Functionalization via Glycerol Transesterification of Polymerized Soybean Oil

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ABSTRACT: An acylglycerol-based molecule was synthesized by the thermal polymerization (bodying) of soybean oil followed by transesterification with glycerol. Transesterification with glycerol at temperatures greater than 200°C provided the desired polyol prepolymers. The extent of bodying and quantity of glycerol added during the transesterification provided tunability of the polyol molecular weight and functionality. The hydroxyl numbers, acidity, and viscosity of the polyols were characterized. The polyols were evaluated in elastomers and rigid foams. Extractability analyses were performed on the polyurethane elastomer wafers to evaluate crosslinking. Rigid foaming results for the processed soy-based polyol showed excellent physicochemical properties suggesting comparability with a petroleum-based polyether polyol. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 19–27, 2009

Key words: crosslinking; elastomers; esterification; oligomers; polyurethanes

INTRODUCTION

Polymers derived from plant oils have attracted major commercial interest and significant attention in scientific research because of the availability, biodegradability, and unique properties of triglycerides. Triglycerides rich in unsaturated fatty acids, such as soybean oil (SBO), are particularly susceptible to chemical modification for desired polymeric materials.

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

Higher molecular weight polyols with corresponding higher hydroxyl equivalent weights are desired in polyurethane production because they lead to larger amounts of B-side components in the urethane formulation. Enzymatic approaches that reduce the use of inorganic catalysts, reduce the use of

amounts of organic reagents or co-reagents, and operate at lower temperatures are considered to be more desirable, greener processes. However, the high costs and relatively low operational productivities of the lipases create economic barriers that offset the advantages.

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

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

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

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

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

EXPERIMENTAL

Materials

Voranol 490 polyether polyol (a petroleum-based polyol made from polypropylene oxide and a sucrose/glycerin base with the following properties: an alcohol functionality of 4.3, an average molecular weight of 460, and a hydroxyl number of 490) and PAPI 27 [a polymeric diphenylmethane diisocyanate (MDI) with an NCO functionality of 2.7, an average molecular weight of 340, and an NCO content of 31.4 wt %] were obtained from Dow Chemical (Midland, MI). Vikoflex 7170 epoxidized soybean oil (ESBO) was supplied by Atofina Chemicals (Philadelphia, PA). Glycerol was obtained from Procter & Gamble Co. (Ivorydale, OH). Catalysts (Polycat 5 and Polycat 8) and a surfactant (Dabco DC 5357) were acquired from Air Products and Chemicals (Allentown, PA) gratis. Distilled water was used as the blowing agent. Refined food-grade SBO with an iodine value of 129 mg of I_2/g of SBO and a viscosity of 28 cP (at 40°C) was obtained from a local wholesaler.

BSBO was synthesized to provide an intermediate that could be further reacted with glycerol to increase the hydroxyl content. BSBO was prepared by the heat polymerization of SBO in batch and continuous processes as described in the Methods section. A gel permeation chromatography analysis of the BSBO intermediate revealed the following com-

ponents by weight: 57.23% oligomer, 34.68% monomer, and 8.09% free fatty acids (with an average molecular weight of 2422 g/mol; SBO has an average molecular weight of 948 g/mol).

Methods

Hydroxyl values of polyols were determined according to American Society for Testing Materials (ASTM) Procedure E222-00, Method A (reapproved in 2005).[7] Acid numbers (mg of KOH/g of sample) of all reaction products were evaluated according to the official American Oil Chemists' Society (AOCS) method (AOCS Te 1a-64).[8] Iodine values (mg of I_2/g of sample) of the polyol samples were determined with ASTM D 1959-97.[9] Epoxy contents of the samples were measured according to the official AOCS method (AOCS Cd 9-57).[10] The dynamic viscosities (cP) of the samples, measured at 200°C, were determined with a model RS100 rheometer (Haake-Thermoelectron, Newington, NH).

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

A Fox 200 heat flow meter instrument (Laser-Comp, Wakefield, MA) was used to measure the thermal conductivity of the PUs according to ASTM Procedure C 518-04.[11] The densities of the foam samples were determined according to ASTM Procedure D 1622-03.[12] Compressive strengths of foam samples were measured with a TA-HDI texture analyzer (Texture Technologies, Scarsdale, NY) according to ASTM Procedure D 1621-04a.[13] Thermal conductivity measurements were performed after the curing of the foams for 24 h, whereas the density and compressive strength measurements were performed after 7 days of sample storage.

