

Hydrophilic Foams Containing Corn Products for Horticultural Use*

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SYNOPSIS

Polyurethane foams containing equal amounts of commercial unmodified cornstarch and a polyisocyanate-terminated polyether exhibit properties suitable for horticultural applications. The use of cornstarch in the foam formulation increased the volume by one-fourth as compared to the foam without cornstarch. This volume increase represents an economic advantage of 20% savings based on material cost. When cornstarch or corn flour is added to the foam formulation, the foams are more resistant to compressive force. Upon wetting and draining, the foams prepared with no auxiliary blowing agent and containing corn products exhibit higher volumes than do the unfilled foams. Radish seeds planted inside 25 mm cubes of foams began to sprout after 1 day. Early developmental growth for the plants was similar in the control and cornstarch-filled foams. Spectroscopic analyses of the starch-containing foams revealed that 60–70% of the cornstarch was metabolized within 4–5 weeks by a microbial consortium. Control polyurethane foams were not affected by the microorganisms tested. © 1994 John Wiley & Sons, Inc.[‡]

INTRODUCTION

Polyurethane (PU) polymers are some of the most versatile polymers ever developed. These polymers are useful for an exceptionally wide range of commercial applications for adhesives, coatings, elastomers, fibers, foams, paints, and other products.¹ In 1989, flexible and rigid PU foams alone represented a major 1.2 billion kg (2.6 billion lb)/year market in the United States.² Most PU foams are hydrophobic although there is a growing interest in hydrophilic foams for a variety of specialty applications such as absorbent material in cleaning pads, disposable diapers, medical supplies, sanitary napkins, sponges, and horticultural products.³

The basic chemistry for the preparation of hydrophobic and hydrophilic foams is somewhat sim-

ilar, involving the reactions of a polymeric isocyanate ($R-N=C=O$) with a polyol ($R'-O-H$) to form the urethane ($R-NH-COOR'$). This chemistry involves the reaction of the NCO groups with hydroxyl groups containing active hydrogens in such polyols as glycerine, methyl glucoside, pentaerythritol, sorbitol, and sucrose.^{4A} The polyols are generally supplied commercially as polyalkoxylated products known as poly(ether polyol)s. In addition to the commercially most important reaction of isocyanates mentioned above, a number of other reactions can be involved in formation of isocyanate-derived foams.^{4B} For example, isocyanate reacts with water to form disubstituted urea plus carbon dioxide, with primary amines to form disubstituted urea without generation of carbon dioxide, and with secondary amines to form trisubstituted urea. Also, isocyanates react with urethanes to form an allophanate, with disubstituted urea to form a biuret, and with itself to form several different compounds. Thus, the PU foam chemistry is quite versatile, depending on the formulated ingredients.

Hydrophilic-type PU prepolymers have been developed under the trade name of Hypol® polymers and they are composed of polyisocyanate-terminated

* 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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polyethers. Compared to the conventional hydrophobic foams, a considerable excess of water may be used, and a catalyst may not be required. The Hypol prepolymers became of considerable interest to us for our present study involving the preparation and evaluation of starch-filled hydrophilic PU foams as a matrix for horticultural applications. The horticultural use of PU foams without cornstarch as a filler has been previously studied.^{5,6}

A foam medium for growing seedlings requires a supportable material with a usable high-water-holding capacity, a well-aerated matrix, and no toxic constituents. Hydrophilic foams made from a Hypol prepolymer appear feasible for this purpose. For the present report, we prepared hydrophilic foams containing equal weights of cornstarch (or corn flour) and a Hypol prepolymer in the presence of water and a surfactant. Control foams without carbohydrate were also prepared. These foams were tested for their physical strength, absorbability, water-holding capacity, drainage, seed germination, and early plant development. As the biodegradation of starch in plastics has received considerable attention,⁷⁻⁹ this property of the foams was also evaluated. The usable water-holding capacity and other properties of the foams containing starch or flour were compared to properties of control foams without a starchy filler. Visual examinations of the seedlings growing in these foams were made to assess availability of the pore space of the foams for root growth. Foams containing these carbohydrates are more compression-resistant and exhibit good hydrophilic properties, and with the carbohydrates, the foams have a degradable component. Due to the increased dry volumes of the starch-filled foams, there appears to be a decided economic advantage for the foams containing starch.

