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## Processing and properties of extruded starch/polymer foams

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### Abstract

Blends of starch and various thermoplastic resins were extruded into foams using a twin-screw extruder. Resins included poly(vinyl alcohol), cellulose acetate (CA), and several biodegradable polyesters. Foams of corn starch with poly(lactic acid) (PLA), poly(hydroxyester ether) (PHEE), or poly(hydroxybutyrate-co-valerate) (PHBV) had significantly lower densities and greater radial expansion ratios than the control starch. Blends with other polyesters and CA had densities and expansion ratios between those of the control starch and the other polyesters. Most of the polymer occupied spherical to elongated domains 1–10  $\mu\text{m}$  long although PLA domains were much smaller. Surface polymer concentrations were larger than the bulk and correlated with foam expansion and resistance to fragmentation.

Foams were also extruded using blends of PLA or PHEE with high amylose starch (70% amylose), wheat starch, and potato starch. Addition of either resin significantly reduced the foam density and increased expansion. At constant relative humidity, compressive strength was a function of foam density only and not the type of resin or starch in the blend. Addition of the resins reduced the water sensitivity of the foams and increased the time needed for complete dissolution. Blends with PLA, PHEE, or PHBV produced foams with densities comparable to commercial starch-based loose-fill foams. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Starch; Blends; Foams

### 1. Introduction

Interest in environmentally friendly materials has stimulated development of extruded starch-based foams as replacements for expanded poly(styrene) in loose-fill packaging applications [1,2]. Extruded starch foams are generally water soluble, and their properties are sensitive to moisture content. Greatest expansions, and lowest densities, are generally achieved through the use of modified high amylose starches. Various synthetic polymers have been blended with unmodified starches, such as corn, wheat, and potato starches, to produce foams with lower densities and increased water resistance, but little systematic examination of the effects of polymer type or amount has been reported.

Extruded foams based on blends of starch with poly(vinyl alcohol) (PVOH) were patented by National Starch [3,4], as well as water-resistant foams from blends of starch with starch esters [5]. Neumann and Seib [6] reported extruded foams from blends of starch with polyglycols. Bastioli et al. [7] at Novamont in Italy reported foams based

on blends of starch with various polymers, including PVOH, poly(ethylene vinyl alcohol), polycaprolactone (PCL), poly(ethylene-co-acrylic acid), and cellulose acetate (CA). The starch/polymer ratios ranged from 9:1 to 3:1. Boehmer [8] reported foams based on graft copolymers of starch with methyl acrylate. Xu and Doane [9] prepared foams using blends of starch with hydroxy functional polyesters (PHEEs). Depending on formulation and processing conditions, the foams reported in the patents cited above had bulk densities in the range of approximately 3–100  $\text{kg}/\text{m}^3$ . Radial expansion data were not reported in these patents.

Bhatnagar and Hanna [10] extruded normal corn starch with either poly(styrene) or poly(methyl methacrylate) (PMMA) at a 70:30 ratio with other additives in a single screw extruder. Foam densities in the range of 29.5–132  $\text{kg}/\text{m}^3$  were obtained, with radial expansions of 8.8–40.1. Subsequently, these authors reported on foams made with poly(styrene) and corn, tapioca, wheat, rice, and potato starches [11]. Depending on starch type and blowing agent, radial expansions ranged from ~10 to ~30, with densities from less than 50 to more than 200  $\text{kg}/\text{m}^3$ . Corn starch gave greater expansions and lower densities than wheat or potato.

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Table 1  
Materials and suppliers

Material	Product name	Supplier
Corn starch	Pure food starch	A.E. Staley
Wheat starch	Midsol 50	Midwest Grain Products
Potato starch	Food grade	Avebe
High amylose starch	Hylon 7 (70% amylose)	National Starch
Poly(lactic acid), PLA	Research grade (241,000)	Cargill-Dow
Poly(hydroxyester ether), PHEE	Adipic acid–diglycidyl ether of Bisphenol A (58,000)	Dow Chemical Co.
Poly(hydroxybutyrate-co-valerate), PHBV	DP300 (5% HV) (445,000), DP600 (12% HV), experimental (18% HV)	Zeneca
Poly(butylene-succinate), PBSA	Bionolle 3001	Showa High Polymer
Poly(caprolactone), PCL	Tone 787 (80,000)	Union Carbide
Butanediol–terephthalate–adipate terpolymer, PBAT	Eastar 14766	Eastman Chemical
Cellulose acetate, CA	398-3 (30,000), 398-30 (50,000)	Eastman Chemical
Poly(vinyl alcohol), PVOH	Airvol 523S (100,000)	Air Products
Poly(ester amide), PEA	BAK 400	Bayer

Average molecular weights are given in parentheses where known.

Hanna and coworkers [12–14] reported that the addition of poly(lactic acid) (PLA) or a commercial starch-based material (Mater-Bi from Novamont) increased radial expansion and decreased water solubility, whereas a butane diol–adipate–terephthalate copolyester (PBAT) showed mixed expansion effects depending on PBAT content when blended with either normal corn starch or waxy corn starch [15]. Foam densities in these studies ranged from about 50 to about 90 kg/m<sup>3</sup>. Cha et al. [16] studied foams from blends of wheat starch, modified corn starch, poly(ethylene vinyl alcohol), and poly(styrene). Bulk densities on the order of 20 kg/m<sup>3</sup> were obtained, with radial expansion ratios of 25–30, depending on formulation and processing variables. The foams in these studies contained up to 30 wt% poly(styrene) which reduced their biodegradability. In addition, chemical blowing agents were used rather than water alone. Shogren [17] demonstrated that acetylated high amylose starch could be extruded into foams with increased water resistance and bulk densities of 40–60 kg/m<sup>3</sup>.

In this work, several biodegradable polymers were blended with starch to better understand how foam properties can be modified. Normal corn starch was primarily used in an effort to develop foams which do not require modified and/or high amylose starches, and water was used as the only blowing agent. Polymers which are reported to be biodegradable were added to avoid compromising the biodegradability of the foams.

## 2. Materials and methods

### 2.1. Materials

Materials used in this study are listed in Table 1. All starches had moisture contents of approximately 10% at ambient conditions and were used as received. Prior to extrusion, talc (MicroTalc IT Extra, Ernstrom Group,

Norway) was added as a nucleating agent at a level of 0.5% by weight to the starch. Deionized water was used to control moisture content during extrusion.

### 2.2. Extrusion

A 30 mm co-rotating twin-screw extruder (Werner Pfleiderer ZSK-30) was used for foam extrusion. The barrel had a length/diameter ratio of 32:1 and eight zones with independent temperature control. A single die (2 mm diameter) was used. Screw speed was fixed at 500 rpm for all formulations. The temperature profile during extrusion was 27/27/50/70/80/90/130/130 °C from the barrel section just after the feed throat to the die. Extrudates were cut at the die face with an attached motorized chopper operating at 600 rpm, yielding essentially cylindrical samples approximately 3 cm in length.

