

Comparative Study of Physical Properties of Water-Blown Rigid Polyurethane Foams Extended with Commercial Soy Flours

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ABSTRACT: The use of renewable resources (mainly carbohydrates) in rigid polyurethane foam has been known to offer several advantages, such as increased strength, improved flame resistance, and enhanced biodegradability. Less attention has been directed to inexpensive protein-based materials, such as defatted soy flour. The objectives of this study were to develop water-blown rigid polyurethane foams, containing defatted soy flour, that have acceptable or improved physical properties which also lower the cost of the foam formulation and to compare the properties of developed foams extended with three kinds of commercial soy flour. Water-blown low-density rigid polyurethane foams were prepared with poly(ether polyol)s, polymeric isocyanates, defatted soy flour, water, a catalyst mixture, and a surfactant. Soy flour and the initial water content were varied from 0 to 40% and from 4.5 to 5.5% of the poly(ether polyol) content, respectively. A standard laboratory mixing procedure was followed for making foams using a high-speed industrial mixer. After mixing, the mixture was poured into boxes and allowed to rise at ambient conditions. Foams were removed from boxes after 1 h and cured at room temperature for 24 h before measurement of the thermal conductivity and for 1 week before other property tests. Foam properties were determined according to ASTM procedures. Measurement of the physical properties (compressive strength, modulus, thermal conductivity, and dimensional stability under thermal and humid aging) of these foams showed that the addition of 10–20% of three kinds of soy flour imparted water-blown rigid polyurethane foams with similar or improved strength, modulus, insulation, and dimensional stability. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 10–19, 2001

Key words: rigid polyurethane foam; soy flour; physical properties

INTRODUCTION

Polyurethane foams have been commercially accepted in a wide variety of applications since the

1940s. These foams surround us in today's society, playing an important role in many industries—from shipbuilding to footwear, construction to cars, insulation to furniture, and car seating to packaging—and contribute greatly to our daily lives.¹ Wirpsza² reported that polyurethane ranks fifth in the production volume of plastics. The use of polyurethane foam is continuing to grow at a rapid pace throughout the world. The

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Table I Specifications of Soyafuff 200W, Nutrisoy Flours, and 200/70 Defatted Soy Flour

| Attributes | Soyafuff 200W ^a (Central Soya) | 200/70 Soy Flour ^b (Cargill) | Nutrisoy Flour ^c (ADM) |
|---|--|--|--------------------------------------|
| Protein (%) | 52 min | 50 min | 53 min |
| Moisture (%) | 8.5 max | 8 max | 9 max |
| Crude Fiber (%) | 4 max | 8.5 max | 8.5 max |
| Ash (%) | 7 max | — | — |
| Fat (%) | 1.5 max | 1.2 max | 1.1 max |
| Particle Size (U.S. Sieve)% through #200 | 90 min | 95 min | — |

^a Adapted from Central Soya Product Description (1996), Central Soya Co., Inc., Fort Wayne, IN.

^b Adapted from Cargill Product Description (1996), Cargill, Inc., Cedar Rapids, IA.

^c Adapted from ADM Product Description (1996), Archer Daniels Midland Co., Decatur, IL.

reasons for the growth are because of its light weight, excellent strength-to-weight ratio, superior insulating abilities, good energy-absorbing performance (including shock, vibration, and sound), and comfort features.³

Polyurethane foams are generally created from a two-phase system that consists of a solid polymer matrix and a gaseous phase gained through blowing agents. There may be more than one solid component present in the solid phase of foams as fillers or extenders, either in fibrous or other shapes. In general, fillers and extenders are incorporated into the plastic materials to either introduce particular characteristics, to improve their physicochemical properties, or to reduce the cost of the product. In the past four decades, many researchers⁴⁻¹¹ have been interested in the use of renewable resources in the plastics industry. Polysaccharides were incorporated into polyurethane systems successfully. However, less attention was directed to inexpensive protein-based materials such as defatted soy flour. Soy flour contains about 50% proteins and 30% carbohydrates which are polyfunctional molecules including many active hydrogens and hydroxyl groups. These active hydrogens and hydroxyl groups can react with isocyanate. Therefore, soy flour can substitute for a small portion of polyols in the polyurethane foam formulation and soy flour is cheaper than are polyols. There exists a great potential for soy flour to be applied to modify or improve the physical and chemical properties of polyurethane foams and to reduce the cost.