Heat polymerization of SBO

The thermal polymerization of SBO was carried out with batch and continuous processes. The batch process was performed in a Parr model 4526 2-L benchtop stirred vessel. About 1500 g of refined SBO was heated in a closed Parr reactor vessel for 6 h at
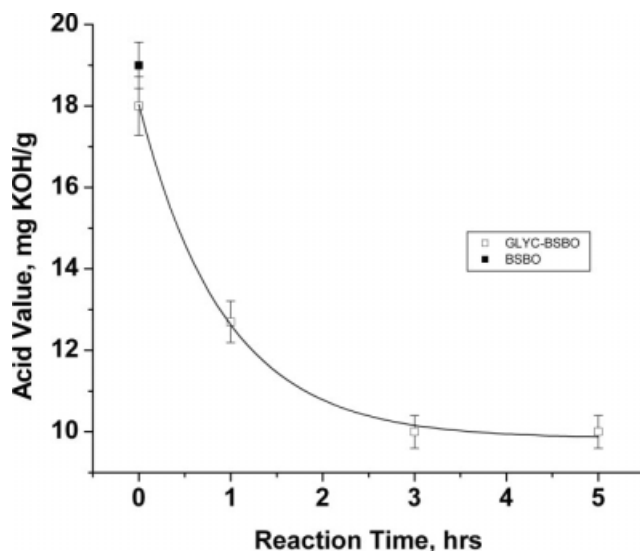
Figure 1 Effect of the reaction time on the polyol acid number for the reaction of BSBO with 5% glycerol at 225°C. The control BSBO (batch-processed) had the following chemical properties: an acid number of 19.0 mg of KOH/g of polyol, a hydroxyl value of 13.2 mg of KOH/g of polyol, and a viscosity of 200 cP.

260°C with constant stirring. A convection oven was used in single-pass continuous bodying of SBO with a flow rate of about 0.32 mL/min at 355°C. The downstream product was cooled below 30°C by direct water cooling of the discharge tube before product collection in an open vessel. The final collected BSBO was mixed well to ensure uniform chemical properties. Decreases in iodine values and increases in viscosities of the batch-processed and continuously processed SBOs were observed. The actual measured values were as follows: for batch-processed SBO, an iodine value of 107 and a viscosity of 200, and for continuously processed SBO, an iodine value of 96.6 and a viscosity of 438. The mechanism has been explained elsewhere.[1]

Synthesis of glycerol-transesterified bodied soybean oil (GLYC–BSBO)

Glycerol transesterification of BSBO for polyurethane production was conducted in a Parr model 4526 2-L bench-top stirred vessel, whereas transesterification of BSBO for a kinetic study was performed in a smaller Parr model 4561 300-mL bench-top stirred vessel. About 1500 g of BSBO was poured into the Parr reactor vessel. Pure glycerol was added to the same vessel in various quantities ranging from 5 to 10 wt % with respect to BSBO. The mixture reacted in a closed Parr vessel with constant stirring in a temperature range of 200–225°C for reaction times of 1–5 h. Kinetic studies were performed on the samples to evaluate the effects of the glycerol concentra-

tion and reaction conditions on the chemical properties of the products.

Polyurethane formation

A foaming procedure described by Tu et al.[14] was used in this study. The Voranol 490, SBO-based polyol, catalysts, surfactant, and blowing agent were added by weighing into a 500-mL disposable plastic cup and mixed at 3450 rpm for 10–15 s. The mixture was allowed to degas for 120 s, and then PAPI 27 was rapidly added with continuous stirring for another 10–15 s at the same speed. The mixture was poured immediately into a wooden mold (11.4 × 11.4 × 21.6 cm³) with aluminum foil lining, and the foam was allowed to rise and set under ambient conditions (23°C).

RESULTS AND DISCUSSION

Effect of the reaction time

Soy-based polyols were prepared by bodying of SBO and then transesterification of BSBO with glycerol. Figures 1 and 2 summarize the dynamics of the transesterification of BSBO with 5% glycerol. The viscosity increased during the 5-h reaction time, approaching asymptotic values at 5 h; this is consistent with crosslinking, which is promoted with the trifunctional glycerol.

