

# Water-Blown Flexible Polyurethane Foam Extended with Biomass Materials

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Received 1 November 1996; accepted 22 November 1996

**ABSTRACT:** Soy protein isolate, soy fiber, and cornstarch (0–40% polyether polyol) were incorporated into a flexible polyurethane foam formulation. Stress–strain curves of the control foam and foams containing 10–20% biomass material exhibit a considerable plateau stress region but not for foams extended with 30–40% biomass materials. An increase in biomass material percentage increases foam density. An increase in initial water content decreases foam density. Foams extended with 30% soy protein isolate, as well as foams extended with 30% soy fiber, have notably greater resilience values than all other extended foams. The comfort factor increases with increasing percentage of biomass material in foam formulation. Foams containing 10–40% biomass materials display significantly lower values in compression-set than the control foam. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 695–703, 1997

**Key words:** flexible polyurethane foam; soy protein isolate; soy fiber; cornstarch

## INTRODUCTION

Use of polyurethane (PU) foams is continuing to grow at a rapid pace throughout the world. This growth can be attributed to their light weight, excellent strength/weight ratio, energy absorbing performance (including shock, vibration, and sound), and comfort features of the polyurethane foams.<sup>1</sup>

Recently, there has been an increased interest in using renewable resources in the plastic industry.<sup>2–10</sup> In addition, many patents covering processes for utilizing the plant components in the preparation of PU foam have been issued in recent years.<sup>11–15</sup> However, most of these studies focused on rigid PU foam. Less attention has been paid to the flexible PU foam system. Two notable renewable raw materials are soybean and corn, but their

major applications are in food and feed. Their utilization in the nonfood industry is still very limited.

Soybeans contain ~40% proteins, which are polyfunctional molecules with many active hydrogens. In addition, soybeans also contain ~35% carbohydrates with many hydroxyl groups. These active hydrogens and hydroxyl groups may react with isocyanate, one of the major components in the PU foam formulation. Corn grain contains ~72% starches and 9% proteins that may also react with the isocyanate. Thus, there is a great potential of using soybean and corn products to modify or improve the physical and chemical properties of flexible polyurethane foams.

A blowing agent is usually required for PU foam formation. There are three types of blowing agents: (1) water that reacts with isocyanate and produces carbon dioxide; (2) low boiling liquid chemicals that can be evaporated due to the exothermic reaction of the polyols and isocyanate; and (3) air blown in or whipped into the polyols and isocyanate mixture. The first reaction, which

Contribution from the Missouri Agricultural Experiment Station, Journal Series No. 12,569.

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uses water as a blowing agent, is preferred for the manufacture of flexible polyurethane foams.<sup>16</sup>

The objectives of this article were to develop flexible polyurethane foams extended with biomass materials such as soybean and corn using water as a blowing agent, to characterize their physical and mechanical properties, and to investigate the effects of biomass concentration on the foam properties.

## EXPERIMENTAL

### Materials

The ingredients used in the preparation of flexible foams were soy fiber (FIBRIM 1250, Protein Technologies International Inc., St. Louis, MO), soy protein isolate (PRO-FAM S955, ADM Protein Specialties, Decatur, IL), and unmodified common cornstarch (PF Powdered Starch, American Maize Products, Hammond, IN). Other components used in the flexible PU foams were toluene diisocyanate (OLIN TDI 80, Olin Corp., Stamford, CT), glycerol-propylene oxide polyether triol (ARCOL LHT-42, Arco Chemical Co., Newtown, PA), tertiary amine (DABCO, Aldrich Chemical Co., Milwaukee, WI), triethanolamine and dibutyltin dilaurate (Aldrich Chemical Co., Milwaukee, WI), stannous octoate (Sigma Chemical Co., St. Louis, MO), surfactant (L-560, Union Carbide Corp., Danbury, CT), and distilled water. The distilled water was used as a blowing agent.

### Experimental Design and Formulations

The effects of the following variables in the foam formulation on the properties of water-blown flexible PU foams were studied. These include (1) Types of soybean and corn products: soybean fiber (FIBRIM 1250), soybean protein isolate (PRO-FAM S955), and corn starch (PF powdered starch); and (2) concentrations of soybean and corn products (parts per hundred weight of polyol): 0, 10, 20, 30, and 40. Other factors in the foam formulation such as catalyst, surfactant, crosslinking agent, and isocyanate index were fixed. They were determined in a preliminary study to assure that all foam products could be produced within 10 min.

