Physical Properties of Water-Blown Rigid Polyurethane Foams from Vegetable Oil-Based Polyols

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ABSTRACT: Fifty vegetable oil-based polyols were characterized in terms of their hydroxyl number and their potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications was evaluated. Polyurethane foams were prepared by reacting isocyanates with polyols containing 50% of vegetable oil-based polyols and 50% of petroleum-based polyol and their thermal conductivity, density, and compressive strength were determined. The vegetable oil-based polyols included epoxidized soybean oil reacted with acetol, commercial soybean oil polyols (soyoils), polyols derived from epoxidized soybean oil and diglycerides, etc. Most of the foams made with polyols containing 50% of vegetable oil-based polyols were inferior to foams made from 100% petroleum-based polyol. However, foams made with polyols containing 50% hydroxy soybean oil, epoxidized soybean oil reacted with acetol, and oxidized epoxidized diglyceride of soybean oil not only had superior thermal conductivity, but also better density and compressive strength properties than had foams made from 100% petroleum polyol. Although the epoxidized soybean oil did not have any hydroxyl functional group to react with isocyanate, when used in 50 : 50 blend with the petroleum-based polyol the resulting polyurethane foams had density versus compressive properties similar to polyurethane foams made from 100% petroleum-based polyol. The density and compressive strength of foams were affected by the hydroxyl number of polyols, but the thermal conductivity of foams was not. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 453–459, 2007

Key words: rigid polyurethane foam; renewable resources; physical properties

INTRODUCTION

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

Polyurethanes are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate). The raw materials of typical polyols, using a diol as an example, are ethylene glycol and propylene oxide; both are derived from petroleum, a nonrenewable and dwindling resource. To meet the need of rapidly increasing polyurethane volume and hence polyol consumption, many researchers are actively searching for alternative resources as raw materials for polyols.

Vegetable oils are renewable resources. They are triglycerides and often have at least one unsaturated fatty acid in its chemical structure. By using enzymes or chemicals to modify the unsaturated fatty acid moiety and introduce one or more hydroxyl functional groups, vegetable oils could be converted into polyols.[3] For example, Leitheiser[4] and Ehrilich[5] reported that castor oil can be used to replace the petroleum-based polyol to make polyurethane foams. Lu[6] used waterborne polyurethane made from rapeseed oil-based polyol to modify glycerol-plasticized starch and develop biodegradable films. Chang[7,8] added commercial soy flours into water-blown rigid polyurethane foams to improve the physical properties and lower the cost of these foams. Petrovic and his colleagues[9,10,11] investigated the structure and properties of vegetable oil-based polyols, their applications in polyurethane foams, and the foam's biodegradation behavior and thermal stability. Although many types of vegetable oils have been tested and reported for polyol and polyurethane applications, soybean oil is the most promising one to partially replacing petroleum to make polyols due to its volume and price stability. Many innovative chemical and/or biological approaches

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are possible to convert soybean oil into polyols but not all will result in polyols with adequate functionality to be useful or considered as the B-side component for polyurethane application. The objectives of this study were to characterize various vegetable oil-based polyols, particularly those made with new chemical and/or biological approaches, in terms of their hydroxyl number, and explore their potential of replacing up to 50% of the petroleum-based polyol in waterborne rigid polyurethane foam applications. The replacement potential was evaluated based on three properties that are important for rigid polyurethane foams: density, compressive strength, and thermal conductivity.

MATERIALS AND METHODS

Materials

Voranol® 490 polyether polyol (a petroleum-based polyol with 4.3 alcohol functionality, 460 average molecular weight, and 490 hydroxyl number) and PAPI® 27 (a polymeric diphenylmethane diisocyanate (MDI) with 2.7 NCO functionality, 340 average molecular weight, and 31.4 wt % of NCO content) were obtained from Dow Chemical (Midland, MI). Soybean oil-based polyols (GC5N, P38N, R2-052, and R3-170) were obtained from Urethane Soy System (Volga, SD). Soybean oil and diglyceride soybean oil (ENOVA®) were from ADM (Decatur, IL). Epoxidized soybean oil (Vikoflex® 7170) was supplied by ATOFINA Chemicals (Philadelphia, PA). Castor oil was from Alnor Oil Company (Valley Stream, NY). Catalysts (POLYCAT® 5 and POLYCAT® 8) and a surfactant (Dabco® DC 5357) were from Air Products and Chemicals (Allentown, PA) gratis. Distilled water was used as the blowing agent.

