Preparation and Properties of Rigid Polyurethane Foams Containing Modified Cornstarches

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SYNOPSIS

Rigid polyurethane foams were prepared containing 20% (based on weight of polyol) unmodified or modified cornstarches. The cornstarches had been modified by breeding or conversion methods and included waxy, acid-modified waxy, malto-dextrin, and canary dextrin. Due to its more favorable role as an extender, canary dextrin was added to additional foam formulations at 10–40%. Foams containing dextrins responded to compressive stress as control foams with yield points before 10% deformation. Foams filled with the unmodified or waxy cornstarches did not give clearly defined yield points and were measured at 10% deformation. After 14 days under 70°C and ambient conditions, volume increases for the filled foams were 4.0–7.1% vs. 4.6% for the control. The foams filled with canary dextrin increased in volume 4.3%. With the addition of 40% canary dextrin, the volume increases for the foams were 4.4% under thermal conditions and 4.5% under humid conditions (38°C and 98% relative humidity). Under humid conditions for 14 days, the foams containing canary dextrin increased in weight as dextrin content increased (1.5, 3.2, 3.4, and 7.6% with 10, 20, 30, and 40% dextrin, respectively). With 40% canary dextrin in the foams, thermal conductivity was 0.0235 vs. 0.0242 W/mK (0.163 vs. 0.168 Btu in/ft^2h°F) for the control.

INTRODUCTION

The polyurethane (PU) market in the United States for 1989 was 3295 million pounds, of which 870 million pounds was rigid foam.[1] A major user of rigid foam is the construction industry for insulation (480 million pounds).[1] Fillers are used in rigid foams to reinforce (fibrous) and to reduce costs and increase compressive strength (mineral).[2a] Investigators have reported success with the incorporation of plant components into PU formulations. Starches and flours have been added to PU foam formulations.[3–7] Kennedy[8] has patented a process for utilizing a gel forming polysaccharide, such as pectin, in the preparation of PU foams. Recently, investigators have examined lignin as a component in other PU systems.[9–12] The availability of large quantities of corn grain for wet milling to obtain cornstarch provides an impetus for investigating corn grain's potential use. PU products are continuing to appear in new industrial markets. The addition of plant components into PU formulations may result in an economical ingredient, beneficial to the properties of a current or new product.

This study evaluates adding modified (either by breeding or conversion) cornstarches in rigid PU foam formulations and the cornstarches' effect on properties. Compressive strength, density, dimensional stability under humid and thermal conditions, open-cell content, and thermal conductivity of foams containing one unmodified and four modified cornstarches were determined.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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EXPERIMENTAL

Materials

The modified cornstarches added to the foam formulations were Amaizo Lo-Dex 10 malto-dextrin,

Table I Foam Formulation

Component	Part by Weight
Poly-G 75–442	45
Triethylenediamine (Aliphatic Tertiary Amine)	0.25
Triethanolamine	0.50
Surfactant (Silicone Polyoxyalkylene Copolymer)	0.90
Dibutyltin Dilaurate	0.05
Water	(0.50–1.61)[a]
Fluorotrichloromethane (y)	(21.4–25.3)[b]
Polymeric Isocyanate	(65.4–84.5)[c]
Filler (Dry Basis) (Carbohydrate)	(4.5–18)[d]

[a] Moisture in filler, but water added as needed to attain 0.50 pbw.
[b] $y = 4 \times$ (OH part by weight + NCO part by weight)/21.
[c] Isocyanate to attain index of 115. Isocyanate index = 100 × (Isocyanate used/Isocyanate required).
[d] Quantity to give 10% to 40%, based on weight of polyol.

1752S canary dextrin, and 890 acid-modified waxy starch (American Maize-Products Co., Hammond, IN), and Amioca waxy cornstarch (National Starch & Chemical Corp., Bridgewater, NJ). Unmodified cornstarch used in the formulation was Buffalo 3401 (CPC International, Englewood Cliffs, NJ). Other ingredients included triethylenediamine, DABCO, (Air Products and Chemicals, Inc., Allentown, PA); dibutyltin dilaurate and fluorotrichloromethane (Aldrich Chemical Co., Milwaukee, WI); polyether polyol, Poly-G 75-442 (Olin Corp., Stamford, CT); polymeric isocyanate, PAPI 27 (Dow Chemical, Laporte, TX); surfactant, 193 (Dow Corning Corp., Midland, MI); and triethanolamine (Union Carbide Corp., Danbury, CT).

