



*Good news  
for your business*

POLYURETHANES MAGAZINE INTERNATIONAL

# magazine

SPECIAL REPRINT

R. Narayan, E. Hablot,  
D. Graiver, V. Sendjarevic

Soy meal-based polyols for  
rigid polyurethane foams

**THINK** SOY  
RESOURCEFUL ▶ RELIABLE ▶ RESPONSIBLE

The United Soybean Board (USB) is committed to supporting innovative soy-based research for new product development.

**THINK RESOURCEFUL.** Since 2000, world production of soybeans has increased by more than 40 percent, or more than twice the rate of population growth.

**THINK RELIABLE.** The molecular structure of soy oil can be readily modified in many applications as a replacement for petrochemicals, and delivers performance that meets or exceeds industry standards.

**THINK RESPONSIBLE.** Life cycle assessment studies show environmental benefits, including lower carbon dioxide emissions, and less energy production costs.

FOR MORE INFORMATION, VISIT  
[WWW.SOYBIOBASED.ORG](http://WWW.SOYBIOBASED.ORG)  
OR  
[WWW.SOYNEWUSES.ORG](http://WWW.SOYNEWUSES.ORG)



[www.pu-magazine.com](http://www.pu-magazine.com)

# Soy meal-based polyols for rigid polyurethane foams

The use of natural oil-based polyols within the PU industry is constantly growing, either as a stand-alone or associated with petroleum-based polyols. Using bio-renewable materials offers the value proposition of a reduced carbon footprint as well as decreasing our dependence to non-renewable resources. Most of the polyols derived from renewable resources that are suitable for polymerization into polyurethanes have been prepared from various vegetable oils. Only limited work has been devoted to the use of protein biomass to produce value added industrial products because of the difficulties associated with their process and their high moisture sensitivity. Research at Michigan State University has recently focused on the development of new polyols derived from soy meal (**fig. 1**) that is suitable for polymerization into rigid PU foams using an inexpensive chemical route. In this process, the soy meal is hydrolyzed to a mixture of amino acids, which are then directly propoxylated and converted to reactive polyols. This amino acid polyol mixture is characterized by a low viscosity and high hydroxyl functionality. The acid, amine and hydroxyl values of these new soy meal-based polyols were determined and were used in a model pour-in place rigid PU foam formulation. The properties of these foams (e. g. compressive strength, compressive strain at yield, flammability) were comparable or better than conventional rigid PU foams.

## 1. Introduction

There has been a growing interest in the last few years to manufacture and use bio-based plastics and products. Switching from petro-fossil feedstocks to bio-renewable carbon feedstocks offers an inherent "value proposition" derived from the reduced petro-fossil carbon and smaller environmental footprint

[1, 2]. This increased awareness in environmentally friendly materials that are produced from annually renewable biodegradable resources has led to intensified research aimed at developing plastic materials from renewable resources. One notable example of a versatile polymer that is commonly used in many of today's applications is polyurethane. Polyurethanes are found in materials such as flexible foams in upholstered furniture, rigid insulation foams in walls and roofs, thermoplastic materials used in medical devices as well as materials for footwear, coatings, adhesives, sealants, and elastomers that are used in flooring and automotive interiors [3].

Many new bio-based polyols have been recently introduced into the polyurethane market. Essentially all these new polyols are derived from natural oils (primarily soybean triglycerides but also some other types of triglyceride oils) and much work has been published in the literature related to the synthesis and use of these polyols for polyurethanes [4, 5]. However, it is desirable to find other bio-based materials that are readily available and are lower in price than these triglyceride oils. Protein biomass is

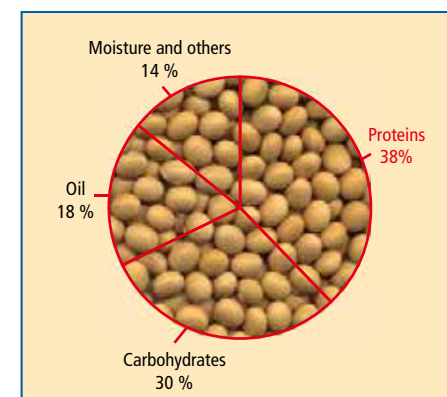
one such candidate although only few examples are available where a protein biomass was converted to yield value added industrial products. The main issues inhibiting progress of this biomass are related to the difficulties associated with processing the proteins and its high sensitivity to moisture. Indeed, soy protein isolate was incorporated into flexible polyurethane foam formulations to produce foams containing up to 40 % biomass material [6, 7]. However, these polyurethane foams were inferior when compared to flexible foams derived from petrochemicals. In order to avoid these difficulties we have used a two-steps process: 1) hydrolysis of the proteins to a mixture of amino acids, 2) propoxylation of the hydrolyzate to yield a final polyol. The overall process leads to polyols having high bio-based content via an economically competitive process when compared to conventional polyols used in rigid polyurethane foams. Furthermore, in soybeans (and most other seeds) the proteins are much more abundant than the triglyceride oils and are usually less expensive than the oil. This work details some of the synthetic strategies we used to manufacture these new polyols and key data related to the properties of rigid polyurethane foams that were prepared from them.

