

# Biodegradable Packaging Foams of Starch Acetate Blended with Corn Stalk Fibers

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Received 19 September 2003; accepted 19 April 2004

DOI 10.1002/app.20843

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Starch acetate–corn fiber foams were prepared by extrusion. Corn starch was acetylated (DS 2) to introduce thermoplastic properties. Corn stalks were treated with sodium hydroxide to remove the lignin and to obtain purified cellulose fibers. Starch acetate was blended with treated fiber at concentrations of 0, 2, 6, 10, and 14% (w/w) and extruded in a corotating twin-screw extruder with 12 to 18% w/w ethanol content and 5% talc as a nucleating agent. The samples were extruded at 150°C and selected physical and mechanical properties were evaluated. Micrographic properties were analyzed using scanning electron micros-

copy to observe the interaction of fiber and starch. Fiber incorporation at the lower concentrations enhanced the physical properties of the foams. Fiber contents greater than 10% decreased expansion and increased density and shear strength. Good compatibility between starch and corn fiber was observed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2627–2633, 2004

**Key words:** fiber; cellulose; starch; foams; extrusion; starch acetate

## INTRODUCTION

There have been increasing efforts to replace synthetic plastics with natural biodegradable polymers. Starch, a biopolymer, has been used to make biodegradable packaging materials.<sup>1</sup> To enhance the properties of starch foams, starch was blended with other polymers such as polylactic acid<sup>2</sup> and Mater-Bi.<sup>3</sup> Further, efforts were made to modify the starch polymer so that it would give a better biodegradable plastic foam. Results are available on hydroxypropylated starch<sup>4</sup> and starch acetate.<sup>5–8</sup>

On the other hand, efforts have been made to include natural fibers in the many synthetic as well as biodegradable polymers, for the manufacture of composites with better mechanical properties. Mohanty et al.<sup>9</sup> reviewed the various aspects of biofibers, biodegradable polymers, and biocomposites and reported the potential and need for the utilization of biofibers in the production of biodegradable plastics and composites. Orts et al.<sup>10</sup> reviewed the industrial potential for agriculturally derived commodities as a controllable and renewable source of fibers and fillers.

Starch-based foams can be produced via a baking process wherein a starch dough containing fiber is

heated under pressure to form a molded foam product. The resulting products are starch-based foam composites with mechanical and thermal properties rivaling those of polystyrene. A key aspect to the strength of the composite is the adhesion between the starch and the fibers. This can be ascertained from the mechanical properties as well as by using tools such as SEM.<sup>11</sup>

Chinnaswamy and Hanna<sup>12</sup> studied the physicochemical and macromolecular properties of starch–cellulose fiber extrudates. They extruded normal starch with commercially available pure cellulose fibers in concentrations from 1 to 10% (w/w). The expansion ratio values decreased with increase in fiber content with the maximum expansion ratio observed at a fiber content of 4% (w/w). There was extensive degradation of the starch with increased fiber content.

Cyras<sup>13</sup> studied polycaprolactone, starch, and sisal fiber biocomposites. An alkaline treatment was performed to improve the adhesion and the compatibility of the fiber with the matrix. Fiber content enhanced the tensile properties of the biodegradable composite. Averous<sup>14,15</sup> formulated plasticized wheat starch (PWS)/cellulose fiber composites and tested them in thermoforming applications. The composites had increased modulus and strength, and improved temperature stability and glass transition shifts. Thermoformed trays were tested under storage conditions from 4°C to ambient temperature. The composites

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showed reduced aging compared with PWS alone. Curvelo<sup>16</sup> used cellulosic fibers from *Eucalyptus urograndis* pulp as reinforcement for thermoplastic regular corn starch to improve its mechanical properties. The composites were prepared with regular corn starch plasticized with glycerin and reinforced with short cellulosic fibers (16% wt) from bleached pulp. The fibers were added to the thermoplasticized corn starch in an intensive batch mixer at 170°C. The mixture was hot-pressed into 2–3-mm-thick plates and then cut to prepare specimens for mechanical tests. The composite showed a 100% increase in tensile strength and >50% increase in modulus, with respect to nonreinforced thermoplastic corn starch. SEM of fractured surfaces revealed a very good adhesion between the fibers and the matrix.