For the gas phase, rigid polyurethane foams containing chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) blowing agents have the lowest apparent thermal conductivity of any nonvacuum insulation currently available.¹² Un-

der a Montreal Protocol (renewed in 1998), the use and production of CFC and HCFC is restricted and is being phased out because CFC and HCFC cause depletion of the ozone layer and contribute to the greenhouse effect.¹³ Therefore, the objectives were to determine the relevant physical properties of the developed plastic foams, to investigate the effects of biomass concentration and water content on the foam properties, and to compare the properties of developed foams extended with three kinds of commercial soy flour.

EXPERIMENTAL

Materials

The soybean flours used in the preparation of water-blown rigid polyurethane foams were Soyafuff 200W (Central Soya Co., Fort Wayne, IN), Nutrisoy flour (Archer Daniels Midland, Decatur, IL), and 200/70 defatted soy flour (Cargill, Cedar Rapids, IA). Their compositions are shown in Table I. The chemicals included polymeric isocyanate (PAPI 27, Dow Chemical Co., Midland, MI), poly(ether polyol) (Voranol 490, Dow Chemical), catalysts (Toyocat-TF and TMF, Tosoh USA, Atlanta, GA), a surfactant (L-5440, OSI Specialties, Sistersville, WV), and a blowing agent (distilled water).

Experimental Design and Formulations

The effects of the following variables in the foam formulation on the properties of water-blown rigid polyurethane foams were studied: (1) concentrations of soybean flour (parts per hundred polyols: 0, 10, 20, 30, and 40; and (2) water con-

Table II Formulations for Water-blown Rigid Polyurethane Foam

| Ingredients | Parts by Weight |
|---------------------------------|-------------------|
| Component A | |
| Polyol | 100 |
| Soy flours | 0, 10, 20, 30, 40 |
| Catalysts | 2.5 and 2.5 |
| Surfactant | 3.0–4.0 |
| Blowing Agent (distilled water) | 4.5, 5.0, 5.5 |
| Component B | |
| Polymeric MDI ^a | 225, 234, 243 |

^a The quantity of isocyanate is based on an isocyanate index 120, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

tents (parts per hundred polyols): 4.5, 5, and 5.5. Other factors in the foam formulation such as catalysts, the surfactant, and the isocyanate index were kept constant. The concentrations of catalysts and the surfactant in the foam formulation were determined first to ensure that all foam products can be prepared within the normal amount of time (10 min). This experiment was a 5 × 3 factorial rearrangement. The foam formulation for water-blown rigid polyurethane foam is shown in Table II. The amount of isocyanate added to each formulation was based on the total hydroxyl content of the poly(ether polyol) and water. Three replicate foams were produced with each formulation.

Foam Preparation

A standard laboratory mixing and pouring procedure for making foams was used.¹⁴ Intensive mixing was generated by a commercial drill press (Buffalo, Colcord-Wright, St. Louis, MO) with a 25.4-cm shaft and a 5-cm impeller. Soybean flours were dried in a vacuum oven at 70°C and 50 mmHg overnight. The poly(ether polyol), catalysts, soybean flour, surfactant, and blowing agent (component A) were added by weight into a 1-qt disposable paperboard container holding a steel frame with four baffles next to the container wall and mixed at 3450 rpm for 60–120 s. Then, stirring was stopped, allowing the mix to degas. After 15 s, polymeric isocyanate (component B) was rapidly added and stirring was continued for another 15–25 s at the same speed. The reacting mixtures were then poured immediately into wooden boxes (20 × 20 × 10 cm) and allowed to

rise at ambient conditions. Foams were removed from the boxes after 1 h and cured at room conditions (23°C) for 24 h before measurement of the thermal conductivity and for 1 week before other property tests.

Foam Properties Measurements

Densities of the samples were determined on the basis of the American Society for Testing and Materials (ASTM) procedure D 1622-88. Each treatment is the average of at least 10 cubes. Compressive strength and modulus were measured according to ASTM D 1621-73 (reapproved 1979) by an Instron universal testing machine (Model 1132, Instron Corp., Canton, MA) with a data-acquisition system. The sample (5.0 × 5.0 × 5.0 cm) was on a flat plate. The voltage versus time output was converted into a digitized load versus deformation relationships. The average of six tests in the direction parallel to the foam rise was reported. Apparent thermal conductivities were determined using a Fox 200 heat flowmeter instrument (LaserComp, Wakefield, MA; ASTM C 518-91). The mean temperature, 22.5°C, and the temperature difference, 25°C, were used. The dimensional stability tests include thermal and humid aging (ASTM D 2126-87). Two Tenney temperature–humidity chambers with a Versatenn (benchtop model, Tenney Engineering, Inc., Union, NJ) were used. At least three samples were determined for the thermal and humid aging tests. The dynamic mechanical properties were obtained using a dynamic mechanical spectrometer 6100 (DMS 6100) (Seiko Instruments, Inc., Koto-ku, Japan) in a compression mode. The approximate cylindrical dimension of the foam samples used was 10.0 mm (D) × 10.0 mm (H). Samples were heated at a rate of 2°C/min over the range of 50–280°C. The sinusoidal oscillation measurement was at the frequencies from 0.1 to 20 Hz and at a compression of 0.05%. The storage modulus (E'), loss modulus (E''), and $\tan \delta$ as a function of temperature at various frequencies were obtained from these runs. Data were the average of at least three samples.