Materials were fed separately into the extruder feed throat either gravimetrically (starch/talc mixture) or volumetrically (resins). Feed rates for starch (ambient moisture content) were 7.6–9.6 kg/h, depending on resin content. Resin feed rates were 0.48, 0.96, or 1.92 kg/h, corresponding to resin contents of 5, 10, and 20 wt%, respectively. Deionized water was injected with a triple piston pump at 0.58 kg/h into the barrel section immediately after the feed throat. Nominal moisture contents ranged from 13.2 to 15.1% during extrusion (see discussion below). When formulations were changed, extrusion was continued until the torque and die pressure stabilized. Samples were collected for a one minute period.

### 2.3. Characterization and analysis

After extrusion, samples were stored in open plastic bags and conditioned in a constant environment room at 22 °C and 50% RH for at least one week before testing. Some samples were also conditioned in environmental chambers at either 10% or 85% RH.

Foam density was measured by weighing a sample of foam and computing its volume after measuring the diameter and length. At least 10 specimens were measured for each formulation. Radial expansion ratio was calculated as the square of the ratio of the measured foam radius  $R_f$  to the die radius  $R_d$ . Specific length  $L_s$  was calculated using the measured length and mass of each foam specimen used for density measurement. Bulk density, which is a function of the extrudate shape, was measured by recording the weight of foam required to fill a box of known volume.

Friability was determined using the apparatus described by Tataraka [2]. Foam specimens were placed in a cubic box ( $190 \times 197 \times 197 \text{ mm}^3$ ) with cubic wooden blocks (19 mm edge) and agitated for 10 min. Friability was determined as the percentage of foam lost by screening through 3 mesh and 5 mesh screens.

Compressive strength was measured on a Instron 4201 universal testing frame. Foam specimens were securely fastened lengthwise and compressed by a metal probe (6 mm diameter) with a hemispherical endcap at a crosshead rate of 30 mm/min for a distance of 3 mm. At that point the crosshead was stopped and the compressive strength determined by dividing the maximum load by the cross-sectional area of the probe [2].

Water absorption and solubility were measured by submerging five preweighed foam samples for 15 min at room temperature. The foam specimens were held under water by a sheet of Parafilm with a beaker placed on top. The foam specimens were strained from the water using a wire mesh and weighed. The samples were then dried for 2–3 days and reweighed. pH measurements were taken by dispersing foam samples (1%, w/v) in deionized water.

Foam samples for scanning electron microscopy were sectioned with a razor blade and then extracted with an appropriate solvent for the polymer (chloroform or chloroform/methanol 9:1 for PHEE) for 1 day at room temperature. Some extracted samples were subsequently resectioned. Samples were mounted on aluminum stubs with graphite filled tape, sputter coated with gold/palladium, and examined with a JEOL JSM 6400V scanning electron microscope.

X-ray diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered  $\text{Cu K}_\alpha$  radiation and a theta compensating slit. Data were acquired in  $0.05^\circ 2\theta$ , 8 s steps. Foam samples were mixed with liquid nitrogen, ground to a powder using an agate mortar and pestle and equilibrated at 23 °C and 50% humidity for 3 days.

X-ray photoelectron spectra were collected with a PHI model 5400 X-ray photoelectron spectrometer (Physical Electronics, Inc., Eden Prairie, MN) equipped with small area electron extraction optics, a spherical capacitor electrostatic energy analyzer and a dual channel plate position sensitive detector. Starch foam samples, both surface and cross-sections, were cut with a razor blade and mounted with double stick Cu tape onto the sample

holder. Samples were excited using characteristic Mg  $\text{K}_\alpha$  X-rays, 1253.6 eV (15 kV, 400 W). Spectra were collected from a  $1 \text{ mm}^2$  area of the surface at a  $45^\circ$  emission angle (relative to surface). Survey spectra were collected using a pass energy of 178.85 eV, 1 eV/step and multiplex spectra were collected using a pass energy of 35.75 eV, 0.1 eV/step. The binding energy scale was calibrated using  $\text{Au}4f_{7/2} = 84.0 \text{ eV}$ ; the scale was shifted by  $\sim 2 \text{ eV}$  to make  $\text{C} (\text{CH}_2) = 285.0 \text{ eV}$  to correct for charging effects.

Chemical state assignments were made based on tabulated energies [18]. Quantitative analyses were carried out by dividing elemental peak areas by the appropriate relative sensitivity factors as reported by the instrument manufacturer. Surface compositions (wt%) were determined from the areas ( $A$ ) of peaks at 289.3 eV (polyester  $\text{C}=\text{O}$ ) and 288.0 eV (starch  $\text{O}-\text{C}_1-\text{O}$ ) according to the equation

Polymer surface concentration

$$= A_{289.3}M_p/n_p / (A_{289.3}M_p/n_p + A_{288.0}M_s/n_s) \times 100 \quad (1)$$

where  $M_p$  and  $M_s$  are molecular weights of the repeating units of the polymer and starch, respectively, and  $n_p$  and  $n_s$  are the numbers of carbonyl groups and anomeric carbons (Eq. (1)) in the polymer and starch repeat units, respectively. Peaks were fit to mixed Gaussian (G)/Lorentzian (L) lineshapes (80–100% G) using PHI instrumental software.

### 3. Results and discussion

#### 3.1. Extrusion conditions

In general, all formulations processed with specific mechanical energy (SME) values between 1200 and 1600 kJ/kg. Addition of resin to the starch reduced SME by 100–200 kJ/kg in most cases. Starch/PHEE melts had the lowest SME (1170 kJ/kg with 20% resin). Melt temperatures increased with increasing SME, and were in the range of 150–155 °C. The fact that the measured melt temperatures exceeded the barrel set points reflects the high levels of SME imparted to the melts. Die pressures ranged from 5 to 6 MPa. In some cases, addition of resin slightly increased die pressure.

The water feed rate was not adjusted when resin was added. Therefore, moisture content based on total feed decreased from 15.1 to 13.2% as the resin content increased, due to reduction in the starch feed rate. However, since starch is considerably more hydrophilic than most of the polymers used, the moisture content in the starch phase of the melts probably increased as resin content increased. Assuming that all water remained in the starch phase, the nominal starch moisture content increased from 15.1 to 16.3% as resin content was increased to 20%. Torque (and SME) contributions from the starch phase would

Table 2  
Density, radial expansion ratios, and specific length for corn starch–resin foams