Mohanty et al.<sup>9</sup> concluded that the most important factors in the formation of a biodegradable polymer industry include cost reduction and public and political acceptance. Application of biodegradable polymers in natural fiber-reinforced composites will broaden their uses. Because of variations in structures and properties of biofibers, more data on the properties of biocomposites are required to establish confidence in their uses.

There is no literature on the use of corn stalk fibers in the production of biofoams. Thus, the objective of this study was to investigate the effectiveness of incorporating corn cellulose fiber into starch acetate for the production of biodegradable foams.

## METHODS

### Materials

Hylon VII (70% amylose starch) was purchased from American Maize Products Co. (Hammond, IN). Talc was purchased from Barretts Minerals Technologies (New York, NY). Denatured ethanol was purchased from Fisher Scientific, Inc. (Fair Lawn, NJ).

Starch acetate, with a degree of substitution of 2, was prepared from 70% amylose cornstarch.<sup>6</sup> To initiate the acetylation process, 110 kg of acetic anhydride (Vopak, Inc., Dallas, TX) was placed in a steam-jacketed reactor with a rotating self-wiping paddle. Then 45.5 kg of 70% amylose starch (dried at 50°C for 48 h) was added into the reactor with 5 min of continuous mixing. Finally, 5 kg of 50% NaOH solution (Harcross Chemicals, Inc., Kansas City, KS) was added during mixing. The temperature of the reactor jacket was maintained at 123°C. After 3 h, the reaction was stopped by quickly adding 200 L of cold water to the reactor. The pH value of the mixture was adjusted to 5.0 by washing with water, before drying at 50°C. After the moisture was constant (4%), the starch was ground in a standard Model No. 3 Wiley mill (Arthur H. Thomas Co., Philadelphia, PA) to pass through a

5-mm opening sieve to obtain uniformly sized particles.

### Fiber extraction from corn stalks

Dry corn stalks, obtained from a university greenhouse, were cut into lengths of 7 to 10 cm and treated with 1 N NaOH solution in the ratio of 1:15 (dry corn stalk:NaOH solution) at boiling temperature for 35–40 min. After this initial treatment, the alkali solution was drained and the fibers were washed with water.

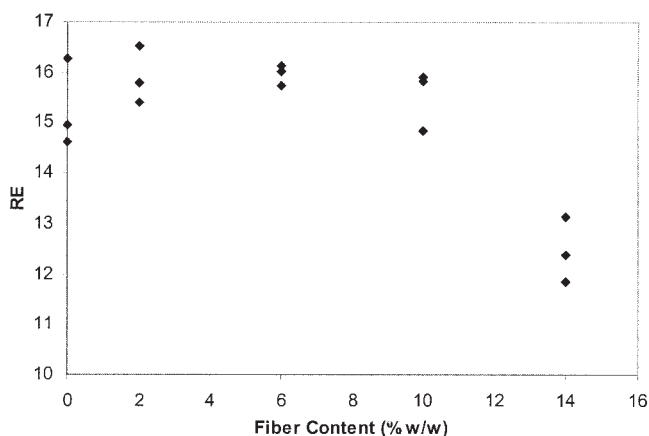
The fibers were reheated to boiling again in 1 N NaOH solution at a ratio of 1:10 (dry fibers:NaOH solution) and held for 10 min. After this second cooking, the fibers were washed thoroughly with water. To neutralize any remaining alkali, the fibers were soaked in 10% acetic acid for 15 min at ambient temperature. Finally, the fibers were rinsed in water and air dried at 105°C. The fibers are not bleached and, therefore, were brownish–yellow in color. The dried fibers were ground in a Wiley mill to pass through a 1-mm mesh. Ground fibers were then blended with starch acetate and extruded into foams.

### Sample preparation

Samples for extrusion were prepared by blending all the constituents together in a Hobart mixer (Model No. C-100, Hobart Corp., Troy, OH). Starch acetate (dried at 105°C for 12 h) was blended with different levels of corn stalk fiber (0, 2, 6, 10, and 14% w/w), different levels of ethanol (12, 15, and 18% w/w) and 5% talc as a nucleating agent. Each sample was 1 kg. The samples were prepared and stored in airtight containers at room temperature for a period of 24 h for the samples to equilibrate.

