent)	3.0	3.0
A-side Material		
Isocyanate Index[b] of PAPI® 27	110	110

[a] The concentration of all ingredients are expressed in parts per hundred parts of polyol, which conventionally dictates that the sum of all polyols adds up to 100 parts.

[b] The amount of isocyanate is based on the isocyanate index. The isocyanate index is the ratio of the actual amount of isocyanate used relative to the theoretical amount times 100. The theoretical amount is an index of 100.

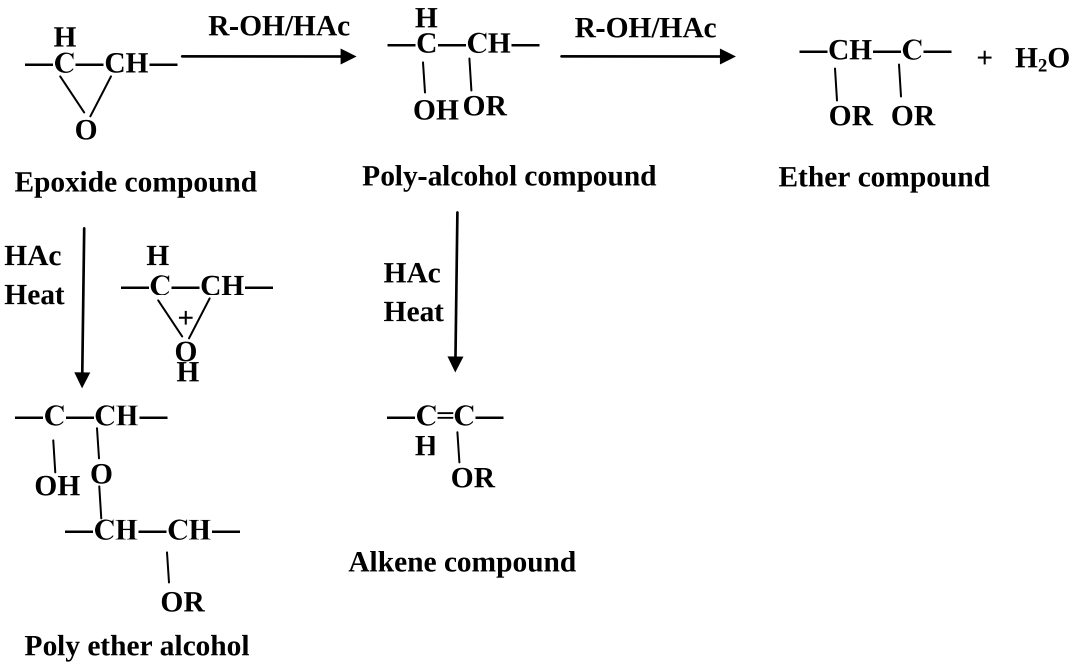


Figure 6.1 General mechanism for the alkoxy hydroxyl reaction (R-OH was an alcohol and HAc was an acid) (Lozada et al 2009b).