EXPERIMENTAL

Materials

The basic materials used in this study were Hypol FHP 3000 polymer (polyisocyanate-terminated

polyether) and BRIJ 72 (surfactant) generously supplied by Hampshire Chemical Corp., Lexington, MA, and ICI Americas Inc., Wilmington, DE, respectively. The carbohydrate additives to the foam formulations were Buffalo 3401 cornstarch, a food-grade starch, supplied by CPC International, Englewood Cliffs, NJ, and corn flour, Product 505, supplied by Illinois Cereal Mills, Inc., Paris, IL. The auxiliary blowing agent was methylene chloride supplied by Fisher Chemical, Fisher Scientific, St. Louis, MO.

Foam Preparation

Foams were formulated as described in Table I using 100 g of Hypol FHP 3000 polymer. Four replicate foams were prepared with each formulation. Surfactant was added to water and mixed with a model TS 2010, Lightnin mixer (General Signal Corp., Rochester, NY) with A-310 impeller (6.35 mm) for 8 min at 500 rpm in a 1.1 L container. For the foams containing the carbohydrate additives, cornstarch or corn flour was added to the surfactant/water mixture and blended using a glass stirring rod. This blend was mixed with the Hypol prepolymer. When the auxiliary blowing agent (methylene chloride) was used, the agent was first mixed with the Hypol prepolymer in a 1.1 L container using a glass stirring rod at room temperature before the above mixture was admixed. Ingredients for the control and cornstarch foams were hand-mixed for 1 min using a glass stirring rod. When the auxiliary blowing agent (0–15% methylene chloride) was used, the ingredients were mixed with the Lightnin mixer for 15 and 30 s at 1800 rpm for the addition of 0 and 10% methylene chloride (based on weight of Hypol polymer), respectively. With the 15% methylene chloride addition, the ingredients were mixed with a glass rod for 1–2 min depending on the time required to obtain a distinct rise in the viscosity. Immediately after final mixing, the ingredients were poured into wooden boxes (178 × 178 × 76 mm) and allowed to rise at room conditions. After 12 h, foams were placed in a Precision Scientific STM 135 Mechanical Convection Oven (Precision Scientific, Chicago, IL) at 70°C for 14.5 h.

Foam Testing Procedures

Specimens of foams with heights of 25 mm were prepared using a band saw. The specimens were then conditioned for 12 h at 23°C and 50% relative humidity (RH). Densities were determined on unpre-flexed foams by American Society for Testing and

Table I Formulation of Ingredients

Ingredients	Grams
Hypol FHP 3000 polymer	100
Water, blowing agent	200
BRIJ 72, surfactant	1.5
Cornstarch or corn flour	100

Materials (ASTM) procedure D 3547-86, Test A. Each foam was cut with a band saw into four specimens of $51 \times 51 \times 25$ mm. Compression force deflection tests were performed on two of these samples from each of four replicate foams according to ASTM D procedure 3574-86, Test C (except for size of sample) using an Instron apparatus (Model 4201, Instron Corp., Canton, MA) equipped with a 5 kN static load cell, type 2518-805. A suspended, self-aligning pressure pad was mounted under the cross arm for the loading platen. These specimens were also used for the biodegradability studies.

Hydrophilicity

Tests were performed on two specimens from each of the four replicate foams. General procedures for determining the suction and draining times of the foams are described by Loew.⁵ The $51 \times 51 \times 25$ mm specimens were immersed in a pan containing a 24 mm depth of water. The time required to saturate the foam with water until the upper surface is wetted is called the suction time. The saturated foam is removed from the water and placed in a beaker at an angle for the foam to drain. The water-draining time is from the time the specimen is removed from the water to the completion of draining (no dripping for 1 min).

Greenhouse Studies

Four replicates of the foams used in the hydrophilicity studies were cut into 25 mm cubes. One round hole with a 0.5 mm diameter and depth of 10 mm was made in the top of each cube and the cubes were placed in growing trays (Growing Systems, Inc., Milwaukee, WI). Two radish seeds were placed in each hole of the cubes and the growing trays were placed in the greenhouse. Temperatures in the greenhouse were 29°C during the day and 24°C at night with 12 h of supplemental lighting (6:00 A.M. to 6:00 P.M.). The foams were watered twice daily and the experiments were terminated after 1 month.