Resin	Foam density (kg/m <sup>3</sup> )	Radial expansion (R <sub>f</sub> /R <sub>d</sub> ) <sup>2</sup>	Specific length (cm/gm)
Starch control	61.4 (0.7)	21.0 (2.6)	24.7 (3.2)
PLA (5%)	47.0	22.6	30.0
PLA (10%)	30.9	29.1	35.4
PLA (20%)	18.8	43.7	38.8
PHEE (5%)	34.9	33.1	27.6
PHEE (10%)	28.2	38.8	29.1
PHEE (20%)	41.9	40.7	18.7
CA (low MW, 10%)	49.1	19.1	33.9
CA (high MW, 10%)	45.6	28.0	24.9
PBAT	69.4	10.6	43.3
PEA	59.6	15.1	35.4
PBSA	51.3	16.0	38.8
PCL	48.2	16.8	39.3
PVOH	35.7	21.0	42.5
PHB-5HV (5%)	36.8	33.4	25.9
PHB-5HV (10%)	33.2	38.1	25.2
PHB-5HV (20%)	25.5	62.4	20.0
PHB-12HV (5%)	36.6	35.8	24.3
PHB-12HV (10%)	29.6	35.3	30.5
PHB-12HV (20%)	31.3	47.9	21.2
PHB-18HV (5%)	36.8	33.3	26.0
PHB-18HV (10%)	31.2	38.2	26.7
PHB-18HV (20%)	31.6	41.9	24.0

consequently be reduced, as the starch would be more highly plasticized by water as the resin content increased. In this regard, it is significant to note that the highest SME was observed in the starch/PVOH blend (1740 kJ/kg), while the starch control SME was 1645 kJ/kg. PVOH is nearly as hygroscopic as starch, and the water would be expected to

Table 3  
Density, radial expansion ratio, and specific length data for foams from corn, wheat, potato, and high amylose starches with either 10% PLA or 10% PHEE

	Control (no resin)	PLA (10%)	PHEE (10%)
<i>Density (kg/m<sup>3</sup>)</i>			
Corn	61.4	30.9	28.2
Wheat	58.6	25.3	28.4
Potato	40.6	23.3	23.9
High amylose	35.5	25.2	23.2
<i>Radial expansion ratio (R<sub>f</sub>/R<sub>d</sub>)<sup>2</sup></i>			
Corn	21.0	29.1	38.8
Wheat	20.1	49.8	45.0
Potato	36.1	58.2	54.2
High amylose	27.7	39.6	41.3
<i>Specific length (cm/gm)</i>			
Corn	24.7	35.4	29.1
Wheat	27.0	25.3	24.9
Potato	21.7	23.5	24.6
High amylose	32.4	31.9	33.2

partition between the starch and PVOH to a greater extent than in the other blends.

### 3.2. Foam density

Densities of foams prepared with normal corn starch (NCS) are shown in Table 2. The density for the NCS control (61.4 kg/m<sup>3</sup>) is the average of four separate extrusion runs, and indicates the variation in data from run to run. The densities shown in Table 2 can be roughly divided into two groups, either greater or less than 35 kg/m<sup>3</sup>. Only one polymer, the PBAT terpolymer, increased foam density relative to the NCS control. Bulk densities (data not shown), which are dependent on sample geometry and reflect the space-filling properties of these shapes, were approximately one-half the magnitude of the foam densities for all formulations.

PLA, PHEE, and the poly(hydroxybutyrate-*co*-valerate)s (PHBVs) effectively reduced density relative to the NCS control, with densities of 33 kg/m<sup>3</sup> or less at starch/resin ratio of 9:1. In general, density decreased with increasing resin content. When PHEE or PHBV content was 20%, the expanded foams contracted somewhat after reaching a maximum radial expansion on exiting the die. Contraction was more pronounced with PHEE, and was least apparent with the PHB-5HV copolymer. This contraction resulted in increased densities and reduced expansions. The observed contraction was probably due to a cooling rate which was not rapid enough to prevent collapse. The impact of cooling rate is consistent with the low *T*<sub>g</sub>s of these polymers: approximately 0 °C for the PHBVs, and near room temperature for the PHEE under these conditions [19].

Foam densities for commercial starch foams are approximately 20 kg/m<sup>3</sup> [2]. The data of Table 2 show that addition of PLA, PHEE, or PHBV to normal corn starch yields foam densities comparable to commercial starch products. Copolymer composition had little effect on foam density for the starch/PHBV blends; any effect at 20% resin content was obscured by contraction after maximum expansion. Since no attempts were made to optimize processing or formulation variables, it is likely that foams with densities lower than those shown in Table 2 could be extruded with NCS.

PVOH, PCL, CA, and PBSA reduced foam density, but gave foams with densities greater than 35 kg/m<sup>3</sup>. CA reduced foam density slightly; CA with higher molecular weight was more effective. PEA had no significant effect on foam density, while the PBAT terpolymer increased the foam density relative to the control (69.4 kg/m<sup>3</sup>), in contrast to the behavior described by Fang and Hanna [15].

Density data for foams prepared using wheat (WS), potato (PS), or high amylose corn (HACS) starches are shown in Table 3. Foams were extruded with 10% of either PLA or PHEE. The addition of either resin significantly reduces the foam density, as with NCS. PS/PHEE and HACS/PHEE foam densities are slightly lower than

densities for WS/PHEE. WS and NCS produce foams of essentially equal density with no resin. It is interesting to note that despite large differences in density between the different starch foams, densities are similar when either PLA or PHEE is present. PLA and PHEE produce foams with densities comparable to commercial starch products when added to potato and high amylose starches. HACS foam extruded using a lower molecular weight PLA ( $M_w = 200,000$ ) had the same density as HACS/PLA foam shown in Table 3 (data not shown). NCS and WS foams have somewhat greater densities. No attempt was made to minimize foam density in this study, so it is possible that foams with densities lower than those in Table 3 could be produced with NCS or wheat starch.

The density and expansion data of Tables 2 and 3 reflect the combined influence of moisture content and partitioning, resin content, and pressure and temperature changes as resin content increases. It has been reported that starch foam density is inversely proportional to moisture content in twin-screw [20–22] and single screw extrusion [23] of starch foams. The large changes in density and expansion shown in Tables 2 and 3 suggest that the presence of the resin phase is the dominant factor in determining foam properties, rather than the relatively minor changes in moisture content, temperature, or pressure. No attempt was made to optimize process conditions to minimize foam density in this work.

### 3.3. Radial expansion and specific length

Radial expansion of extruded starch foams can be described by the ratio of the cross-sectional area of the foam to the die cross-section ( $R_f/R_d$ ), where  $R_f$  is the radius of the foam and  $R_d$  is the radius of the die. It has been suggested that radial expansion of extruded starch is dependent on the melt elasticity [20,23]. Radial expansion ratios for the NCS blends are given in Table 2. The value for the control starch is the average of four separate extrusion runs. The relative error is greater than that of the density since the measured foam/die diameter ratios are squared.

The foams can be separated into two categories: those with radial expansion ratios greater than the control (21.0), and those with reduced radial expansion. For the former case, radial expansion increased with increasing resin content (PLA, PHEE, and PHBV). The lowest density foam with a radial expansion ratio less than the control was 48.2 kg/m<sup>3</sup> (10% PCL); its density is only 21% lower than the control starch. PBAT had a radial expansion only half that of the starch control. Despite their increased density due to partial collapse, foams with 20% PHEE or PHBV had radial expansion values twice as great as the control starch.

Addition of either PLA or PHEE significantly increases the radial expansion for wheat, potato, and high amylose starches, as seen in Table 3. Radial expansion values are increased by more than 100% for the wheat and potato starches when either PLA or PHEE are present.

