Polyurethane Foams Extended with Corn Flour

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ABSTRACT

Five levels of unmodified corn flour (5, 10, 20, 30, and 40%, based on weight of polyether polyol) were evaluated as fillers-extenders in rigid polyurethane foams. Densities of the flour-filled and control foams were similar (0.025–0.026 g/cm^3) except for the foams containing 10% flour (0.029 g/cm^3). The moisture in the flours at the various levels of addition appeared to have a significant effect on the structural formation of the foams. Force-deformation curves of foams with 5 and 10% flour were similar to those curves of the controls. Thermal conductivity of the foam filled with 10% flour was slightly lower (thus having greater insulating value) than were the values for the foam filled with 5% flour or the control foam (0.0232 versus 0.0242 W/m·K) (0.161 versus 0.168 BTU in./[ft^2·hr·°F]). Foams containing 5 and 10% flour did not increase more than 5% in volume when subjected to thermal or humid conditions for 14 days. At the 40% level, foams expanded 14 and 16% under thermal and humid conditions, respectively, after 14 days.

Corn flour, cornmeal, or grits have been used industrially in the manufacture of adhesives, explosives, textile sizing, core binders, and soaps (Leonard and Martin 1963). Another industrial use of corn flour may be as a filler or extender for polyurethane (PU) foams. Fillers are used in many kinds of PU products for various reasons (Woods 1987), such as to to reduce flammability; lower costs; improve heat resistance; and increase weight, stiffness, and comprehensive and tensile strength.

Corn flour was once considered a possible source of starch for the reaction of an organic polyisocyanate with degraded starch polyoxalkylene ethers to make PU foams (Otey and Mehltretter 1965). Starch-containing material such as flour was mentioned in the process for preparing resins of polyether-PU-starch (Otey et al 1968). Cunningham and Carr (1990) evaluated six cornstarches and corn flours as fillers for rigid PU foams. The favorable position of corn flour in the preliminary study merited additional evaluation.

The purpose of this investigation was to study compressive strength, density, dimensional stability under thermal and humid aging, thermal conductivity, and open-cell content of PU foams containing five levels of unmodified corn flour. The vital role of PUs in many industries and the increasing diversity of their uses require a continuing search for potential ingredients to meet the needs of current and future products. Thus, corn flour may have the functionality required for incorporation into PU foams and be economically feasible as well. With insulating foam selling for \$162/m^3, inexpensive extenders such as corn flour (\$0.20/kg) could be beneficial.

MATERIALS AND METHODS

Materials

The materials used in the foam formulations were corn flour (Product 505, Illinois Cereal Mills, Inc., Paris, IL), 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).

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[2]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.

Preparation of PU Foams

Foams were prepared by adding polymeric isocyanate to a mixture of polyether polyol, triethylenediamine, corn flour, triethanolamine, surfactant, dibutyltin dilaurate, water, and a blowing agent (Table I). Ingredients were added in sequence as listed above, with corn flour additions of 5, 10, 20, 30, and 40%. The quantities of corn flour (dry basis) were based on the weight of the polyether polyol. No water was added to foams with 10–40% levels of flours other than the moisture in the flours. The quantity of isocyanate added in each formulation is dependent on available hydroxyl content. Therefore, additional isocyanate was added for the increased water in the flours (Table II). Four replicate foams were prepared with each formulation with and without flour additions. After each addition, the materials were mixed for 1 min at 2,500 rpm in a Waring Blendor (model 34BL97, Waring Products Division, Dynamics Corp. of America, New Hartford, CT) equipped with a variable autotransformer (type 3PN1010V, Staco Energy Products Co., Dayton, OH). Isocyanate was added during mixing for 15 sec at 2,500 rpm. The mixtures were poured immediately into wooden boxes (178 × 178 × 76 mm) and allowed to rise at room conditions. Foams were removed from the boxes after 2–3 hr and allowed to cure at room temperature for one week before being cut into test specimens.

Foam Test Procedures

The foams were tested according to standards of the American Society for Testing and Materials (ASTM). The replicate foams were cut with a band saw into four specimens of 152 × 152 × 51 mm. The specimens were conditioned for two days at 23°C and 50% relative humidity and then were tested for thermal conductivity according to ASTM procedure C 518. Tests were performed with a Rapid-k heat-flow meter (Holometrix, Inc., Dynatech R/D Co., Cambridge, MA) at a mean temperature of 25°C. After completing the thermal conductivity measurements, each specimen was cut into nine 51-mm cubes (36 cubes per condition) and conditioned as described above for an additional two days. These specimens were calipered and weighed to determine density. Twenty of the 36 cubes were tested for compressive strength, four for thermal aging, eight for humid aging, and four for open-cell content. For the open-cell test, the 51-mm cubes were cut into 25-mm cubes and conditioned for another two days at 23°C and 50% relative humidity. Density and dimensional stability were tested according to ASTM D 1622-83 and ASTM D 2126-87, respectively. Compression was tested with an Instron apparatus (model 4201, Instron Corp., Canton, MA) equipped with a 5-kN static load cell, type 2518-805, ASTM D 1621-73 (reapproved in 1979), procedure A. A suspended, self-aligning pressure pad was mounted under the cross arm for the loading platen. A Beckman air comparison pycnometer (model 930, Beckman Instruments, Inc., Scientific and Process Instruments Division, Fullerton, CA) was used to test the open-cell content of the foams according to ASTM D 2856-87, procedure C.