Foam Preparation

Foams were prepared by adding isocyanate to a premix of polyether polyol, triethylenediamine, starch or dextrin, triethanolamine, surfactant, dibutyltin dilaurate, water, and blowing agent (Table I). Ingredients were added as listed with starch or dextrin added at the 20% level (dry basis) based on the weight of the polyol. Canary dextrin, 1752S, was added at the 10, 20, 30, and 40% levels. The quantity of isocyanate added in each formulation was based on total hydroxyl content of the polyether polyol, triethanolamine, surfactant, and water, including water as moisture in the starch products. The total water in fillers at each addition are reported in Table II. Four replicate foams were prepared with each formulation. Materials were mixed in a Waring Blendor, Model 34BL97 (Waring Products Division, Dynamics Corp. of America, New Hartford, CT), which was equipped with a Variable Autotransformer, Type 3PN1010V (Staco Energy Products Co., Dayton, OH) for one min at 2500 rpm after each addition. Isocyanate was added during mixing for 15 s at 2500 rpm, after which the mixtures were poured immediately into wooden boxes (178 × 178 × 76 mm) and were allowed to rise at room conditions. Foams were removed from the boxes after 2–3 h and were allowed to cure at room temperature one week before cutting into test specimens.

Foam Testing Procedures

Testing procedures are ASTM Standards. The replicate foams were cut with a band saw into 152 × 152 × 51 mm specimens. The specimens were conditioned for two days at 23°C and 50% relative humidity (RH) and then were tested for thermal conductivity by ASTM C 518. Tests were performed

Table II Corn Products

Description	Moisture Content (%)	Level of Addition to Foam Formulation (%)	Total Water in Filler (g)
Unmodified cornstarch	9.8	20	0.98
Amioca (Waxy)	15.2	20	1.61
Amaizo 890 (Acid-modified Waxy)	12.0	20	1.22
Amaizo Lo-Dex 10 (Malto-Dextrin)	6.2	20	0.59
Amaizo 1725S Dextrin (Canary Dextrin)	3.1	10	0.14
		20	0.28
		30	0.43
		40	0.57

Table III Properties of Polyurethane Foams with 20%[a] Corn Products

Property	Control	Cornstarch	Amioca	Amaizo 890	Amaizo Lo-Dex 10	Amaizo 1752S Dextrin
Density, (g/cm^3)	0.0264	0.0251	0.0202	0.0238	0.0278	0.0276
Standard Deviation[b]	0.0010	0.0006	0.0002	0.0007	0.0007	0.0005
Compressive Strength, (kN/m^2)	196				141	158
Standard Deviation[b]	15				8	9
At maximum point						
Compressive Strength, (kN/m^2)		137	86	97		
At 10% deformation						
Standard Deviation[b]		6	4	7		
Thermal Conductivity, (W/mK)	0.0242	0.0249	0.0272	0.0258	0.0236	0.0236
Open Cells, (%)	13	13	15	15	12	12

[a] Based on weight of polyol.

[b] ASTM E 691-87, s = cell standard deviation $\sqrt{\sum_{1}^{n} (x - \bar{x})^2/(n-1)}$.

with a Rapid-k heat flow meter (Holometrix, Inc. Dynatech R/D Co., Cambridge, MA) at a mean temperature of 25°C using 152 × 152 × 51 mm cubes. After thermal conductivity testing, each of the four specimens was cut into nine, 51-mm cubes and was conditioned as described above for an additional two days. The specimens were calipered and weighed to determine density. Twenty of the 36 cubes were tested for compressive strength, 4 for thermal aging, 8 for humid aging, and 4 for open-cell content. For

Table IV Effect of Aging Polyurethane Foams Containing Various Additives[a]

