J Mater Sci (2006) 41:4914–4920
DOI 10.1007/s10853-006-0310-6

Structure–property relationships in polyurethanes derived from soybean oil

Andrew Guo · Wei Zhang · Zoran S. Petrovic

Received: 19 September 2005 / Accepted: 31 October 2005 / Published online: 27 May 2006

Abstract Two types of soy polyols have been prepared, one with secondary OH groups resulted from epoxidation of soybean oil followed by methanolysis (polyol type I) and the other with primary OH groups created from hydroformylation of soybean oil followed by hydrogenation (polyol type II). Cast polyurethane resins were prepared from these two types of polyols with Isonate 2143L, and rigid polyurethane foams were prepared from a blend of soy polyol and glycerol with PAPI 2901. Polyol II is much more reactive than polyol I towards polyurethane formation. This is evidenced from studies on polyurethane gel-times, glass transitions and rigid foam mechanical strengths. The reaction for the polyurethane formation is more complete for polyol II resulted from its higher reactivity than polyol I, although a less rigid polyurethane material is resulted from polyol II than from polyol I. Polyol type II also requires lower amounts of catalysts for rigid foam formulation. Both rigid foam systems produce foams having the required mechanical strength. The polyol II foam system behaves much like conventional rigid foam systems where the strength are proportional to system OH content, while the less reactive polyol I system does not.