The experiment was a  $3 \times 5$  factorial design. The foam formulation for water-blown flexible PU

foam is shown in Table I. The amount of isocyanate added in each formulation was based on the total hydroxyl content of polyether polyol, triethanolamine, and water, including water originally present in the soybean and corn products. The amount of water was varied to maintain the same isocyanate index in each formulation (Table II). Two replicate foams were produced with each foam formulation.

### Foam Preparation

Foams were prepared by adding a mixture of toluene diisocyanate, dibutyltin dilaurate, and stannous octoate (component B) to a premix of glycerol-propylene oxide polyether triol, tertiary amine, soybean products or cornstarch, triethanolamine, and distilled water (component A). A standard mixing procedure for making foams was used in this study.<sup>17</sup> This procedure involved intensive mixing using a commercial drill press (Colcord-Wright, St. Louis, MO) fitted with a 25.4 cm shaft with a 5 cm impeller arranged to turn at 1845 and 3450 rpm. Component A was sequentially weighed and placed into a disposable paperboard container ( $0.95 \text{ dm}^3$ ) fitted with a steel frame with four baffles, and mixed at 3450 rpm for 30 s. The stirring was then stopped, allowing the mix to degas. After 15 s, component B was rapidly added and stirring was continued for another 10 s at the same speed. The reacting mixtures were then poured immediately into wooden boxes with a dimension of  $200 \times 200 \times 100 \text{ mm}$  and allowed to rise at ambient conditions. Foams were removed from boxes after 3 h and allowed to cure at room temperature ( $23^\circ\text{C}$ ) for 1 week before cutting into test specimens.

### Foam Property Measurements

Foam density, defined as mass per unit volume, was tested according to ASTM D3574 (section 9–15). The test specimens ( $100 \times 100 \times 50 \text{ mm}$ ) were calipered and weighed to determine the density in kilograms per cubic meter. Four specimens were tested and the average value was reported.

The resilience test is also referred to as the “ball rebound test.” The instruments and the methods used conform to the ASTM D3574 (section 68–75). This instrument consists of a 38-mm inside diameter vertical clear plastic tube and a 16-mm diameter steel ball (16.3 g). The height of drop is 500 mm. Since it is most convenient to note the position of the top of the ball on rebound,

**Table I Foam Formulations for Flexible Polyurethane Foams**

Ingredients	Parts by Weight
Component A	
Glycerol-propylene oxide polyether triol	100.0
Tertiary amine	0.1
Soybean and corn products	0, 10, 20, 30, 40
Triethanolamine	0.7
Surfactant (L-560)	1.0
Blowing agent (distilled water)	4.5
Component B	
Toluene diisocyanate	(105) <sup>a</sup>
Dibutyltin dilaurate	0.1
Stannous octoate	0.3

<sup>a</sup> The quantity of isocyanate is required to meet an isocyanate index 105, defined as the actual amount of isocyanate used over the theoretical amount of isocyanate required, multiplied by 100.

the scale on the back of the tube was calibrated directly in percent as follows: every 5% a complete circle was scribed and every 1% a 120° arc was scribed. The reason for using the complete circle is to eliminate parallax error. The test specimen with a dimension 100 × 100 × 50 mm was placed at the base of the tube. The specimen was centered and the height of the tube was adjusted so that zero rebound was 16 mm above the surface of the specimen. The steel ball was released from the base of a magnet, located at the top of the tube, and the maximum rebound height was marked. The experiment was repeated if the ball stuck to the tube when it dropped or rebounded.

The median of three rebound values was recorded. If any value deviated >20% from this median, two additional drops were made and the median for all five drops was recorded. Finally, the ball rebound resilience value of the foam sample was recorded as the median of the three specimen medians.