RESULTS AND DISCUSSION

Density

Table III shows the density of water-blown rigid polyurethane foams containing 0–40% of soy

Table III Density of Water-blown Rigid Polyurethane Foams Extended with Soy Flours

| Water Content (%) | Biomass (%) | Density (kg/m ³) | | |
|-------------------|-------------|------------------------------|------------------|----------------|
| | | Soyafluff 200W | 200/70 Soy Flour | Nutrisoy Flour |
| 4.5 | 0 | 33.8 | 33.8 | 33.8 |
| | 10 | 34.1 | 34.1 | 34.5 |
| | 20 | 40.9 | 36.4 | 36.2 |
| | 30 | 43.3 | 38.2 | 38.0 |
| | 40 | 45.2 | 42.6 | 41.9 |
| 5.0 | 0 | 32.1 | 32.1 | 32.1 |
| | 10 | 32.5 | 34.4 | 33.9 |
| | 20 | 34.9 | 35.9 | 35.3 |
| | 30 | 40.4 | 37.4 | 35.6 |
| | 40 | 41.5 | 38.4 | 36.2 |
| 5.5 | 0 | 30.5 | 30.5 | 30.5 |
| | 10 | 31.2 | 31.6 | 32.4 |
| | 20 | 34.8 | 33.8 | 34.2 |
| | 30 | 36.2 | 35.7 | 34.4 |
| | 40 | 38.8 | 36.9 | 36.1 |

flour at a 4.5, 5.0, and 5.5% initial water content based on the weight of poly(ether polyol). For Soyafluff 200W, the foam density at three levels of the initial water content increased with increasing percentage of the soy flour. The density of water-blown rigid foam is dominated by the weight and volume of the plastics consisting of the matrix of the foam and the gases entrapped in the foam cells. The solid-phase composition contains all additives such as the surfactant, catalysts, stabilizers, and fillers/extenders (soy flour in this study) as well as the pure polymer. Each of foam-making formulations has the same amount of blowing agent (water) and other components, except the weight percentages of Soyafluff 200W. As expected, the density increases with an increasing level of Soyafluff 200W. Moreover, the gas phase is carbon dioxide produced by the reaction of isocyanate and water. Water functions as a kind of blowing agent. The more water added to the foam system, the more carbon dioxide was generated and filled in the same system. Therefore, increasing the initial water content from 4.5 to 5.5% decreases the foam density at five levels of soy flour. The trends were similar for the foams with Nutrisoy flours and 200/70 defatted soy flour.

Compressive Strength

The compressive strength of a foam is the maximum compressive stress which the foam is capa-

ble of withstanding, based on the original area of the cross section, for a short time at a fixed point in the compression-loading cycle.¹⁵ The samples were compressed parallel to the foam rise direction. According to Table IV, the initial water content increased as the compressive strength decreased. This is a commonly observed rule in many cellular foam systems.¹⁶ At a 4.5% initial water content, an increase in the Soyafluff 200W percentage up to 30% resulted in an increase in the compressive strength. For others, an increase in the Soyafluff 200W percentage caused an increase in the compressive strength. In addition, there was an increase of compressive strength with increasing 200/70 soy flour and Nutrisoy flour percentage up to 30% for all levels of initial water content. Further increase in their percentage led to a decrease of the compressive strength.

A comparison of Table IV with Table III shows that the foam density was closely related to the compressive strength. Typical values of the compressive strength as a function of the density for conventional foams (the shaded area in Fig. 1) have been provided.¹⁷ Figure 1 shows the relationship between the density and compressive strength for all foams with three levels of the initial water content and five levels of the Soyafluff 200W percentage. In general, foams with up to 20% Soyafluff 200W were higher in