Biodegradability

Foam specimens of the control (no starch or flour) and starch-filled foams were cut into 25 mm cubes. Each sample was placed in a 250 mL Erlenmeyer flask and autoclaved at 121°C for 15 min. After the sample cooled, 100 mL of minimal medium and 2 mL of the culture LD 76⁷ (a proprietary mixed bacterial culture composed of amylolytic bacteria) were added to each flask and the flasks were placed on

an orbital shaker (Lab-line Instruments, Inc., Melrose Park, IL) at 28°C and 180 rpm. The designated times for removal of the residue were 2, 5, 10, 20, and 35 days. To collect larger particulates, the samples were centrifuged at 15,300*g* for 15 min with Model J2-21, JA-14 rotor (Beckman Instruments, Inc., Palo Alto, CA). The samples were rinsed twice with sterile media and once with sterile H₂O and recentrifuged after each wash. To collect minute solid material, supernatants were filtered through disposable filterware (Type S cellulose nitrate, 0.2 micron pore size, Nagle Co., Subsidiary of Sybron., Rochester, NY). Each sample including solids on filters was placed in a dish, dried in an oven at 80°C overnight, and weighed. Where indicated, the control, cornstarch-, and corn flour-filled foams were shredded into 3 mm pieces to increase surface availability. Such samples were autoclaved, exposed to the bacterial consortium, collected, and analyzed as described above.

Scanning Electron Microscopy

Shredded specimens were mounted on aluminum stubs using double-sided carbon tape and were coated with gold-palladium (60 : 40) to a thickness of about 0.015 micron in a sputter coater. The coated specimens were observed in a scanning electron microscope (SEM) (Model JSM-6400, JEOL Inc. Peabody, MA) at a specimen angle of 0°. Accelerating voltage was 10 kV, and final aperture was 200 microns.

Fourier Transform Infrared (FTIR) Spectrometric Analysis

Prior to FTIR analysis, all foam samples were dried under vacuum at 60°C for 24 h. Test samples were ground, mixed with KBr, and pressed into transparent KBr disks. Special effort was made to minimize the particle size of the powders to give clear homogeneous KBr disks. This was accomplished by pulverizing 5.0 mg of sample for 3 min at liquid nitrogen temperature in a stainless-steel vial containing two stainless-steel ball-bearings on a mixer mill (Brinkmann Instruments Inc., Subsidiary of Sybron Corp., Westbury, NY). After warming to ambient temperature, 95.0 mg of spectral grade KBr (Spectra-Tech Inc., Samford, CT) was added to the vial. All weighings and transfers of samples were done in a dry box to prevent moisture absorption by the hygroscopic KBr. The sample in KBr was then pulverized on the amalgamator (Wig-L-Bug, Crescent Dental Mfg. Co., Lyons, IL) for 60 s at liquid nitro-

Table II Properties of Hydrophilic Foams Containing Cornstarch

Foam Properties	Control	Cornstarch ^a
Density (g/cm ³)	0.136	0.202
Compression force deflection		
Thickness (mm)		
(after contact load)	25.6	25.2
Compression deflection (50%) (Pa)	10,200	20,100
Hydrophilicity		
Time (s)		
Suction	834	456
Drainage	165	78.0
Increase (%)		
Weight	162	236
Density	96.2	112
Volume	32.4	58.5

^a Fifty percent, by weight.

gen temperature in the same vial. At ambient temperature, 25 mg of the pulverized KBr mixture was diluted to 750 mg in KBr and pulverized on the amalgamator. Finally, 300 mg of the pulverized KBr mixture was transferred in the dry box to a 13 mm

KBr die (Perkin-Elmer Corp., Analytical Instruments, Norwalk, CT), and the box was evacuated for 5 min before pressing *in vacuo* at 110 MPa on a laboratory press (Fred S. Carver, Menomonee Falls, WI). Infrared spectra were measured on a spectrometer (Model RFX-75, FTIR, KVB-Analect, Irvine, CA) equipped with a TGS detector. Interferograms were processed on an APT-824 array processor using triangular apodization for linear response. Spectra were acquired at 4 cm⁻¹ resolution and signal averaged over 64 scans with no zero filling. The interferometer and sample chambers were purged with dry nitrogen to remove spectral interference from water vapor and carbon dioxide.