The indentation force deflection (IFD value) was determined according to ASTM D3574 (section 16–22) by the Instron Universal Testing Machine, Model 1132 (Instron Corporation, Canton, MA) with a data acquisition system. The foam sample with a dimension 200 × 200 × 20 mm was placed between two flat plates. The foam area to be tested was preflexed by twice lowering the in-

**Table II Toluene Diisocyanate and Water Added to Foam Formulation at Different Levels of Biomass Materials Addition**

Biomass Materials	Level of Addition in Foam Formulation (%)	Added Water (g)	Toluene Diisocyanate (g)
Soy fiber	0	4.5	54
	10	3.8	54
	20	3.1	54
	30	2.4	54
	40	1.7	54
Soy protein isolate	0	4.5	54
	10	3.9	54
	20	3.3	54
	30	2.7	54
	40	2.1	54
Cornstarch	0	4.5	54
	10	3.5	54
	20	2.5	54
	30	1.5	54
	40	0.5	54

dentor foot to a total deflection of 75–80% of the original thickness at a rate of 0.9 mm/s. The location of the test area was marked with a pen by circumscribing the indenter foot while under 4.5 *N* force. The specimen was allowed a 6-min rest after the reflex. Then, the indenter foot was brought into contact with the specimen and the thickness of the specimen was determined after applying a contact force of 4.5 *N* to the indenter foot. The specimen was indented 25% of its thickness at a rate of 0.9 mm/s and the force in *N* after 1 min was recorded. Then, the deflection was increased to 50% without removing the specimen and the force after 1 min was recorded. The procedure was repeated again with the deflection increased to 65%, allowing the force to drift while maintaining the 65% deflection. Again, the force in *N* after 1 min was recorded. The IFD values at 25, 50, and 65% were calculated by dividing the forces at 25, 50, and 65% deflections, respectively, by the indented area. The comfort or support factor is calculated as the ratio of the 65% indentation force deflection to the 25% indentation force deflection.

The compression set test under constant deflection was conducted according to ASTM D3574 (section 37–44). This instrument consisted of two flat plates arranged so that the plates were held parallel to each other and the space between the plates was adjustable to the required deflection thickness by means of calipers. The initial thickness (~ 50 mm) of a specimen sample (100 × 100 × 50 mm) was measured. The sample was compressed by 50% of its original thickness between plates and held for 22 h in an oven at conditions of 70 ± 2°C and 5 ± 1% relative humidity. Thickness was measured 30 min after removal of the plates. The compression set value was calculated as follows:

$$C = \frac{(T_o - T_f)}{T_o} \times 100\%$$

where *C* is the compression set expressed as a percentage of the original thickness, *T<sub>o</sub>* is the original thickness of test specimen, and *T<sub>f</sub>* is the final thickness of the test specimen. Three samples were tested and the median was reported.

### Data Analyses

A least significant difference (LSD) rule was applied to compare the means of the foam properties

of different treatments and different types of biomass (soybean protein isolate, soybean fiber, and cornstarch).

## RESULTS AND DISCUSSION

### Density

Table III shows that the density of biomass extended flexible foam rises with increasing weight percentage of biomass added to the foam formulation. This may be explained in terms of formulation and structure difference among these foams.

The density of a plastic foam is determined by the density or specific gravity of the material making up the matrix of the foam, the density of the gas in the cells, and the percentage of the material made up of foam network. The plastic phase composition includes polyol, isocyanate, and all additives such as surface active agents, stabilizers, crosslinking agents, and biomass extenders. The gas phase composition includes gases, either generated by the physical blowing agents that liberate gases as a result of elevated temperatures (e.g., thermal decomposition sodium bicarbonate), or produced by chemical blowing agents that release gases through chemical reactions (e.g., the chemical reaction between isocyanate and water), and the air, which is either introduced into the reaction vessel during the foaming process or diffuses into the cells during the aging process. In this study, with the exception of the percentage of biomass material, each foam formulation has the same amount of water (blowing agent) and other components. As expected, the density increased with increasing the amount of extender. The incorporation of soybean fiber into the foam formulation had a greater effect on the foam density than those foams containing the soybean protein isolate or cornstarch. This might have been caused by less active hydrogen atoms to react with the isocyanate for soybean fiber as compared to soy protein isolate and cornstarch.

