

# Physicomechanical and Hydrophobic Properties of Starch Foams Extruded with Different Biodegradable Polymers

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Received 2 September 2004; accepted 27 December 2004

DOI 10.1002/app.22127

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

**ABSTRACT:** Blends of hydroxypropylated high amylose starch and various functional aids listed below were extruded into foams using a twin-screw extruder ZSK - 30. In this study, the hydrophobic character and mechanical properties of starch foams were improved by using other biodegradable polymers, such as poly-caprolactone (PCL), poly (butylene adipate-co-terephthalate) (PBAT), cellulose acetate (CA), methylated pectin (MP), and polyvinyl alcohol (PVA), and crosslinkers like glyoxal. The hydrophobic character was improved in terms of a reduction in steady state weight gain, and an increase in dimensional stability (reduction in loss of radial and longitudinal dimensions) on moisture sorption. At the same time, efforts were made to maximize the expansion ratios by reduction of unit densities. Formulations of these foams (in terms of additive content and other processing parameters) were optimized. Particular formula-

tions with PVA, polyesters like PCL and PBAT, and glyoxal with PVA gave foams with unit densities lower than 25 kg/m<sup>3</sup>. The dimensional stability increased with an increase in the polyester content, but the density increased beyond an optimum polyester content, too. The loss in radial and longitudinal dimensions under steady state conditions was 12–20% with polyesters as compared to about 50–55% for control starch. Addition of these processing aids did decrease the water sensitivity of the starch foams. Foams with CA and methylated pectin, in the presence/absence of glyoxal, had marginally lower unit densities and slightly higher expansion ratios, as compared to those of control starch. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 58–68, 2006

**Key words:** biodegradable; foam extrusion; hydrophobicity; moisture sorption; polyester; starch

## INTRODUCTION

Foam plastic packaging is experiencing growing pressure from existing and proposed environmental and disposal regulations, and market based sustainability initiatives. It presents a major disposal problem for companies and municipalities as it is lightweight and bulky and so does not lend itself to a viable economic and environmentally responsible recycling operation due to expensive handling and transportation costs. It is not biodegradable, which makes disposal in soil or composting operations untenable. Further, issues such as sustainability, industrial ecology, biodegradability, and recyclability are becoming major considerations in a company's product packaging design, especially with single use disposable packaging. There is, thus, a market need for bio-based, biodegradable foam plastic packaging that can be safely and effectively disposed of in soil or in composting operations, but retains all of the current foam plastics performance requirements. In previous work, we have reported on the rationale, design, and engineering of bio-based, biodegradable polymer materials.<sup>1–4</sup>

Starch, an anhydroglucose polymer from corn, offers a structural platform to manufacture sustainable, biodegradable foam packaging. Extruded starch foams with polyvinyl alcohol (PVA) were first patented by Lacourse and coworkers.<sup>5,6</sup> Starch granules, however, exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The hydrophilicity and thermal sensitivity renders the starch molecule unsuitable for thermoplastic applications.

To impart hydrophobicity to the starch foams, some researchers have reported the melt blending of thermoplastic starch with nonbiodegradable hydrophobic polymers, such as polystyrene, poly(methyl acrylate), and so forth. For example, Chinnaaswamy and Hanna<sup>7,8</sup> hold U.S. and Australian patents on manufacturing loose-fill foams made of 70% starch and 30% polystyrene. The combination of polystyrene with starch reduced the use of petroleum-based plastic and rendered the material disintegrable, while providing water resistance. Bhatnagar and Hanna<sup>9</sup> extruded regular cornstarch with either polystyrene or poly(methyl methacrylate) at a 70 : 30 ratio with other additives in a single screw extruder. Foam densities in the range of 29.5–132 kg/m<sup>3</sup> were obtained, with radial expansions of 8.8–40.1. Cha and colleagues<sup>10</sup>

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studied the moisture adsorption isotherms, bulk densities, and expansion ratios of starch-based foams involving about 33% synthetic polymers (polystyrene), which reduces its biodegradability. Also, chemical blowing agents were used in addition to water as the physical blowing agent. Cha and coworkers<sup>11,12</sup> conducted extrusions to study the rheological properties of blend melts and the effects of temperature and moisture contents on mechanical properties of starch-based foams containing wheat and corn starches, polyethylene-*co*-vinyl alcohol, polystyrene, plasticizers, and nucleating and blowing agents. However, the resultant starch-based foams were not completely biodegradable.

The following authors report the use of hydrophobic biodegradable polymers such as poly(caprolactone) (PCL), cellulose acetate (CA), aliphatic-aromatic copolyesters, and so forth in starch-based foam formulations. Altieri and Tessler<sup>13</sup> patented water-resistant foams from blends of starch with starch esters. Bastioli and colleagues<sup>14–17</sup> patented foams from blends of starch with 10–30% of polymers such as PVA, poly (caprolactone), cellulose acetate, poly (ethylene vinyl alcohol), and poly (ethylene-*co*-acrylic acid). Neumann and Seib<sup>18,19</sup> patented the technology to make biodegradable starch-based foams using polyalkylene glycols. Xu and Doane<sup>20,21</sup> prepared starch foams using hydroxy functional polyesters as a processing aid. Depending on the formulation and processing conditions, the foams reported in the patents cited above had bulk densities in the range of approximately 3–100 kg/m<sup>3</sup>. Wang and Shogren<sup>22</sup> extruded cornstarch blended with biodegradable polymers to make loose-fill foams. The effects of nucleating agent (talc), blowing agents (water, ethanol, and propanol), and different polymers (polylactic acid, polycaprolactone, polyvinyl alcohol, polybutylene succinate-adipate, and polyester-amide) and extrusion conditions on foam density, resilience, and compressibility were examined. Results indicated that 0.5–1% talc addition was the optimum range. No significant differences existed between the blowing agents. Hanna and coworkers reported that the addition of PLA,<sup>23</sup> Eastar Bio copolyester (poly (butylene adipate-*co*-terephthalate)) (PBAT),<sup>24,25</sup> or a commercial starch-based material (Mater-Bi from Novamont)<sup>26</sup> increased radial expansions for the starch-based foams for particular compositions and moisture contents. These foams also showed improved flexibility and water resistance. Willett and Shogren<sup>27</sup> extruded blends of normal cornstarch, as well as high amylose cornstarch, wheat starch, and potato starch, with resins such as PVA, cellulose acetate, and several biodegradable polyesters, such as poly (lactic acid) (PLA), poly (hydroxyesterether) (PHEE), poly (caprolactone), poly (ester amide) (PEA), and poly (hydroxybutyrate-*co*-valerate), among others.