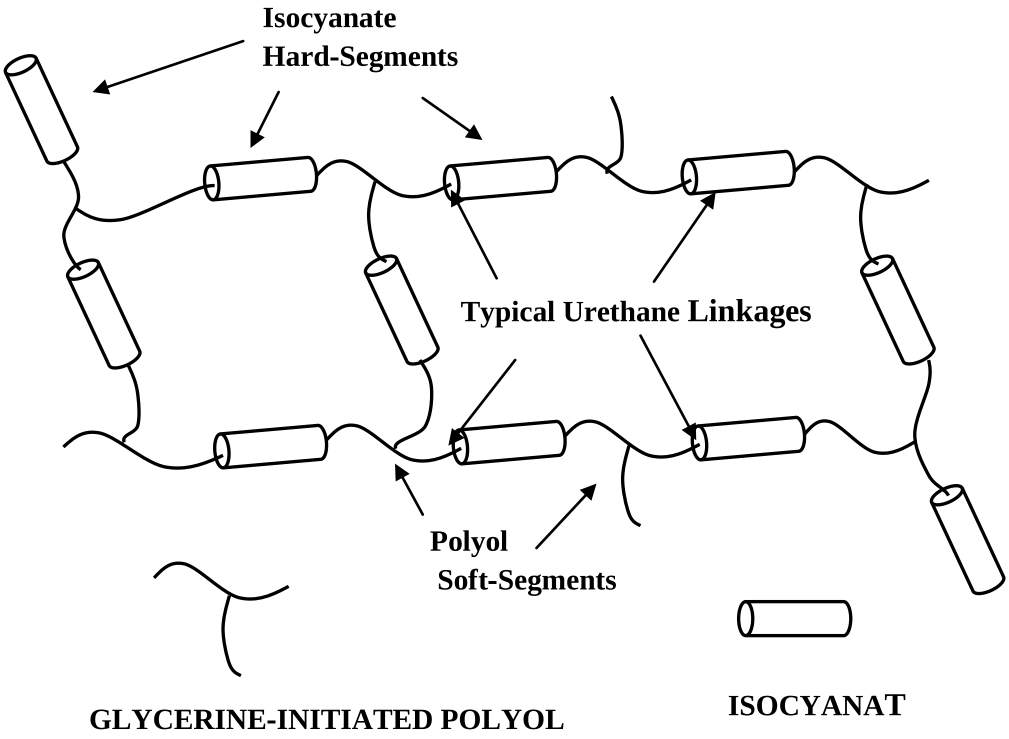


Figure 6.2 Cross-linking structure in polyurethane (Klempner and Sendijarevic 2004).

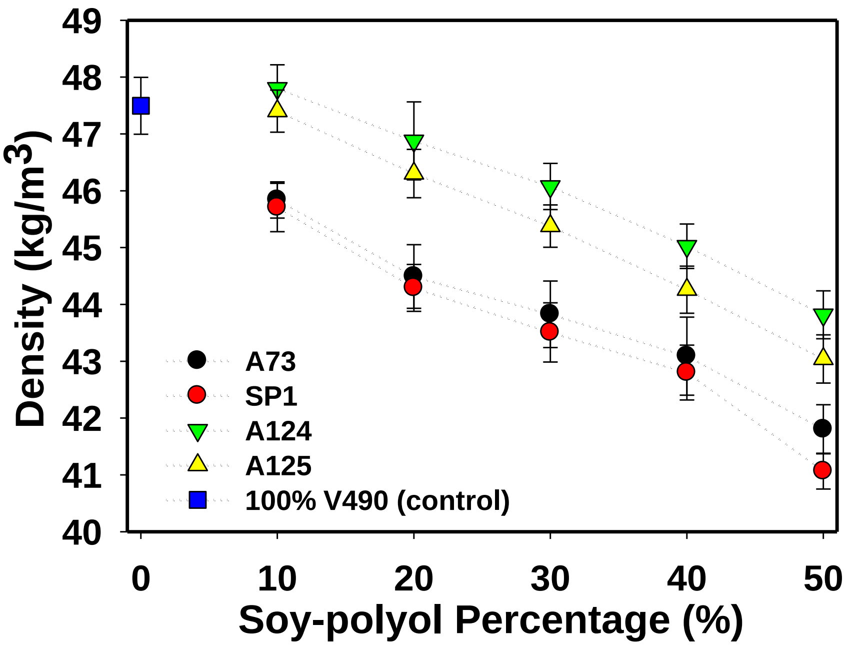


Figure 6.3 Density of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

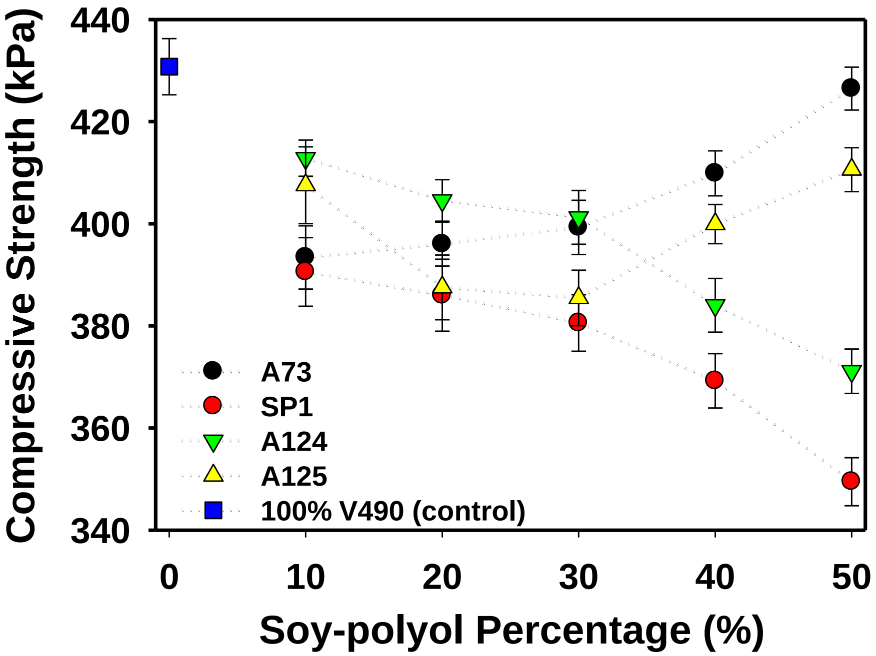


Figure 6.4 Compressive strength of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