Day	Control	Cornstarch	Amioca	Amaizo 890	Amaizo Lo-Dex 10	Amaizo 1752S Dextrin
	70°C and Ambient Volume Changes (%)					
1	+1.5	+3.3	+1.0	+2.1	+2.3	+1.5
7	+3.8	+6.2	+3.3	+5.5	+4.6	+3.5
14	+4.6	+7.1	+4.0	+6.6	+5.7	+4.3
	70°C and Ambient Weight Changes (%)					
1	−0.4	−0.2	−0.3	−0.5	−0.7	−0.4
7	0.0	−0.2	+0.1	−0.1	−0.6	−0.1
14	−0.1	−0.1	0.0	0.0	−0.7	0.0
	38°C and 98% Relative Humidity Volume Changes (%)					
1	+2.1	+3.2	+0.8	+3.4	+3.0	+2.8
7	+3.2	+4.7	+2.5	+5.0	+4.6	+4.0
14	+4.3	+6.4	+3.4	+6.2	+5.6	+4.7
	38°C and 98% Relative Humidity Weight Changes (%)					
1	+0.5	+0.9	+0.4	+1.0	+2.5	+2.2
7	+0.8	+0.8	+0.7	+1.3	+4.3	+3.3
14	+0.5	+1.0	+0.7	+1.4	+4.4	+3.2

[a] Twenty percent based on weight of polyol.

the open-cell test, the 51-mm cubes were cut into 25-mm cubes and conditioned another 2 days at 23°C and 50% RH. Density tests were performed according to ASTM D 1622-83 and dimensional stability by ASTM D 2126-87, except 51-mm cubes were used. Thermal aging was accomplished in a Precision Scientific STM 135 Mechanical Convection Oven (Precision Scientific, Chicago, IL). A Temperature–Humidity Chamber Model 434304 (Hotpack Corp., Philadelphia, PA) was utilized for humid aging. The compressive testing apparatus was an Instron Model 4201 (Instron Corp., Canton, MA), equipped with a 5kN static load cell Type 2518-805, ASTM D 1621-73 (Reapproved 1979) Procedure A. A suspended, self-aligning pad was mounted under the cross arm for the loading platen. The Beckman Air Compression Pycnometer Model 930 (Beckman Instruments, Inc., Scientific and Process Instruments Division, Fullerton, CA) was used for testing the open-cell content of the foams ASTM D 2856-87, Procedure C.

RESULTS AND DISCUSSION

Molecular differences in fillers include unmodified cornstarch (27% amylose/73% amylopectin), waxy (amylopectin), acid-modified waxy (highly acid-modified amylopectin), malto-dextrin (high molecular weight saccharides and low reducing sugar), and canary dextrin (fine particle size). The compressive strength, density, open-cell content, and thermal conductivity of the control and foams containing 20% (based on weight of polyol) corn product are reported in Table III. Effects of humid and thermal aging on these foams are reported in Table IV; effects on foams containing 10–40% Amaizo 1752S Dextrin are given in Table V.

Compressive Strength

Responses to compressive strain, expressed as compressive stress, for the control and filled foams at the 20% level are shown in Figure 1. The control and foams containing dextrins exhibit yield points before 10% deformation as foams collapse suddenly under an increasing stress. Foams containing the same quantity of the cornstarches (unmodified cornstarch, waxy, and acid-modified waxy) do not give sharply defined peak stress levels at failure. Foams containing each of these three fillers were less dense, resulting in some loss of compressive strength. Moisture in these starches (9.8, 15.2, and

Table V Effect of Aging Polyurethane Foams Containing Amaizo 1752S Dextrin

	Level of Dextrin (%)[a]				
Day	0	10	20	30	40
	70°C and Ambient Volume Changes (%)				
1	+1.5	+1.9	+1.5	+1.6	+1.3
7	+3.8	+4.4	+3.5	+6.5	+3.5
14	+4.6	+5.4	+4.3	+5.1	+4.4
	70°C and Ambient Weight Changes (%)				
1	−0.4	+0.1	−0.4	−0.4	−0.6
7	0.0	+0.3	−0.1	−0.3	−0.4
14	−0.1	+0.6	0.0	−0.3	−0.4
	38°C and 98% Relative Humidity Volume Changes (%)				
1	+2.1	+2.4	+2.8	+2.4	+2.2
7	+3.2	+3.7	+4.0	+3.8	+3.4
14	+4.3	+5.1	+4.7	+4.9	+4.5
	38°C and 98% Relative Humidity Weight Changes (%)				
1	+0.5	+1.0	+2.2	+2.1	+3.8
7	+0.8	+1.2	+3.3	+4.1	+7.0
14	+0.5	+1.5	+3.2	+3.4	+7.6

[a] Based on weight of polyol.