Some reactive modifications of starch itself have also been performed to impart hydrophobicity. Boehmer and colleagues<sup>28</sup> patented foams based on graft copolymers of starch with methyl acrylate. Shogren<sup>29</sup> reported that extruded foams made from acetylated high amylose starch had higher water resistance, but high bulk densities of 40–60 kg/m<sup>3</sup>.

Starch-based foams, due to their hygroscopic nature, tend to gain weight on moisture sorption in a humid environment. This is also accompanied by shrinkage in the foam dimensions. Studies on determining the weight gain and the dimensional stability of starch-based foams, which are critical for cushion packaging applications, have not been performed earlier. The objective of this study was to use water-resistant biodegradable polymers, such as PCL, PBAT, PVA, CA, and MP, to improve the hydrophobic character of these starch foams. Hydrophobicity was imparted by decreasing the weight gain and the loss in dimensions by shrinkage on moisture sorption, without sacrificing the physicomechanical properties, such as lower densities and higher resilience (spring indices). Weight gain and shrinkage (loss in dimensions) in starch foams on moisture sorption adversely affects its performance in cushioning as well as the insulation, and hence, is critical. The best formulations were determined based on their lower weight gains, high dimensional stability, low densities, and improved mechanical properties such as compressibility and resilience.

In this study, the operating conditions were almost fixed based on preliminary studies<sup>30</sup> (the moisture content and the temperature profile had to be slightly manipulated to achieve foams with the best physicomechanical properties). Physical properties, such as unit densities, expansion ratios, equilibrium weight gains, and dimensional stability on moisture sorption, were studied.

## EXPERIMENTAL

### Materials

The type of starch used was hydroxypropylated high amylose cornstarch (70% amylose content). The starch was purchased from National Starch and Chemicals (Indianapolis, IN), under the trade name of HYLON 7. The density of HYLON 7 starch is 1.2 g/cm<sup>3</sup>. The inherent moisture content of the starch is 11.2% under ambient conditions. Water was used as the plasticizer as well as the blowing agent. Water content was maintained at 8–10% of the starch used. Talc (magnesium silicate), used as the nucleating agent, was obtained from Luzenac (Ontario, Canada). It has a specific gravity of 2.76 and a bulk density of 150 kg/m<sup>3</sup>. The talc content was maintained at 1% for all the experiments. Semicrystalline polycaprolactone (PCL) resin of  $M_n$

80,000, under the trade name Tone 787, was purchased from Union Carbide Chemicals and Plastics (South Charleston, WV). Poly (butylene adipate-*co*-terephthalate) (PBAT) resin of  $M_n$  51,100 and PDI of 2.214, under the trade name Ecoflex FBX 7011, was purchased from BASF Chemicals (Ludwigshafen, Germany). Cellulose acetate (grade JLF-68) (degree of substitution = 2.0) was acquired from Hoechst Celanese Corp (Somerville, NJ). It had a weight-average molecular weight,  $M_w$ , of  $\sim 55,100$ , an  $M_n$  of  $\sim 11,800$ ,  $T_g$  of  $191^\circ\text{C}$ , and a melting temperature of  $230^\circ\text{C}$ . The melting endotherm started at  $218^\circ\text{C}$ . PVA was purchased from Air Products and Chemicals (Allentown, PA), under the trade name Airvol 325 (degree of hydrolysis of 98.3%,  $M_w \sim 85,000$ – $146,000$ ). Glyoxal and methylated pectin (93% methylated) were from Sigma-Aldrich Chemical Co. (St. Louis, MO).

### Experimental setup

The experimental setup used in this study was a twin-screw extrusion system. The twin-screw extrusion system consisted of an extruder driver with a speed control gearbox, a CENTURY ZSK-30 twin-screw corotating extruder with a screw diameter of 30 mm, an L/D of 42, a positive displacement pump for injecting water into the extruder, and ACCURATE single-screw feeders for feeding starch, and the processing aids and talc were fed individually. The screw configuration is shown in Figure 1. This specific screw configuration was selected to get the best physicomaterial properties based on our previous work.<sup>30</sup> A cylindrical filament die 2.7 mm in diameter and 8.1 mm in length, with a cooling sleeve, was assembled to the extruder. The sensors were mounted on the die to measure the temperature and pressure of the melt. A high-speed cutter was used to get cylindrical foam extrudates of required size.

### Procedure

The temperatures in the extruder zones were set up to reach the required temperatures. The temperature profile is as follows:

- Zone 1:  $20^\circ\text{C}$  (cold feed)
- Zone 2:  $100^\circ\text{C}$
- Zone 3:  $115^\circ\text{C}$
- Zone 4:  $120^\circ\text{C}$
- Zone 5:  $125^\circ\text{C}$
- Zone 6:  $125^\circ\text{C}$
- Zone 7:  $120^\circ\text{C}$
- Zone 8:  $120^\circ\text{C}$
- Zone 9:  $115^\circ\text{C}$
- Die:  $115^\circ\text{C}$
- Melt Temperature:  $112$ – $115^\circ\text{C}$

The feeder for starch was calibrated and set at a particular speed to feed at  $11.2 \text{ kg/h}$  ( $\sim 25 \text{ lb/h}$ ). The other feeder/feeders were calibrated and set at feeding rates accordingly. Initially, during start-up, water was pumped into the system at 15–20% of the starch fed, and later its flow rate was reduced to about 8–10% of the starch. The inherent moisture (11.2%) present in starch also helped in the plasticization of the starch. Thus, the total moisture content was 18.5%. The screw speed was maintained at 200 rpm. The processing aids were used individually, or in combination with each other. When formulations were changed, extrusion was continued until the torque and the die pressure stabilized. Extrusions were carried out at a torque of 70–75% and a pressure of 700–1000 psi.