Another expansion parameter is the specific length  $L_s$ ,

which is a measure of expansion in the flow direction. Specific length of expanded starch products is thought to be dependent on the viscous nature of the melt [20,23]. In general, addition of resin to normal corn starch increased the specific length of the resulting foam (Table 2). The only NCS foams with specific lengths less than the control starch were blends with 20% PHEE or PHBV. As noted above, these foams experienced collapse after maximum expansion. All NCS foams with radial expansion ratios less than the control starch had specific lengths greater than the control.

Specific length data for wheat, potato, and high amylose starches are given in Table 3. The addition of either polymer has little effect on specific length for any of these starches. PLA and PHEE decrease starch foam density primarily by increasing radial expansion, suggesting that these polymers significantly alter melt elasticity. Higher melt elasticity is generally associated with improved foaming properties.

It is known that polymers which exhibit strain hardening during extension have improved foaming properties [24], consistent with the extensional deformation experienced by the melt during bubble growth in the foaming stage. In this regard, it has been reported that the addition of as little as 10 wt% of one polymer into another can significantly alter strain hardening in poly(ethylene) blends [25]. It has recently been shown that PLA similar to the one used in this work shows strong strain hardening at high test rates [26]. Strain hardening is often associated with branching, which is known to exist in PHEE. The fact that PLA and PHEE gave the lowest density foams suggests that their presence may significantly alter the rheological properties of the melt during bubble growth. While no data available for the PHBVs used in this work, it is not unreasonable to expect that the high molecular weight indicated in Table 1 may be sufficient to induce strain hardening in these polymers.

### 3.4. Foam structure

Scanning electron micrographs of the foam surfaces and cross-sections are shown in Fig. 1. The surfaces of starch foams containing no added polymer generally have many small holes, suggesting that the starch outer wall burst during extrusion foaming. This reflects the low melt strength and elasticity of starch melts and is consistent with previous studies indicating that starch foams have open cells [2,3]. Cell sizes were about 0.3–1 mm in diameter. Surfaces of starch foams containing some polymers, particularly higher levels of PHEE and to a lesser extent, PHBV and PLA, had fewer or no holes. This suggests that these foams have greater melt strength and resistance to bubble rupture. The average cell size is much larger for foams containing PHEE, PHBV and PLA (up to 2 mm), reflecting the higher volume expansion of these foams than the control (no polymer). In contrast, foams containing

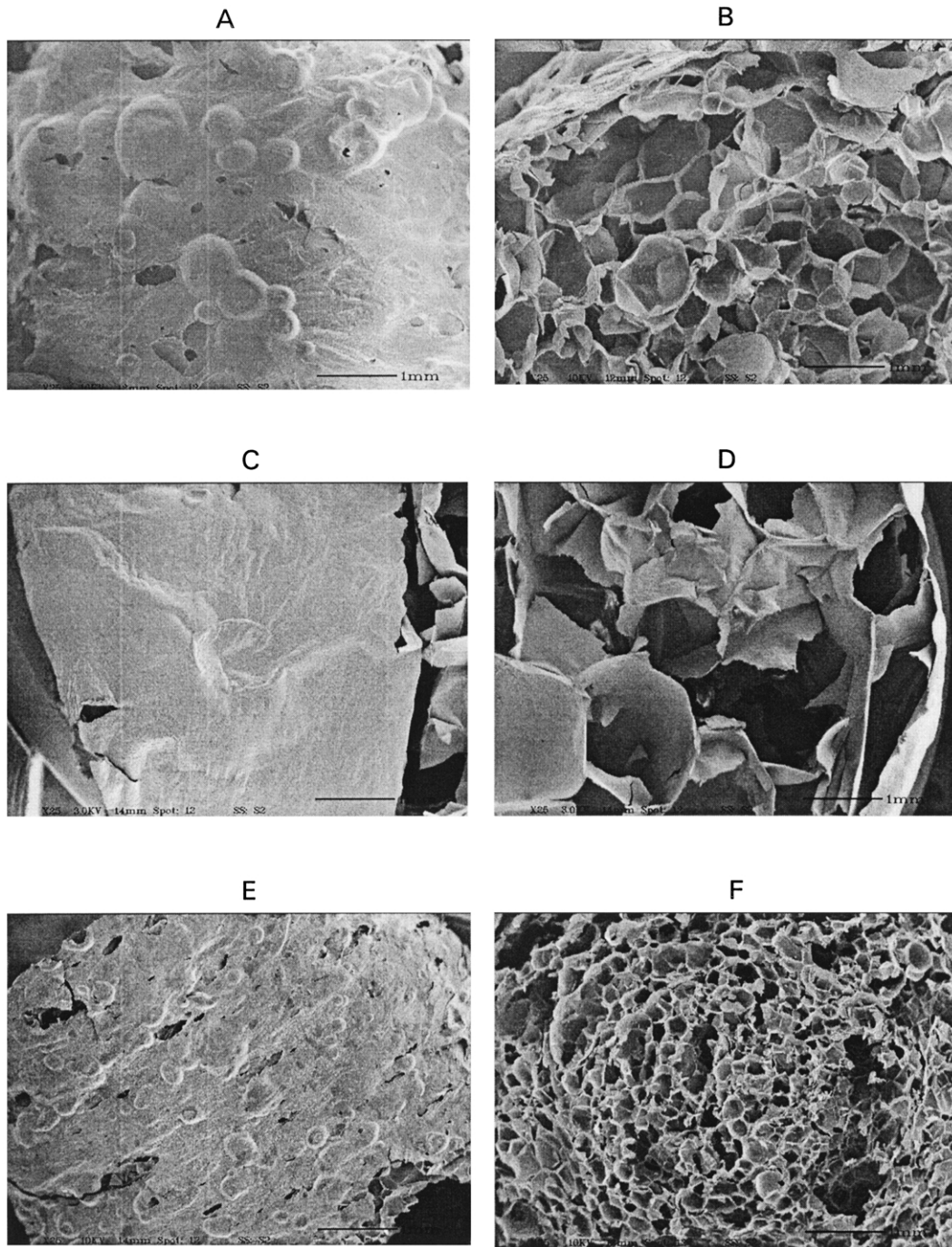


Fig. 1. Scanning electron micrographs of surfaces (s) and cross-sections (x) of starch/polymer foams: no polymer surface (A), cross-section (B); 10% PHEE surface (C); cross-section (D); 10% PBAT surface (E), cross-section (F). Magnifications were  $25\times$ .

PBSA and PBAT resins had small cell sizes (0.1–0.4 mm) and a lower volume expansion than the control.

Fig. 2 shows scanning electron micrographs of foams after sectioning, extraction of the polymer component and then resectioning or fracturing. The latter step was necessary since the starch seemed to ‘heal’ over the cut areas after drying of the solvent, giving rounded, blurred images. A micrograph of an internal starch/20% PHEE foam strut in Fig. 2A and B shows that the PHEE occupies

spherical to slightly elongated domains 1–2  $\mu\text{m}$  in size. The starch/20% PHBV-12 foam in Fig. 2C and D has a similar morphology but with slightly larger domain sizes (1–10  $\mu\text{m}$ ). Foams containing 20% PLA (Fig. 2E and F) have very small PLA domain sizes, in the order of 0.1  $\mu\text{m}$ , suggesting better compatibility of starch with PLA than the other polymers examined.