RESULTS AND DISCUSSION

Compression Force Deflection

The force necessary to produce a 50% compression over the entire top area of the foam specimens are shown in Tables II and III. More force was required to compress foams containing cornstarch (2×) or corn flour (4×) than for the control foams. With 15% addition of methylene chloride (based on weight of Hypol polymer) to the formulation, the corn flour-

Table III Effect of Methylene Chloride on Foam Properties

Properties	Foam								
	Control			Corn Flour ^a Methylene Chloride (%) ^b			Cornstarch ^a		
	0	10	15	0	10	15	0	10	15
Density (g/cm ³)	0.140	0.128	0.096	0.245	0.254	0.182	0.210	0.251	0.225
Compression force deflection									
Thickness (mm) ^c	27.5	26.9	26.6	28.9	26.9	25.8	28.3	26.6	24.3
Compression deflection (50%) (Pa)	14,000	15,100	6,780	58,000	72,100	20,600	27,600	32,600	6,370
Hydrophilicity									
Time (s)									
Suction	471	1,140	748	1,000	2,040	2,520	539	184	20.6
Drainage	71.6	415	837	66.9	338	1,820	79.4	164	709
Increase (%)									
Weight	218	369	380	327	394	336	173	272	180
Density	119	151	156	133	184	160	63.5	114	71.6
Volume	45.8	79.6	90.1	83.2	74.3	68.0	67.9	72.8	69.8

^a Fifty percent, by weight.

^b Based on weight of Hypol.

^c After contact load.

filled foams still required more force to achieve 50% compression than did the control with no auxillary blowing agent. Compressive behavior is affected by polymer composition, density, and cell structure and size.¹⁰

Density and Volume

The addition of cornstarch or corn flour in the foam formulation increased foam density (Tables II and III). Table II shows a 48% increase in density with the addition of cornstarch in the formulation. The use of methylene chloride as an auxillary blowing agent had more of an effect in decreasing density of the control foam than of the cornstarch- or corn flour-filled foams. The interaction of cornstarch with the Hypol prepolymer, surfactant, and water in foam making increases the dry foam volume by one-fourth over foam without cornstarch. With the economical cornstarch at \$0.22/kg, this volume increase contributes up to 20% savings based on material cost.

Hydrophilicity

With hand mixing of the ingredients (Table II), the suction and drainage times were higher for the control foams than for foams containing cornstarch. Increases in weight, density, and volume of the foams occurred with the addition of cornstarch to the formulation. Mixing differences affected foam

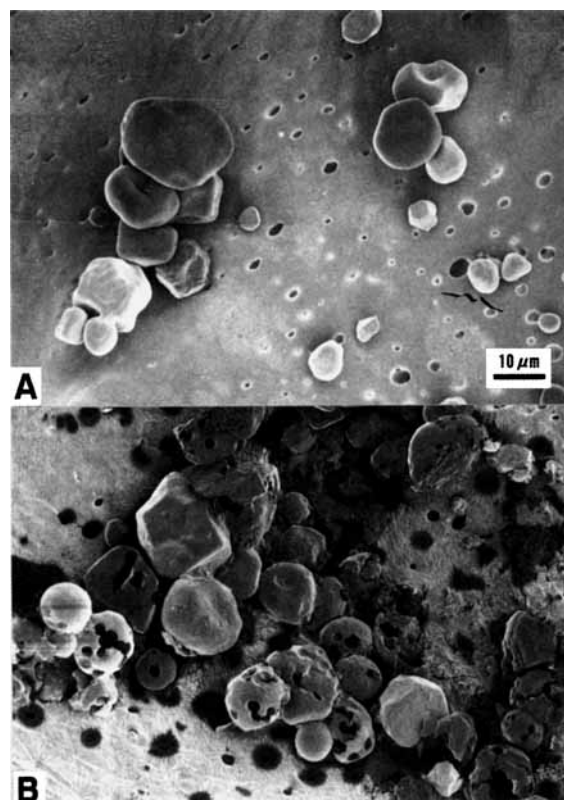


Figure 1 SEM photomicrographs of 50% cornstarch-filled foam (3 mm pieces) (A) before and (B) after 28 days of incubation with a mixed bacterial culture (LD 76, amyolytic bacteria isolated by USDA) at 28°C and shaken at 180 rpm.