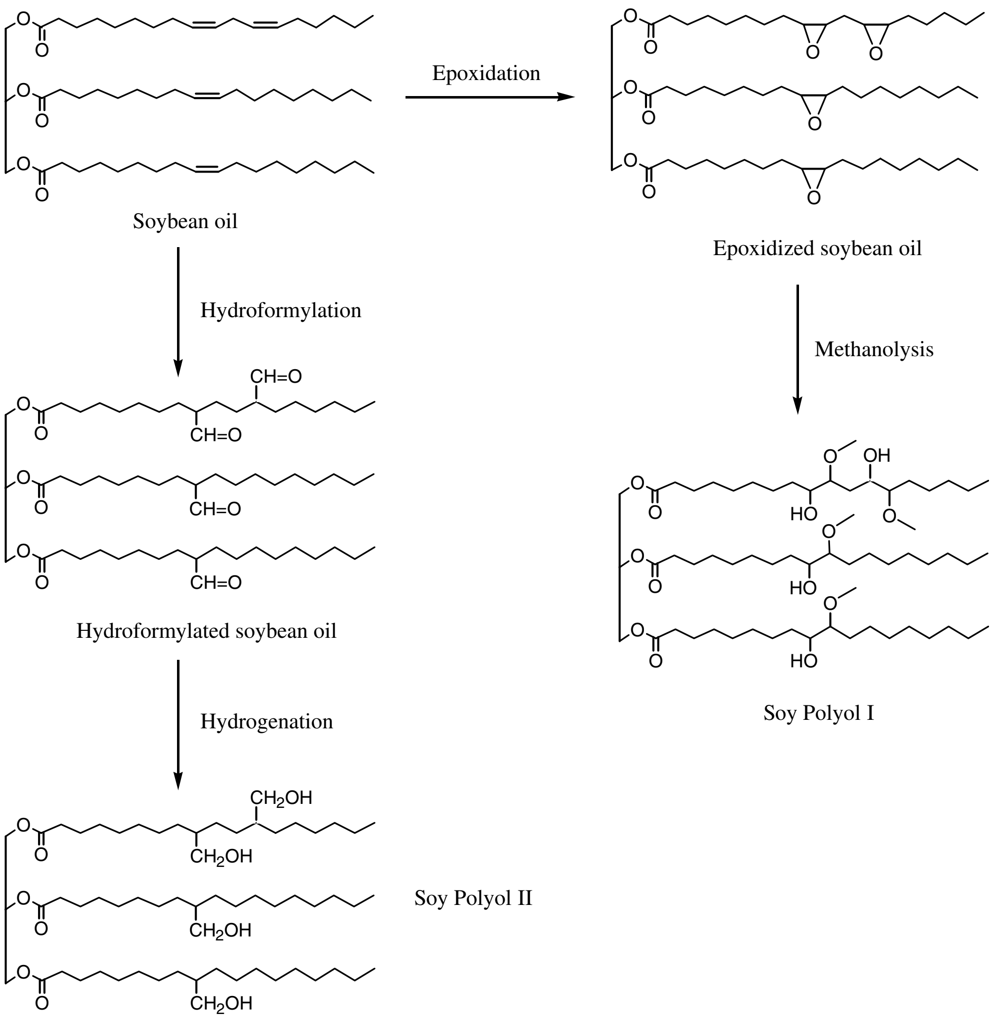
Introduction

Polyurethane materials created from vegetable oils such as cast resins and rigid foams has been in exist for some time [1–6]. Regarding soybean oil, polyols with secondary as well as primary OH groups are known. For example, polyols with primary OH groups have been reported by Frankel [7, 8]. Some rigid foam systems based on such polyols and a number of crosslinkers have also appeared in the literature [9, 10]. However, a comparison between the properties of the polyurethane materials created from polyols having different structures or having different types of OH groups has been lacking. This report constitutes our continuation on the studies of structure–property relationships in polyurethanes based on vegetable oils [11, 12].

The goal of this study is to compare the performance of two types of polyols: one prepared from epoxidation of soybean oil followed by methanolysis (polyol type I) and the other prepared from hydroformylation of soybean oil followed by hydrogenation (polyol type II). These transformations have been outlined in Scheme 1, where the structures of all the molecules have been idealized (a typical soybean oil molecule of North America origin contains 11% of palmitic, 4% of stearic, 23% of oleic, 54% of linoleic, and 8% of linolenic acid, plus some minor fatty acids, which gives rise to an average double-bond functionality of 4.4). Since the former polyol contains secondary hydroxy groups while the latter contains primary hydroxy groups in the molecule, polyol II is expected to be much more reactive than polyol I towards polyurethane formation. Polyol II has also been introduced one additional carbon atom to the crosslinking loop after hydroformylation, while polyol I bears methoxy groups as side-chains. Therefore the polyurethane materials prepared from these two types of polyols

---

A. Guo (✉) · W. Zhang · Z. S. Petrovic
Kansas Polymer Research Center, Pittsburg State University,
1501 S. Joplin Street, Pittsburg, KS 66762-7560, USA
e-mail: aguo@pittstate.edu



Scheme 1

may exhibit different physical and mechanical properties coming from these origins.

Experimental procedures

Soybean oil (RBD, IV = 130) was supplied by Riceland Foods, Inc. (Stuttgart, AR). Rhodium dicarbonyl acetylacetonate was purchased from Johnson Matthey (Ward Hill, MA). Syngas (1:1 CO/H_2, certified), hydrogen gas (USP zero), DBTDL (dibutyltin dilaurate) T-12 and DABCO^{TM} DMEA (a mixture of 1,4-diazabicyclo[2,2,2]octane with dimethylethylamine) were from Air Products (Allentown, PA). Triphenylphosphine and Raney nickel (50% slurry in water) were from Strem (Newburyport, MA). Hydroxyl number reagent (a mixture of phthalic anhydride and imidazole in pyridine), and deuterated chloroform $CDCl_3$ were purchased from Aldrich (Milwaukee, WI). Sodium hydroxide (1.000 N) and isopropanol (laboratory grade) were purchased from Fisher (Pittsburgh, PA). Isonate 2143L (NCO functionality of 2.1, 29.0% NCO) and PAPI 2901 (NCO functionality of 2.3, 31.6% NCO) were from Dow Chemicals (Midland, MI). Surfactant B-8401 was from Goldschmidt (Hopewell, VA). Genetron 141b was from Allied Signals (Morristown, NJ). Glycerol was from HUMCO (USP 99.5%, Texarkana, TX). All chemicals were used as received.