### Characterization

The samples obtained were in the form of cylindrical blocks of a length of about 3 cm. The samples collected were conditioned as per ASTM D-4332,<sup>31</sup> in a constant environment room at  $23 \pm 1^\circ\text{C}$  ( $73.4 \pm 3.6^\circ\text{F}$ ) and  $50 \pm 2\%$  RH for at least 72 h before testing.

### Density

The density of the foam was calculated from the mass and volume of a regularly shaped specimen according to test method ASTM D-3575 (section 43, Method A).<sup>32</sup> Ten samples were measured for each formulation.

The dimensions of the sample were measured using a Vernier Calipers graduated to permit measurements accurate to 0.0254 mm. The expansion ratio (ER) was calculated as the ratio of the cross-sectional area of the foam to that of the die.

### Compressive strength and resiliency<sup>5,33</sup>

Compressive strength and resiliency describe the mechanical integrity of the foam. Compressive strength of the lab-scale specimens was measured on a UTS SFM –20 tensile testing machine. Foam specimens were securely fastened lengthwise and compressed by a steel probe (0.635 cm diameter) with a hemi-spherical end-cap. By lowering the piston to the foam surface, an initial load of 0.5N was applied on the specimen for approximately 5 s. From this point, the probe was lowered at a rate of 30 mm/min for a distance of 3 mm. The maximum load was recorded. After 60 s had elapsed, a relaxation load was recorded. Compressive strength was determined by dividing the maximum load by the cross-sectional area of the probe. Resiliency is the percentage of the compressive force after the 60 s hold period divided by the maximum force required to compress the foam by 3 mm. Averages were calculated from ten specimens for each starch foam formulation.

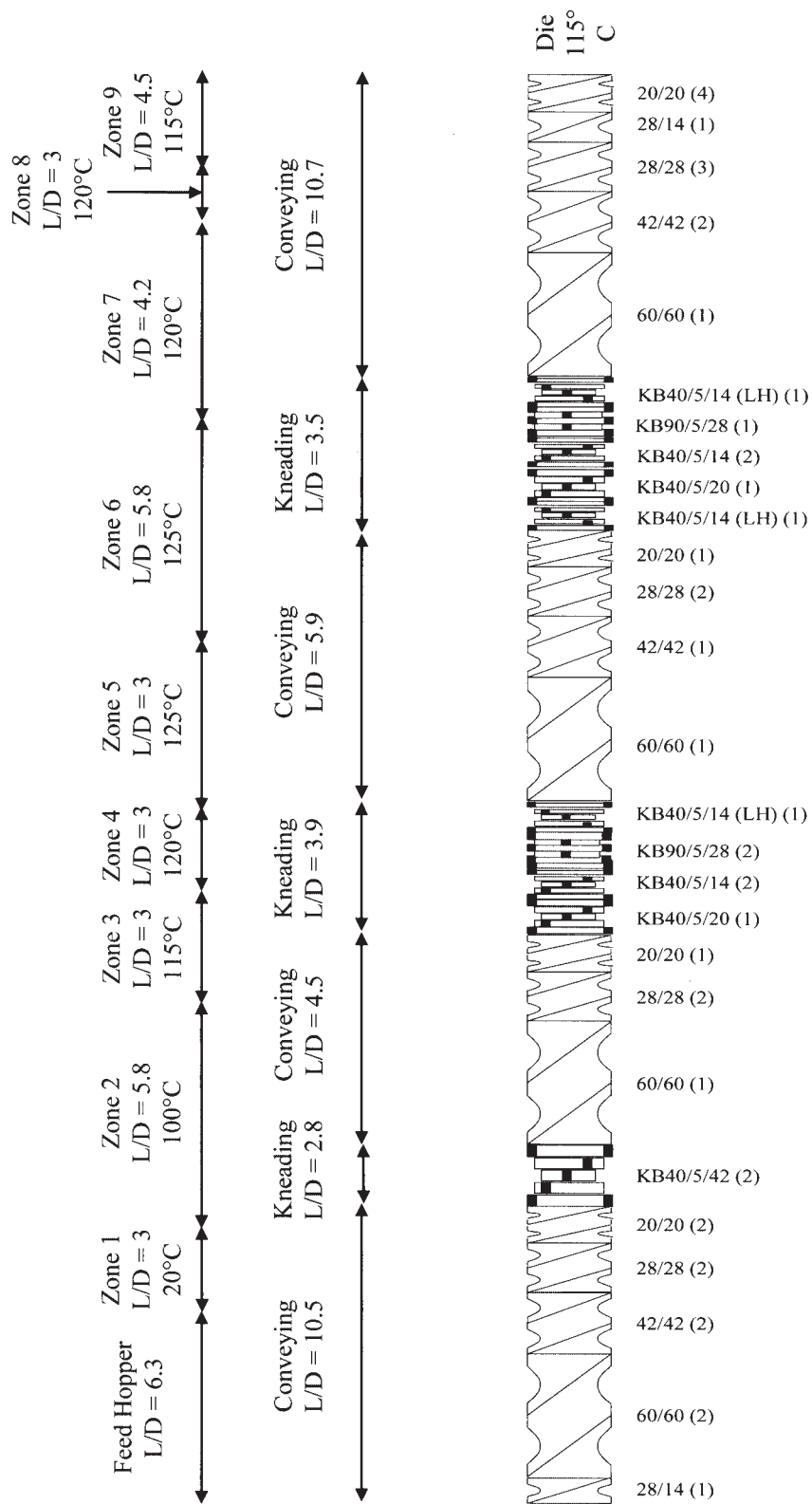


Figure 1 Screw configuration used for making starch foams.