X-ray powder diffraction patterns for ground corn starch/polymer foams are shown in Fig. 3. Starch foams

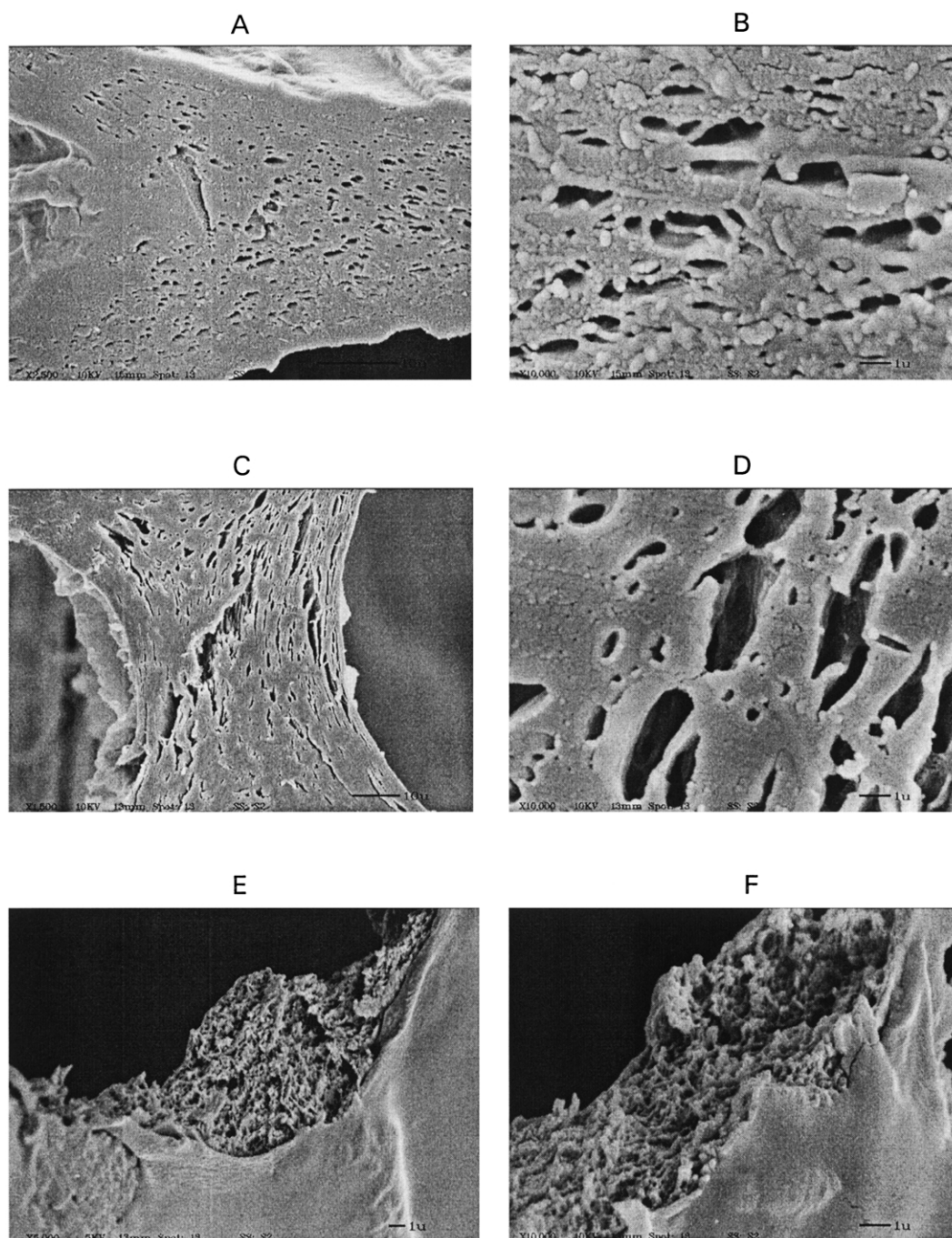


Fig. 2. Scanning electron micrographs of starch/polymer foams after solvent extraction and sectioning: starch/20% PHEE (A,B); starch/20% PHBV-12 (C,D); starch/20% PLA (E,F). Magnifications were: (A) 2500  $\times$ ; (B) 10,000  $\times$ ; (C) 1500  $\times$ ; (D) 10,000  $\times$ ; (E) 5000  $\times$ ; (F) 10,000  $\times$ .

containing no polymer have reflections at approximately 12, 13 and 17.5°  $2\theta$ . This pattern, observed previously for starch extruded at low (<19%) moisture, was termed 'E' type starch and was thought to result from helical inclusion complexes of amylose with native starch lipids [27]. The pattern is similar to the  $V_6$  hydrate pattern normally seen for amylose/fatty acid complexes [28] except that the peaks are shifted to lower angle suggesting larger interhelical spacings. Complexes of amylose with bulky molecules such as *tert*-butanol which form  $7_1$  helices have such larger

spacings and have reflections similar to those observed here [29]. It is unknown why such structures form preferentially during extrusion at low moisture contents.

Foams containing added polymer also show the diffraction peaks due to amylose/lipid complexes. Additional peaks were observed for foams containing PCL, PBAT, PEA and PBSA. These reflections occur at similar scattering angles to the most intense X-ray diffraction peaks of neat polymer films which were prepared by casting from chloroform or blowing: 21.6–22.3, 23.9° for PCL; 19.9,

Table 4  
Surface compositions of normal corn starch/polymer foams

Polymer	Polymer concentration (wt%)	Surface C/O ratio (number/number) <sup>a</sup>	Surface polymer concentration (wt%) <sup>b</sup>	Surface energy (dyn/cm)
None	0	1.41	0	53.7 <sup>c</sup> ; 43.0 <sup>d</sup>
PLA	10	1.40	28	43.9 <sup>c</sup> ; 43.5 <sup>d</sup>
PHEE	5	2.20	48	–
PHEE	10	2.49	70	34.7 <sup>d</sup>
PHEE	20	3.19	97	–
PHEE (powder)	100	3.38	100	–
PBSA	10	1.66	26	–
PCL	10	1.67	33	39.6 <sup>c</sup> ; 45.5 <sup>d</sup>
PBAT	10	1.45	22	44.2 <sup>d</sup>
PHBV-5	10	1.62	40	41.5 <sup>c</sup> ; 42.2 <sup>d</sup>
PHBV-18	10	1.67	45	41.5 <sup>c</sup> ; 42.2 <sup>d</sup>

<sup>a</sup> Data are average of two measurements: one outside, one inside (cut) foam; average standard deviation:  $\pm 0.14$ .

<sup>b</sup> Data are average of two measurements: one outside, one inside (cut) foam; average standard deviation:  $\pm 2.3$  wt%.

<sup>c</sup> From Ref. [34].