During the SBO bodying reaction, the acidity increased such that the resulting BSBO reagent acidity was 19 mg of KOH/g of sample. The acidity decreased rapidly during glycerol transesterification, with a nearly constant value of about 10 obtained at 5 h (see Fig. 1). These trends are consistent with the
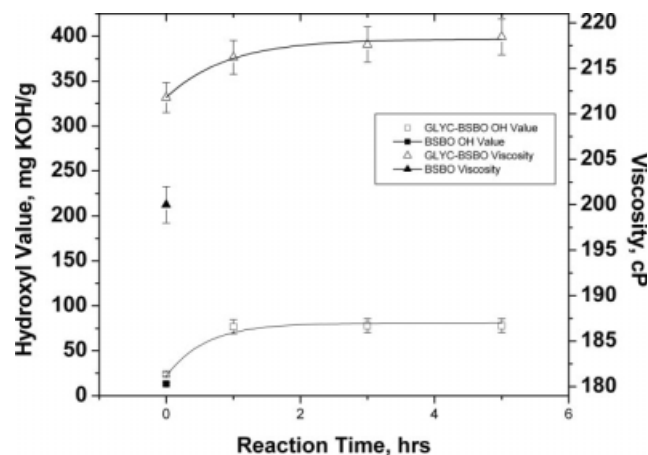

Figure 2 Effect of the reaction time on the polyol hydroxyl value and viscosity for the reaction of BSBO with 5% glycerol at 225°C. The control BSBO (batch-processed) had the following chemical properties: an acid number of 19.0 mg of KOH/g of polyol, a hydroxyl value of 13.2 mg of KOH/g of polyol, and a viscosity of 200 cP.
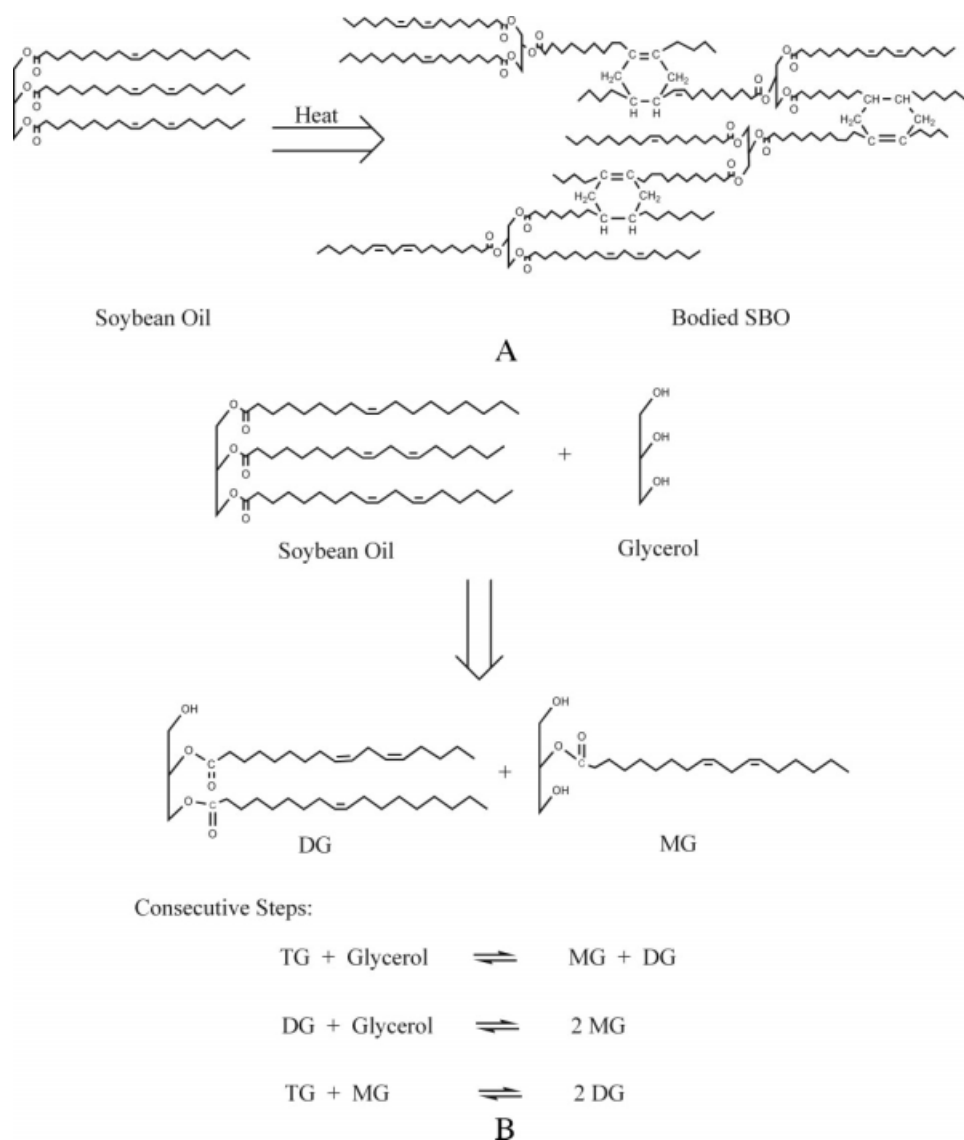
Figure 3 Reaction schemes for the hydroxylation process of BSBO: (A) unreacted SBO is polymerized to BSBO and (B) SBO and glycerol react to form acylglycerols of SBO [monoglycerides (MG), diglycerides (DG), and triglycerides (TG)].