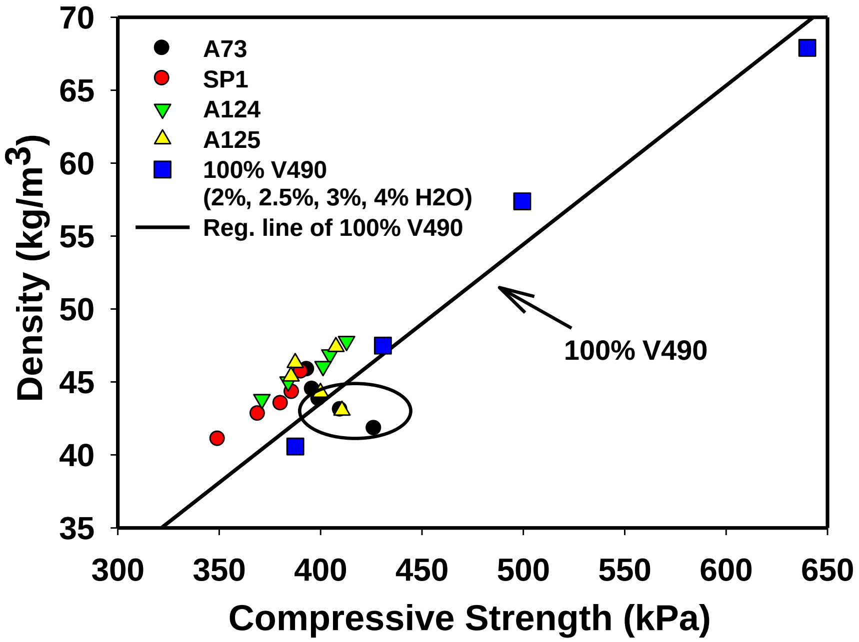


Figure 6.5 Density-compressive strenth of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

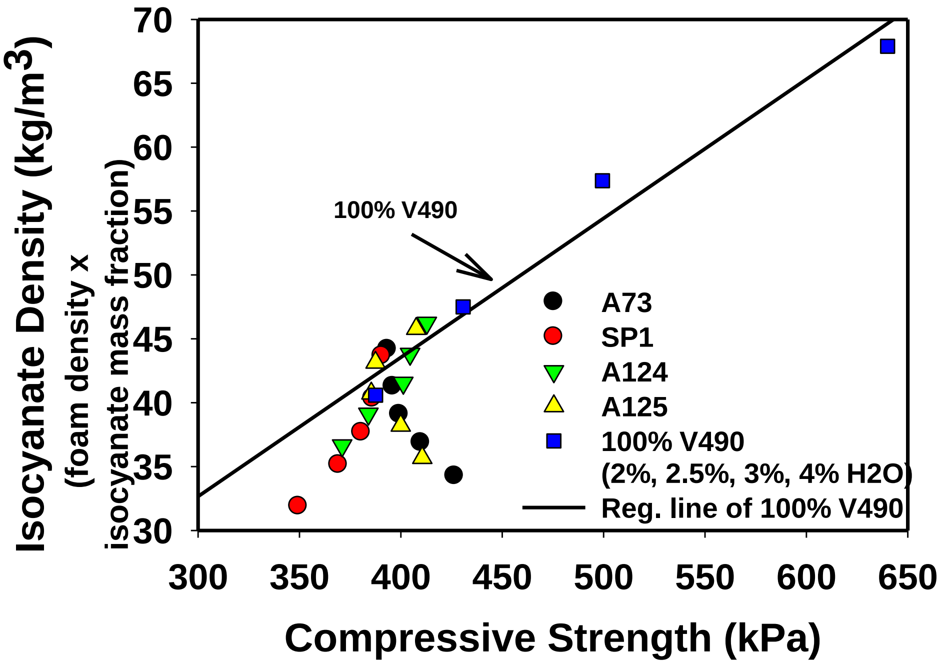


Figure 6.6 Isocyanate density-compressive strenth of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