The derivatives of soybean oil, epoxidized soybean oil, and castor oil (Table I) were prepared at Chemical Engineering Department, University of Missouri-Columbia, and briefly described as follows:

1. *DG SBO:* ENOVA® oil contains >80% of diglycerides (DGs) used and designated as diglyceride soybean oil (DG SBO).
2. *Epoxidized DG SBO:* DG SBO was epoxidized using the method developed by Suppes and Dasari.[12]
3. *Oxidized SBO, oxidized DG SBO, and oxidized epoxidized DG SBO:* The starting raw materials (SBO, DG SBO, and epoxidized DG SBO) were oxidized by oxygen bubbling and heating at 100–110°C for 30 h. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng et al.[13]
4. *Blown SBO:* Blown SBO (680 Blown SBO) was from Cargill (Chicago, IL). It contains soybean oil-based oligomers produced by heat polymerization and oxygen oxidation. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng et al.[13]
5. *Bodied soybean oil (BSBO):* To produce bodied soybean oil (BSBO), nonoxidized soy-based oligomers, soybean oil was heated at 330°C for 30–60 min with vigorous stirring in a closed system (no air/oxygen circulation). The process of making BSBO was reported by Erhan et al.[14,15] The bodying process increased viscosity by 23% and reduced the iodine number by 45%. The iodine value and viscosity of BSBO were 67 and 80 cS, respectively.[16]
6. *Epoxidized BSBO:* The method used to prepare epoxidized BSBO was similar to that for epoxidized DG SBO except the staring raw material was BSBO.
7. *Selectively hydrolyzed BSBO:* This polyol was derived from BSBO by enzyme hydrolysis. Lipase from *Candida rugosa* (''Amano'' AY, a gift from Amano Enzyme, Elgin, IL) was used at a loading unit of 1 mg enzyme per g of BSBO and the weight ratio of BSBO to phosphate buffer (pH 7.0) was 1 : 1. The reaction was carried out in a well-mixed reactor at 45°C for 4 h. The lipase selectively hydrolyzed saturated fatty acids, especially palmitic acid from BSBO, and introduced hydroxyl functional groups. Sodium bicarbonate solution (0.5*M*) was used to wash and remove fatty acids from the polyol products after the enzyme hydrolysis.
8. *SBO/acetol and BSBO/acetol:* They were synthesized in a closed, well-mixed reactor. SBO (or BSBO) was mixed with acetol (20 wt %) at

TABLE I
The Derivatives from Soybean Oil, Epoxidized Soybean Oil, and Castor Oil Used in This Study

Raw materials	Derivatives
Soybean oil (SBO)	Diglyceride soybean oil (DG SBO)
	Oxidized DG SBO
	Oxidized epoxidized DG SBO
	Blown SBO
	Oxidized SBO
	Bodied SBO (BSBO)
	Epoxidized BSBO
	Selectively hydrolyzed BSBO
	SBO/acetol
	BSBO/acetol
Epoxidized SBO (ESBO)	Oxidized ESBO
	Hydroxy methoxy SBO
	Hydroxy SBO
	ESBO/acetol
	Selectively hydrolyzed ESBO
Castor oil	DG castor oil
	Oxidized DG castor oil

180°C for 9 h with rigorous agitation to produce SBO/acetol (or BSBO/acetol). The reason to use acetol is that acetol is expected to be an inexpensive material due to high volume of glycerin in the market from the expanding of biodiesel manufacturing.[17] The products were washed by water to remove unreacted acetol and then neutralized.