glycerol alcohol moieties esterifying with the acid moieties and thereby reducing the acid number. Low acidity in polyols is important because high-acid-number polyols tend to neutralize the urethane formulation catalysts.

The hydroxyl groups were introduced primarily by the glycerol reagent to the mixture. Consequently, the hydroxyl number remained essentially constant throughout the reaction, as shown in Figure 2. The primary reaction having an impact on the hydroxyl content was esterification with acid in the solution. The amount of alcohol moieties lost by the reaction with the acids had a negligible impact on the hydroxyl number. Starting with the same BSBO as the control (hydroxyl value = 13.2 mg of KOH/g, viscosity = 200 cP), transesterification with 5% glycerol produced a polyol with a hydroxyl value of 78 and a viscosity of about 400 after a 5-h reaction time.

A study by Erhan et al.[5] confirmed through gas chromatography/mass spectroscopy analysis of volatile byproducts (from bodying of SBO) that the more reactive linolenic and linoleic acids are consumed at an early stage of the bodying process to produce the polymeric materials. This was evident from the decrease in the iodine value (from 129 to 107) and increase in the viscosity (from 29 to 200) of SBO after the bodying process.

The three reactions shown in Figures 3 and 4 are possible when glycerol is reacted with BSBO at 225°C. They include (1) further polymerization of unreacted SBO triglycerides to BSBO, (2) formation of SBO monoglycerides and diglycerides, and (3) transesterification of BSBO to GLYC–BSBO. The
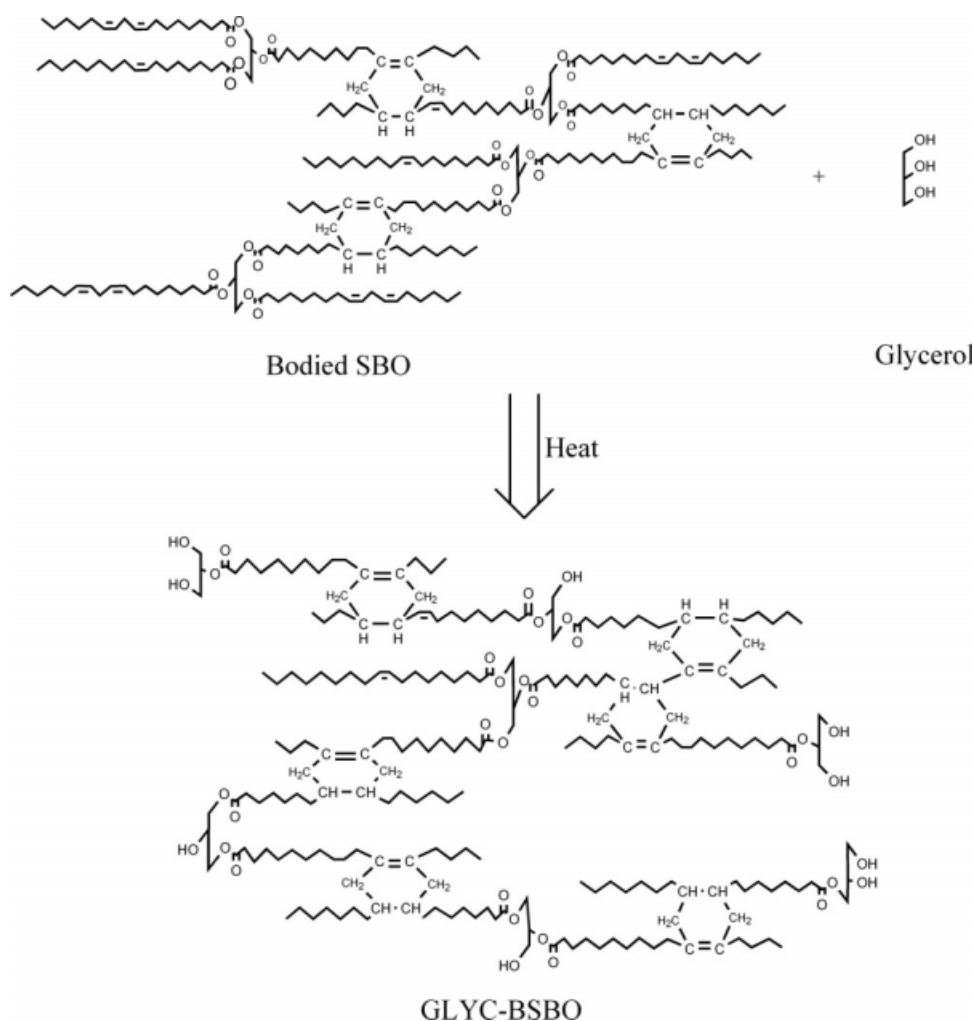
Figure 4 Major reaction in the hydroxylation process in which BSBO and glycerol react to form GLYC–BSBO.

latter is assumed to be the dominant, but not sole, reaction when the amount of moisture (water) is negligible.