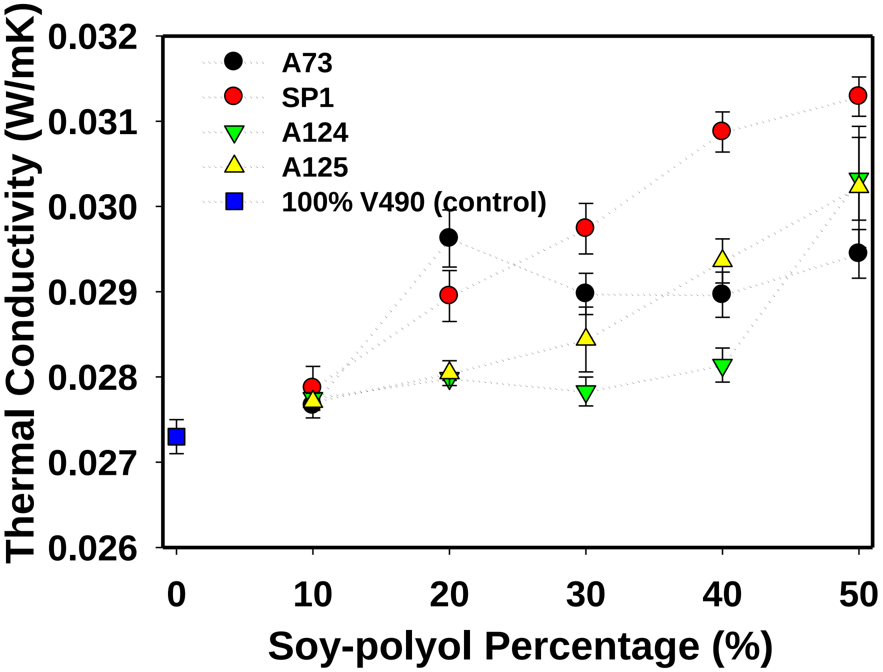


Figure 6.7 Thermal conductivity of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

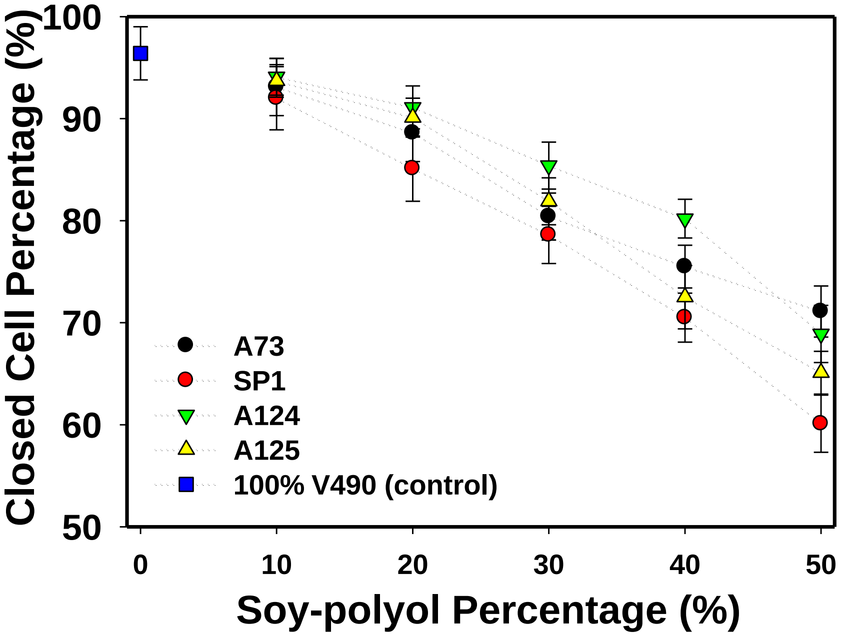


Figure 6.8 Closed cell percentage of rigid PU foams made from high viscosity soy-polyols mixed with VORANOL 490.

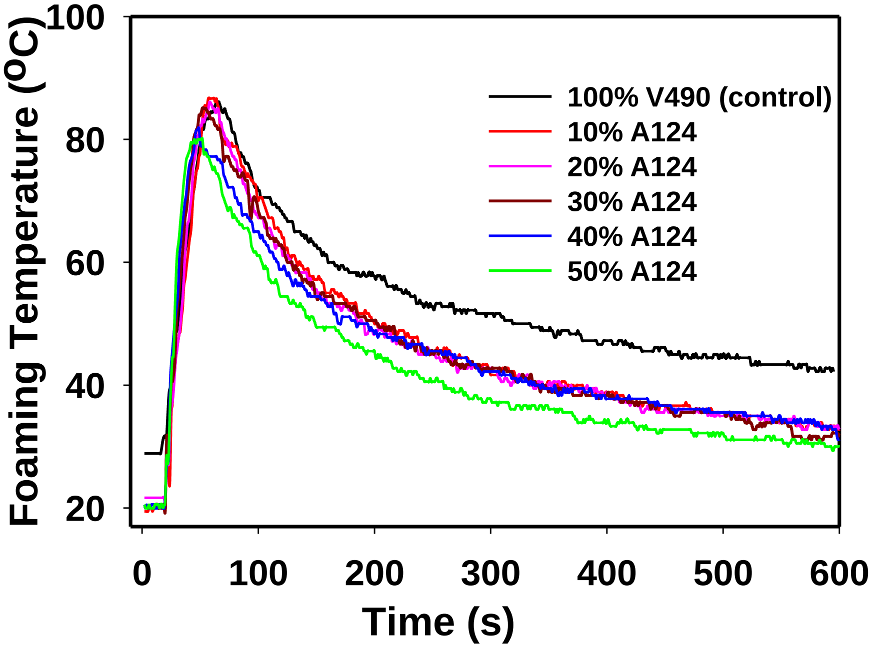


Figure 6.9 Foaming temperature of rigid PU foams made from high viscosity soy-polyol mixed with VORANOL 490.