<sup>d</sup> From Ref. [35].

22.3–24.2° for PBAT; 20.3, 23.1° for PEA; and 19.7, 21.7–22.7° for PBSA. This indicates that the above polymers have phase separated from starch and partially crystallized. This is consistent with previous studies by microscopy and DSC which showed that starch is incompatible with polyesters [19,30,31]. Polymer crystallization was not observed for

PLA, PHEE, PVOH or 10% PHBV. These polymers have low crystallinity or are slow to crystallize at room temperature. Peaks at 9.2 and 28.2° in the starch/PBAT sample are due to talc and reflect the relatively large amount of talc which was present in the sample of PBAT provided by the supplier. (Starch/PBAT peanuts contained 4.9% talc as measured by weight remaining after ashing at 550 °C.)

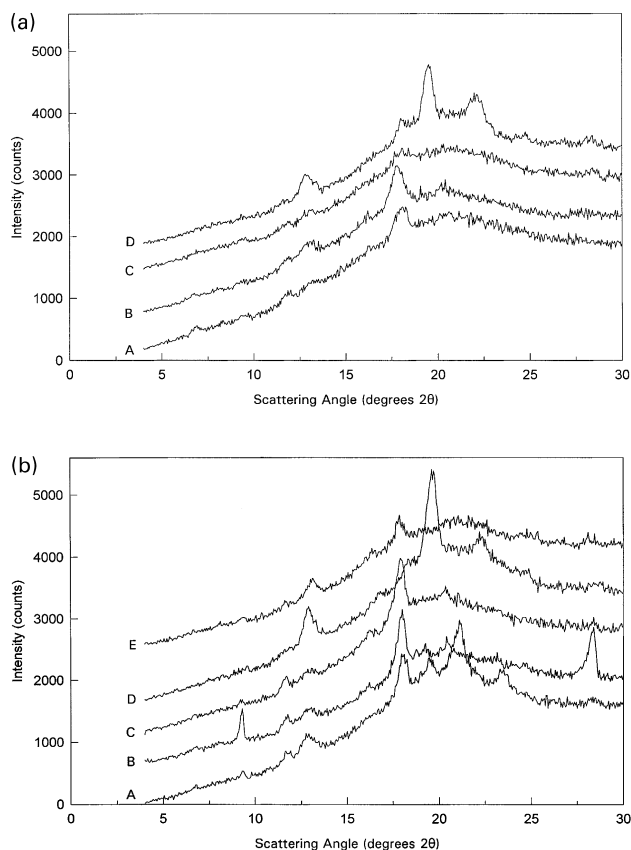


Fig. 3. (a) X-ray diffraction of starch/polymer foams: no polymer (A), 10% PLA (B), 10% PHEE (C), 10% PBSA (D). (b) X-ray diffraction of starch/polymer foams: 10% PCL (A), 10% PBAT (B), 10% PVOH (C), 10% PEA (D), 10% PHBV-12 (E).

### 3.5. X-ray photoelectron spectroscopy

From the areas under the peaks, one can calculate the relative numbers of carbon and oxygen (or other electron dense atoms) on the foam surface (Table 4). Due to the strong interaction of the emitted electrons with the matter, XPS detects only electrons released from the approximately 50 Å nearest the surface and hence the composition measured reflects only the top several molecular layers. From the data in Table 4, it can be seen that there is more carbon on the foam surface than expected from starch molecular composition (6 carbons/5 oxygens). This is due to absorption of adventitious hydrocarbons from the air onto the starch and has been observed previously [32]. Therefore, one cannot calculate the starch/polymer surface composition from just the C/O ratio.

However, the electron binding energies of carbon are influenced by the chemical nature of adjacent atoms and peaks can be assigned to different carbon atoms as shown in Fig. 4. Aliphatic carbons, carbons with one oxygen attached, carbons with two oxygens attached and carbonyl carbons were assigned to peaks at 285, 287, 288.1 and 289.3 eV, respectively [33]. Thus, the starch/polymer compositions can be estimated from the ratio of area of the starch anomeric carbon peak (O–C1–O, 288.1 eV) to the polyester carbonyl carbon peak (C=O, 289.3 eV).

Surface compositions of the starch/polymer foams calculated as described above are also shown in Table 4. In all cases, the surface concentration of polymer is higher than that of the bulk concentration, suggesting that the



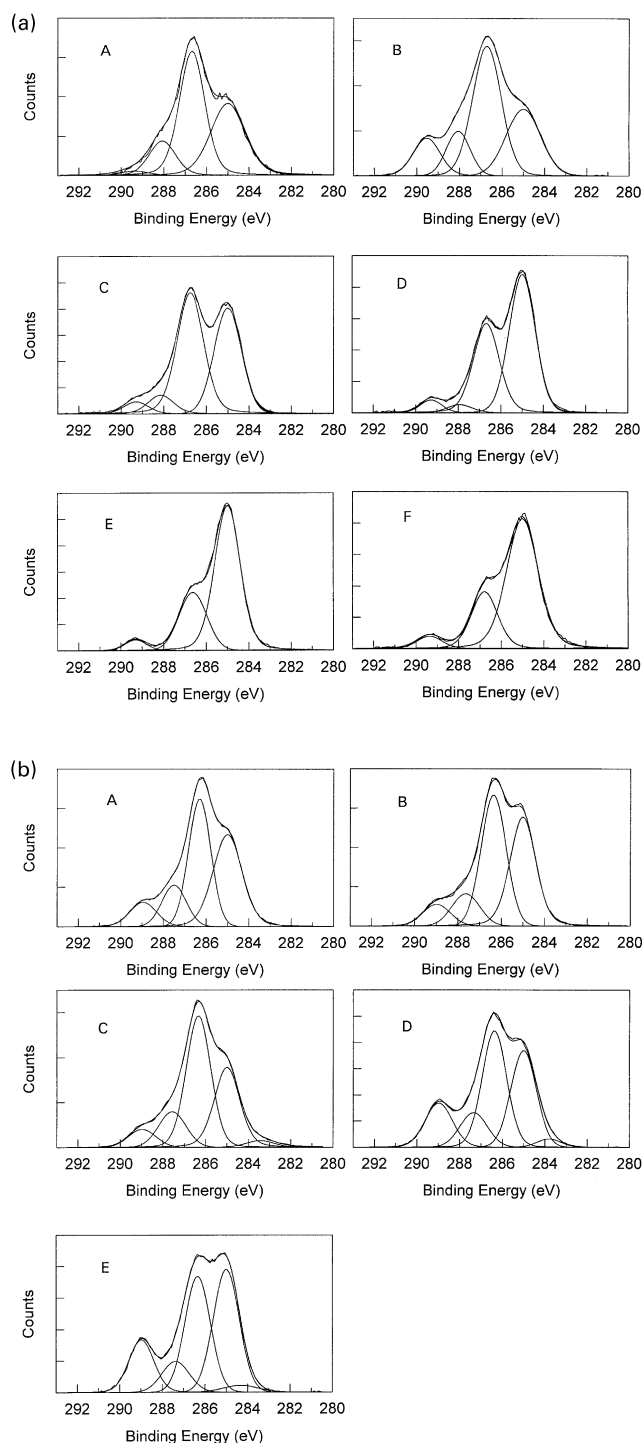


Fig. 4. (a) X-ray photoelectron spectra of carbon region of starch/polymer foams: no polymer (A), 10% PLA (B), 5% PHEE (C), 10% PHEE (D), 20% PHEE (E), neat PHEE powder (F). (b) X-ray photoelectron spectra of carbon region of starch/polymer foams: 10% PBSA (A), 10% PCL (B), 10% PBAT (C), 10% PHBV-5 (D), 10% PHBV-18 (E).