9. *DG of castor oil:* Diglycerides (DG) of castor oil were produced by transesterification of castor oil triglycerides and glycerol. Sulfuric acid was used as the catalyst at a high temperature (>120°C) in a closed well-mixed reactor.
10. *Oxidized DG castor oil:* To produce oxidized DG castor oil, DG products from the transesterification of castor oil were oxidized for 30 h by heating (100–110°C) and oxygen bubbling. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng et al.[13]
11. *Oxidized ESBO:* It was synthesized by applying heat and oxygen bubbles to ESBO at 100–110°C for 30 h. The oxidation mechanism and the heat-oxidized products from soybean oil were studied and reported by Teng et al.[13]
12. *Hydroxy methoxy SBO:* It was produced via alcoholysis of epoxidized soybean oil (ESBO) by reacting ESBO with methanol using an acid catalyst according to the method of Suppes and Dasari.[12] One epoxy group in ESBO was opened producing one hydroxyl group and one methoxyl group.
13. *Hydroxy SBO:* It was produced by reacting ESBO with water using an acid catalyst according to the methods of Suppes and Dasari.[12] One epoxy group in ESBO was opened producing two hydroxyl groups.
14. *ESBO/acetol:* It was synthesized similarly to the production of SBO/acetol, or BSBO/acetol except ESBO was used instead of SBO or BSBO.
15. *Selectively hydrolyzed ESBO:* It was derived from ESBO by enzyme hydrolysis using lipase from *Burkhloderia cepacia* (a gift from Amano Enzyme) according to the methods of Kiatsimkul, Sutterlin and Suppes.[18] ESBO triglycerides and phosphate buffer pH 7.0 (1 : 1) was mixed with the lipase (67.5 enzyme units per g of ESBO) in a well-mixed reactor at 50°C for 2–4 h. The lipase selectively replaced saturated fatty acid (palmitic and stearic) moieties with hydroxyl functional groups. The product was washed and neutralized by sodium bicarbonate solution (0.5*M*).

Hydroxyl number test

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

TABLE II
Formulations for Water-Blown Rigid Polyurethane Foam

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

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

Experimental design and formulations

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

Foaming procedures

A standard laboratory mixing and pouring procedure for making water-blown polyurethane foams was used.[19] The petroleum polyol (VORANOL® 490), vegetable oil-based polyol, catalysts, surfactant, and blowing agent (B-side materials) were added by weighing into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s. PAPI® 27 (A-side material) was then added rapidly and stirring was continued for another 10–15 s at the same speed. The mixtures were poured immediately into a wooden mold (11.4 × 11.4 × 21.6 cm) with aluminum foil lining and the foam was allowed to rise and set at ambient conditions (23°C). Figure 1 illustrates the foaming procedures.

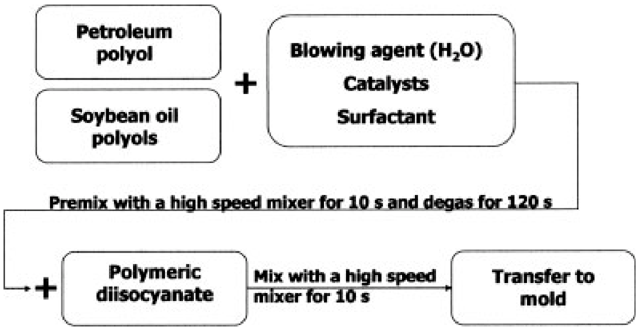

Figure 1 Procedures of preparing polyurethane foams in the laboratory.

Foam properties measurements

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

RESULTS AND DISCUSSION

Hydroxyl number

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

TABLE III
Hydroxyl Numbers of Soybean Oil, Epoxidized Soybean Oil, and Castor Oil Based Polyols

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

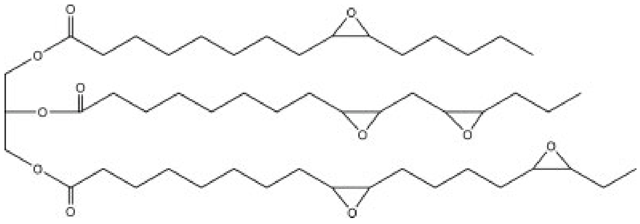

Figure 2 Representative chemical structure of ESBO.