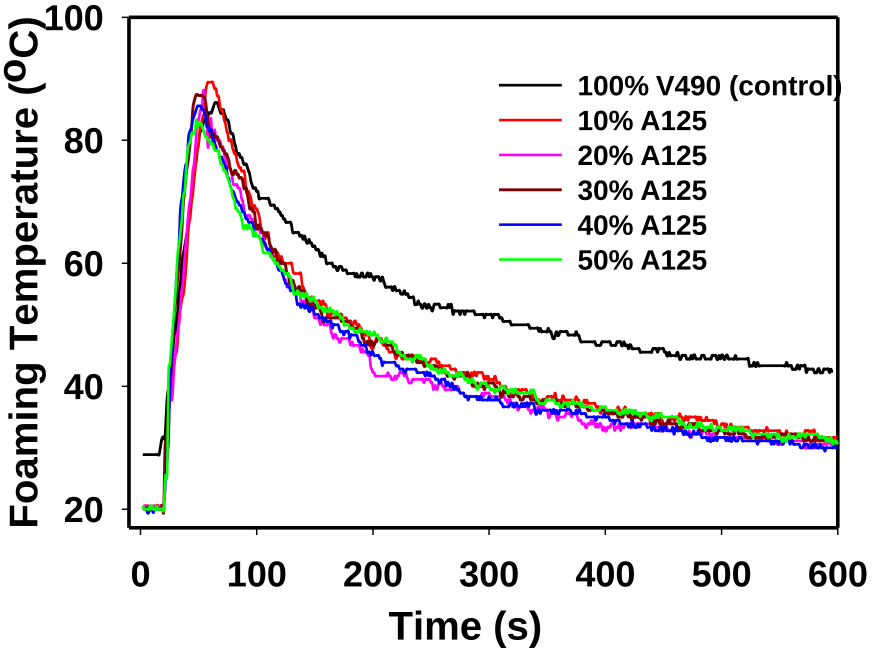


Figure 6.10 Foaming temperature of rigid PU foams made from high viscosity soy-polyol mixed with VORANOL 490.

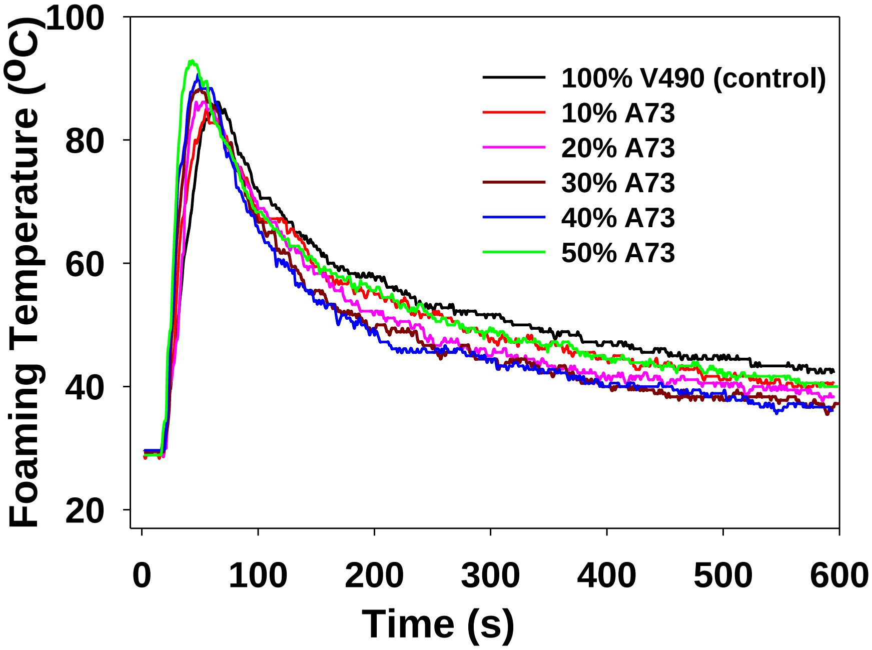


Figure 6.11 Foaming temperature of rigid PU foams made from high viscosity soy-polyol mixed with VORANOL 490.