**Moisture sorption analysis**

Ten blocks of each formulation, collected at different times, were placed in an environmental humidity

chamber, subject to a relative humidity of  $95 \pm 5\%$  and a temperature of  $38 \pm 5^\circ\text{C}$ . The weight and the dimensions (length and diameter) of the samples were monitored. They were measured at regular intervals using

**TABLE I**  
**Unit Densities, Radial Expansion Ratios, Specific Lengths, Compressive Strengths, and Spring Indices (Resilience)**  
**with Different Functional Aids (10 samples were measured for each formulation)**

Entry	Processing aids	Unit density (kg/m <sup>3</sup> )	Radial expansion ratio	Specific length (cm/gm)	Resiliency (%)
1	None (control)	30.2 (±0.8)	39.6 (±1.1)	14.6 (±0.6)	69.8 (± 2.1)
2	3% PVA	24.5 (±0.5)	45.1 (±1.0)	15.8 (±0.5)	72.8 (± 1.8)
3	6% PVA	29.2 (±0.6)	39.7 (±0.9)	15.1 (±0.8)	72.4 (± 1.2)
4	9% PVA	32.2 (±0.9)	36.7 (±0.9)	14.8 (±0.4)	71.0 (± 1.2)
5	12% PVA	34.2 (±1.3)	34.2 (±0.6)	14.9 (±0.5)	71.6 (± 1.3)
6	15% PVA	36.4 (±1.6)	31.8 (±0.9)	15.1 (±0.3)	71.2 (± 0.8)
7	0.1% Glyoxal + 3% PVA	24.4 (±0.4)	44.9 (±1.8)	15.9 (±0.6)	66.2 (± 3.9)
8	0.2% Glyoxal + 3% PVA	24.1 (±0.4)	46.8 (±2.3)	15.5 (±0.6)	66.6 (± 4.2)
9	0.3% Glyoxal + 3% PVA	23.5 (±0.6)	48.5 (±1.7)	15.3 (±0.5)	66.3 (± 3.7)
10	0.4% Glyoxal + 3% PVA	25.8 (±0.3)	44.8 (±2.1)	15.1 (±0.9)	66.4 (± 3.1)
11	1.0% Glyoxal + 3% PVA	30.5 (±1.3)	39.1 (±1.4)	14.6 (±0.8)	65.4 (± 5.1)
12	3% CA	30.2 (±1.2)	39.6 (±2.1)	14.6 (±0.9)	74.7 (± 3.2)
13	6% CA	29.7 (±1.0)	40.4 (±1.6)	14.6 (±1.1)	76.7 (± 2.7)
14	10% CA	29.6 (±1.3)	40.5 (±2.2)	14.6 (±1.4)	77.5 (± 3.5)
15	3% methylated pectin	30.1 (±1.9)	39.7 (±2.6)	14.6 (±1.3)	71.0 (± 2.8)
16	6% methylated pectin	29.9 (±1.6)	40.2 (±1.9)	14.6 (±1.1)	70.0 (± 2.3)
17	10% methylated pectin	29.8 (±1.5)	40.3 (±2.1)	14.6 (±1.6)	70.9 (± 3.2)
18	0.1% glyoxal + 10% CA	30.1 (±0.6)	39.7 (±1.3)	14.6 (±0.9)	73.1 (± 2.1)
19	0.2% glyoxal + 10% CA	29.7 (±0.5)	40.5 (±1.1)	14.6 (±0.7)	74.3 (± 2.3)
20	0.3% glyoxal + 10% CA	28.6 (±0.5)	42.3 (±0.8)	14.4 (±0.9)	74.4 (± 2.8)
21	0.4% glyoxal + 10% CA	31.1 (±0.8)	38.3 (±0.9)	14.7 (±1.1)	71.6 (± 2.4)
22	1.0% glyoxal + 10% CA	32.7 (±1.4)	36.0 (±1.7)	14.8 (±1.5)	67.5 (± 3.8)
23	0.1% glyoxal + 10% methylated pectin	29.9 (±0.8)	40.0 (±1.5)	14.6 (±0.8)	66.2 (± 3.9)
24	0.2% glyoxal + 10% methylated pectin	29.6 (±0.7)	40.5 (±1.5)	14.6 (±1.0)	67.5 (± 3.6)
25	0.3% glyoxal + 10% methylated pectin	28.8 (±0.5)	42.0 (±1.2)	14.5 (±0.9)	66.9 (± 4.1)
26	0.4% glyoxal + 10% methylated pectin	32.1 (±1.1)	36.9 (±1.4)	14.8 (±1.3)	68.4 (± 4.3)
27	1.0% glyoxal + 10% methylated pectin	34.8 (±1.9)	33.5 (±2.4)	15.0 (±2.1)	66.8 (± 4.9)
28	1% PCL	27.4 (±0.5)	41.0 (±0.6)	15.5 (±0.4)	75.3 (± 1.2)
29	3% PCL	26.2 (±0.3)	42.7 (±0.4)	15.6 (±0.2)	78.2 (± 1.3)
30	7% PCL	37.4 (±1.1)	28.2 (±0.9)	16.6 (±0.7)	75.7 (± 0.8)
31	10% PCL	47.1 (±1.5)	19.3 (±1.5)	19.2 (±0.9)	73.6 (± 1.1)
32	1% PBAT	26.2 (±0.3)	45.3 (±0.4)	14.7 (±0.5)	80.3 (± 0.8)
33	3% PBAT	24.5 (±0.3)	46.5 (±0.3)	14.8 (±0.3)	83.6 (± 1.2)
34	5% PBAT	24.2 (±0.2)	46.7 (±0.5)	15.5 (±0.4)	84.2 (± 1.1)
35	7% PBAT	24.7 (±0.4)	46.0 (±0.4)	14.8 (±0.6)	85.9 (± 0.8)
36	10% PBAT	28.7 (±0.2)	41.1 (±0.3)	14.8 (±0.5)	83.1 (± 0.7)

an accurate weighing balance and a pair of Vernier Calipers, to the third decimal place. The entities measured at different time intervals were normalized using the value measured before placing the samples in the humidity chamber (time,  $t = 0$ ). The initial weight, diameter, and length were assigned  $W_0$ ,  $D_0$ , and  $L_0$ , respectively. The weight and dimensions of the samples were recorded until a steady state value was reached (approximately 30 days). The steady state weights and dimensions of the samples were assigned  $W$ ,  $D$ , and  $L$ , respectively. The results for a formulation were obtained as an average over the ten samples used for that formulation.