### Extrusion of foams

Samples were extruded in a laboratory corotating twin-screw extruder (Model No. CSTE-V, C. W. Brabender, Inc., Hackensack, NJ). Conical screws had diameters decreasing from 43 to 28 mm along a length of 365 mm from the feed end to the exit end. Rotational speeds, for both screws, were set at 140 rpm for all extrusions. Barrel temperature for the feed zone was set to 50°C. The other two barrel sections and the die were maintained at 150°C. Extrusions were carried out maintaining full feed, ensuring that the flights and feed port were full throughout the extrusion runs. Extrudates were collected when the system stabilized, with constant backpressure at the die, constant torque, and constant output flow rate. All extrusion runs were duplicated.



**Figure 1** Radial expansion (RE) values of the foams with increase in fiber content.

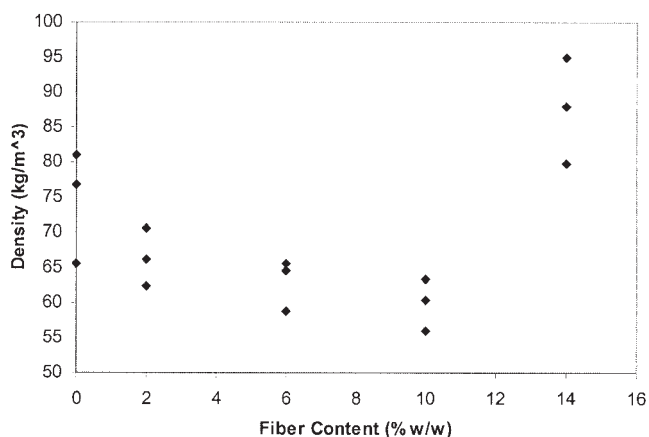
### Physical properties

Radial expansion ratio (RE) was calculated by dividing the mean cross-sectional area of the extrudates by the cross-sectional area of the die nozzle. Each mean value was the average of 30 measurements.

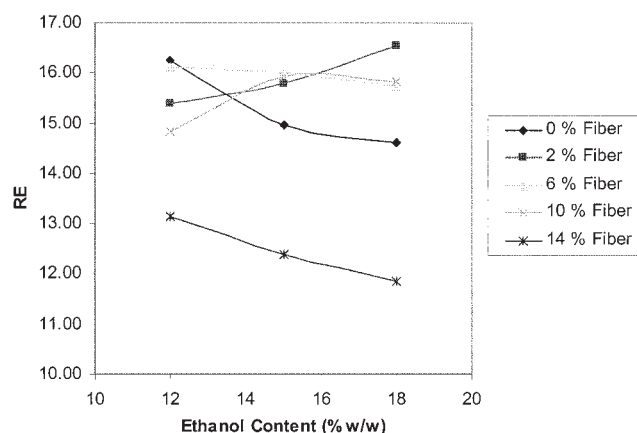
Unit density (UD) was determined using a glass bead displacement method.<sup>17</sup> Glass beads, 0.1 mm in diameter, were used as the displacement medium to determine the volume of the extrudate. Unit density was obtained by dividing the mass by the volume of the extrudate being measured.

### Shear strength

Samples were conditioned at  $43.2 \pm 0.4\%$  relative humidity in a desiccator with saturated potassium carbonate ( $K_2CO_3$ ) aqueous solution for 10 days at  $25^\circ C$ . Weight changes of the samples were monitored. After 7 days, the sample weights were constant, an indication of equilibrium. Shear strengths of the extrudates



**Figure 2** Unit density (UD) values of the foams with increase in fiber content.



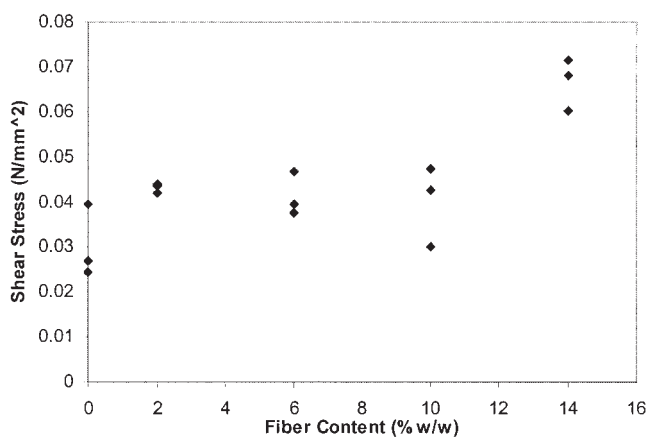
**Figure 3** Radial expansion (RE) values of the foams with increase in ethanol content.

were determined. The force required to shear an individual extrudate was recorded with an Instron universal testing machine (Model No. 5566, Instron Engineering Corp., Canton, MA) with a 10 kN load cell operating at a speed of 2 mm/min. Shear strength was calculated by dividing the shear force by the total cross-sectional area of the surface sheared. Each value was taken as an average of five samples.