Table IV Compressive Strength of Water-blown Rigid Polyurethane Foams Extended with Soy Flours

| Water Content (%) | Biomass (%) | Compressive Strength (kPa) | | |
|-------------------|-------------|----------------------------|------------------|----------------|
| | | Soyafluff 200W | 200/70 Soy Flour | Nutrisoy Flour |
| 4.5 | 0 | 218 | 218 | 218 |
| | 10 | 234 | 243 | 225 |
| | 20 | 264 | 243 | 244 |
| | 30 | 265 | 247 | 253 |
| | 40 | 244 | 242 | 246 |
| 5.0 | 0 | 202 | 202 | 202 |
| | 10 | 217 | 227 | 210 |
| | 20 | 221 | 239 | 221 |
| | 30 | 229 | 240 | 245 |
| | 40 | 234 | 226 | 224 |
| 5.5 | 0 | 186 | 186 | 186 |
| | 10 | 187 | 190 | 215 |
| | 20 | 189 | 216 | 233 |
| | 30 | 200 | 216 | 243 |
| | 40 | 224 | 199 | 217 |

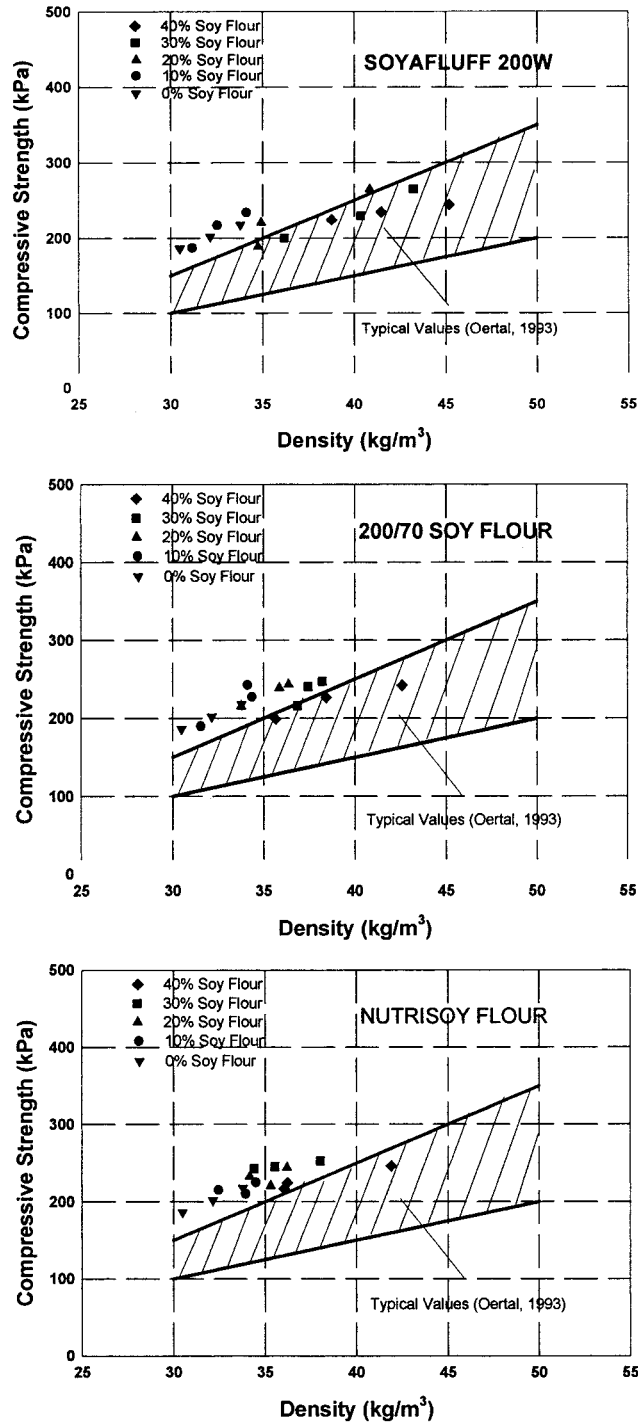


Figure 1 Relationship between the density and compressive strength for foams without and with Soyafuff 200W.

compressive strength than were conventional foams with a similar density. When compared against the control, only foams with 10% Soyafuff 200W show promise, with slightly higher com-

pressive strength with a similar density. The foams extended with 200/70 soy flour up to 20% were the same or better in compressive strength when compared with the control foams. The foams extended with Nutrisoy flour up to 30% had the same or better compressive strength than that of the control foams.

Compressive Modulus

The compressive modulus is the ratio of stress to the corresponding strain in a material loaded below its proportional limit.¹⁸ For rigid foams, the definition of the compressive modulus is the maximum slope of the stress–strain curve. Its value is a hardness index of a material. A higher slope in the stress–strain curve means that a larger increase in stress is required for the same amount of deformation. As a result, the higher the compressive modulus is, the harder the material.