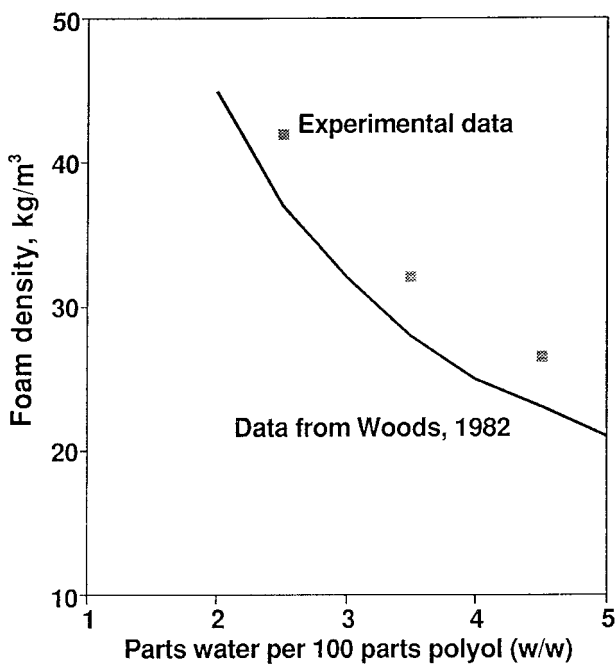
Water, when used as a blowing agent, plays an important role in PU foam formulation. Figure 1 shows the effect of increasing water content on the density of flexible PU foams without biomass materials. The filled square points were experimental data from this study, while the solid line was obtained from Woods.<sup>18</sup> The density of flexible PU foam could be dramatically reduced by increasing the initial water content in foam formulation and by adding sufficient isocyanate to react

**Table III Densities (kg/m<sup>3</sup>) of Water-Blown Flexible Polyurethane Foams Containing Biomass Materials**

Biomass	Biomass (%)				
	0	10	20	30	40
Soy protein isolate	27(a)	34(b)	37(c)	40(d)	42(e)
Soy fiber	27(a)	33(b)	39(c)	45(d)	48(e)
Cornstarch	27(a)	29(b)	31(c)	33(d)	37(e)

Means with the same letter in the same row are not significantly different at 5% level.

with water. Unfortunately, water's effectiveness in reducing PU foam's density was limited. If the water content exceeded 4.5 parts per 100 parts (w/w) of polyether polyol, the foam self-ignited immediately after foam preparation. As a result, the surface of the foam exhibited small holes or cracks and the inside of the foam block had large holes and flaws. The strong exothermic isocyanate-water reaction, producing excessive heat buildup in the foam block, thus limited the amount of water to a ratio of 4.5 parts per 100 parts (w/w) of polyether polyol in the formulation of this study. To make a lower-density flexible foam, a different formulation, or a blowing agent other than water, will be needed.



**Figure 1** Effect of initial water content on flexible water-blown polyurethane foam density.

## Resilience

For flexible PU foams, the resilience is defined as the rebound height of the ball over the drop height of the ball multiplied by 100. A higher percentage corresponds to a foam having better resilience. Foams containing biomass material all have higher resilience values when compared to those of the control foam (Table IV). For soy protein isolate and soy fiber-extended flexible foams, the resilience values increased with the increasing concentration of biomass material up to a maximum addition of 30% biomass material, and then decreased. For cornstarch-extended flexible foam, the maximum resilience occurred at 20% cornstarch addition. This property is particularly important in determining the degree of comfort in a cushion material. Comfort, however, is a subjective property that can vary from one person to another. Fortunately, Hartings and Hagan<sup>19</sup> demonstrated that the resilience value obtained from the ball-rebound test was correlatable to sitting comfort rated by a panel of judges. As the resilience increases, the comfort rating of the cushion foam also increases. Therefore, the incorporation of biomass material into the water-blown flexible foam system increased the comfort value of the foam, a desirable trait in cushioning application.

Table IV shows that soybean products had a better effect on foam resilience than cornstarch. The resilience values of foams extended with soybean products increased with increasing concentration of soybean materials up to 30%, and then decreased. At the lower level (10%) addition, soy protein isolate had the greatest effect, while at 20% addition all three biomass materials had a similar effect on the resilience value. At the higher level (30%) addition, soy products had a better effect on the foam resilience than the cornstarch, while at 40% addition, the soy fiber had the highest value of resilience.