## 2. Experimental

### 2.1 Materials

Soy meal was obtained from Zeeland Farm Services. The equilibrium moisture content

▼ **Fig. 1:** Typical soybean composition



in the meal was relatively constant at about 15 wt%. Hydrochloric acid and sodium hydroxide were purchased from Sigma-Aldrich and used as received. Propylene oxide, Poly-G 74-376 (a sucrose-based polyol) Dabco DC193 (a blowing catalyst), Dabco 33LV (a gelling catalyst), Niox A1 (an amine catalyst), and Rubinate M (a polyisocyanate) were kindly provided by Troy Polymers, Inc.

### 2.2 Polyol synthesis

The soy meal was first hydrolyzed with water and 3N HCl under reflux at 110 °C. Then, the hydrolyzate was filtered to remove any unreacted humin, neutralized using a 36 % NaOH solution and the water was then striped out of the reactor under vacuum. This hydrolyzate mixture thus ob-

tained was mixed with a sucrose-based polyol (Poly-G 74-376) and reacted with propylene oxide. Poly-G 74-376 was found to improve the compatibility of the soy meal polyol with propylene oxide. It should be emphasized that the propoxylation step further reduced the viscosity of the polyol and provided better economics since it eliminated the need to separate the carbohydrates present in the meal and allowed for higher yields.

### 2.3 Preparation of rigid PU foams

Water-blown, pour-in-place rigid foams were prepared from the soy meal polyols. The properties of these foams were compared to foams prepared with a commercial sucrose-based polyol having a hydroxyl value in the range of 360 mg KOH/g and used as a control. Some selected formulations of the foams prepared with the soy meal-based polyols in comparison to a reference foam prepared with Poly-G 74-376 are presented in **figure 2** and listed in **table 1**.

In a typical process the polyol component of the polyurethane system was prepared by blending a predetermined amount of the soy meal polyol with the other formulation components using a high torque mixer. The polyol side was then mixed with the isocyanate, poured into a paper box and the foaming reaction profile was determined (**tab. 1**). The core density, the compressive strength, the compressive strain at yield, and the burning rate of the resulting rigid foam were also determined following ASTM D 1622-03, ASTM 1621-00, ASTM D 1621-00, and ASTM D 635-03, respectively.

**Tab. 1:** Typical formulation of rigid foams derived from SPH polyol

Sample	Eq. wt.	Control	Foam 1	Foam 2
<b>Polyol system*</b>				
Poly-G 74-376	155.40	100	80	80
Soymeal polyol	103.13	0	20	20
Water	9.00	4.5	4.5	4.5
Dabco DC193		2.5	2.5	2.5
Dabco 33LV		1.8	1	0.6
Niox A1		0.1	0.05	0.08
<b>Isocyanate system</b>				
Rubinate M	135.50	168.69	171.07	170.55
Isocyanate index		105	105	105
<b>Reaction profile</b>				
Mix time / s		10	10	10
Cream time / s		20	18	18
Gel time / s		40	28	27
Rise time / s		116	63	80
Tack-free time / s		160	57	69



◀ **Fig. 2:** Samples of PU foams with A) 0 % of soy meal-based polyol, B) 20 % of soy meal-based polyol, C) 50 % of soy meal-based polyol.

## 3. Results and discussion

The hydrolysis of soy meal proteins was accomplished using relatively mild hydrolysis conditions in order to minimize premature degradation of the amino acids (3M HCl solution, 100 °C). Consequently, a relatively long reaction time was used to ensure complete hydrolysis of the proteins to individual amino acids. The composition of the amino acids in the soy proteins is well-known and is reported in the literature [8].

The hydrolyzate was mixed with a sucrose-based polyol (Poly-G 74-376) and propoxylated with propylene oxide to yield the final polyol. The polyol thus obtained is generally characterized by a hydroxyl value of 442 mg KOH/g, an amine value of 102 mg KOH/g and a water content lower than 0.2 %. It should further be emphasized here that this polyol was readily miscible with the other components in the foam formulation. Furthermore, this soy meal-based polyol was also miscible with many other commercial polyols currently on the market, which allows the formulator to choose a blend of polyols to reach specific foam properties. One of the most noticeable properties in the reaction profile of foams formulated with the soy meal-based polyol was a self-catalytic property. This self catalytic property was evaluated for different ratios of soy meal polyol/Poly-G 74-376 blends by measuring the gel time as shown in **figure 3**. Apparently, the soy meal polyols were found to be self-catalytic due to the presence of tertiary amine and imine groups present in the polyol structure.