12.0%, respectively) were high and therefore the additional water could have provided additional blowing, since one water molecule reacts with two −NCO groups. Since there are no definite yield points in compressive tests for the foams containing these starches, the values at 10% deformation, based on the original thickness, are reported. Among the filled foams, the dextrin foams exhibited higher values for compressive strength than the starch-filled foams (141–158 vs. 86–137 kN/m^2), but less than the control with 196 kN/m^2. Foams containing unmodified cornstarch responded better to the external compressive strain than the foams containing either of the waxy starches (137 vs. 86–97 kN/m^2). Among all of the filled foams, the ones filled with Amaizo 1752S Dextrin (yellow or canary corn dextrin) responded best to the external compressive strain (158 kN/m^2). At this level of addition of corn flour, Cunningham et al.[13] reported a compressive strength of 139 kN/m^2. The compressive stress values did not improve with less (10%, based on weight of polyol) or more (30–40%) canary dextrin, as shown in Figure 2. Bennett et al.[4] reported that in the foam system, an increase in cornstarch resulted in a decrease in compressive strength. Typically, compressive strength is a function of density.[14] There appears to be a relationship between compressive stress and density, as shown in Figure 2, until the dextrin is added at a level of 30% or above.

Density

With the exception of the foams filled with the dextrins, the filled foams were less dense than the control foam (Table III). Amioca and Amaizo 890 (waxy cornstarches) contained more moisture than the regular cornstarch or corn dextrins, and additional moisture would contribute to the formation of CO_2 from an isocyanate/water reaction, and therefore would create some CO_2 blowing. A slight increase in the open-cell content was observed (15 vs. 12–13%), which is to be expected from CO_2 blowing. The densities of the foams filled with dextrins were essentially the same (0.028 g/cm^3), but were slightly more dense than the control (0.026 g/cm^3).

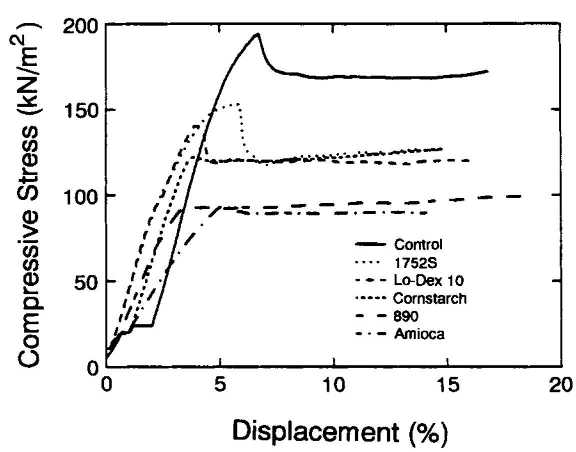

Figure 1 Effect of corn product fillers in polyurethane foams on compressive stress. Stress is calculated as force per unit initial area. Representative cubes of control and foams containing 20% corn product (dry basis) based on the weight of the polyol.

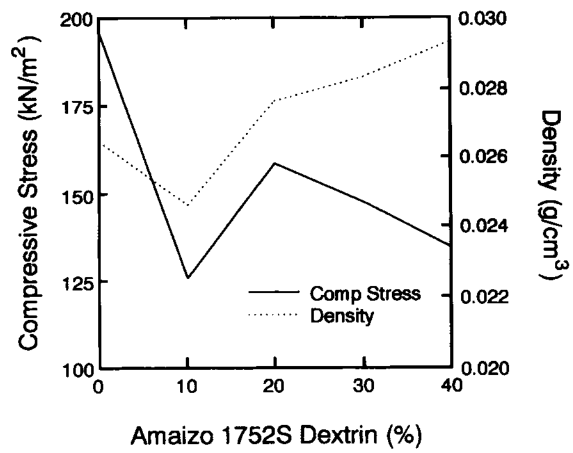

Figure 2 Relationship of compressive stress and density with increased Amaizo 1752S Dextrin in rigid polyurethane foams.

Dimensional Stability

Thermal Aging

Essentially no change in weight was observed during the thermal aging of the control and foams containing 20% (based on weight of polyol) corn product (Table IV). Some variations in volume increases were observed for the filled foams. After 14 days, the control foam increased in volume 4.6% and the filled foams increased 4.0–7.1%. When Amaizo 1752S Dextrin was added to the foam formulations over a range of 10–40%, only 4–5% increases in volume were noted after 14 days (Table V).