**Table IV Resilience (%) of Water-Blown Flexible Polyurethane Foams Containing Biomass Materials**

Biomass	Biomass (%)				
	0	10	20	30	40
Soy protein isolate	22(a)	31(c)	31(c)	34(d)	30(b)
Soy fiber	22(a)	26(b)	31(c)	34(e)	32(d)
Cornstarch	22(a)	26(b)	31(e)	27(c)	29(d)

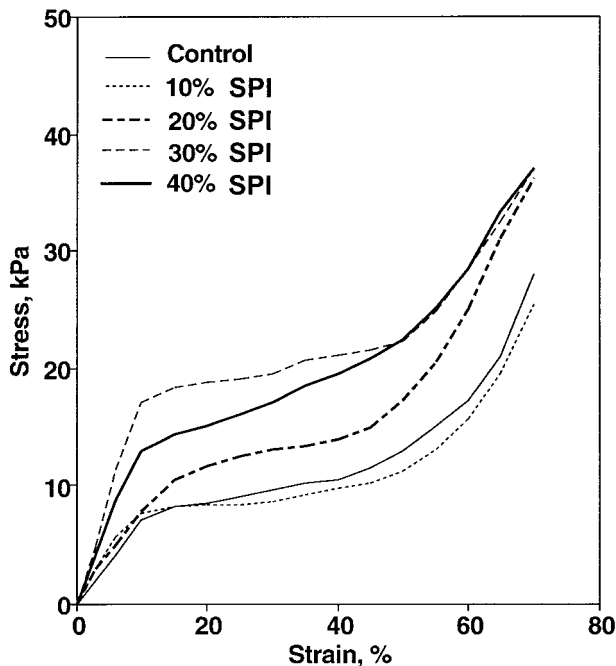
Means with the same letter in the same row are not significantly different at 5% level.

### Indentation Force Deflection

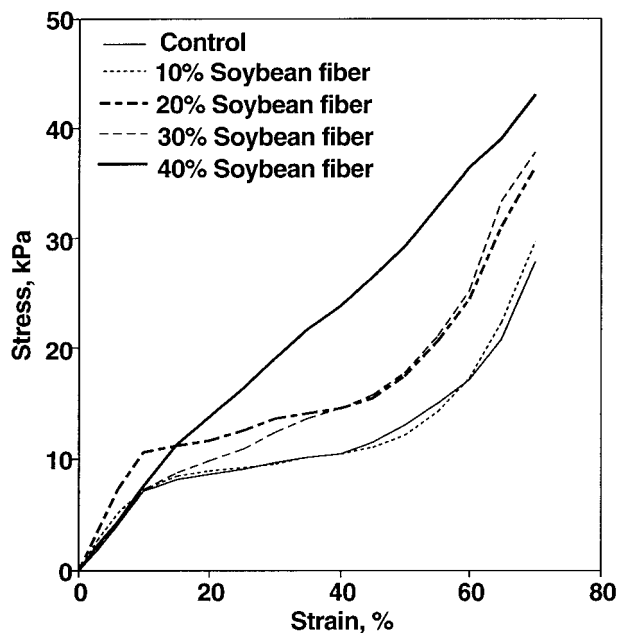
The major market for flexible PU foam is as a cushioning material in furniture, bedding, and automotive seating applications. The load-bearing properties of a flexible foam can be determined by studying the manner in which the structure deflects under a known applied load.<sup>18</sup> Figures 2–4 show the behavior of the load-deformation, stress–strain relationship under indentation for PU foams containing soy protein isolate, soy fiber, and cornstarch, respectively. In general, these curves can be divided into three regions. At a lower strain, the foam deforms in a linear-elastic manner and is reversible. The slope of this portion is initial modulus or Young's modulus. This initial linear elasticity region is due to the elastic bend-

ing of the cell walls and the struts comprising the foam matrix. The second region exhibits a plateau of deformation at almost constant stress. This occurs as a result of the unstable elastic buckling, plastic yielding, or brittle fracture of the struts. The final region shows steeply rising stress. This occurs when opposing cell walls meet after they have completely collapsed upon compression. The interaction of the struts once they compact forms a much denser foam system. This has been described in the literature.<sup>20–23</sup>