#### Environmental scanning electron microscopy (ESEM)

Foam samples were sectioned with a razor blade and mounted on aluminum stubs with graphite filled tape,

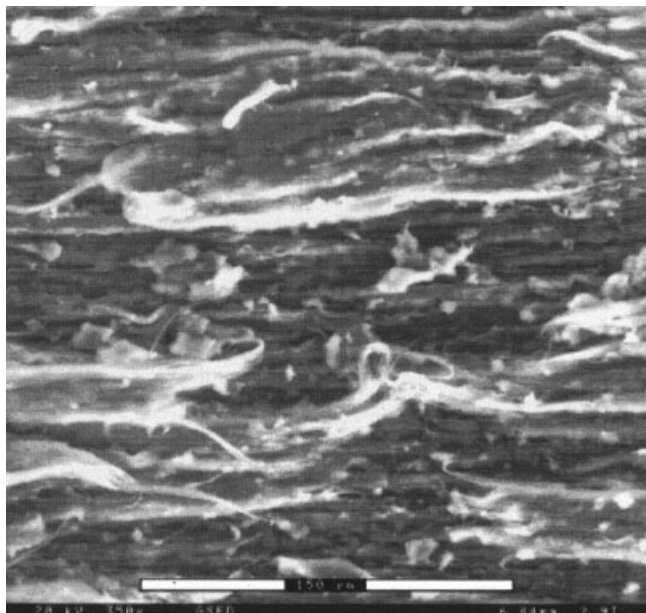
sputter coated with gold, and examined with a Philips Electroscan 2020 environmental scanning electron microscope. The surfaces of the foam samples with polyesters as processing aids were used.

#### RESULTS AND DISCUSSION

An optimum formulation had to be reached with each functional aid, to get the most hydrophobic foam without sacrificing physicomechanical properties. The unit densities and the ERs for the foam formulations using the biodegradable polymers as functional aids are reported in Table I. Densities lower than 25 kg/m<sup>3</sup> were obtained for some formulations.

#### Effect of functional aids on the density and ER of the starch foams

In the case of PVA, it was observed that the ER increased with an increase in the PVA content, but just



**Figure 2** ESEM of the surface of starch foams with 12% PVA.

up to a certain level, and then decreased again (Table I, Entries 2–6)). The maximum ER of 45.1 and minimum unit density of  $24.5 \text{ kg/m}^3$  was obtained at a PVA content of 3% of the starch used. Addition of PVA to starch reduced its melt flow index (MFI) value,<sup>34</sup> indicating an increase in the viscosity of the melt, indicated by a rise in the torque on the extruder, and thus the specific mechanical energy (SME). This was in accordance with the behavior observed by Willett and colleagues,<sup>27</sup> that an increase in SME was observed in the starch/PVA blend as compared to the starch control. Also, PVA, a high molecular weight molecule, being soluble in water, would decrease its diffusivity. This led to a more controlled expansion, and the increased stiffness of the starch matrix supported this expansion. With an increase in the PVA content, there was a lowering effect on the flow behavior. This negative deviation was due to a phase separation in the system. An improvement in mechanical properties was not realized due to the poor interface adhesion between the fibrous PVA structure and the starch matrix (Fig. 2). Also, an increase in the PVA content may have reduced the diffusivity of water (the blowing agent), considerably resulting in lower values of the ER.

Glyoxal has found applications as a crosslinker in the production of moisture resistant glues and adhesives, as well as moisture resistant foundry binders. Hence, glyoxal was used as a crosslinker for starch to improve its hydrophobic character. 3% PVA was used in the formulations to obtain a product with lower unit density. As seen in Table I (Entries 7–11), the ER increased while the density decreased with an in-

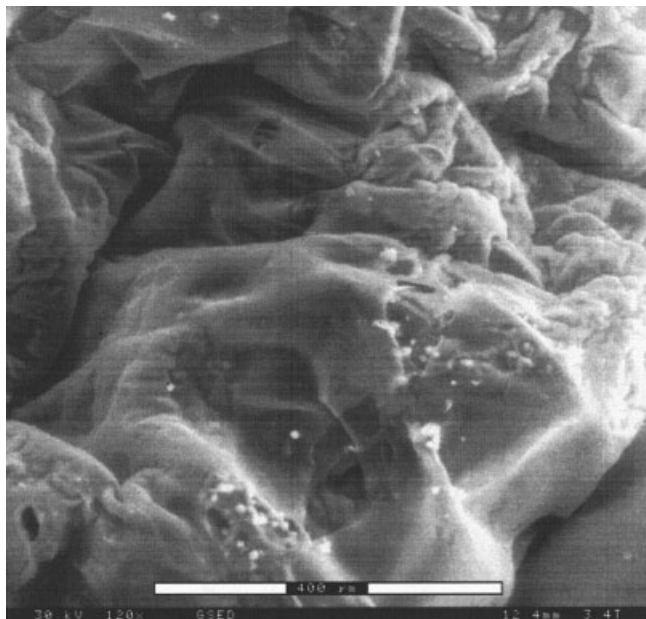
crease in glyoxal content, but beyond a certain amount the ER decreased and the unit density increased. A maximum ER of 48.5 and a minimum density of  $23.5 \text{ kg/m}^3$  were obtained at a glyoxal content of 0.3%.

The increase in ER can be attributed to the fact that glyoxal acted as a crosslinker within starch and with PVA and increased the molecular weight of the starch matrix, thus making it stiffer. This helped in preventing the loss of moisture through the surface. Also, an increase in melt strength due to crosslinking prevented the loss of moisture due to cell rupture. At higher glyoxal contents, however, the stiffness increased considerably, restricting the expansion due to loss of flexibility. Thus, an optimum amount of glyoxal (0.3%) was required to give maximum ER and a minimum unit density, in addition to some hydrophobic character.

Cellulose acetate and methylated pectin did not have a significant effect on the density and the ER of the starch foams (Table I, Entries 12–17). A minimum unit density of  $29.6 \text{ kg/m}^3$  and a maximum ER of 40.5 were obtained with the formulation containing 10% CA. A minimum unit density of  $29.8 \text{ kg/m}^3$  and a maximum ER of 40.4 were obtained with 10% methylated pectin. When glyoxal was used as a crosslinker between CA and MP, the response was similar to the one obtained by using glyoxal with PVA (Table I, Entries 18–27).