As expected, lower hydroxyl numbers were found for soybean oil and BSBO. On the other hand, some vegetable oil polyols made from epoxidized soybean oil reacted with acetol, diglycerides, and epoxidized soybean oil had a relatively high hydroxyl number. It is interesting to note that even though epoxidized soybean oil does not have the alcohol functional group in its chemical structure as shown in Figure 2, its hydroxyl number of 404 is close to that of Voranol® 490. The hydroxyl number of epoxidized soybean oil was determined by placing the oil in the acidic solution (a mixture of pyridine and acetic anhydride) for 2 to 4 h and then titrated with 0.5N of sodium hydroxide for 30 to 60 s. Further study will be needed to investigate the role of epoxidized soybean oil on polyurethane foaming.

Thermal conductivity

Figure 3 shows the thermal conductivity of the foams that were made with 50 different vegetable oil polyol samples. All samples used a combination of 50% Voranol® 490 and 50% vegetable oil polyol as the polyol component (B-side) for the polyurethane foam, except the first one, which was 100% Voranol® 490

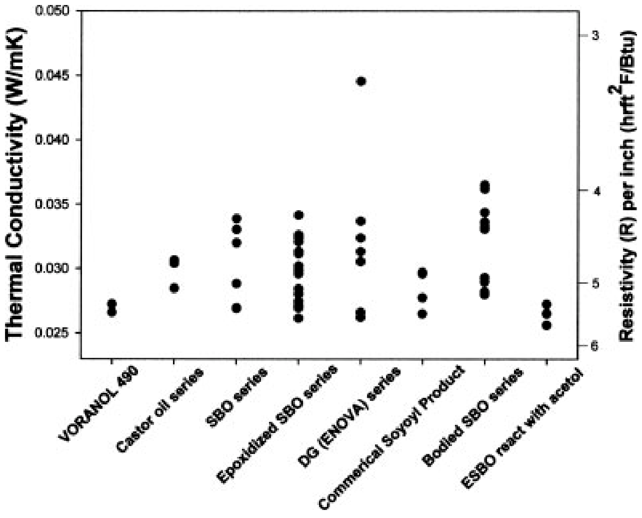

Figure 3 Thermal conductivity of foams made with polyols containing 50% Voranol® 490 and 50% of various vegetable oil-based polyols.

and served as the control for comparison. In addition, 3% of distilled water, based on the amount of polyol, was used as the blowing agent. It is interesting and encouraging to note that some foams made with 50% of epoxidized SBO series polyols, DG (ENOVA) series polyols, commercial soyoils, and ESBO reacted with acetol polyols had a thermal conductivity as low as foams made with 100% Voranol® 490.

Most foams, however, had a thermal conductivity higher than foams made with 100% Voranol® 490. This could be attributed to the slower reaction rate of soybean oil polyols with isocyanate. Unlike Voranol® 490, which has the majority of its functional group (OH group) as primary alcohols, the majority of functional group in soybean oil polyols is secondary. The reaction rate of primary alcohols with isocyanate is about 3.3 times faster than that of secondary ones in the polyurethane reaction.[20] During polyurethane foaming reaction, carbon dioxide is generated by the reaction between water and isocyanate, which is faster than the reaction between the primary hydroxyl group in Voranol® 490 and isocyanate. Since the soybean oil polyols in this study contain only secondary hydroxyl group, they react with isocyanate at a slower rate than do the primary hydroxyl group in Voranol® 490. A slower reaction rate might weaken the three-dimensional network of the polyurethane foam, which is less capable of holding up the pressure of carbon dioxide generated from the polyurethane reaction and cells in polyurethane foam are more open (data not shown). Carbon dioxide contributes to the low thermal conductivity in water-blown rigid polyurethane foam and open cells increases air convection and increases thermal conductivity. Therefore, foams with lower carbon dioxide content and more open cells would have a higher thermal conductivity.

Density and compressive strength

Figure 4 shows the density and compressive strength of polyurethane foams made with 50 different soybean oil polyols. The data shown as solid square symbols are polyurethane foams made with 100% Voranol® 490 with 2–5% of distilled water as the blowing agent. The compressive strength of these foams increased linearly with foam density. This is a commonly observed phenomenon in many cellular foam systems.[21] Increasing the water content, which acted as a blowing agent, expanded the foam volume resulting in thinner foam cell walls and larger foam cells. Therefore, the compressive strength decreased. Similar results have been reported.[22] The data shown on the left side of solid square symbols had inferior density and compressive strength property to foams made with 100% Voranol® 490 while the data on the right side had superior one.