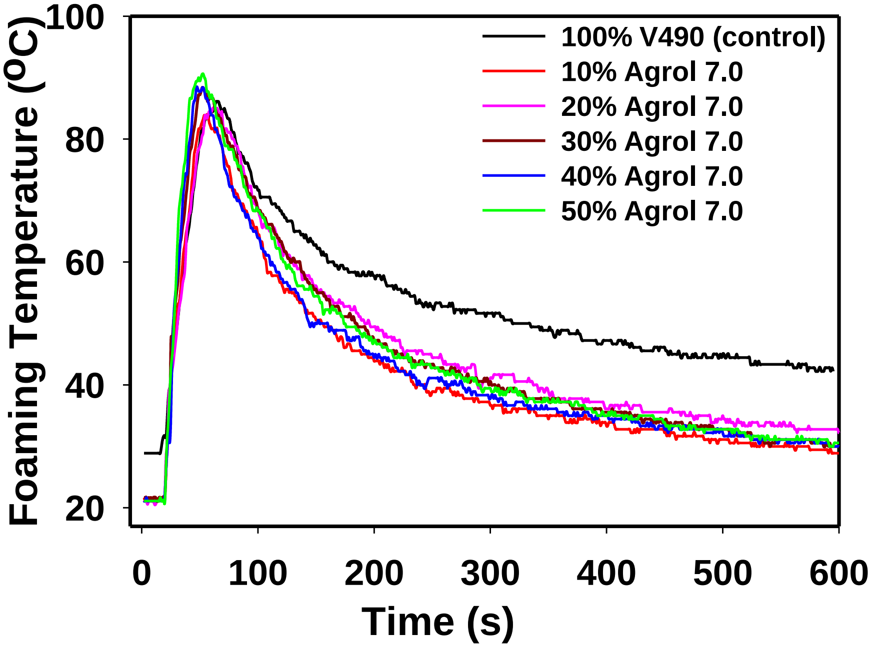
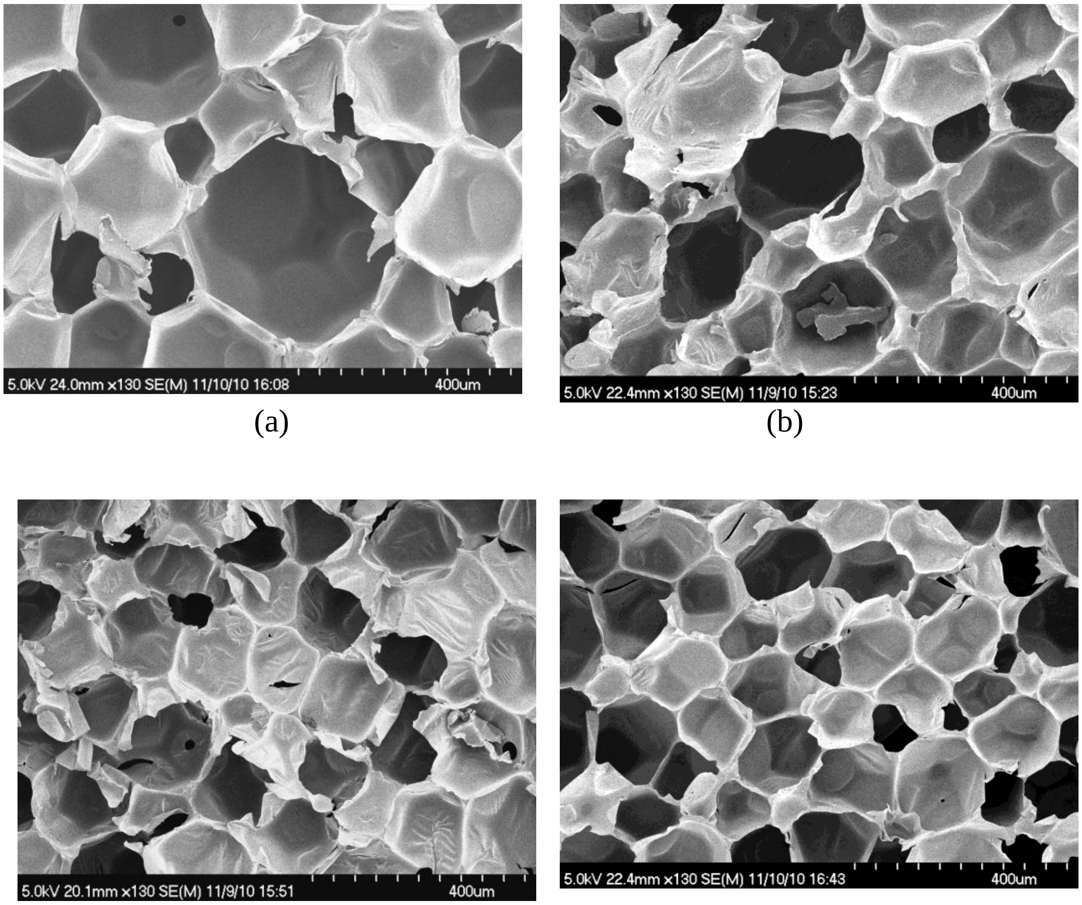