The compressive modulus values of the extended foams were higher than that of the control foam for each initial water content (Table V). The foam’s compressive modulus increased with an increasing Soyafuff 200W and 200/70 soy flour or decreasing initial water content. The compressive modulus of the foam with a 4.5% initial water content increased with an increasing Nutrisoy flour percentage. The LSD test shows that foams

Table V Compressive Modulus of Water-blown Rigid Polyurethane Foams Extended with Soy Flours

| Water Content (%) | Biomass (%) | Compressive Modulus (kPa) | | |
|-------------------|-------------|---------------------------|------------------|----------------|
| | | Soyafuff 200W | 200/70 Soy Flour | Nutrisoy Flour |
| 4.5 | 0 | 8925 | 8925 | 8925 |
| | 10 | 9494 | 9096 | 9022 |
| | 20 | 12,261 | 9822 | 9478 |
| | 30 | 12,873 | 10,395 | 9806 |
| | 40 | 12,867 | 10,684 | 12,317 |
| 5.0 | 0 | 8447 | 8447 | 8447 |
| | 10 | 9110 | 8695 | 8636 |
| | 20 | 9134 | 9048 | 8963 |
| | 30 | 10,076 | 10,020 | 9163 |
| | 40 | 11,733 | 10,106 | 10,122 |
| 5.5 | 0 | 7718 | 7718 | 7718 |
| | 10 | 7963 | 8291 | 7829 |
| | 20 | 8618 | 8788 | 8136 |
| | 30 | 8660 | 9210 | 8962 |
| | 40 | 10,382 | 9216 | 9588 |

Table VI Apparent Thermal Conductivity of Water-blown Rigid Polyurethane Foams Extended with Soy Flours

| Water Content (%) | Biomass (%) | Apparent Thermal Conductivity (W/mK) | | |
|-------------------|-------------|--------------------------------------|------------------|----------------|
| | | Soyafuff 200W | 200/70 Soy Flour | Nutrisoy Flour |
| 4.5 | 0 | 0.0248 | 0.0248 | 0.0248 |
| | 10 | 0.0254 | 0.0258 | 0.0258 |
| | 20 | 0.0257 | 0.0258 | 0.0259 |
| | 30 | 0.0264 | 0.0266 | 0.0263 |
| | 40 | 0.0266 | 0.0268 | 0.0267 |
| 5.0 | 0 | 0.0251 | 0.0251 | 0.0251 |
| | 10 | 0.0259 | 0.0262 | 0.0260 |
| | 20 | 0.0261 | 0.0264 | 0.0261 |
| | 30 | 0.0264 | 0.0265 | 0.0263 |
| | 40 | 0.0266 | 0.0265 | 0.0265 |
| 5.5 | 0 | 0.0256 | 0.0256 | 0.0256 |
| | 10 | 0.0258 | 0.0267 | 0.0264 |
| | 20 | 0.0266 | 0.0272 | 0.0271 |
| | 30 | 0.0278 | 0.0279 | 0.0286 |
| | 40 | 0.0280 | 0.0289 | 0.0293 |

containing 30 and 40% Nutrisoy flour had significantly greater modulus values than that of the control. The compressive moduli of foams with a 5.0 and 5.5% initial water content had the same trend as that of the foams with a 4.5% initial water content.

Apparent Thermal Conductivity

Rigid polyurethane foams have remarkably excellent thermal insulation resulting from their low apparent thermal conductivity.¹⁹ The apparent thermal conductivity (k value) of a material is characterized by its ability to transport heat from one side of the material to the other for a unit difference in temperature. The insulating capacity increases as the k value decreases.

The thermal conductivities (k values) shown in Table VI were measured at a mean temperature of 22.5°C and a temperature difference of 25°C (upper, 35°C, and lower, 10°C). The k value was lower for the control foam than it was for the extended foams and increased as Soyafuff 200W was increased in the foam formulation. Statistical analyses using LSD rules with 95% confidence showed no significant difference in the k value between the control foam and foams containing Soyafuff 200W up to 30%. The k value also in-

creased as the percentage of 200/70 soy flour and Nutrisoy flour in the foam system increased, but there was no significant difference of the apparent thermal conductivity with 95% confidence in statistical analyses using LSD rules between the control and extended foams. This trend probably resulted from the decrease in the number of cells per unit area and the increase in the polymer phase content, which had 10 times or more thermal conductivity than that of the gas phase content,²⁰ with an increase of the foam density.