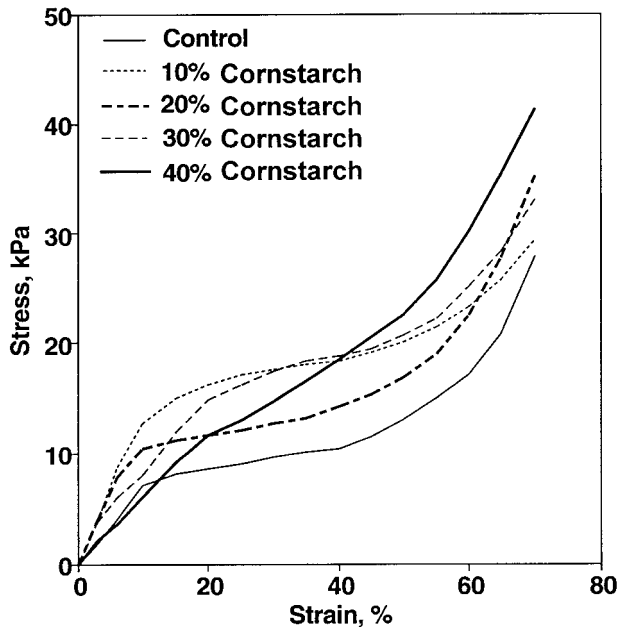
The control foam and the foam containing 10% soy protein isolate had a similar load-deformation relationship (Fig. 2). Foams containing 20 and 30% soy protein isolate also exhibited a similar stress–strain shape, but with a higher indentation hardness. With the exception of the foam with 40% soy protein isolate, all others contained a significant and almost constant plateau stress re-



**Figure 2** Stress–strain curves of flexible water-blown polyurethane foams containing soy protein isolate.



**Figure 3** Stress–strain curves of flexible water-blown polyurethane foams containing soy fiber.



**Figure 4** Stress–strain curves of flexible water-blown polyurethane foams containing cornstarch.

gion. At 70% indentation, the indentation hardness increased with increasing concentration of soy protein isolate in foam formulation, since the foam had a higher density at a higher level of soy protein isolate addition (Table III). Therefore, the foam had a higher indentation hardness.

Figure 3 indicates that the control foam and the foam containing 10% soy fiber addition had almost the same stress–strain behavior under the indentation load deflection. With the exception of a higher indentation hardness, the foam containing 20% soy fiber was similar to that of the control. They all contained the constant stress plateau region. The foams containing > 30% soy fiber addition did not show a significant plateau region, especially for the foam extended with 40% soy fiber. For indentation hardness property, again the foam containing 40% soy fiber had the greatest value.

A series of typical stress–strain curves for foams containing 0–40% cornstarch are shown in Figure 4. Foams containing < 20% cornstarch exhibited a plateau stress region. The stress–strain shape for the foam extended with 40% cornstarch did not show any significant plateau region and had the highest indentation hardness.

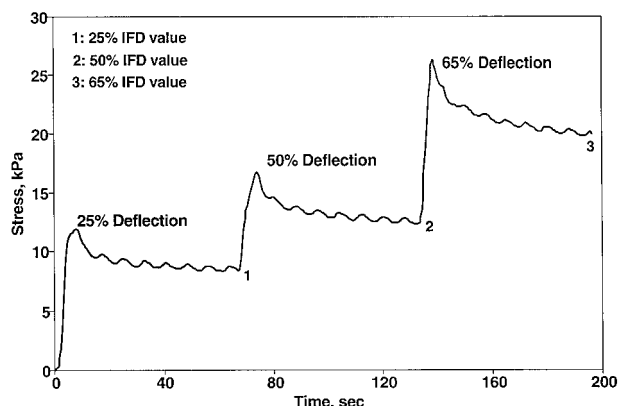
When the stress–strain curve of a foam contains a considerable plateau stress region, it will have a low comfort value.<sup>24</sup> Therefore, the addi-

tion of 30–40% biomass material into the flexible foam system appeared to increase the foam comfort value. This is also supported by the results obtained in the resilience study in the previous section.