TABLE I
Foam Formulated by Adding Polymeric Isocyanate to a Mixture of Ingredients

Ingredient	Part by Weight
Polyether polyol	45
Tertiary amine	0.25
Triethanolamine	0.50
Surfactant	0.90
Dibutyltin dilaurate	0.05
Water	0.50[a]
Total	47.2
Fluorotrichloromethane	Y(21.4)[b]
Polymeric isocyanate	65.4[c]
Corn flour (dry basis)	2.25, 4.5, 9.0, 13.5, 18

[a] Value for control and foam containing 5% corn flour. For other foams extended with corn flour, see Table II.
[b] Calculated value based on quantity of ingredients (47.2) with polymeric isocyanate (65.4), as follows $Y = 0.16(47.2 + Y + 65.4)$.
[c] Quantity necessary to give an isocyanate index of 115 for the control and for the foam containing 5% flour. The isocyanate index is determined by dividing the actual amount of isocyanate used by the theoretical amount of isocyanate required and multiplying by 100. An isocyanate index of 115 indicates a 15% excess of isocyanate.

TABLE II
Polymeric Isocyanate Added to Foam at Different Levels of Flour Addition

Flour		Water Source, g		Polymeric	Fluorotri-
(%)[a]	(g)	Flour Moisture	Added Water	Isocyanate (g)	chloromethane (g)
0	0.00	0.00	0.50	65.4	21.4
5	2.25	0.27	0.23	65.6	21.5
10	4.50	0.56	0.00	66.4	21.6
20	9.00	1.13	0.00	76.2	23.6
30	13.50	1.69	0.00	85.9	25.6
40	18.00	2.25	0.00	95.6	27.5

[a] Dry basis, percent of polyether polyol.

RESULTS AND DISCUSSION

The properties of rigid PU foams containing five levels of corn flour addition are reported in Table III. Density, compressive strength, thermal conductivity, and open-cell content are considered essential properties of foams for determining their suitability for most applications. The effects of aging on dimensional stability and weight changes, under two combinations of temperature and relative humidity, are reported in Tables IV and V.

TABLE III
Properties of Polyurethane Foams with Added Corn Flour

	Added Corn Flour, %[a]					
Property	0	5	10	20	30	40
Density, g/cm^3	0.0264	0.0259	0.0291	0.0250	0.0250	0.0246
Standard deviation[b]	0.0010	0.0005	0.0015	0.0005	0.0009	0.0009
Compressive strength, kN/m^2	196	160	192	139[c]	120[c]	104[c]
Standard deviation[b]	15	16	17	5	6	6
Thermal conductivity, W/mK	0.0242	0.0242	0.0232	0.0246	0.0259	0.0275
Open cells, %	13	14	12	13	15	17

[a] Percent of corn flour is based on the weight of polyether polyol.
[b] ASTM E 691-87, s = cell standard deviation = $\sqrt{\sum_{1}^{n}(x-\bar{x})^2/(n-1)}$
[c] Measured at 10% deformation.

TABLE IV
Effect of Aging Rigid Polyurethane Foams Containing Corn Flour at 70°C and Ambient Room Conditions

	Added Corn Flour, %[a]					
	0	5	10	20	30	40
Volume changes, %						
Day						
1	+1.5	+1.8	+1.3	+2.4	+4.0	+8.9
7	+3.8	+3.8	+3.3	+4.5	+7.7	+12.5
14	+4.6	+4.7	+4.1	+5.4	+8.7	+13.8
Weight changes, %						
Day						
1	−0.4	−0.5	−0.5	−0.6	−0.6	−0.8
7	0.0	−0.1	−0.2	−0.4	−0.8	−1.1
14	−0.1	−0.1	−0.3	−0.3	−0.9	−0.9
Compressive strength, kN/m^2						
Day						
14	199	183	212	158[b]	145[b]	111[b]
Standard deviation[c]	13	18	14	12	5	5

[a] Percent of corn flour is based on weight of polyether polyol.
[b] Measured at 10% deformation.
[c] ASTM E 691-87, s = cell standard deviation = $\sqrt{\sum_{1}^{n}(x-\bar{x})^2/(n-1)}$