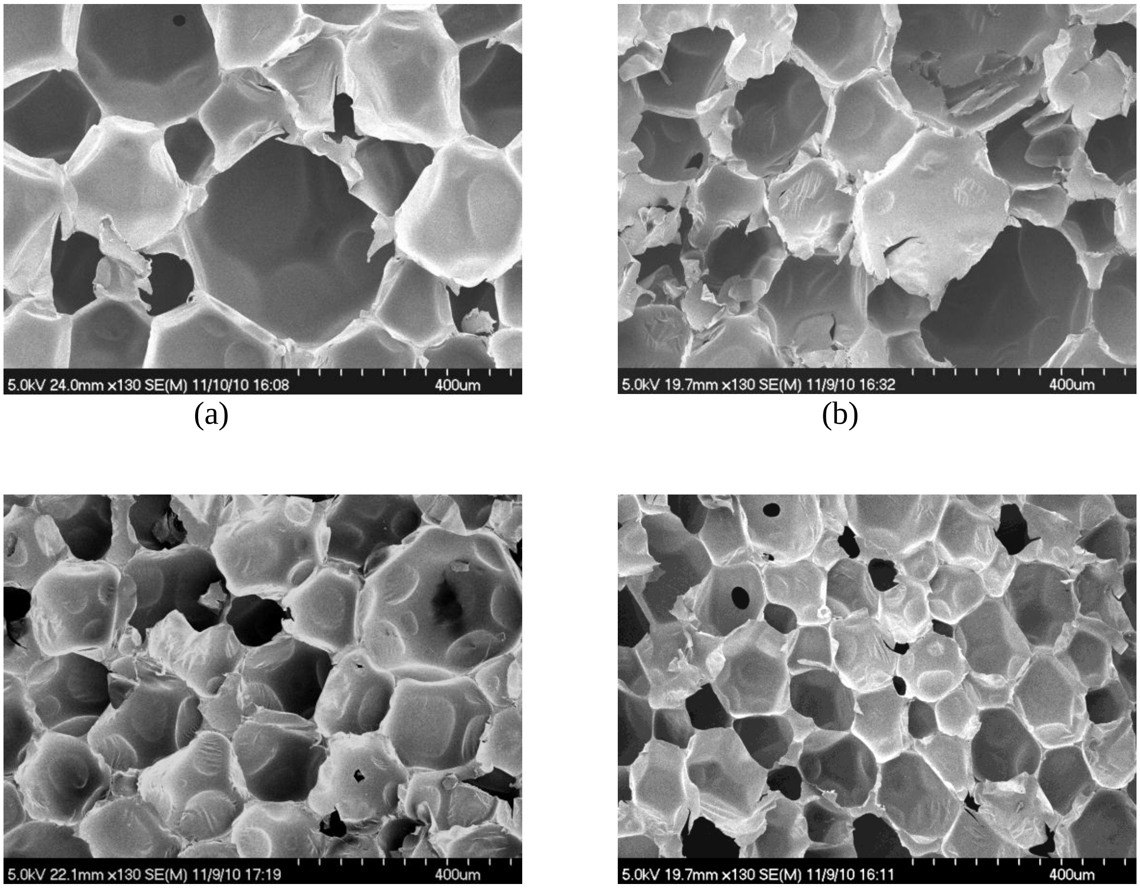
Figure 6.12 Foaming temperature of rigid PU foams made from high viscosity soy-polyol mixed with VORANOL 490.



(a) (b)

(c) (d)

Figure 6.13 Scanning electron micrographs of rigid PU foams made from high viscosity soy-polyol, A73, mixed with VORANOL 490
(a) 100% VORANOL 490 (control); (b) 10% A73; (c) 30% A73; (d)50% A73.



(a) (b)

(c) (d)

Figure 6.14 Scanning electron micrographs of PU foams made from high viscosity soy-polyol, SP1, mixed with VORANOL 490
(a) 100% VORANOL 490 (control); (b) 10% SP1;
(c) 30% SP1; (d) 50% SP1

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Polyurethane (PU) foams are important polymers, and they have many commercial applications in industry. Traditionally, the main raw materials to produce PU foams, polyol and isocyanate, are derived from petroleum. Bio-based polyols are gaining popularity due to the increasing costs of petrochemical feedstocks and public desire for renewable green products. In the United States, soybeans account for about 90% of the whole country oilseed production. The refined soybean oils contain 99% triglycerides with a variety of carbon-carbon double bonds, which are amenable to chemical reactions for designing polymers. Therefore, soybean oils have great potentials to prepare bio-based polyols for PU foams.

This research focused on the study of PU foams made from soy-polyols. In this project, PU foams were made from commercial soy-polyols, and lab-scale soy-polyols prepared at Dr. Suppes‘s lab. The commercial Soy-Polyols (SP), were obtained from Biobased Technologies, LLC (Rogers, AR). They were derived by converting the alkene groups of the unsaturated molecules into hydroxyl groups. Two types of soy-polyols are prepared at Dr. Suppes's lab: soy-phosphate polyol (SPP), and soy-polyol made from fully epoxidized soybean oil (ESBO). The SPP was made from soybean oil epoxides with the presence of phosphate acid as catalyst by acidolysis reaction. The other soy-polyol was made from ESBO combined with ethylene glycol, and using p-toluenesulfonic acid as catalyst to promote the oxirane ring opening and form a hydroxyl group molecule.