Another indicator of comfort of the cushion foam is the comfort (SAG) factor. According to ASTM D3574, seating foams with low support factors will usually bottom out and give inferior performance. Figure 5 shows the stress–strain curve of PU foams containing 20% cornstarch under indentation test and indicates the 25, 50, and 65% IFD values. Table V shows the data of indentation force deflection values and comfort factor for PU foams containing soybean protein isolate, soybean fiber, and cornstarch.

All soy protein isolate-extended foams had a higher comfort factor than the control foam, and their value increased with increasing the concentration of soy protein isolate. However, at a lower level of addition (<20%), there was no significant difference between the control and the extended foams. At a higher level (>30%), the extended foams had a significantly higher comfort value than the control foam.

Foams extended with soybean fiber exhibited a greater comfort factor than the control foam, and again, its value increased by increasing the percentage of soybean fiber. But, at a lower level of addition (10%), no significant difference was evident between the control and the extended foam. At a higher level (>20%), all biomass-extended foams had a higher comfort value. Foams containing cornstarch also displayed a greater comfort factor than the control foam. Only foam con-



**Figure 5** Load-deflection curve of flexible water-blown polyurethane foam containing 20% cornstarch under indentation force deflection test.

**Table V The Indentation Force Deflection (IFD) Values (kPa) and Comfort Factor of Water-Blown Flexible Polyurethane Foams Containing Biomass Materials**

Foam Properties	Biomass (%)				
	0	10	20	30	40
Soy protein isolate					
IFD values, kPa					
25% deflection	6.7	5.6	7.1	6.2	6.0
50% deflection	8.9	7.8	10.3	9.8	10.4
65% deflection	13.5	13.6	17.2	17.4	20.0
Comfort factor	2.0(a)	2.4(ab)	2.5(ab)	2.8(bc)	3.3(c)
Soy fiber					
IFD values, kPa					
25% deflection	6.7	6.5	8.0	7.9	8.9
50% deflection	8.9	8.8	12.2	13.5	16.0
65% deflection	13.5	14.7	22.1	25.9	33.5
Comfort factor	2.0(a)	2.3(a)	2.7(b)	3.3(c)	3.8(d)
Cornstarch					
IFD values, kPa					
25% deflection	6.7	7.0	8.7	6.5	9.9
50% deflection	8.9	9.9	12.4	9.1	15.4
65% deflection	13.5	15.9	20.0	15.5	25.8
Comfort factor	2.0(a)	2.3(ab)	2.3(ab)	2.4(ab)	2.6(b)

Means with the same letter in the same row are not significantly different at 5% level.

taining 40% cornstarch exhibited a significant improvement in the comfort factor.

Generally speaking, all extended foams had a higher comfort factor than the control foam. Among them, soy fiber-extended foams had the greatest comfort factor, soy protein isolate next, and then cornstarch. Moreover, the comfort factor increased as the biomass concentration increased. Table V also shows the effect of adding biomass at different levels on the comfort factor of foams. The foam extended with 40% soy fiber had the highest comfort factor while cornstarch, the least. Since the foam with 40% soy fiber had the highest density (Table III), this might have contributed to the highest strength value. Again, the comfort factor property further confirms the results obtained from the resilience test and the stress-strain curve. The comfort value of a cushion foam can be improved by incorporating a higher level of biomass material (>30%) into the foam formulation.

### Compression Set Value

Compression set value is a measure of the non-recoverable loss in the thickness of a flexible foam

after a static load is removed. This property is important for material-handling applications, such as an interplant container or where this foam is designed for multiple uses. Table VI shows the compression set results for different biomass materials at different levels of addition. All extended foams had smaller compression set values than the control foam. The compression set values for the foam-extended soybean products decreased with increasing concentration of soybean products. Foams containing cornstarch, however, exhibited a minimum compression set value at 20% addition. Thus, incorporating the biomass materials into the flexible foam improved the compression set value. It should be cautioned, however, the compression set results obtained in this study were under an accelerated test environment. Further tests under real end-use situations need to be conducted to confirm these results.

In conclusion, this article demonstrated that the foam properties in cushioning applications are improved by adding biomass materials. Further studies are needed to determine the causes of the differences in the properties of flexible PU foams resulting from adding different biomass materials such as soy protein isolate, soy fiber, and cornstarch.