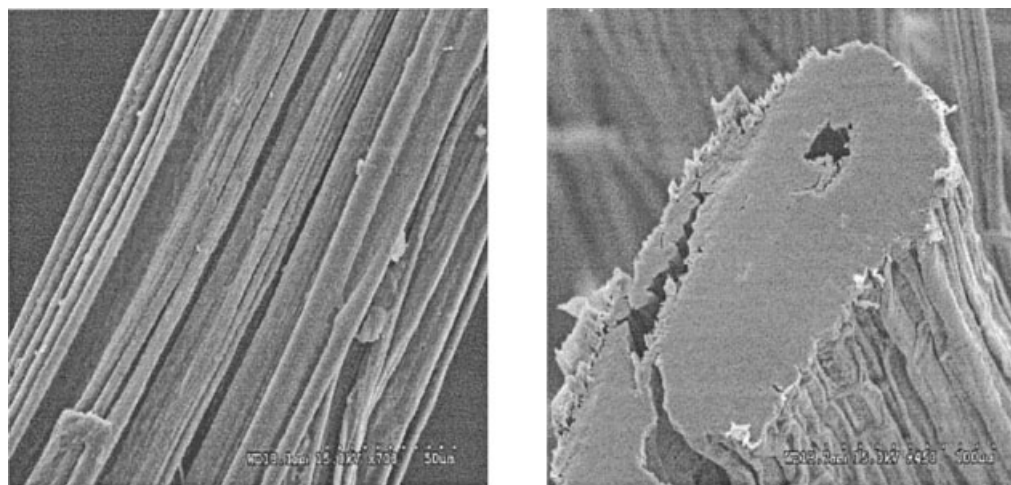
Data were analyzed using the SAS statistical software package (SAS Institute). General Linear Model procedure was used to detect differences among the treatments, with the level of significance set to 0.05.

### Micrographic properties

Micrographs were obtained by using a Model No. S2000N scanning electron microscope (SEM) (Hitachi, Tokyo, Japan). Samples were dried in a vacuum oven at  $40^\circ C$  for 12 h and cooled in a desiccator. Cross sections of the samples were cut horizontally for viewing and were mounted on SEM studs using silver



**Figure 4** Shear strength values of the foams with increase in fiber content.



(a) Longitudinal section

(b) Cross-section

**Figure 5** SEM of the corn stalk fiber before extrusion.

colloidal paste and sputter coated with gold palladium. Sections were prepared in order to observe the differences in pore structures and the interaction of fiber and starch in the extrudates. Micrographs were obtained at magnifications ranging between 100 and 2000 $\times$  to look at the foam cells and the distribution of corn fibers in the starch matrix.

## RESULTS AND DISCUSSION

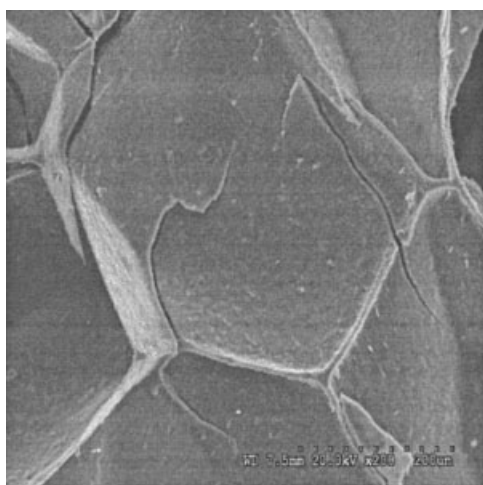
### Physical properties

RE values of the extrudates are shown in Figure 1. RE values ranged between 12 and 16 for different fiber concentrations. RE values increased initially with increase in fiber content. But, with fiber content above

8%, the RE decreased. Considerable decrease was observed in the RE of samples with 14% fiber content. The unit densities decreased with increase in fiber content from 0 to 10% and increased remarkably as the fiber content was increased further to 14% (Figure 2). The expansions and densities results were consistent. There were significant differences between the RE and UD values between the samples with 14% fiber content and the rest of the samples.