Table IV Effect of Mixed Bacterial Culture on the Weight Loss (%) of Foams^a

Days	Additives		
	None	Cornstarch	
Foam, 25 mm cubes			
0	1	1	
2	2	3	
5	2	6	
10	1	10	
20	2	12	
35	1	36	
	None	Corn flour	Cornstarch
Foam, shredded (3 mm)			
28	3	34	33
28 ^b	3	40	29

^a Incubated at 28°C in a liquid culture (LD76, composed of amyolytic bacteria) and shaken at 180 rpm.

^b Not inoculated.

properties. The hand mixing permitted better observation of the starch incorporation with viscosity changes of the foam. With the mechanical mixing of the ingredients as shown in Table III, longer suction times were required for foams filled with corn flour than for either the control or cornstarch-filled foams. Short suction times are beneficial in wetting the foams and the length of drainage times are important in providing the proper amount of water to the seedlings for the necessary time. The optimum moisture for seed germination varies with the plant species. Corn flour blended into the foam formulation well. Some leaching of cornstarch from the foam during drainage was noted.

Greenhouse Plantings

Some of the radish seeds began to sprout the first day after planting in the foams. On the fourth day after seeding, plants in the foams with and without cornstarch had leaves, while plants in the corn flour

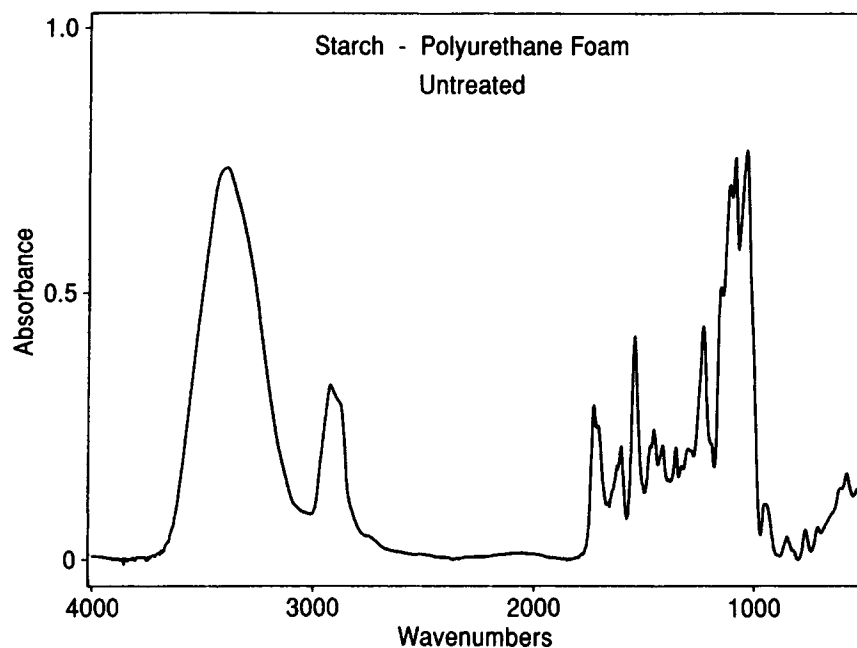


Figure 2 Fourier transform infrared spectrometric analysis of a 50% cornstarch-filled foam (3 mm pieces).

foams were nearly leaved out. After 1 week, root hairs were observed on the bottoms of the control and cornstarch foams and some mold was observed on the bottom of the corn flour foams. After 17 days, roots extending below the foams with and without cornstarch looked similar.

Biodegradability

Efforts to develop products to alleviate disposal problems have included the use of cornstarch in plastic products to increase their susceptibility to degradative processes.⁷ Degradability of products