The Infrared spectra were recorded on a Perkin-Elmer Spectrum-1000 FT-IR spectrometer. Samples were prepared as thin liquid films on KBr or NaCl salt plate. The GPC chromatograms were acquired on a Waters model 510 pump system equipped with a model 410 differential refractometer using THF as the eluent operating at 1.00 ml/min at room temperature (ca. 23°C). Three Styragel HR columns from Waters covering a molecular weight range of 10^2–10^6 Da were used and calibrated using five polystyrene narrow standards from BF Goodrich (Richfield, Ohio). Molecular weights and molecular weight distributions for the polyols were calculated using the Millennium 2010 software from Waters and were reported as polystyrene-equivalent values. The polyol viscosities and polyurethane gel-times were measured on a Rheometrics model SR-500 Dynamic Stress Rheometer between two parallel plates of 25 mm in diameter having a gap of 1 mm. The hydroxyl values of polyols were determined following a modified ASTM titration method D 1957-86 (Reapproved 1990) using a hydroxyl number reagent from Aldrich and sodium hydroxide as the titrant [13]. Isopropanol was also used as the co-solvent for all titrations. DSC was measured on a TA Instruments model 2910 differential scanning calorimeter. The apparent densities of the foams were measured according to ASTM D1622-93 procedures. Compressive strengths of the foams were measured according to ASTM D1621-94 on a Q-Test II tensile tester using a custom-made fixture. For easy comparison, the strength for all foams has been normalized to 30 kg/m^3 since it is found that for our soy foam systems compressive strength linearly increases with density in the range of 20–40 kg/m^3 and carries a slope of approximately 9.0 kPa per kg/m^3 [9].

Preparation of soy polyol type I

The procedure for the preparation of soy polyol type I has been reported previously [6, 9].

Preparation of soy polyol type II

Soybean oil (100 g, 0.512 mol of double bond), rhodium dicarbonyl acetylacetonate (0.129 g, 5×10^{-4} mol), and triphenylphosphine (0.660 g, 2.5×10^{-3} mol) were charged sequentially into a Teflon-lined 500-ml reactor. The reactor was flushed three times with syngas at ca. 1.0 MPa, and then pressurized to 13.4 MPa with the same gas. The reactor was heated to 90 °C in 25 min by which time the pressure increased to 15.0 MPa. The content of the reactor was stirred for 2 h at 90 °C maintaining a pressure of 13.3 MPa and a stirring rate of 1,000 rpm, and an additional hour at 110 °C maintaining a pressure of 13.8 MPa. The reactor was cooled to 60–70 °C. After the release of the pressure, it was flushed three times with hydrogen gas at ca. 1.0 MPa and then pressurized to 3.4 MPa with the same gas. It was heated to 130 °C for 30 min to deactivate the catalyst and then cooled to 30 °C. After the release of the pressure, the reactor was opened and Raney nickel (9 g) and isopropanol (50 ml) were charged into the reactor. The reactor was again flushed three times with hydrogen gas at ca. 1.0 MPa and then pressurized to 4.1 MPa with the same gas. The hydrogenation reaction was maintained at 110 °C, 2.8–5.5 MPa of H_2 pressure and 1,000 rpm of stirring rate for 5.5 h. The reactor was cooled to room temperature and the pressure was released. The content was filtered through Celite® and the solvent was removed on a Rotavapor® followed by high vacuum. A brown oily liquid was obtained in 107 g yield (93%) which has an OH number of 228 mg KOH/g (conversion of 92%) and a viscosity of 14.2 Pa s at 23 °C. GPC showed the following polystyrene-equivalent molecular weight: Mp = 1,000, Mn = 440, Mw = 820, and Mw/Mn = 1.8. Samples were taken at different stages of the reactions. After hydroformylation, FT-IR indicated the disappearance of carbon–carbon double bond band at 3,011 cm^{-1}, and the emerging of the aldehyde band at 2,701 cm^{-1} (broad, weak) and 1,728 cm^{-1} (shoulder, strong). These bands disappeared after hydrogenation and the broad hydroxyl band emerged at 3,362 cm^{-1}.