polymers have a lower surface energy than starch [34] and thus overall energy is minimized by a migration of the polymer to the foam surface. Reported surface energies for starch range from 39 to 43 dyn/cm [34,35]. Surface concentrations of PHEE are the highest followed by

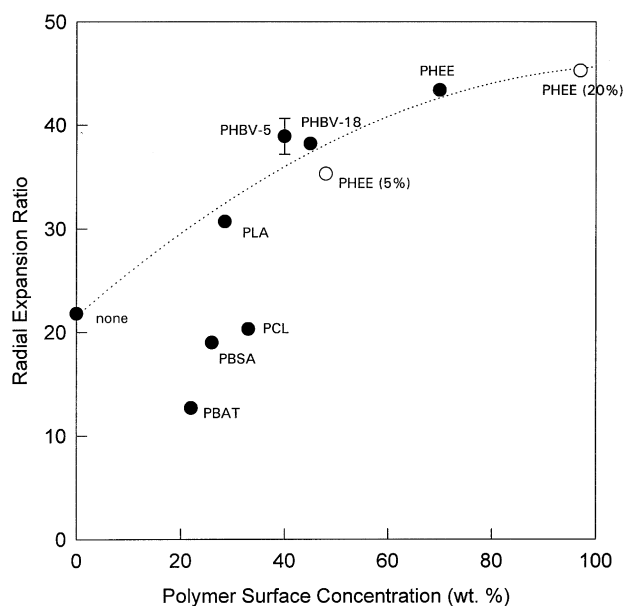


Fig. 5. Correlation of foam radial expansion ratio (foam diameter/die diameter)<sup>2</sup> with polymer surface concentration. Foams contain 10% of the indicated polymers unless noted otherwise.

PHBV, PCL, PLA, Bionolle and Eastar, consistent with fact that PHEE has the lowest reported surface energy of the polymers in Table 4 [35]. Rates of surface migration would tend to increase as molecular weight decreases [36]. PHEE molecular average molecular weights are  $M_n = 9500$  and  $M_w = 65,000$  [37]. PHBV [38] and PLA [39] are both known to degrade in the presence of high temperature/moisture conditions. Indeed, pH values of starch/PLA foams in particular decreased as PLA level increased, probably due to hydrolysis of ester linkages to form carboxylic acids (see below). The thickness of the surface layer of polymer is unknown but is likely to be quite thin since most of the polymer appears to be localized as inclusions inside the starch as seen in scanning micrographs (Fig. 2).

Plots of radial expansion ratio versus polymer surface composition are shown in Fig. 5. The data show that foam expansion increases with increasing polymer surface concentration though two different lines are seen for two polymer groups. Data for PLA, PHEE and PHBV fall along a line with an overall higher expansion while PBAT, PBSA and PCL fall along a lower line. The reasons for this difference are not clear although the former polymers are amorphous or slowly crystallizing while the latter crystallize rapidly. PBAT, PBSA and PCL are also relatively high molecular weight, low  $T_g$  ( $-33$ ,  $-45$ ,  $-60$  °C, respectively) blown film grade polymers which would tend to have high melt viscosities and elasticities.  $T_g$  values for PLA, PHEE and PHBV are higher (60, 37,  $\sim 0$  °C, respectively). The foaming process is complex in that temperatures and water contents are changing rapidly upon exiting the die, molecular weights are changing and rheological properties of the polymers are not well characterized so it is difficult to come to a definitive conclusion. While it seems likely that

Table 5  
Friability data for corn starch foams

Resin	Friability 10% RH	50% RH
Starch control	100 (0)	7 (3.9)
PLA (5%)	–	34 (14)
PLA (10%)	98 (0.4)	22 (4.3)
PLA (20%)	–	12 (1.3)
PHEE (5%)	–	0.7 (0.7)
PHEE (10%)	56 (7.9)	0.2 (0.3)
PHEE (20%)	–	0.7 (0.0)
CA (low MW, 10%)	51 (15.9)	1 (0.0)
CA (high MW, 10%)	49 (8.2)	1 (0.3)
PBAT	95 (2.0)	14 (3.2)
PEA	100 (0)	66 (10.8)
PBSA	96 (1.2)	11 (1.7)
PCL	79 (7.9)	3 (1.0)
PVOH	100 (0)	29 (1.7)
PHB-5HV (5%)	–	5 (0.5)
PHB-5HV (10%)	91 (1.0)	3 (0.5)
PHB-5HV (20%)	–	53 (3.4)
PHB-12HV (5%)	–	2 (0.6)
PHB-12HV (10%)	76 (5.8)	1 (0.3)
PHB-12HV (20%)	–	0 (0.0)
PHB-18HV (5%)	–	1 (0.3)
PHB-18HV (10%)	67 (13.3)	0 (0.0)
PHB-18HV (20%)	–	0 (0.0)

Standard deviations are in parentheses.

polymer on the foam surface would decrease foam surface tension and increase expansion, the data of Table 4 indicate that factors other than surface tension are operative, since PLA and PHEE give comparable densities despite the difference in surface energies. Polymer on the surface would also tend to resist tears and hole formation during blowing since the polymer should be more elastic than the highly branched starch molecules. Surface polymer might also decrease the permeability of the cell walls to water vapor

Table 6  
Friability data for corn, wheat, potato, and high amylose starch foams at 10, 50, and 85% RH

	10% RH	50% RH	85% RH
Corn control			
10% PLA	98 (0.4)	22 (4.3)	–
10% PHEE	56 (7.9)	0.2 (0.3)	–
Wheat control	100 (0.2)	37 (5.7)	2.4 (0.0)
10% PLA	96 (0.8)	7 (0.9)	0.7 (0.7)
10% PHEE	97 (1.0)	1 (0.4)	2.6 (4.6)
Potato control	100 (0.0)	74 (0.9)	1.3 (0.6)
10% PLA	32 (8.0)	0.6 (0.0)	0.4 (0.3)
10% PHEE	73 (0.7)	1 (0.4)	0 (0.0)
High amylose control	40 (2.9)	0.4 (0.4)	2 (0.2)
10% PLA	33 (2.1)	0.2 (0.3)	0.2 (0.3)
10% PHEE	23 (0.7)	1.3 (0.0)	0 (0)

Standard deviations are in parentheses.

and thereby increase pressure inside the cells during expansion. Measurement of moisture contents of foams just after extrusion showed that foams containing 10% PLA/PHEE mixtures had slightly higher moisture contents (8–9.5%) versus 7–8% without added polymer. Previous work has suggested that additives which migrate to the surface of polyethylene foams can decrease blowing agent permeability and contribute to foam dimensional stability [40]. The morphology or arrangement of polymer on the surface of the starch foam is unknown but could also be an important factor.