The k value increased with increasing initial water content for five levels of Soyafuff 200W. An increase in the initial water content led to an increase in the k value, except for the foams with 30 and 40% 200/70 soy flour at a 5.0% initial water content. For Nutrisoy flour, the thermal conductivity increased with an increasing Nutrisoy flour percentage and decreased with an increasing initial content, except for the foam extended with 30% Nutrisoy flour at a 5.0% initial water content. This might have been caused by increased convection heat transfer due to larger foam cells and increased open-cell content.

Dimensional Stability

Rigid polyurethane foams are particularly suitable for structural or foamed-in-place application because of their capacity of being molded to size. Generally, foams of this type do not allow preconditioning prior to installation. In this condition, the dimensional stability of rigid foams, where they are subjected to accelerated aging at a standard temperature and relative humidity, is the most important property to be carefully considered, especially for low-density foams. The changes in the volume of the sample were determined. According to the data shown in Table VII, the changes in volume are increased, but are less than 2% for all foams with 200W Soyafuff. The diffusion of air into the foam cells is accelerated at a higher temperature. Since the pressure inside the cell is different from the atmospheric pressure, the developed stress will result in a deformation of the foam if the foam structure is not strong enough. All foams were expanded. Some variations in volume were noted for all foams with 200W Soyafuff during the aging period. For most foams with 70/200 soy flour, the volume changes are increased, but are less than 1.0%. All foams are expanded. Small variations in volume were stated during the aging period for all foams with 70/200 soy flour. After 14 days, the foams

Table VII Effect of Thermal Aging on Dimensional Stability of Water-blown Rigid Polyurethane Foams Extended with Soy Flours at 70°C and 5% Relative Humidity

| Volume Change (%) | Soyafuff 200W ^a (%) | | | | | 200/70 Soy Flour ^a (%) | | | | | Nutrisoy Flour ^a (%) | | | | |
|---|--------------------------------|-------|-------|-------|-------|-----------------------------------|-------|-------|-------|-------|---------------------------------|-------|-------|-------|-------|
| | 0 | 10 | 20 | 30 | 40 | 0 | 10 | 20 | 30 | 40 | 0 | 10 | 20 | 30 | 40 |
| 4.5% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | +1.65 | +1.70 | +0.73 | +1.36 | +1.13 | +1.65 | +0.80 | +0.38 | +0.27 | +1.25 | +1.65 | +0.47 | +0.47 | +0.51 | +0.69 |
| 7 | +1.19 | +1.49 | +1.02 | +1.31 | +1.17 | +1.19 | +0.52 | +0.33 | +0.06 | +1.48 | +1.19 | +0.48 | +0.73 | +0.87 | +0.92 |
| 14 | +0.67 | +0.84 | +1.04 | +1.29 | +1.05 | +0.67 | +0.60 | +0.06 | +0.01 | +1.55 | +0.67 | +0.45 | +0.83 | +0.95 | +0.99 |
| 5.0% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | +0.55 | +1.25 | +0.39 | +1.15 | +1.66 | +0.55 | +0.08 | +0.01 | +0.31 | +0.32 | +0.55 | +0.35 | +0.38 | +0.50 | +0.57 |
| 7 | +0.97 | +1.03 | +0.53 | +1.05 | +1.29 | +0.97 | +0.26 | +0.05 | +0.18 | +0.74 | +0.97 | +0.46 | +0.74 | +0.65 | +0.85 |
| 14 | +1.00 | +0.62 | +0.41 | +0.75 | +0.91 | +1.00 | +0.44 | +0.04 | +0.23 | +0.88 | +1.00 | +0.49 | +0.67 | +0.76 | +0.91 |
| 5.5% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | +1.06 | +0.58 | +1.52 | +1.38 | +1.47 | +1.06 | +0.07 | +0.62 | +0.31 | +0.34 | +1.06 | +0.50 | +0.67 | +0.67 | +0.48 |
| 7 | +1.07 | +1.01 | +0.90 | +0.96 | +1.14 | +1.07 | +0.02 | +0.77 | +0.51 | +0.73 | +1.07 | +0.79 | +0.68 | +0.92 | +0.80 |
| 14 | +0.84 | +1.31 | +0.36 | +0.82 | +1.21 | +0.84 | +0.23 | +0.52 | +0.81 | +0.96 | +0.84 | +0.75 | +0.75 | +0.89 | +0.92 |

^a Percent of soy flours is based on weight of polyether polyol.

^b Foams containing 4.5, 5.0, and 5.5% initial water content, respectively.

with up to 30% 70/200 soy flour were more stable in volume change than were those of the control foams. Thus, the foams extended with 70/200 soy flour have a greater dimensional stability than that of the control foam. For all foams with Nutrisoy flour, the volume changes are decreased, but are less than 1.0%. All foams are expanded. An increase in the soy flour content increases the volume change for all the foams. After 14 days, the foams with up to 20% Nutrisoy flour were more stable in volume change than that for the control foams, except the foams with a 4.5% initial water content.