A typical proton NMR spectrum of polyol type II is shown in Fig. 1. The NMR measurement was made on a Bruker DPX-300 NMR spectrometer using $CDCl_3$ as the solvent with 0.03% TMS as the internal standard. The peak assignments are as follows: δ5.27 (m, 1H); δ4.30 (m, 2H); δ4.15 (m, 2H); δ3.54 (d, 2H); δ2.32 (t, 6H); δ1.62 (m, 6H); δ1.46 (m, 3H); δ1.29 (m, 60H); δ1.26 (m, 16H); δ0.89 (t, 9H).

Polyurethane casting procedures

For polyol type I, the polyol and Isonate were mixed at ca. 50 °C. The mixture was then poured into a 100 × 100 × 1 mm mold and vacuumed. Final curing of the material was accomplished by keeping it in a forced-air oven at 110 °C overnight. For polyol type II, the mixing is done at room temperature (21–25 °C), and both mixing and vacuuming time were shortened accordingly to avoid gelling.

Rigid polyurethane foam preparation procedures

The procedure for the preparation of rigid polyurethane foams based on soy polyols has been reported previously [9].

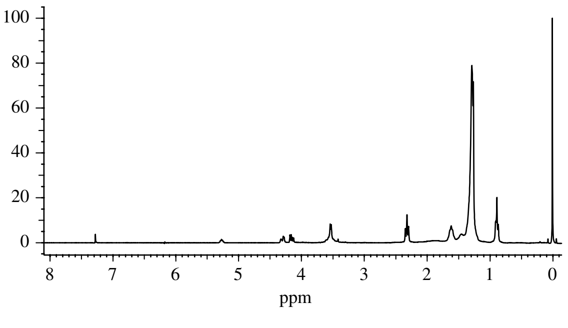


Fig. 1 A typical proton NMR spectrum of polyol type II

Results and discussion

Cast polyurethane resins

We have prepared four cast polyurethane resins for each type of polyol by reacting it with Isonate 2143L and compared the glass transition temperatures (Tg), the results of which is presented in Fig. 2. Since Tg is a measure of rigidity for plastics, cast resins created from Polyol II are less rigid than those prepared from polyol I. This lower rigidity is presumably attributed to the larger crosslinking loop originated from the one additional carbon introduced during hydroformylation. Both curves tend to plateau out at a polyol hydroxyl functionality of 3.8–4.0 (i.e., the number of OH groups per triglyceride molecule), and below this range both polyurethane materials suffers from a lower glass transition temperature and thus rigidity.

Polyurethane gel-times

Gel-times for polyurethane formation are a measure of the reactivity of the polyols if the same isocyanate used. We have thus conducted studies on the gel-times of polyurethanes created from the two different types of polyols and Isonate 2143L, the results of which are listed in Table 1. Polyol II was observed to be much more reactive than polyol I. For example, the mixture of polyol II (OH number = 209 mg KOH/g) and Isonate gelled within minutes at the temperature range we handled the material (from room temperature to 80 °C), accompanied by a large exotherm, while the mixture of polyol I (OH number = 215 mg KOH/g) and Isonate takes 4 h to gel at room temperature, and 41 min at 60 °C. The origin for the difference in reactivity between the two types of polyols is the different types of OH groups, i.e., primary in polyol II versus secondary OH groups in polyol I, as is pointed out earlier.