Densities

Foam containing 5% corn flour was similar in density to the control (0.0259 versus 0.0264 g/cm^3). Although the foams extended with 20–40% corn flour were slightly less dense than the control (0.0246–0.0250 versus 0.0264 g/cm^3), the foam with 10% flour was denser (0.0291 g/cm^3) than the control. This is because the quantities of water in the foam formulations were similar for the foam containing 10% flour and for the control, whereas the quantities of water from the natural moisture content of the flours was greater with 20–40% addition. The effect of decreasing water content on density of foam formulations is shown in Figure 1. Kennedy (1985) adjusted the density of foams by varying the amounts of water in the mixture. Although a 10% flour addition provided 0.56 g of water, this foam was denser than foam made with a formulation containing only 0.2 g of water. When added water is in the form of moisture in the flour, the water-density relationship is probably different from that shown in Figure 1 for formulations that do not contain flour.

TABLE V
Effect of Aging Rigid Polyurethane Foams Containing Corn Flour at 38°C and 98% Relative Humidity

	Percent of Corn Flour[a]					
	0	5	10	20	30	40
Volume changes, %						
Day						
1	+2.1	+2.7	+2.4	+3.7	+4.7	+9.5
7	+3.2	+4.1	+3.5	+5.3	+6.5	+11.8
14	+4.3	+5.1	+4.4	+6.5	+8.1	+16.0
Weight changes, %						
Day						
1	+0.5	+0.6	+1.0	+0.6	+1.0	+0.6
7	+0.8	+0.9	+1.2	+0.8	+0.4	+0.3
14	+0.5	+0.8	+1.0	+1.0	+0.3	+0.9
Compressive strength, kN/m^2						
Day						
14	176	164	182	137[b]	114[b]	96.3[b]
Standard deviation[c]	15	18	11	3	4	4

[a]Percent of corn flour is based on weight of polyether polyol.
[b]Measured at 10% deformation.
[c]ASTM E 691-87, s = cell standard deviation = $\sqrt{\sum_{1}^{n}(x-\bar{x})^2/(n-1)}$

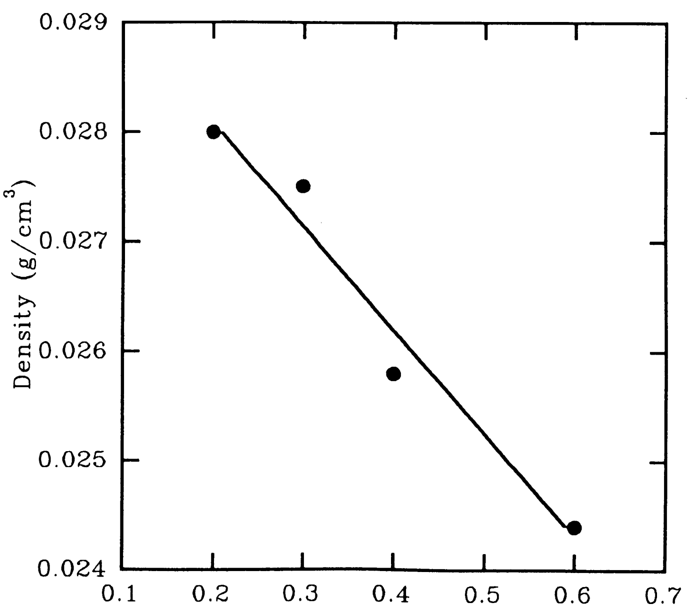

Fig. 1. Relationship of formulation water and density of rigid polyurethane foam.

Compressive Strength

Figure 2 illustrates the behavior of these cellular plastics under compressive loads. The control foam and foams containing 5 and 10% corn flour exhibit a yield point before 10% deformation. Even though the compressive-strength value is lower for the foam containing 5% flour than for the control foam, the value for foam with 10% flour is nearly equal to that of the control. Their patterns on the graph represent foams that collapse suddenly under increasing stress, showing the same typical force-deformation curve. The higher density of the foam containing 10% flour compared with the foam containing 5% flour may contribute to its higher compressive strength. Since no compressive-strength yield points were observed for foams containing 20, 30, and 40% flour, strength values are reported at 10% deformation, as discussed by Zollner (1985). These foams would be more cushionlike.

Thermal Conductivity

Foams containing 5 and 20% flour were similar to the control in their thermal conductivities (0.0242 and 0.0246 versus 0.0242 W/m·K) (0.168 and 0.171 versus 0.168 BTU in./[ft^2·hr·°F]). The conductivity of foam containing 10% flour was 0.0232 W/m·K (0.161 BTU in./[ft^2·hr·°F]). Thermal conductivity of foams containing 30 and 40% flour were 7 and 14% higher, respectively, than those of the control foams.