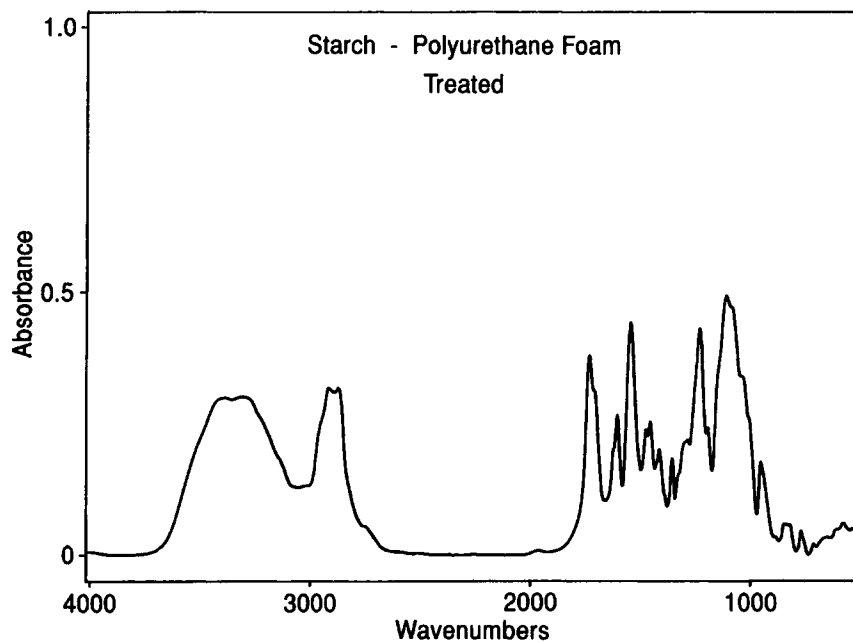


Figure 3 Fourier transform infrared spectrometric analysis of a 50% cornstarch-filled foam (3 mm pieces) after 28 days of treatment with a mixed bacterial culture at 28°C and shaken at 180 rpm.

used in the soil for the starting plants would be highly desirable and, if susceptible to biological attack over time, could alleviate accumulation of unwanted debris. Using equal parts by weight of cornstarch and the Hypol polymer (Table I), 36% of the weight (25 mm cubes) was lost after being incubated with a mixed bacterial culture for 35 days (Table IV). When the foam was shredded into 3 mm pieces to increase surface area, the losses in weight of the cornstarch- and corn flour-filled foams were 33–34% after 28 days of incubation, indicating that the cornstarch/corn flour is easily accessible to the microbes. Weight loss of shredded foams containing corn products without added bacteria indicate that endogenous microbes are probably present in the foams and are difficult to senesce using standard sterilization procedures. The SEM photomicrographs of the foams after treatment are shown in Figure 1. Untreated cornstarch-filled foams (A) show the intact granules, whereas the foams treated with amylolytic bacteria (B) have openings in the granules, indicating sites of attack by the bacteria. FTIR spectra of the cornstarch-filled foam before and after bacterial treatment are shown in Figures 2 and 3, respectively. Loss of cornstarch is indicated by the decrease in both the starch hydroxyl absorption bands at 3350 cm^{-1} and the C—O absorption bands in the carbohydrate fingerprint region ($1000\text{--}1200\text{ cm}^{-1}$). The carbohydrate band at 1023 cm^{-1} was used to measure the loss since this band contained relatively little interference from PU and water in the sample and, therefore, satisfied the assumptions of the absorbance ratio method for analysis of infrared spectra of polymer mixtures.^{11–13} For comparison of the foams before and after bacterial treatment, the 1023 cm^{-1} bands in Figures 2 and 3 were ratioed against the relatively constant methylene absorption bands at 2870 cm^{-1} from PU. The decrease in the absorbance ratio corresponded to a loss of approximately 60% of the cornstarch after bacterial treatment. This agreed with the weight loss value of 30% (33% minus 3%) (Table IV), as the foam contained 50% cornstarch in the formulation.

CONCLUSIONS

The addition of an equal weight of cornstarch or corn flour to the Hypol polymer in a formulation produces a hydrophilic foam more dense and more resistant to compression. Foams containing corn flour had higher densities and required more force to deflect 50% of their height than did foams con-

taining cornstarch. When foams prepared without an auxiliary blowing agent were wetted and drained, the increases in volumes were greater for the foams containing cornstarch or corn flour than those for the control. After 1 day in the greenhouse, radish seeds placed within the foams had begun to sprout. Cornstarch- and corn flour-filled foams (3 mm pieces) on an orbital shaker at 28°C and 180 rpm for 28 days with a mixed bacterial culture lost one-third of their weight, attributed to biodegradation of the carbohydrate. Foams filled with corn products exhibit good hydrophilicity and physical properties of interest to horticulture. Based on the increased volume that results from the incorporation of starch, the economical advantage also is attractive.

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