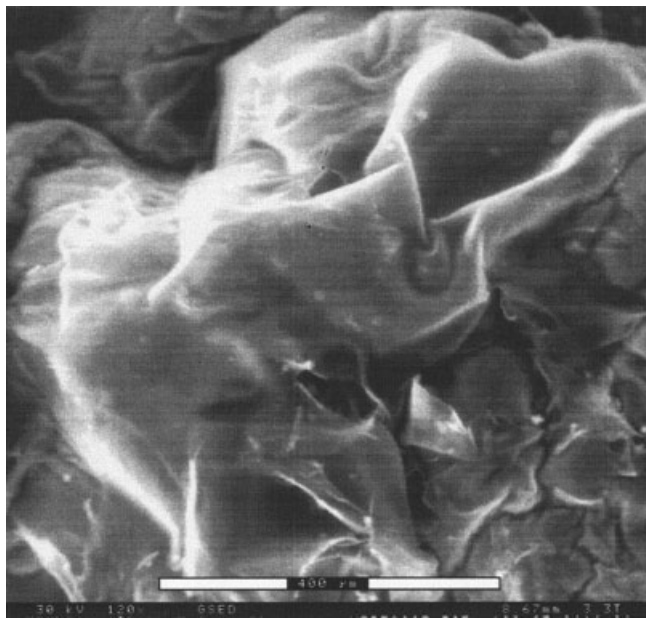
When PCL was used in the starch-based foam formulations, the ER increased initially and reached a maximum of 42.7 at a PCL content of about 3% (Table I, Entry 29). The density of the corresponding formulation was  $26.2 \text{ kg/m}^3$ . The density increased to  $47.1 \text{ kg/m}^3$  with an increase in PCL content to 10%, with a low ER of 19.3 (Table I, Entry 31). PCL was not compatible with starch, and phase separated, and most of it migrated to the surface into the skin. The polyester migrated to the surface because of the lower surface tension in the melt, thus forming a hydrophobic coating. PCL ( $39.6 \text{ dynes/cm}$ )<sup>35</sup> has a lower surface energy than starch ( $53.7 \text{ dynes/cm}$ ),<sup>36</sup> and, thus, the overall energy is minimized by the migration of the polymer to the foam surface. Figures 3 and 4 show the scanning electron micrographs of the starch foam surface in the absence of any functional aids, and with 3% PCL, respectively. Figure 4 shows the presence of a smooth skin on the surface of the starch foams, as compared to the surface of the control starch foam without any processing aids (Fig. 3). This finding was consistent with the results seen by Willett and colleagues,<sup>27</sup> where X-ray photoelectron spectroscopy was used to show the manifestation of the polyester on the surface of starch foams. This prevented the loss of water (blowing agent) through the skin, resulting in an increase in the ER and a reduction in unit density.

However, further increase in the PCL content led to poorer densities and ERs due to a nonhomogeneous

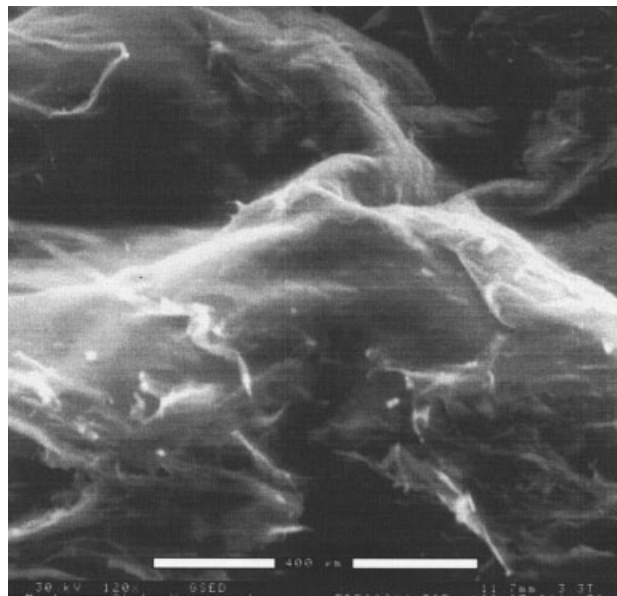


**Figure 3** ESEM of the surface of starch foams with no additives.

melt phase involving the starch plastic and the PCL. This resulted in much denser foam, since water did not function as a blowing agent for PCL. Thus, the un-foamed PCL phase separated, resulting in an increase in the density. Chemically modifying either starch or PCL, and grafting one onto the other, could increase the compatibility between starch and PCL. This could result in a molecule that is hydrophobic by itself.



**Figure 4** ESEM of the surface of starch foams with 3% PCL.

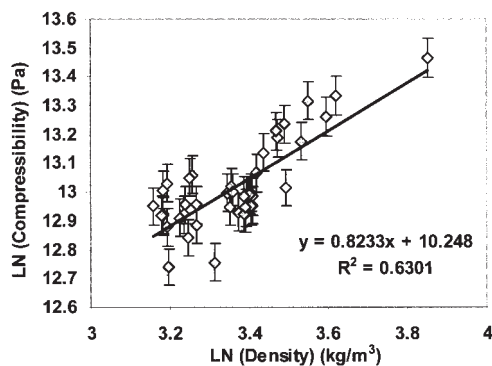


**Figure 5** ESEM of the surface of starch foams with 7% PBAT.

The effect of PBAT on the starch foams was very much similar to that due to PCL. But higher values of ER were obtained in the case of PBAT, because of the higher flexibility of PBAT. These results were contrary to those observed by Willett and colleagues.<sup>27</sup> Also, the densities obtained were much lower than those reported by Fang and coworkers.<sup>24</sup> Foams with 5% PBAT were extruded at a unit density of 24.2 kg/m<sup>3</sup> at an ER of 46.7. There is a possibility that the PBAT showed higher compatibility than PCL with the starch matrix. Maximum ERs were obtained at a PBAT content of 3–7% as shown in Table I (Entries 32–36). The ER was higher in this range because PBAT migrated to the surface, which was evident from the scanning electron micrograph of the starch foam surface in Figure 5, thus providing a finer and more stable surface, preventing the rapid loss of moisture through the surface. PBAT (44.2 dynes/cm)<sup>35</sup> has a lower surface energy than starch (53.7 dynes/cm),<sup>36</sup> and thus the overall energy is minimized by the migration of the polymer to the foam surface.