The free fatty acids in BSBO will react with glycerol to form acylglycerols, as illustrated in Figure 3(B). This is an important reaction as it results in a product with two functional alcohols, which react with isocyanates to propagate a urethane reaction. Residual triglyceride and diglyceride in BSBO would be converted to similar acylglycerols. Trace amounts of diglyceride and triglyceride would be expected with the reaction products.[15]

A number of factors can contribute to the formation of free fatty acids in the bodying process of SBO. The presence of moisture in the reaction mixture would yield free fatty acids by triglyceride hydrolysis.[16] Fatty acids with no olefin groups could also incorporate into the end product as they can easily volatilize at high bodying temperatures.[5] The presence of water would lead to an esterification equilibrium of fatty acids balanced with water and glycerides.[17] The decrease and eventual plateau in the acid number value of the polyol in Figure 1 may be indicative of residual water content; however, this is unlikely. The residual acid was present in the batch and flow reactor BSBO product. In the batch reactor product, the combination of a nitrogen purge and temperatures in excess of 300°C would drive off essentially all water.

The major reaction in the glycerol transesterification process is the reaction between BSBO and glycerol, which is shown in Figure 4. BSBO is a macromolecule of polymerized SBO with a moderate molecular weight, and it can be readily cleaved by glycerol at the ends of its branches. Because BSBO has a higher molecular weight than SBO, it requires less glycerol per mole to achieve a given average functionality.

For every mole of glycerol reacting with a glyceride, the concentration of alcohol moieties in solution remains the same. This explains the nearly constant hydroxyl value as a function of the reaction time, as illustrated in Figure 2. An alcohol moiety on a triglyceride is known to increase the viscosity (e.g.,