With the inclusion of fiber at lower concentrations there was good distribution along with good interaction between the fiber and the starch. The even distribution of fiber in the starch matrix led to an initial increase in expansion values. The fibers were compatible with the starch and were distributed very well in the starch matrix during extrusion. With an increase in the fiber content there was difficulty in maintaining uniform distribution of the fibers in the starch matrix during extrusion. This may have resulted from aggregation of fibers at different places, due to which there were discontinuities in the starch matrix during expansion. The distribution and aggregation of corn fibers are observed and discussed later.

The effect of ethanol also was observed. It is generally seen from Figure 3 that expansion decreased with increases in ethanol content, although the differences were not significant. There were increases in the RE values by only 1 unit. For the samples with 2% fiber content the RE values increased when the ethanol content was increased. The effect was reversed for samples with 10% fiber content. These differences in the trend were due to the complex behavior of the extrusion of starches.<sup>18</sup> However, there were significant differences in RE values between the samples



**Figure 6** SEM of extruded starch with 0% fiber.



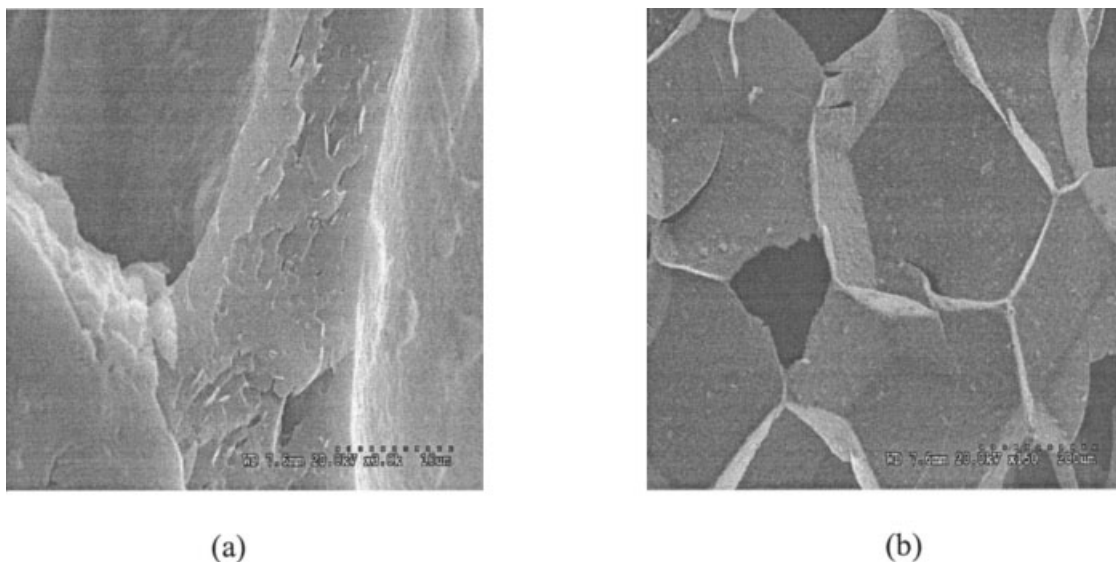


Figure 7 SEM of foams with 2% fiber.

with 14% fiber content and all samples with lower fiber contents. There is a need to investigate further the effect of ethanol on the expansion of starch–fiber matrices.

#### Mechanical properties

Shear strength of the foams was measured as described earlier. Figure 4 shows the values of shear strength of the extrudates as a function of fiber content. The values followed a pattern close to that of the densities. The force required to shear the extrudates increased with increase in fiber content from 1 to 10%. There was a drastic increase in the force required to

shear the extrudates with 14% fiber content. This suggests that although the fibers would have aggregated at certain places due to improper distribution, there was a very strong interaction between the fiber and the starch. This further indicated that the alkali-treated fibers were compatible with the starch molecules. To further justify this observation, micrographs of the extrudates were observed.