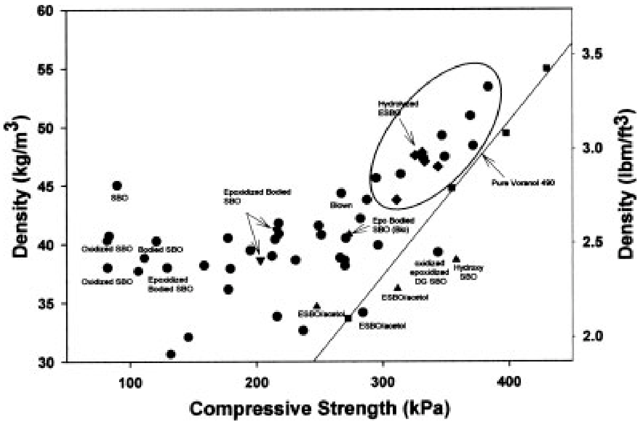

Figure 4 Density versus compressive strength of polyurethane foams made with soybean oil polyols.

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

Some foams had encouraging and better density and compressive strength properties than had foams from 100% Voranol® 490, as shown in Figure 4. These foams were made with 50% replacement of Voranol® 490 by: (1) hydroxy SBO, (2) ESBO/acetol, and (3) oxidized epoxidized DG SBO. Therefore, some derivatives of epoxidized soybean oil and diglyceride show the potential to make high-quality rigid polyurethane foams. Again, additional study is needed to elucidate the reaction chemistry of these new soyoil polyols with isocyanate.

Hydroxyl number effects

Figures 5–7 show the results of thermal conductivity, density, and compressive strength of foams from

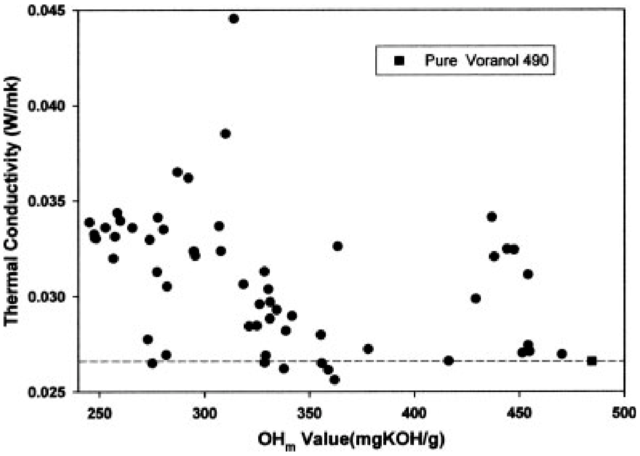

Figure 5 Thermal conductivity of foams versus hydroxyl number of soybean oil polyols.

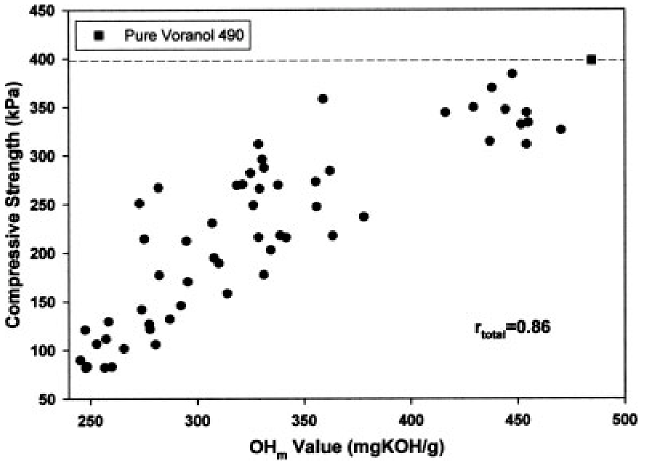

Figure 7 Compressive strength of foams versus hydroxyl number of soybean oil polyols.

polyols with various hydroxyl numbers. Except the control foam which used 100% Voranol® 490, all foams were made with 50% of Voranol® 490 and 50% of vegetable oil-based polyols as the B-side components and 3% water was used as a blowing agent. The OH number of each mixture was calculated as follows:

$$\mathrm{OH}_m = \frac{\text{OH of Voranol}^{\circledR}\ 490 \times 50 + \text{OH of vegetable oil-based polyols} \times 50}{100}$$

where OH$_m$ is the hydroxyl number of polyol mixture, OH of Voranol® 490 = 484.4 mgKOH/g.