TABLE I
Polyol Product Synthesis Details for Polyurethane Production

Polyol	Description	Unreacted oil phase (%)
Voranol 490	Commercial	0.38
GLY10	10 wt % glycerol in BSBO and heat-processed at 220°C/2 h, Parr	0.77
BSBO	Heat treatment of SBO at 355°C, continuous-flow process at 0.32 mL/min	4.92
ESBO	Commercial	17.78
SBO	SBO	~ 100
SBOGLY10	SBO and 10% glycerol, 220°C/2 h	Does not set
GLY5–BO	GLY5 (below) neutralized with a stoichiometric amount of 1,2-butylene oxide at 170°C/2 h, Parr	5.20
GLY10–BO	GLY10 neutralized with a stoichiometric amount of 1,2-butylene oxide at 170°C/2 h, Parr	1.77
GLY10–ESBO	GLY10 neutralized with a stoichiometric amount of ESBO at 170°C/1 h, N_2 flowing	0.81
GLY10–KOH	GLY10 with 1% KOH, 225°C/5 h, Parr	1.90
SBOGLY5[a]	SBO (57 cP) and 5% glycerol, 220°C/2 h	Does not set
GLY5a[a]	BSBO (384 cP) and 5% glycerol, 220°C/2 h	4.70
GLY5b[a]	BSBO (438 cP) and 5% glycerol, 220°C/2 h	4.58
GLY5c[a]	BSBO (451 cP) and 5% glycerol, 220°C/2 h	4.40
GLY5d[a]	BSBO (510 cP) and 5% glycerol, 220°C/2 h	4.10
GLY5e[a]	BSBO (984 cP) and 5% glycerol, 220°C/2 h	3.42
GLY5f[a]	BSBO (3936 cP) and 5% glycerol, 220°C/2 h	3.05

The different extractability values are expressed as the percentage of the unreacted oil phase of the synthesized soy polyols and controls.

[a] With starting BSBOs of various viscosities (Fig. 6).

castor oil vs SBO). The viscosity trend in Figure 2 reflects an increase in the viscosity due to the alcohol functionality. The leveling-off of the viscosity after the first hour could reflect nearly complete transesterification at 1 h.

Preliminary crosslinking test on GLYC–BSBO

The reactivities of GLYC–BSBO products were evaluated through the reaction of GLYC–BSBO with polymeric MDI followed by an extraction test to determine the percentage of the unreacted oil phase, as described in the Methods section. The extraction tests are summarized in Table I, with a graphical comparison of the different product categories shown in Figure 5. Low extractability is believed to correlate with high crosslinking, whereas high extractability is believed to correlate with the presence of nonfunctional or single-functional components in the B-side (alcohol side) of the urethane formulation.

According to Figure 5, the crosslinking of GLY10 (synthesis and property details are shown in Tables I and II, respectively, and extraction result details are shown in Table I) is greater than that of GLY5. In view of the amount of fatty acid groups in BSBO, 5% glycerol is apparently not adequate to ensure that most of the molecules have at least two functional alcohol groups.

A series of controls were run to evaluate the crosslinking performance of the GLYC–BSBO polyols. Petroleum-based Voranol 490 achieved the highest

reactivity with polymeric MDI on the basis of its 0.38% unreacted oil phase. Its crosslinking performance reflects its high hydroxyl functionality and ordered polymeric structure.

ESBO exhibited the lowest crosslinking (of the systems that set to polymers) with a 17.8% unreacted oil phase. Depending on the means of evaluating the hydroxyl value, each epoxy group in ESBO can register as two alcohol groups corresponding to the cleavage of the epoxy group with water to yield a
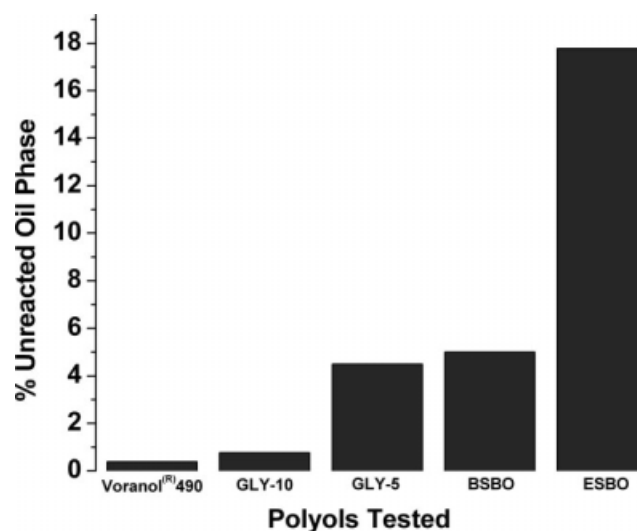

Figure 5 Preliminary crosslinking test results presented as the percentage of the unreacted oil phase recovered after organic solvent extraction. The extractability of GLY5 and GLY10 is shown in comparison with controls.