PBAT on the surface resisted tears and the formation of holes on the surface, as it has a higher elasticity as compared to thermoplastic starch. Similar to PCL, at higher PBAT contents, slightly denser foam was obtained, since water did not function as a blowing agent for PBAT, resulting in lower values of the ER. However, the densities were still lower than that measured for the control.

Efforts are on to chemically modify either PBAT or starch for better compatibility between the two, thus producing a resulting entity (molecule) that is hydrophobic by itself and also exhibits better mechanical properties.



**Figure 6** Compressive strength (Pa) of the starch-based foams as a function of their density ( $\text{kg/m}^3$ ).

### Compressive strength and resiliency

Typically, a power-law relationship is observed between compressive strength,  $\sigma_c$ , and foam density,  $\rho$  ( $\sigma_c \sim \rho^n$ ). Denser foams tend to have thicker cell walls and, hence, resist deformation better than lower density foams with thinner cell walls. A strong relation existed between foam density and compressive strength (Fig. 6). The regression line in Figure 6 was drawn and a slope of 0.82 was obtained ( $n = 0.82$ ). A value of  $n = 0.92$  was obtained by Willett and coworkers,<sup>27</sup> while Hutchinson and colleagues<sup>37</sup> report exponents of 1.5–1.6 for compressive strengths of foams prepared from maize grits. The variation in the value of the slope obtained (0.82) and the values reported in literature was due to a different type of starch used, and probably also due to a different experimental twin-screw extrusion configuration.

The resiliency of the foam samples is listed in Table I. The control starch foams provided a resiliency (spring index) of 69.7%. The addition of PBAT improved the resiliency considerably, from 69.7% to 85.9% at a PBAT content of 7% of the starch used. PCL and CA helped increase the spring index up to  $\sim 78\%$ , while PVA and methylated pectin barely increased the resiliency to  $\sim 71\text{--}72\%$ . When glyoxal was added as a crosslinker, it increased the rigidity of the starch foams and, thus, the resiliency of the foams decreased by  $\sim 3\%$ .

Thus, PBAT provided the best properties in terms of its lower densities ( $\sim 24\text{--}25 \text{ kg/m}^3$ ), better hydrophobic properties, and spring indices as high as 85%.

### Effect of functional aids on the weight gain and dimensional stability of the starch foams on moisture sorption

Table II (Entries 2–6) exhibits the response of the PVA modified starch foams to a humid environment. A lower final weight gain value implies more hydropho-

bic character. It was observed that the hydrophobic character increased with an increase in PVA concentration, but just up to a certain extent. Minimum weight gain was observed at a PVA content of 12%. The samples with 15% PVA showed higher moisture absorption as compared to those with 12%.

Starch foams shrink in the presence of moisture. The dimensional stability of the product is important in packaging applications. The lower the loss in dimensions, the better is the dimensional stability. Thus, a higher ordinate value indicates better dimensional stability. Results indicated that the samples with 6% polyvinyl alcohol exhibited maximum dimensional stability (minimum radial and longitudinal shrinkage).

The steady state weight gain by samples containing 6% PVA was not considerably higher as compared to those with 12% PVA (12.2% as compared to 11.2%). The loss in radial dimensions at 6% PVA was about 20%, while the shrinkage in the longitudinal direction was 25%, as compared to 35% for samples containing 12% PVA and 50% for control starch.

The free hydroxyl groups from starch were capable of forming hydrogen bonds with surrounding moisture, resulting in its hygroscopic nature. In the presence of polyvinyl alcohol, hydrogen bonding may have taken place between the free hydroxyl groups of PVA and those on starch, thus reducing the absorption of moisture. However, addition of an excess of PVA led to a large number of free hydroxyl groups, which were capable of absorbing moisture themselves. This increased the hydrophilicity of the foam, and hence resulted in higher weight gains.

When glyoxal was used in combination with 3% PVA, as a result of the crosslinking of starch by glyoxal, the moisture sorption decreased. Thus, the steady state weight gain reduced from about 12.2% to about 11.4% with an increase in the glyoxal content from 0% up to 0.3%, but beyond that moisture sorption increased again (Table II, Entries 7–11).

These results were consistent with those showing the dimensional stability of these samples. The samples with 0.3% glyoxal showed minimum loss of radial and longitudinal dimensions, as well as lowest gain in weight under steady state conditions. The dimensional stability improved from 40% (at 0% glyoxal and 3% PVA) to 25% (at 0.3% glyoxal and 3% PVA). Also, the maximum ER is obtained at a glyoxal content of 0.3%. Thus, an optimum amount of glyoxal to be used would be 0.3%.

Cellulose acetate imparted some hydrophobic character, evident from the steady state weight gain data (Table II, Entries 12–14). The steady state weight gain decreased with an increase in the cellulose acetate content, due to the hydrophobic character of CA. Hence, further efforts were made to crosslink cellulose acetate (10%) with starch using glyoxal. The nature of



**TABLE II**  
**Normalized Steady State Weight Gains, Diameters, Lengths of the Starch-Based Foams with Different Functional Aids (10 samples were measured for each formulation)**