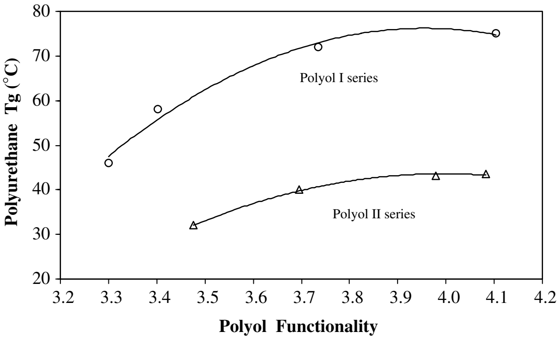


Fig. 2 Polyurethane glass transition temperature versus polyol functionality for the two types of polyols

Table 1 Gel-times of polyurethanes prepared from polyols I and II, and Isonate 2143L

Temperature (°C)	Polyol I (min)	Polyol II (min)
R. T.	240	6
40	—	4
60	41	3
80	14	2
100	10	—
120	5	—

Polyurethanes prepared from a blend of soy polyol and glycerol

We have also prepared a series of polyurethane resins from a blend of glycerol and each type of polyol reacted with PAPI 2901. Their glass transition temperatures (Tg) are presented in Fig. 3. The incorporation of glycerol into soy polyols obviously enhances the rigidity of both series of polyurethanes, as is evidenced by the increase in Tg's. Although the polyurethane created from Polyol II are less rigid than the one prepared from polyol I, polyol II system reacts completely, which is evidenced by the linear increase in polyurethane Tg and thus rigidity with the increase in glycerol/soy-polyol equivalent ratio or in polyol mixture functionality. This is the result of the presence of more reactive primary OH groups in polyol II than in polyol I. The Tg of the polyurethane originated from polyol II eventually reaches that of the polyurethane originated from polyol I (the two curves is about to cross at a glycerol/soy-polyol equivalent ratio of 2.0, or ca. 25 pph of glycerol, Fig. 3). On the other hand, the Tg's of the polyurethane originated from polyol I do not increase linearly, indicating (1) the polyol may not be compatible with glycerol, and (2) the curing temperature (110 °C) may have limited the degree of crosslinking for the polyurethanes.

Rigid polyurethane foams

We have chosen polyols with the same functionality for both polyol types for the purpose of easy comparison. The

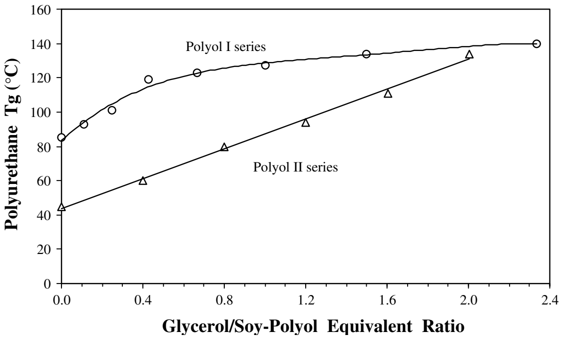


Fig. 3 Polyurethane glass transition temperature versus glycerol/soy-polyol equivalent ratio for the blends of the two types of polyols and glycerol

characteristics of the two polyols used in the formulation are listed in Table 2. As is stated previously, soy polyols do not have sufficient OH content to create a rigid foam, and a crosslinker is required. A blend of soy polyol and glycerol has proved to be our best choice [9]. We have conducted two series of studies, one varying the relative amount of glycerol and water, and the other varying the relative amount of the two catalysts employed in the formulation, as is presented in Table 3, and the foam density and compressive strength were measured. Foam cream time, set time and tack-free time were also noted. Special care has been taken to avoid shrinkage of the foams, as a shrunk foam leads to poor correlation of foam strength and experimental parameters. Both studies were aimed at finding the best combination or optimized conditions for preparing a foam with sufficient rigidity.