TABLE II
Chemical Properties of the Polyols Used in the Preparation of the Polyurethanes

Polyol	Acid number (mg of KOH/g)	Viscosity (cP at 22°C)	Hydroxyl number (mg of KOH/g)	Epoxy content (%)
Voranol 490	<1.0	11,239.4	484.4	<0.10
ESBO	<1.0	362.1	403.8	6.1
BSBO	30.4	438.0	16.0	<0.10
GLY5	2.1	732	91.1	<0.10
GLY10	1.4	2,000 (gelled)	162.2	<0.10
GLY5–BO	2.5	732.4	91.2	0.10
GLY10–BO	1.4	997.1	163.0	0.13
GLY10–ESBO	1.6	1,664	90.3	<0.10
GLY10–KOH	8.0	2,791 (gelled)	153.4	<0.10

diol. The fact that the epoxy polymerizes is an interesting artifact of these results. When SBO is used as the B-side in the wafers used for extraction tests, the system does not set (100% extractability).

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

When BSBO is transesterified with glycerol, alcohol functionality is imparted, and some of the acids are reacted into esters. A decrease of about 7% in the extracted oil phase was observed when BSBO was further processed by the addition of 5% glycerol. The 5% glycerol increased the hydroxyl value of BSBO by about 80%. The addition of 10% glycerol to BSBO enhanced its hydroxyl value by 90% and further decreased the extracted oil phase.

In theory, an increase in bodying would increase the hydroxyl equivalent weights at the same hydroxyl number, and this should decrease the extracted oil phase of the test wafers. To evaluate this, SBO and BSBO with various degrees of oligomerization (viscosity) were evaluated after transesterification with 5% glycerol.

Figure 6 illustrates the correlation between the percentage of the unreacted oil phase and the viscosity of the starting BSBO used to prepare the GLY5 polyol. As expected, higher degrees of oligomerization result in a reduced unreacted oil phase. Better crosslinking performance is related to higher hydroxyl equivalent weights of the soy polyols (at the same hydroxyl number), which can be achieved primarily by initial bodying of the SBO and the addition of glycerol to increase alcohol functional groups. This clearly illustrates that the primary goal of the bodying process is achieved: a higher molecular weight monomer is produced.

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

Properties of polyurethanes based on GLYC–BSBO polyols

Rigid foams were prepared with the GLYC–BSBO polyols and several controls as summarized in Table I. Properties of resulting polyurethane foams are shown in Table III. In each case, 50% by mass of the B-side was the indicated polyol, and 50% was Voranol 490. Figure 7 summarizes the foaming performances graphically, and the traditional trade-off in compressive strength versus density can be observed. The line indicates the Voranol 490 that was created by the variation of the water content (2.5–4.5% water as a blowing agent) in the formulation.

The BSBO control was inferior to the other polyols. The very low hydroxyl functionality (16) created
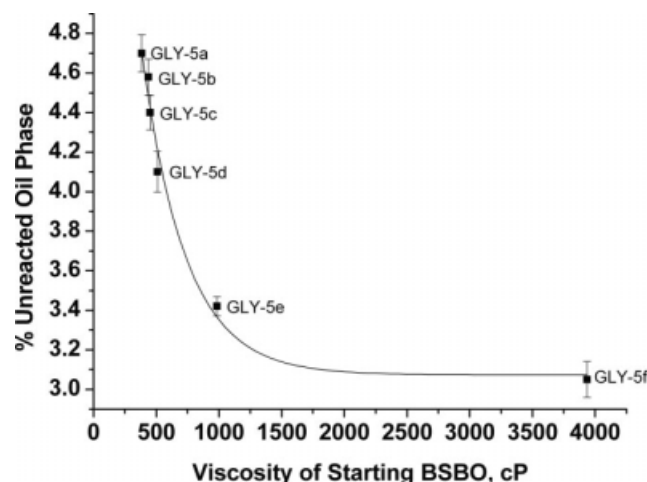

Figure 6 Effect of the viscosity of the starting BSBO on the extractability of the final GLY5 polyol.

a poorly crosslinked foam with a very low compressive strength.