Entry	Processing aids	Normalized steady state weight gain	Normalized steady state diameter	Normalized steady state length
		$\left[ \frac{W - W_0}{W_0} \right]$ ( $\pm 0.032$ )	$\left[ \frac{D}{D_0} \right]$ ( $\pm 0.041$ )	$\left[ \frac{L}{L_0} \right]$ ( $\pm 0.046$ )
1	None (control)	0.128	0.564	0.498
2	3% PVA	0.122	0.682	0.655
3	6% PVA	0.122	0.769	0.743
4	9% PVA	0.120	0.740	0.682
5	12% PVA	0.113	0.717	0.659
6	15% PVA	0.114	0.697	0.631
7	0.1% glyoxal + 3% PVA	0.117	0.715	0.718
8	0.2% glyoxal + 3% PVA	0.117	0.721	0.729
9	0.3% glyoxal + 3% PVA	0.114	0.738	0.774
10	0.4% glyoxal + 3% PVA	0.118	0.670	0.726
11	1.0% glyoxal + 3% PVA	0.123	0.657	0.738
12	3% CA	0.119	0.614	0.525
13	6% CA	0.112	0.651	0.566
14	10% CA	0.105	0.691	0.632
15	0.1% glyoxal + 10% CA	0.099	0.725	0.636
16	0.2% glyoxal + 10% CA	0.094	0.714	0.638
17	0.3% glyoxal + 10% CA	0.093	0.751	0.658
18	0.4% glyoxal + 10% CA	0.100	0.683	0.641
19	1.0% glyoxal + 10% CA	0.110	0.679	0.587
20	3% methylated pectin	0.124	0.610	0.515
21	6% methylated pectin	0.116	0.637	0.541
22	10% methylated pectin	0.110	0.678	0.614
23	0.1% glyoxal + 10% methylated pectin	0.106	0.697	0.619
24	0.2% glyoxal + 10% methylated pectin	0.105	0.719	0.628
25	0.3% glyoxal + 10% methylated pectin	0.104	0.734	0.642
26	0.4% glyoxal + 10% methylated pectin	0.108	0.653	0.620
27	1.0% glyoxal + 10% methylated pectin	0.114	0.621	0.573
28	1% PCL	0.096	0.581	0.672
29	3% PCL	0.094	0.638	0.736
30	7% PCL	0.092	0.654	0.798
31	10% PCL	0.090	0.752	0.869
32	1% PBAT	0.095	0.689	0.696
33	3% PBAT	0.094	0.743	0.752
34	5% PBAT	0.094	0.788	0.808
35	7% PBAT	0.094	0.826	0.829
36	10% PBAT	0.091	0.855	0.876

the response was similar to that obtained using glyoxal with 3% PVA (Table II, Entries 15–19). However, the steady state weight gain was lower, suggesting that some hydroxyl groups on starch were used up in crosslinking with the cellulose acetate molecules, due to which the moisture sorption would have been lower, though marginally.

The loss of radial and longitudinal dimensions was about 35–40% at 10% CA as compared to 50–55% in the case of control starch foams (Table II, Entries 12–14). The dimensional stability was maximum at a CA content of 10%. In the presence of glyoxal, maximum dimensional stability was obtained at 0.3% glyoxal (Table II, Entries 15–19). The loss in radial dimensions was improved to 25%.

The carboxylate groups in the pectin molecule tend to expand its structure as a result of their charge. Methylation of these carboxylic acid groups forms their methyl esters, which take up a similar space but are much more hydrophobic. Thus, esterified pectin would also impart hydrophobic character to the starch foams. The steady state weight gain decreased with an increase in the pectin content (Table II, Entries 20–22). Hence, glyoxal was used as a crosslinking agent between starch and pectin. Glyoxal helped improve the hydrophobic character, though not considerably, which is evident from Table II (Entries 23–27).

The steady state loss of radial and longitudinal dimensions when MP was used in the foam formula-

tions was similar to the response in the presence of CA and is shown in Table II (Entries 20–27).

The addition of PCL did have a slight advantage in decreasing the weight gain of these starch foams. The equilibrium weight gains were about 8.8–9.5% of the original weight of the sample, as compared to ~ 13% in the case of the control starch foams, as shown in Table II (Entries 28–31). Also, the addition of PCL helped increase the dimensional stability of the starch foams considerably. The loss of radial and longitudinal dimensions (Table II, Entries 28–31) decreased from 50% to about 25 and 13%, respectively, (at 10% PCL), with an increase in the PCL content.

The PCL migrated to the surface because of the lower surface tension in the melt,<sup>35,36</sup> thus forming a hydrophobic coating. This was evident from the scanning electron micrographs of the surface of the foams in Figures 3 and 4 as seen earlier. However, there was a limitation involved in the addition of PCL. The maximum ER and minimum density for the foams was obtained at a PCL content of 3%. Hence, a compromise has to be reached in adding PCL to the formulation.

Like PCL, the purpose of adding PBAT was to improve the hydrophobic character and water endurance of the starch foams. The results obtained by using PBAT were very similar to those obtained by using PCL.

As shown in Table II (Entries 32–36), the steady state weight gain was about 8.5–9.5% of the original weight of the foam samples on addition of PBAT, but dimensional stability increased significantly.

The loss of radial and longitudinal dimensions (Table II, Entries 32–36) decreased from 50% to about 12% with an increase in the PBAT content. This could imply that most of the PBAT in the foam samples manifested at the surface (Fig. 5) and not in the core. Thus, the core of these samples continued to absorb as much moisture as it used to.

The aliphatic-aromatic copolyester PBAT provided the best properties in terms of low densities, higher resilience, and better hydrophobic properties (low steady state weight gain and high dimensional stability).

## CONCLUSIONS

Hydroxypropylated high amylose cornstarch was extruded into foams using various functional aids, such as PCL, PBAT, PVA, CA, glyoxal, and methylated pectin. The different formulations were successfully optimized to give foams with the lowest densities. Some formulations with PVA and PBAT gave foams with densities lower than 25 kg/m<sup>3</sup>. The starch foams were subjected to a relative humidity of 95 ± 5% and a temperature of 38 ± 5°C to determine the change in weight and dimensions on moisture sorption. The

functional aids, such as PVA, CA, MP, and their combinations with glyoxal, did not significantly affect the weight gain on moisture sorption. However, the weight gain could be reduced from about 13% for control starch to a minimum of about 9% for formulations involving PCL and PBAT. Also, the shrinkage in radial and longitudinal dimensions could be reduced from about 50% for control starch to about 12–20% for certain formulations involving biodegradable polyesters, and to about 25–40% in formulations involving PVA, glyoxal, CA, pectin, and combinations thereof. There is a possibility that most of the polyester migrates to the surface of the foams, restricting the shrinkage of the starch foams, while the core continues to absorb as much moisture. Thus, the hydrophobic character of the starch-based foams in terms of its weight gain and dimensional stability on moisture sorption was improved considerably.

Current efforts focus on improving the compatibility between the starch and polyesters to improve the physicomachanical as well as the hydrophobic properties of the starch-based foams. This would be done using reactive extrusion as a tool to chemically modify the starch or the polyester. The chemically modified entities would act as compatibilizers between the starch and the polyester.

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