Soy meal-based polyols for rigid polyurethane foams

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

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 or www.soynewuses.org
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 biorenewable materials offers the value proposition of a reduced carbon footprint as well as decreasing our dependence on 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.

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 involving 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) propoxylolation 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 oils. 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. Materials

Soy meal was obtained from Zeeland Farm Services. The equilibrium moisture content of 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), and Rubinate M (a polyisocyanate) were kindly provided by Troy Poly-mer, Inc.

2.2 Polyol synthesis

The soy meal was first hydrolyzed with water and 3% HCl under reflux at 110 ºC. Then, the hydrolyzate was filtered to remove any unreacted reactant, neutralized using a 36% NaOH solution and the water was then stripped out of the reactor under vacuum. This hydrolyzate mixture thus obtained was mixed with a sucrose-based polyol (Poly-G 74-376) and reacted with propylene oxide. Poly-G 74-376 was found to have 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 (Fig. 3). The core density, the compressive strength, the compressive strain at yield, and the burning rate of the resulting rigid foam were also determined following the ASTM D 1620-03, ASTM 1621-03, ASTM D 1621-00, and ASTM D 635-03, respectively.

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 ºC). 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 110 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 formed 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 as shown in figure 3. Apparently, the soy meal polyols were found to be self-catalystic 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 the foaming reaction profile (cream time, gel time, rise time, and tack-free time). The results indicate that all foams 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 polyol 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


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