Effect of the relative amount of glycerol and water on foam strength

While both additions of glycerol and water increase the hydroxyl content of the foam systems dramatically, the amount of water carries a larger effect. The extremely rigid polyurea structure formed between water and isocyanate boosts up the rigidity of the foams, but the foam thermo-insulating properties suffer if the addition of water exceeds a certain level. Normally 1–2 pph (part per hundred part of soy polyol) of water is incorporated into a rigid foam formulation, thus we varied this amount in between 0 and 2 pph. On the other hand glycerol, being a trifunctional crosslinker, enhances foam rigidity, as is illustrated in Fig. 3. We varied the glycerol amount in between 10 and 30 pph. Under the lower limit a shrunk foam would be resulted, and above the upper limit the foam becomes too brittle. The theoretical calculations of OH contents of the foam systems based on polyol type I and polyol type II are presented in Figs. 4 and 5. For conventional rigid foam systems, the OH content should be 450–500 mg KOH/g to produce a foam with sufficient rigidity and mechanical strength.

Our experimental results indicated that the two polyols behaved much differently. As are shown by Figs. 6 and 7, the mechanical strengths for both polyol foam systems are satisfactory and comparable within the OH content range of 450–500 mg KOH/g. However, the compressive strength curves of the polyol II system (Fig. 7) essentially are proportional to the OH content curves (Fig. 5) since the contour lines in Fig. 7 are parallel to those in Fig. 5, indicating the system has reacted well during foam formation. This system was also found to be less sensitive to

Table 2 Characteristics of soy polyols used in rigid foam formulation

Type of soy polyol	Polyol I	Polyol II
Hydroxyl number (mg KOH/g)	212	223
Equivalent weight	265	252
Functionality	4.0	4.0
Viscosity (Pa s at 30 °C)	10.4	6.4
Density (g/cm^3)	1.018	—
Color	Pale yellow	Brown

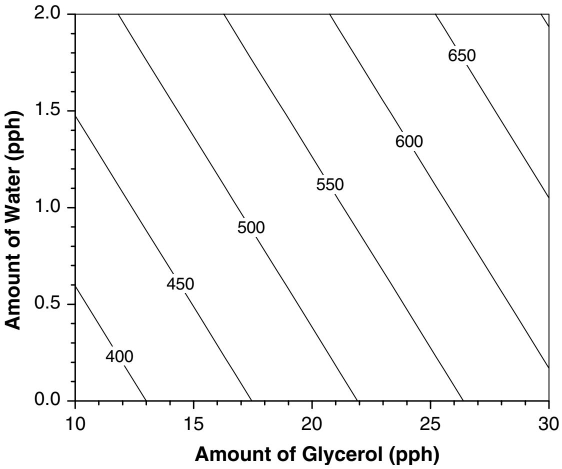


Fig. 4 Dependence of total OH number (mg KOH/g) on the amount of glycerol and water for the rigid foam system based on polyol type I (contour plot)

Table 3 Rigid foam formulation

Type of soy polyol	Series 1		Series 2	
	Polyol I	Polyol II	Polyol I	Polyol II
Soy polyol	100 part	100 part	100 part	100 part
Glycerol	Varied	Varied	23.5	20
Water	Varied	Varied	2	2
Surfactant B8404	2	2	2	2
DBTDL T-12	1	0.5	Varied	Varied
DABCO DMEA	1	0.5	Varied	Varied
Crude MDI Index	1.2	1.2	1.2	1.2
Genetron-141b	11–14%	11–14%	11–14%	11–14%

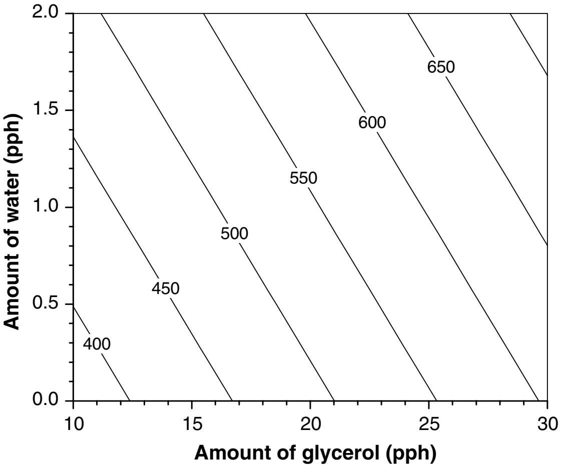


Fig. 5 Dependence of total OH number (mg KOH/g) on the amount of glycerol and water for the rigid foam system based on polyol type II (contour plot)