Figure 5 shows the relationship between thermal conductivity of foams and the hydroxyl number of polyol mixtures. As shown, the hydroxyl number did not significantly affect the thermal conductivity of foams ($r = -0.46$). This is not surprising since the hydroxyl number alone does not provide information whether the hydroxyl group in polyol mixture is primary or secondary, which has very different reaction rates with isocyanate causing differences in open cell content. The thermal conductivity of foams is contributed by the thermal conductivity of gas trapped in the foam cells, thermal conductivity of foam cell membrane material, convection of cell gas, cell size, cell orientation, closed cell content, foam density, and thermal radiation.[21] While the hydroxyl number of polyol mixtures (OH$_m$) influences the crosslinking density of foams, the convection of gas is mainly governed by the open cell content.

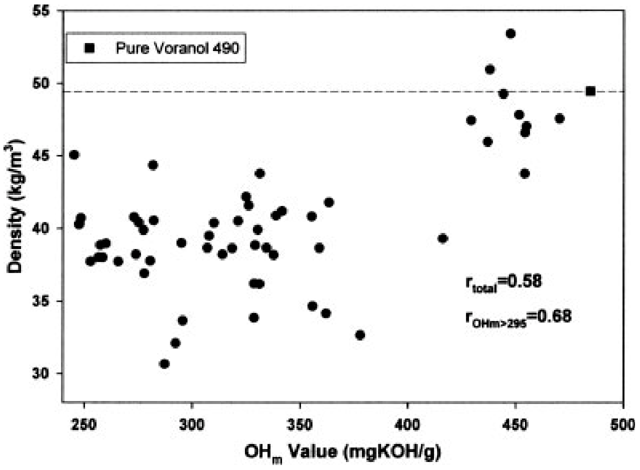

Figure 6 Density of foams versus hydroxyl number of soybean oil polyols.

It is interesting to note that while the majority of foams made with 50% vegetable oil-based polyols and 50% Voranol® 490 had inferior or higher thermal conductivity than had the control foam made with 100% Voranol® 490, some were equal or superior and show the potential for further study. These polyols were: (1) hydroxy SBO, (2) ESBO/acetol, and (3) oxidized epoxidized DG SBO. It is also interesting to note that the foams made with 50% of these three vegetable oil-based polyols and 50% Voranol® 490 also had encouraging and better density and compressive strength properties than foams made from 100% Voranol® 490 as shown in Figure 4.

Figure 6 shows the relationship between density of foams and the hydroxyl number of polyol mixtures. As shown, the hydroxyl number of polyol mixtures seems did not significantly affect density of foams ($r = 0.58$). However, it was noted that foams made from vegetable oil based polyols having hydroxyl number below 100, or polyol mixtures having OH$_m$ lower than 292, usually shrank within a few days of storage at room temperature. The shrinkage reduced the dimensions of foams resulting in higher density of foams (Fig. 6). If these data (having OH_m lower than 292) were ignored, foams made from a higher OH_m number of polyol mixture appeared to have a higher density ($r = 0.68$).

Figure 7 shows the relationship between OH_m number of polyols and compressive strength of foams. It is evident that compression strength of foams increased with increasing OH_m number of polyols ($r = 0.86$). As mentioned previously, a higher OH_m number of polyols will consume more isocyanate causing foams to have a higher crosslinking density of foams. Both higher crosslinking density and higher foam density (Fig. 6) will result in foams with a higher compressive strength.[1] In addition, it should be noted here that density and compressive strength should be used together to compare the foams made from 50% vegetable oil-based polyols and 50% Voranol® 490 against foams made from 100% Voranol® 490 as shown in Figure 4.

CONCLUSIONS

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

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