Humid Aging

The changes in weights of the filled foams were slightly higher than for the control after 14 days (Table IV). Control foam increased in weight only 0.5%, whereas the filled foams increased 0.7–4.4% during this period. Foams containing dextrins increased in weight from 3.2–4.4 as compared with 0.7–1.4% for the foams containing starches. Typically, the water vapor permeability of rigid PU foam is low.[2b] The increases in volumes for the filled foams during the 14 day period were 3.4–6.4% vs. 4.3% for the control foam. Even with a 40% addition of Amaizo 1752S Dextrin, the increase in volume was 4.5% vs. 4.3% for the control (Table V). However, weight increases of 1.5 to 7.6% were observed as the dextrin content was increased from 10 to 40%.

Open-Cell Content

The cells in a PU foam can be open and/or closed, depending on the blowing process. Testing of a foam for its open-cell content is of interest as it affects properties, especially thermal conductivity, water vapor permeability, and liquid water uptake.[2c] The open-cell content of foams filled with unmodified cornstarch was the same as for the control foam (13%) (Table III). Foams filled with the modified starches (waxy and acid-modified waxy) contained 15% open cells. When dextrins were added in the foam formulations, the foams contained fewer open cells (12%).

Thermal Conductivity

Foams containing starches (unmodified, waxy, and acid-modified) exhibited higher thermal conductivity values than did the foams containing no starch (Table III). However, the foams containing dextrins had a slightly lower thermal conductivity value than the control 0.0236 vs. 0.0242 W/mK (0.164 vs. 0.168 Btu in/ft^{2}h °F). Table III shows the relationship between the thermal conductivities of the foams and their open-cell contents. With fewer open cells, thermal conductivities values are lower. Closed celled foams containing fluorotrichloromethane have a low coefficient of thermal conductivity.[14] This same relationship is exhibited by the addition of Amaizo 1752S Dextrin in a range from 10 to 30% (based on weight of polyol) as shown in Figure 3. Even at the 40% addition level of Amaizo 1752S Dextrin, the thermal conductivity value was 0.0235 W/mK (0.163 Btu in/ft^{2}h °F), or 3% below the control.

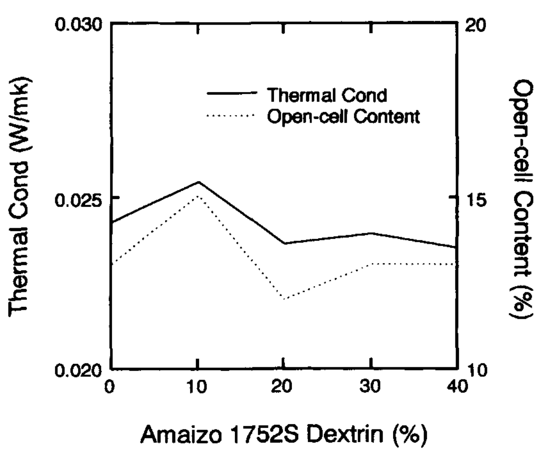

Figure 3 Relationship of thermal conductivity and open-cell content with increased Amaizo 1752S Dextrin in rigid polyurethane foams.

CONCLUSIONS

The foams containing canary dextrin exhibited a higher compressive strength value than any foams filled with unmodified, waxy, acid-modified waxy, or malto-dextrin. Foams containing malto-dextrin and canary dextrin (20%, based on weight of polyol) responded to compressive stress as the control foam in exhibiting yield points before 10% deformation. Upon application of additional levels of canary dextrin, foams containing 40% (based on weight of polyol) gave compressive strength values of 134 kN/m^2. Under thermal and humid conditions, the volume changes for the foams containing 40% canary dextrin was only 4% after 14 days of aging. Under humid conditions, the foams increased in weight by 8% during the same time period. Foams containing 40% canary dextrin retained a thermal conductivity of 0.0235 W/mK (0.163 Btu in/ft^{2}h °F).

Application of canary dextrin in rigid polyurethane foam formulations provided foams with similar or improved thermal stability, open-cell content, and thermal conductivity. This was characteristic of the properties even at applications of the canary dextrin at 40% (based on weight of polyol).

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