Water-blown flexible PU foams (SP PU foams) were produced with a mixture of petroleum polyol and commercial Soy-Polyols (SP) with different functionalities. The effect of hydroxyl number and functionality of soy-polyols, and the effect of tin catalyst and cross-linker levels on properties of SP PU foams were investigated. Compared to the control foams made from 100% petroleum polyol, SP PU foams had lower density, higher compression force deflection (CFD) and tear resistance (TR). In addition, SP PU foams displayed lower resilience and higher 50% constant deflection compression set (CDC) due to less flexibility to the control foams. The glass transition temperature, T_g, was constant at approximate -54^{o}C, independent of isocyanate index and Soy-Polyol percentages. The results of FTIR images indicated that SP PU foams became firmer with increasing Soy-Polyol percentage.

Water-blown rigid polyurethane foams (SPP PU foams) were produced by combining 0 to 50% soy-phosphate polyol (SPP) with petrochemical polyol, VORANOL® 490, using 2-4% water as the blowing agent. The effect of water content (blowing agent) and isocyanate index on physical properties of SPP PU foams were studied. The water content significantly affected the foam properties, such as density, thermal conductivity, and compressive strength. The lowest thermal conductivity was obtained at 3% water content and 20% SPP percentage. The compressive strength increased with increasing isocyanate index or isocyanate density.

Water-blown rigid polyurethane foams (SBO PUF) containing 15% soy-polyol were incorporated with different loadings of glass microspheres and nanoclay. The properties, including density, compressive strength, thermal conductivity, foaming temperature and morphology, were characterized. Since filler surface provided nucleation sites for bubble formation, larger volume and thus lower density were obtained in PU foams incorporated with fillers. It was encouraging that at 7% microsphere concentration, SBO PUF displayed the comparable compressive strength to the control foams made from 100% petroleum polyol. With regard to the property of density-compressive strength, the filler did reinforce the cell walls and improved mechanical properties of SBO PUF.

Water-blown rigid polyurethane foams (SBO PU foams) were prepared from petroleum polyol mixed with 0-50% high viscosity (13,000 to 31,000 cP at 22^{o}C) soy-polyols. The compressive strength decreased, decreased and then increased, and remained the same and then increased, when soy-polyol had viscosity of 13,000 cP, 21,000 cP, and 31,000 cP, respectively. These results indicated that the soy-polyol ether bonds could replace the urethane linkage to support the polymer structure. Also, the hydroxyl number of polyols is important to the foam structure in addition to their viscosity. With regard to the isocyanate density-compressive strength, most SBO PU foams displayed comparable or superior value to the control foams. Especially, rigid PU foams could be made from 50% replacement of petroleum polyol and a 30% reduction in isocyanate content. Images from SEM presented that foam cell size decreased and cell number increased with increasing soy-polyol percentage.

Recommendations

1. Reformulate commercial Soy-Polyol based PU foams (SP PU foams)

Commerical Soy-Polyols, especially SP2, SP3, are promising substitutes of petroleum polyol in making water-blown flexible PU foams. Because Soy-Polyols have different chemical structures, hydroxyl numbers, and other properties compared to petroleum polyether polyols, it is recommended to explore new foaming formulation processes in future studies, such as changing the gelling catalyst, blowing catalyst, surfactant and their ratio to improve the performance of SP PU foams.

2. Improve the properties of soy-phosphate polyol (SPP) to expand its applications in PU

By changing reacting conditions, such as the ratio of reactants, SPP could be a mono-ester, di-ester or tri-ester. The di-ester form was selected as the polyol to partially replace the petroleum polyol and make water-blown PU foams because of its hydroxyl number, molecular weight and viscosity. The properties of polyol play an important role in determining physical properties of the PU foams. In future studies, SPP properties should be further improved for different kinds of rigid PU foams.

3. Modify the surface properties of fillers

The natures of fillers play a significant role in modifying PU foam properties. The final foam properties depend on the combined effects of filler characteristics and PU polymer network. In future study, fillers could be treated with hydroxyl groups on the surface, and these hydroxyl groups would participate in the polyol-isocyanate reactions. The properties of PU foams modified with treated fillers should be investigated.

4. Reformulate and modify foaming methods for high viscosity soy-polyols

Soy-polyol with ultra high viscosity is extremely viscous at ambient temperature. Therefore, preheating of soy-polyols is mandatory to thoroughly blend the foaming ingredients. In future study, the foaming formulations and preparing methods for making SBO PU foams need to be improved in accordance with attributes of high viscosity soy-polyols.

VITA

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