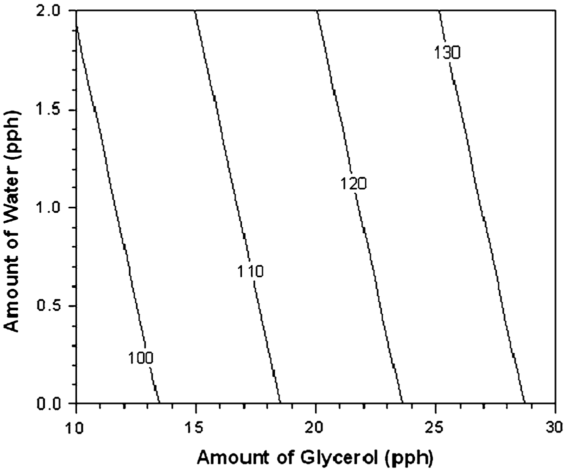


Fig. 6 Effect of the amount of glycerol and water on compressive strength (kPa) of rigid foams based on polyol type I (contour plot)

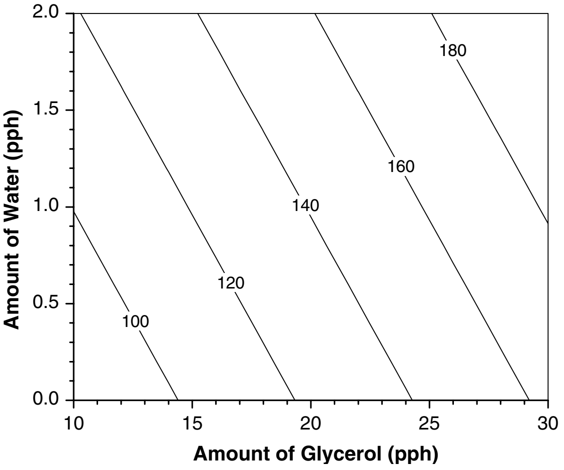


Fig. 7 Effect of the amount of glycerol and water on compressive strength (kPa) of rigid foams based on polyol type II (contour plot)

variations in mixing efficiency, even when a large sample was made. Such was not the case for the polyol I system, and the foams suffered from some shrinkage if agitation was not sufficient. This is another indication that polyol II is much more reactive than polyol I, and vice versa. On the other hand, the curves for the polyol I system are not proportional to the system OH content and are less responsive to the addition of both crosslinkers, and even much less so with the addition of water (Fig. 6) since the contour lines in Fig. 6 are not parallel to those in Fig. 4), indicating that the polyol I–glycerol–water system does not react well. This is in line with our observation in the case of polyurethane cast resins created from soy polyol–glycerol blends mentioned above.

Effect of the relative amount of catalysts on foam strength

While DBTDL T-12 catalyzes both urethane and urea formation, DABCO DMEA preferentially catalyzed urea formation, and traditionally both catalysts are added to the rigid foam formulation to provide optimal cream time, set time and tack-free time. On the other hand, the polyol II system is expected to require lower amounts of catalysts owing to the presence of more reactive primary OH groups. Our results are presented in Figs. 8 and 9 for polyol type I and polyol type II, respectively. As is seen, the polyol I system requires 1 pph for each catalyst to have an optimized mechanical strength (this refers to the coordinates to the center circle of Fig. 8), while the polyol II system requires much less: 0.4–0.5 pph of DBTDL T-12 and 0.3 pph of DABCO DMEA (i.e., the coordinates to the center circle of Fig. 9). While these data were all compared at a level of approximately 20 g of soy polyol, it was also observed that generally a lower amount of catalysts are needed if a larger sample is made. Since catalysts are generally much more