There is shrinkage of foams with 200W Soyafuff in accordance with the results shown in Table VIII. After 14 days, the foams with up to 40% 200W Soyafuff were more stable in volume change than were those of the control foams, except for the foam with a 5.5% initial water content and 20% biomass. During the aging period, the changes in volume for most of foams increased, then decreased. Moreover, all foams with 70/200 soy flour are expanded and the changes in volume are less or equal than 1.20%. After 14 days, the volume changes of all foams with biomass are smaller than those of the control foams. During the aging period, there are some variations in the change in volume for those foams. According to Table VIII, the results indicate that the change in volume varies between 1.0 and 2.0 for foams with Nutrisoy flour. All foams are expanded. After 14 days, the volume changes, for most of foams with Nutrisoy flour are larger than are those for the control foams. There are small variations of volume changes during the aging period.

Benning²¹ indicated that rigid polyurethane foam will absorb water to equilibrate with water vapor in a surrounding atmosphere (97% relative humidity in this study). The changes in dimensions, weight, and physical properties will result from the water absorption. In addition, the amount of absorbed water depends on whether the cell structure of a foam is closed or open and whether or not the foams have skin. When the molded foam has continuous foam skins, this will dramatically prevent water diffusion into the inside of the foam. In these experiments, the foams were divided by a band saw into the size 10.0 × 10.0 × 5.0 cm. The continuous skin surface was removed. Klempner and Frisch³ asserted that this mechanical trapping in cut or ruptured cells will vastly enhance the diffusive rate of water vapor into the foam system. Thus, the foams during humid aging absorb a great quantity of mois-

ture. Furthermore, according to Tables VII and VIII, the increase in volume at high relative humidity (humid aging) is higher than that under a dry condition (thermal aging) in results of the absorption of moisture, which plasticizes the foam system. Similar results were reported by Hildado.²² The dimensional stability and performance characteristics of a rigid polyurethane foam are significantly affected by the testing environmental conditions.

For a comparison of dimensional stability among foams with three different kinds of soy flours, the foams with 70/200 soy flour give the best performance of dimensional stability. Two reasons, such as particle size and amount of crude fiber, may contribute to dimensional stability in accordance with the results of Tables VII and VIII and the specifications of the three types of soy flour shown in Table I.

Glass Transition Temperature

The glass transition temperature is an important indicator for applications of polymeric materials. The selection of the glass transition temperature from the DMA data is usually either the peak loss modulus, E'' , or peak $\tan \delta$ and the glass transition temperature is dependent on the frequency.²³ In this study, peak $\tan \delta$ and 1 Hz were used for choosing the glass transition temperature. Table IX shows the glass transition temperature of the rigid polyurethane foams with 0–40% of soy flour at a 4.5, 5.0, and 5.5% initial water content. The glass transition temperatures of most of the extended foams were higher than those of the control foams and increased with increasing Soyafuff 200W and Nutrisoy flour. No systemic trend was found for each level of the initial water content, but most foams with 200/70 soy flour had a higher glass transition temperature than that of the control foams, except the foams with 10 and 20% biomass at a 5.5% initial water content. It seemed that adding soy flour into the foam system imparted a higher glass transition temperature than that of the control foams and the results were in agreement with the compressive strength.

Moreover, the glass transition temperature of most foams extended with Soyafuff 200W and Nutrisoy flour increased with increase of the initial water content. There also was no clear trend for each level of 200/70 soy flour. An increasing initial water content formed more urea bonds and fewer urethane bonds simultaneously in the rigid

Table VIII Effect of Humid Aging on Dimensional Stability of Water-blown Rigid Polyurethane Foams Extended with Soy Flours at 38°C and 97% Relative Humidity