The self-catalytic property of this soy meal-based polyol was further confirmed by recording recording the foaming reaction profile (cream time, gel time, rise time, and tack-free time). The results indicate that all were significantly shorter for foams prepared with the soy meal-based polyol compared to the reference foam (**tab. 1**). Typical final physical properties of the foams (e. g. density, compressive strength, compressive strain, and friability) were deter-

mined and are presented in **figure 4**. Foams prepared with the soy meal-based polyol exhibited equal or better properties compared with the reference foam. Of particular interest are the flammability measurements (measured as burning rate with no flame retardant additives), where the foams prepared with the soy meal-based polyol were found to be better than the reference foam.

#### 4. Conclusions

We prepared polyols from protein soy meal that are suitable for rigid PU foams. The preparation process includes hydrolysis of the proteins to a mixture of amino acids followed by the direct propoxylation of the hydrolyzate. The reaction profile and the physical properties of the foams obtained with this new polyols were compared to a reference foam prepared from a commercial Poly-G 74-376 polyol.

This new soy meal-based polyol has several advantages including:

- Low cost process and raw materials.
- Readily available and stable source of domestic raw materials.
- High bio-based content in the final polyol.
- Self catalytic property during the foaming reaction (due to the presence of tertiary amines and imines).
- Compatibility with other polyols, blowing agents and other foam additives.

- Physical properties similar to conventional rigid PU foams.
- Low flammability (charring upon burning) in synergy with flame retardant additives.

#### 5. Acknowledgments

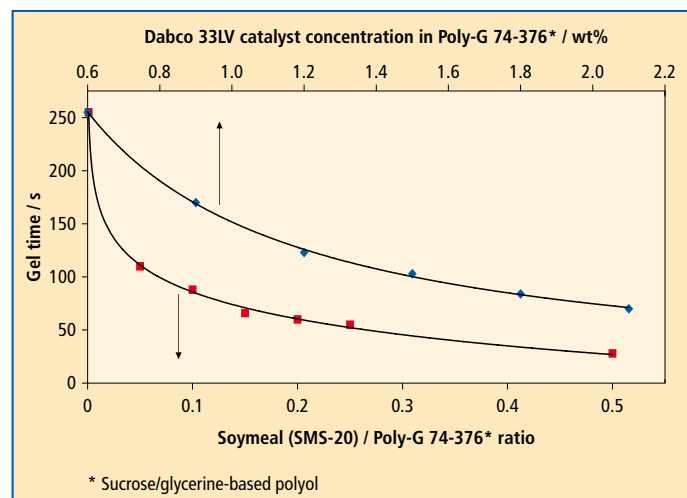
This research work was supported by a generous grant #1481 from the United Soybean Board as well as the NSF Award IIP-1214595.

#### 6. References

- [1] Narayan R., 2000. "Reactive Extrusion Process Produces Biodegradable Films & Injection Molded Products Based on Soy Protein-Polyester", MRS (Materials Research Society), Bulletin 28, Vol. 10.
- [2] Narayan R., 2006. "Rationale, Drivers, Standards, and Technology for Biobased Materials in Renewable Resources and Renewable Energy", CRC Press, Ed Mauro Graziani & Paolo Fornasiero.
- [3] Szycher M., 1999. Handbook of Polyurethanes. Boca Raton, FL.
- [4] Shogren R. L., Petrovic Z. S., Liu Z., Erhan S. Z., 2004. "Biodegradation Behavior of Some Vegetable Oil-Based Polymers", Journal of Polymers and the Environment, Vol. 12, p. 173.
- [5] Zlatanovic A., Lava C., Zhang W., Petrovic Z. S., 2004. "Effect of Structure on Properties of Polyols and Poly-

urethanes Based on Different Vegetable Oils", Journal of Polymer Science Part B: Polymer Physics, Vol. 42, p. 809.

- [6] Lin Y., Hsieh F., Huff H. E., 1997. "Water-blown flexible polyurethane foam extended with biomass materials", Journal of Applied Polymer Science, Vol. 65, No. 4, p. 695–703.
- [7] Lin Y, Hsieh F, Huff HE, Iannotti E. 1996. "Physical, Mechanical And Thermal Properties Of Water-Blown Rigid Polyurethane Foam Containing Soy Protein Isolate. Cereal Chemistry", Vol. 73, No. 2, p. 189–196.
- [8] Tomita H., Sanda F., Endo T., 2001. "Self-Polyaddition of Six-Membered Cyclic Carbonate Having Fmoc-Protected Amino Group: Novel Synthetic Method of Polyhydroxy-urethane", Macromolecules, Vol. 34, No. 22, p. 7601.



◀ **Fig. 3:** Auto-catalysis effect of the soy meal-based polyol

**Fig. 4:** Physical properties of the reference foam (control, table 1) and foams prepared with 20 % of soy meal polyol (foam 2, table 1)