**Table VI Compression Set (%) of Water-Blown Flexible Polyurethane Foams Containing Biomass Materials**

Biomass	Biomass (%)				
	0	10	20	30	40
Soy protein isolate	46(d)	45(c)	43(b)	42(a)	42(a)
Soy fiber	46(d)	45(c)	42(b)	42(b)	40(a)
Cornstarch	46(d)	44(c)	42(a)	43(b)	43(b)

Means with the same letter in the same row are not significantly different at 5% level.

The authors gratefully acknowledge generous financial support from the Missouri Soybean Merchandising Council and Missouri Corn Merchandising Council for this project.

## REFERENCES

1. D. Klempner and K. C. Frisch, *Handbook of Polymeric Foams and Foam Technology*, Oxford University Press, New York, 1991.
2. S. Bhatnagar, R. R. Hilton, and M. A. Hanna, *Physical, mechanical, and thermal properties of starch based plastic foams*. Paper No. 936532. ASAE International Winter Meeting, Chicago, IL, Dec. 14–17, 1993.
3. C. E. Carraher, Jr. and L. H. Sperling, *Polymer Applications of Renewable Resource Materials*, Plenum Press, New York, 1981.
4. R. L. Cunningham and M. E. Carr, in *Corn Utilization Conference III Proceedings*, National Corn Growers Association and Ciba-Geigy Seed Division, St. Louis, MO, 1990, pp. 1–16.
5. R. L. Cunningham, M. E. Carr, and E. B. Bagley, *Cereal Chem.*, **68**, 258–261 (1991).
6. R. L. Cunningham, M. E. Carr, and E. B. Bagley, *J. Appl. Polym. Sci.*, **44**, 1477–1483 (1992).
7. R. L. Cunningham, M. E. Carr, E. B. Bagley, and T. C. Nelsen, *Starch / Staerke*, **44**, 141–145 (1992).
8. M. J. Donnelly, J. L. Stanford, and R. H. Still, *Carbohydr. Polym.*, **14**, 221–240 (1991).
9. H. Yoshida, R. Morck, K. P. Kringstad, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **34**, 1187–1198 (1987).
10. H. Yoshida, R. Morck, K. P. Kringstad, and H. Hatakeyama, *J. Appl. Polym. Sci.*, **40**, 1819–1832 (1990).
11. L. P. Dosmann and R. N. Steel, U.S. Pat. 3,004,934 (October 7, 1961).
12. F. Hostettler, U.S. Pat. 4,156,759 (May 29, 1979).
13. R. B. Kennedy, U.S. Pat. 4,520,139 (May 28, 1985).
14. Y. Lin, F. Hsieh, H. E. Huff, and E. Iannotti, *Cereal Chem.*, **73**, 189–196 (1996).
15. F. H. Otey, L. Bennett, and C. L. Mehlretter, U.S. Pat. 3,405,080 (October 8, 1968).
16. D. Dieterich, E. Grigat, W. Hahn, H. Hespe, and H. G. Schmelzer, Principles of polyurethane chemistry and special applications, in *Polyurethane Handbook*, G. Oertel, Ed., Hanser Publishers, Munich, 1993.
17. F. E. Bailey and F. E. Critchfield, *J. Cell. Plast.*, **17**, 333–339 (1981).
18. G. Woods, *Flexible Polyurethane Foams: Chemistry and Technology*, Applied Science Publishers, London, 1982.
19. J. W. Hartings and J. H. Hagan, *J. Cell. Plast.*, **14**, 81–86, 105 (1978).
20. M. F. Ashby, *Metall. Trans.*, **14A**, 1755–1769 (1983).
21. R. Chan and M. Nakamura, *J. Cell. Plast.*, **5**, 112–118 (1969).
22. A. N. Gent and A. G. Thomas, *J. Rubber Chem. & Technol.*, **36**, 597–610 (1963).
23. N. C. Hilyard and L. K. Djiauw, *J. Cell. Plast.*, **7**, 33–42 (1971).
24. H. W. Wolfe, Cushioning and Fatigue, in *Mechanics of Cellular Plastics*, N. C. Hilyard, Ed., Applied Science Publishers, Barking, Essex, England, 1982.