| Volume Change (%) | Soyafuff 200W ^a (%) | | | | | 200/70 Soy Flour ^a (%) | | | | | Nutrisoy Flour ^a (%) | | | | |
|---|--------------------------------|-------|-------|-------|-------|-----------------------------------|-------|-------|-------|-------|---------------------------------|-------|-------|-------|-------|
| | 0 | 10 | 20 | 30 | 40 | 0 | 10 | 20 | 30 | 40 | 0 | 10 | 20 | 30 | 40 |
| 4.5% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | -0.96 | -0.10 | -0.40 | -0.14 | -0.30 | -0.96 | +0.89 | +0.49 | +0.40 | +0.43 | -0.96 | +1.08 | +1.10 | +1.24 | +1.11 |
| 7 | -1.23 | -0.19 | -0.47 | -0.55 | -1.02 | -1.23 | +1.03 | +0.76 | +0.80 | +0.78 | -1.23 | +1.09 | +1.18 | +1.54 | +1.42 |
| 14 | -1.32 | -0.07 | -0.68 | -0.50 | -0.72 | -1.32 | +1.04 | +0.62 | +0.63 | +0.58 | -1.32 | +1.23 | +1.28 | +1.52 | +1.54 |
| 5.0% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | -1.11 | -0.68 | -0.56 | -0.76 | -0.51 | -1.11 | +0.54 | +0.68 | +0.65 | +0.79 | -1.11 | +1.46 | +1.30 | +1.51 | +1.12 |
| 7 | -1.87 | -1.49 | -1.27 | -1.59 | -1.00 | -1.87 | +0.69 | +0.78 | +0.82 | +1.06 | -1.87 | +1.48 | +1.15 | +2.02 | +1.10 |
| 14 | -1.45 | -1.20 | -0.94 | -1.30 | -0.64 | -1.45 | +0.49 | +0.66 | +0.67 | +0.75 | -1.45 | +1.49 | +1.33 | +1.89 | +1.12 |
| 5.5% Initial water content^b | | | | | | | | | | | | | | | |
| Day | | | | | | | | | | | | | | | |
| 1 | -0.80 | -0.22 | -0.65 | -0.19 | -0.33 | -0.80 | +0.59 | +0.72 | +0.60 | +0.57 | -0.80 | +1.30 | +1.75 | +1.17 | +1.49 |
| 7 | -1.23 | -0.53 | -0.56 | -0.65 | -0.71 | -1.23 | +0.82 | +1.20 | +0.88 | +0.73 | -1.23 | +1.34 | +1.92 | +1.43 | +1.80 |
| 14 | -0.87 | -0.41 | -0.97 | -0.38 | -0.58 | -0.87 | +0.57 | +0.86 | +0.42 | +0.44 | -0.87 | +1.57 | +1.85 | +1.41 | +1.71 |

^a Percent of soy flours is based on weight of polyether polyol.

^b Foams containing 4.5, 5.0, and 5.5% initial water content, respectively.

Table IX Glass Transition Temperature of Water-blown Rigid Polyurethane Foams Extended with Soy Flours

| Water Content (%) | Biomass (%) | Glass Transition Temperature (°C) | | |
|-------------------|-------------|-----------------------------------|------------------|----------------|
| | | Soyafuff 200W | 200/70 Soy Flour | Nutrisoy Flour |
| 4.5 | 0 | 220.3 | 220.3 | 220.3 |
| | 10 | 223.2 | 224.2 | 225.0 |
| | 20 | 225.2 | 224.6 | 225.4 |
| | 30 | 225.5 | 225.1 | 225.5 |
| | 40 | 229.5 | 222.1 | 228.6 |
| 5.0 | 0 | 223.8 | 223.8 | 223.8 |
| | 10 | 226.7 | 224.4 | 227.1 |
| | 20 | 229.9 | 225.9 | 228.5 |
| | 30 | 227.8 | 224.8 | 228.5 |
| | 40 | 229.5 | 228.8 | 228.7 |
| 5.5 | 0 | 227.0 | 227.0 | 227.0 |
| | 10 | 227.3 | 221.0 | 228.6 |
| | 20 | 227.5 | 225.0 | 228.7 |
| | 30 | 229.4 | 230.0 | 230.3 |
| | 40 | 223.2 | 232.2 | 230.4 |

polyurethane foam system. Oertel¹⁷ reported that the urea bonds were more stable thermally (to 250°C) as compared to the urethane bonds (to 180°C).

Although the glass transition temperature increased with increase of the initial water content, the compressive strength decreased (Table IV). This was probably because the effect of decreasing foam density (Table III) reduced the foam's compressive strength more than did the effect of increasing the glass transition temperature. Therefore, the glass transition temperature alone could not be used directly to predict the compressive strength of the low-density foams.

CONCLUSIONS

According to the results of the measurements, the addition of 10% Soyafuff 200W, 20% 200/70 soy flour, or 20% Nutrisoy flour imparted water-blown rigid polyurethane foams with similar or improved strength, modulus, insulation, and dimensional stability. Moreover, the addition of soy flour in the rigid polyurethane foam system contributed to a higher glass transition temperature.

Also, increasing the initial water content resulted in an increase of the glass transition temperature. The compressive strength of rigid polyurethane foam could not be predicted by the glass transition temperature data.

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