#### Micrographic characteristics

Figure 5a and b show micrographs of the raw fiber. From Figure 5a it can be seen that an individual fiber had a width of about  $150\ \mu\text{m}$ . The fibers had striations

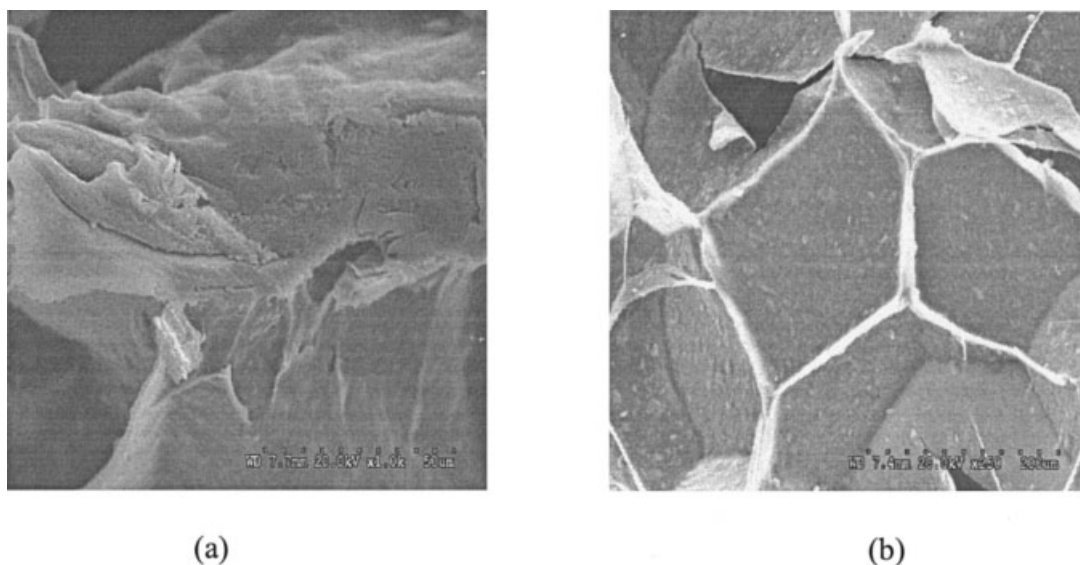
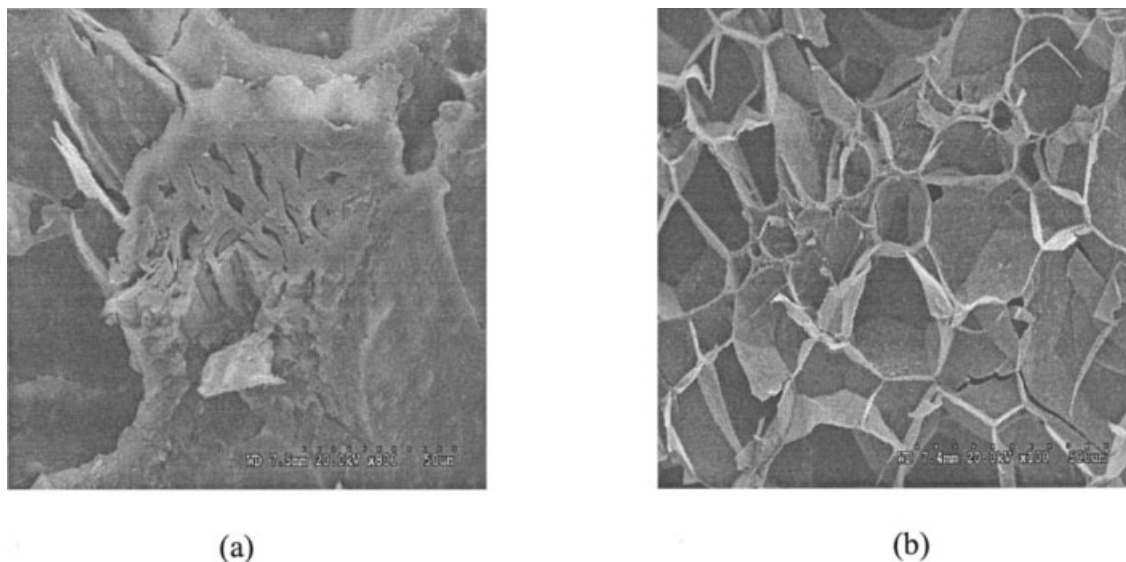


Figure 8 SEM of foams with 6% fiber.