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

The remaining five soy-based polyols (GLY5, GLY10, GLY10–BO, GLY10–ESBO, and GLY10–KOH) exhibited similar behavior when the dependence of the rigid foam density on the urethane-formulation water content was taken into account. The products exhibited a decrease in the compression strength of about 17%. In some applications, the lower compression strengths are acceptable. The advantage of these products is that they can be synthesized with a nearly 100% yield from relatively inexpensive renewable materials in a relatively simple process.

A comparison of the GLY10 product with GLY10–BO reveals that only minor changes in physical properties occurred when butylene oxide was used to neutralize residual acidity. Both samples eventually gelled, and they had similar viscosities before gelling. Butylene oxide is believed to slow down the reactivity of the alcohol groups (it converts primary alcohols into secondary alcohols), and this results in higher densities. In the case of GLY10–BO versus GLY5–BO, the higher glycerol content of the GLY10–BO product could have provided enough added functionality to maintain crosslinking at a level consistent with the better of the other products.
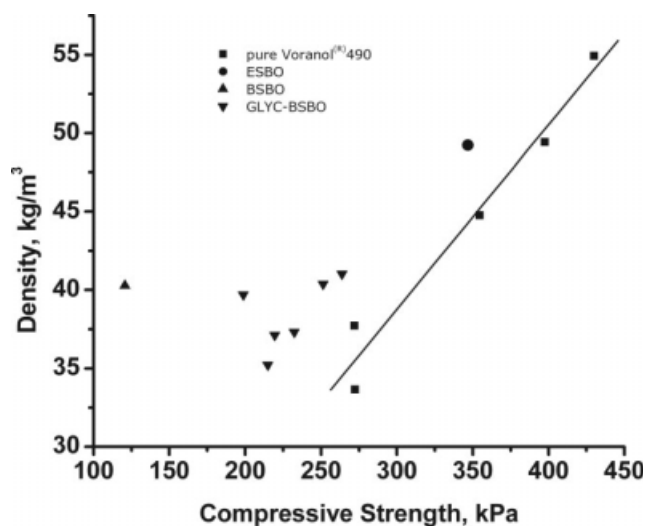
TABLE III
Properties of the Polyurethane Products Obtained from the Synthesized Soy-Based Polyols

Polyol	Thermal conductivity (W/mK)	Density (kg/m^3)	Compressive strength (kPa)
Voranol 490	0.02660	49.44	397.59
ESBO	0.03247	49.25	346.89
BSBO	0.03326	40.27	120.74
GLY5	0.02930	37.11	219.46
GLY10	0.02820	37.31	232.47
GLY5–BO	0.02805	39.70	198.80
GLY10–BO	0.02955	41.02	263.83
GLY10–ESBO	0.02665	40.38	251.43
GLY10–KOH	0.03058	35.23	214.95

Three percent water was used as the blowing agent.

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

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

From best to worst thermal conductivity, the GLY10–ESBO and Voranol 490 control had similarly good thermal conductivities. The GLY10 product also had good thermal conductivity with acceptable combinations of density and compressive strength. Good thermal conductivity appeared to correlate with the molecules having the highest average functionality. In the complex gelling and blowing reactions of the rigid foaming process, an early high degree of crosslinking is critical to keep the foam cells closed (this leads to low thermal conductivities).

CONCLUSIONS

Polyurethanes made from the transesterification of glycerol with BSBO exhibited good physicochemical properties. The better attainable performances were comparable to those of petroleum-based Voranol 490, except for an 18% reduction in compressive strength. The advantages of a GLYC–BSBO polyol series include (1) simple nonhazardous processing to

Figure 7 Properties of soy polyol foams versus a control (pure Voranol 490) with various quantities of water as the blowing agent (2.5, 3.0, 3.5, 4.0, and 4.5%).

form polyols, (2) yields of polyols approaching 100%, and (3) feedstock costs that are considerably less than those of the propylene oxide and butylene oxide used to prepare petroleum-based polyols.

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

In comparison with the synthesis and use of monoglycerides in rigid foams, 10% BSBO materials require less glycerol (10 vs 30%) and have the potential for attaining functionalities in excess of 2. It has been noted that free fatty acids formed during the preparation of BSBO, and so some monoglycerides were in most of the formulations evaluated in this study. A reduction in the free fatty acid content of BSBO should lead to improved performances.

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

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