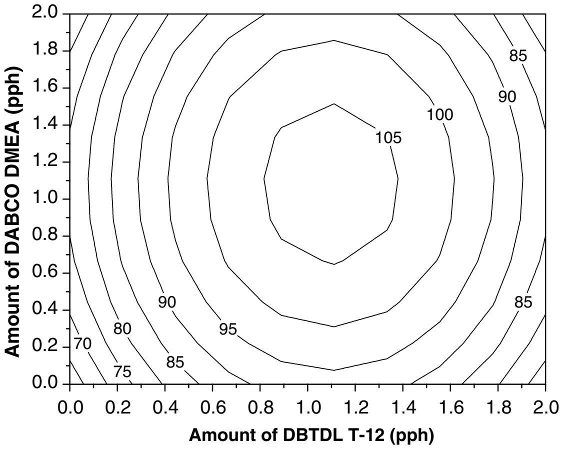


Fig. 8 Effect of the amount of catalysts on compressive strength (kPa) of rigid foams based on polyol type I (contour plot)

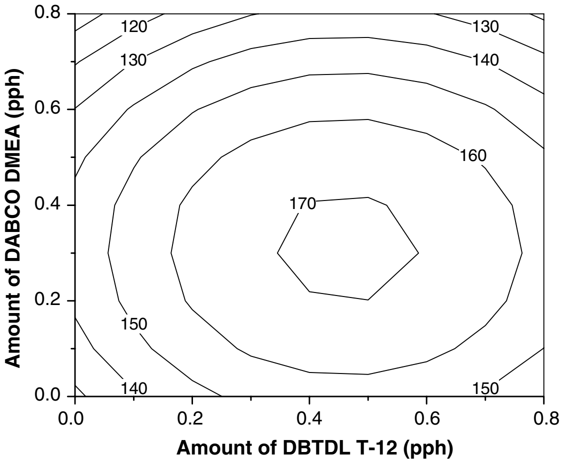


Fig. 9 Effect of the amount of catalysts on compressive strength (kPa) of rigid foams based on polyol type II (contour plot)

costly than other materials used in the foam formulations, the economics of rigid urethane foams systems based on polyol type II will be more favorable.

In summary, we have prepared two types of soy polyols, one with secondary OH groups and the other with primary OH groups. The latter polyol is much more reactive towards polyurethane formation. The reaction for the polyurethane formation is more complete for polyol II, although a less rigid polyurethane material is resulted. The latter polyol also requires lower amounts of catalysts for rigid foam formulation.

Acknowledgements We are indebted to The United Soybean Board for financial support. We also thank Riceland Foods, Goldschmidt, Air Products, Allied Signals, and Dow Chemicals for their generous donation of some chemicals.

References

1. Saggese EJ, Scholnick F, Zubillaga M, Ault WC, Wrigley AN (1967) J Am Oil Chem Soc 44:43
2. Khoe TH, Otey FH, Frankel EN (1972) J Am Oil Chem Soc 49:615
3. Lyon CK, Garrett VH, Frankel EN (1974) J Am Oil Chem Soc 51:331
4. Hoefer, R, Gruber, B, Meffert, A, Gruetzmacher, R, US Patent 4,826,944
5. Chian KS, Gan LH (1998) J Appl Poly Sci 68:509
6. Petrovic, Z, Guo, A, Javni, I, US Patent 6,107,433
7. Frankel EN, Thomas FL (1972) J Am Oil Chem Soc 49:10
8. Frankel, EN, US Patent 3,787,459
9. Guo A, Javni I, Petrovic ZJ (2000) Appl Polym Sci 77:467
10. Guo A, Demydov D, Zhang W, Petrovic ZS (2002) J Polym Environ 10:49
11. Guo A, Cho Y-J, Petrovic ZS (2000) J Polym Sci, Part A: Polym Chem 38:3900
12. Petrovic ZS, Guo A, Zhang W (2000) J Polym Sci, Part A: Polym Chem 38:4062
13. Carey MA, Wellon SL, Elder DK (1984) J Cell Plast (1–2). Available at: http://www.polyurethane.org/standards/purmac_docs/article1.asp