Open-Cell Content

Cellular plastics have walls of polymer separating cells and are interconnecting (open cells), nonconnecting, or a combination (ASTM D 2856-87). In the open-cell test (procedure C), the cut-cell volume at the surface of the test specimen (cells opened during sample-cutting preparation) are uncorrected. This test showed that the experimental foams containing corn flour had only 12–17% open cells. The lowest percentage (12%) of open cells was obtained with a foam containing 10% corn flour.This foam formulation contained no added water except for the natural moisture in the corn flour. Carbon dioxide from the isocyanate-water reaction contributed to the foam blowing and probably to the open-cell content, since foams blown with carbon dioxide are preponderantly to exclusively open celled (Dahm and Uhlig 1985). Foam formulations containing 20, 30, and 40% flour had additional water and therefore more carbon dioxide but the percentage of open cells increased only slightly (Table III).

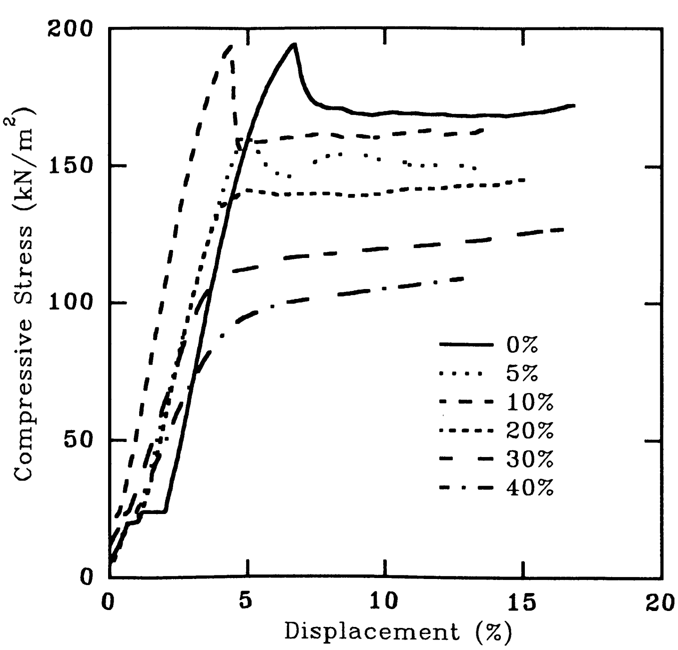

Fig. 2. Effect of corn-flour fillers on compressive stress in rigid polyurethane foams. Stress is calculated as force per unit initial area. Data are for representative cubes of the control foam and foam supplemented with 5, 10, 20, 30, and 40% corn flour (based on the weight of polyether polyol).

Dimensional Stability

Thermal aging. The changes in volume and weight during thermal aging of the control and the foams containing 5% flour were similar (Table IV). After 14 days of thermal aging at 70°C, the 10% flour-filled foams were 11% more dimensionally stable than the control foams. With foams containing 20, 30, and 40% flour, volume increases were 5, 9, and 14%, respectively, after 14 days. Weight losses for all foams during the aging period never exceeded 1%. Compressive-strength values increased for the foams tested after thermal aging for 14 days, compared with their respective foams tested before aging, probably because of a curing effect.

Humid aging. Volume changes of foams containing 10% flour were similar to those of the control foams after 14 days of humid aging (Table V). Other flour-filled foams increased 5–16% in volume versus 4% for the control foams after 14 days of exposure. None of the foams ever exceeded 1% in weight gain. Generally, compressive-strength values were lower for the foams after humid aging.

CONCLUSIONS

Rigid PU foams containing 5 and 10% corn flour (polyol weight basis) exhibited force-deformation curves similar to those of the control foams. Compressive stress of these foams rose to a maximum and then dropped rapidly. At the 10% level of addition, compressive strength was similar to that of the control. Only the 10% flour-filled foam was denser than the control (0.0291 versus 0.0264 g/cm^3). Thermal conductivity of the 10% flour-filled foam was slightly lower than that of the control or the 5% flour-filled foams (0.0232 versus 0.0242 W/m·K) (0.161 versus 0.168 BTU in./[ft^2·hr·°F]). Because of the moisture in the flour at the 10% level of addition, no water was added in the formulation, but the moisture absorbed in the flour apparently resulted in a modified chemical reaction, with slightly higher density and insulating value. Dimensional stability of foams filled with 5 and 10% flour were similar to that of the control foams when exposed to humid or thermal aging conditions. Thus, 10% corn flour (polyol basis) added to the formulation served not only as filler but as a promising contributive material for maintaining specific properties of PU foams, especially compressive strength and insulating properties.

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