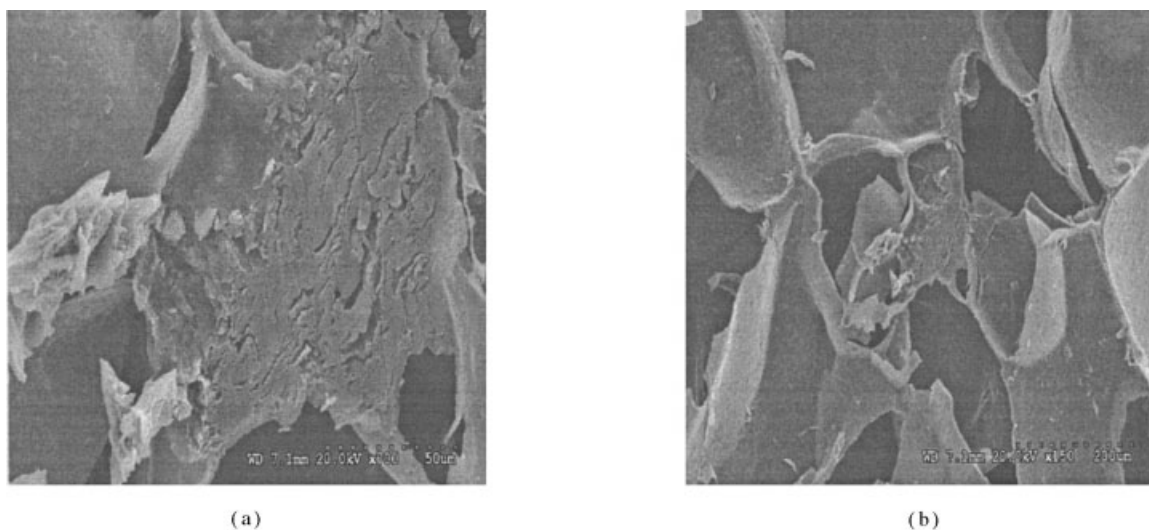
**Figure 9** SEM of foams with 10% fiber.

running along the entire length of the fiber. Such striations increase the surface area of the fiber and provide better interactions with other polymers in composites. Figure 5b shows the cross section of a single fiber. The fiber had an irregular oval shape with striations at the edges and a small lumen, which is characteristic of all natural cellulosic fibers. The diameter of the fibers ranged between 100 and 150  $\mu\text{m}$ .

Extrudates also were scanned under the SEM. Figure 6 is the micrograph of a starch extrudate without any fiber. Typical starch structure is observed.

Figure 7a, which shows the SEM of foam with 2% fiber, does not show clearly any presence of fiber. This suggests that the fibers were very compatible with starch acetate. The extrudates were better than the

extrudates without any fiber when the physical and mechanical properties were considered along with the micrographic characteristics. Figures 8 to 10 are the SEM of extrudates with 6, 10, and 14% concentrations of fiber. There was aggregation of fibers at different places in the cross section of the extrudates when fiber concentrations were high. At 14% fiber concentration, the fiber was not well distributed in the starch matrix, which led to aggregation of fibers as seen in Figure 10. When the aggregated fiber sections were observed closely at higher magnification it was seen that the fibers were not easily distinguishable, suggesting good compatibility of the fibers and starch. These micrographs support the behavior of the properties of extrudates with increased concentrations of fiber.



**Figure 10** SEM of foams with 14% fiber.

## CONCLUSION

Starch acetate was blended with corn stalk fibers at different concentrations for the production of biodegradable extruded foams. Corn fibers were found to be compatible with the starch acetate molecules. Corn fibers at concentrations less than 10% were well distributed in the starch acetate matrix during extrusion, leading to foams with good physical and mechanical properties. The results revealed that the corn stalk fibers were compatible with starch acetate. When the concentration of corn fiber exceeded 10%, nonuniform fiber distributions were observed, with aggregates of fiber in the starch matrix. It is expected that, with higher concentration of fibers, better mixing is needed to uniformly distribute the fiber.

We thank Sitaramraju Palwai (graduate student, Mechanical Engineering, UNL) and Nathan Weise (undergraduate student, Mechanized Systems Management, UNL) for their help in conducting the extrusions discussed in this article.

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