Studies of other polymer foam systems have shown that initial bubble growth is accelerated by a low melt viscosity while stabilization of the bubbles is enhanced by strain hardening (an increasing elongational viscosity with strain) [41]. Strain hardening is normally associated with long chain branching and enhanced entanglements in polyolefins though for some other polymers, such as polystyrene, it is attributed to intermolecular non-bonded ( $\pi$ – $\pi$ ) interactions. PHEE is branched and also has aromatic rings and hydroxyl groups which could associate during elongation, perhaps leading to strain hardening. It is unknown whether the PLA or PHBV were branched though the relatively high  $T_g$  for PLA would tend to give a high viscosity as the extruded foam cooled to near that temperature. Recent work has shown that PLA similar to that used in these experiments did indeed exhibit strain hardening at high test rates [26]. PBAT, PBSA and PCL are probably linear polyesters and, with low  $T_g$  values, might not show significant strain hardening effects or have melt viscosities which are high enough that initial bubble growth is slow.

### 3.6. Friability

Friability is a measure of the fragmentation of foam during handling. It is an important parameter for foams intended for use in loose-fill packaging. Friability was measured by tumbling foam samples in a box with small wooden blocks. Foams were conditioned at 10, 50, or 85% relative humidity before tumbling. Friability data are presented in Tables 5 and 6.

Friability is high for all formulations and starches at 10% RH. Of the control starch foams, only the high amylose starch has friability of less than 95%. Under these conditions, the starch matrix is well below its glass transition temperature and is brittle. As the relative humidity increases to 50%, the equilibrium moisture content of the starch rises, and the foams are consequently less brittle. The friability decreases significantly, but only the high amylose starch foam displays negligible friability (0.4%).

The addition of resin generally reduces friability at 50% RH. Corn starch foams with the greatest density also exhibited greater friability, as seen in Table 5, while corn starch foams with low densities had insignificant levels of friability.

Plots of foam friability (% fines after tumbling with

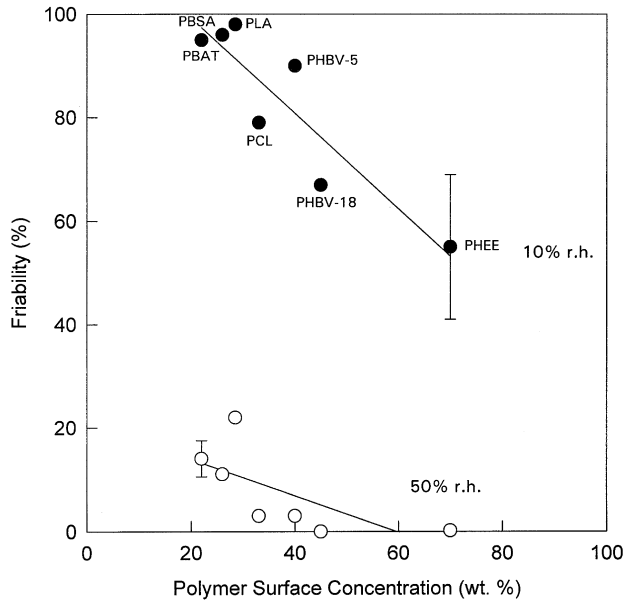


Fig. 6. Correlation of foam friability with polymer surface concentration. Foams contain 10% of the indicated polymers. RH refers to relative humidity.

wooden blocks) versus polymer surface concentration are shown in Fig. 6. Friability decreases as polymer surface concentration increases, although the level of scatter is high. The presence of a ductile polymer on the foam surface may retard the formation of cracks and fragments under impact by the wooden blocks. One cannot, however, rule out indirect effects of the polymer on foam structure, i.e. lower

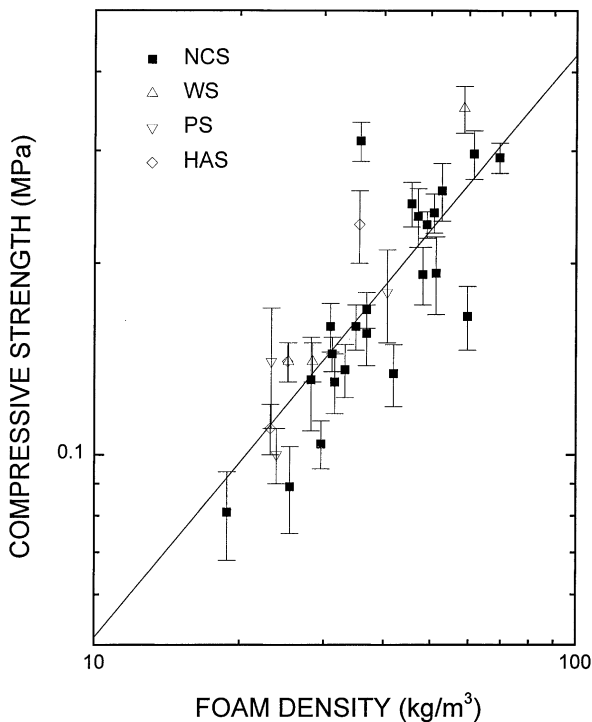


Fig. 7. Double logarithmic plot of compressive strength and foam density at 50% relative humidity. Least squares fit is drawn; slope = 0.92(±0.12).

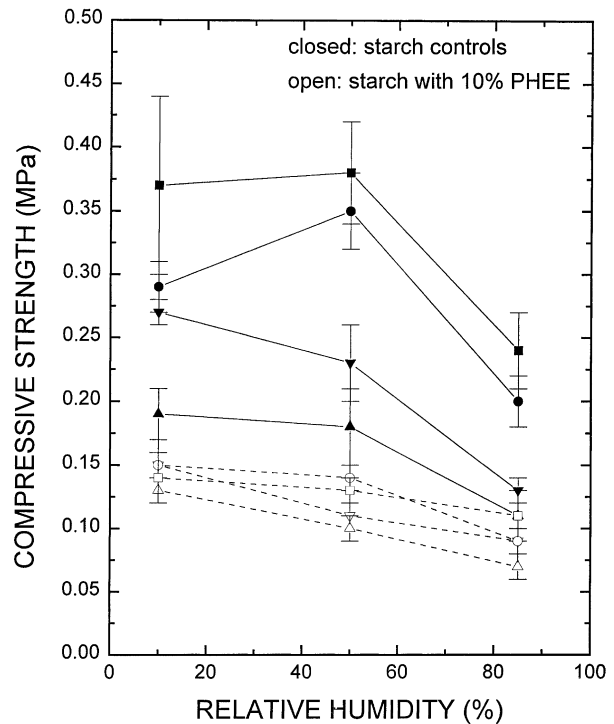


Fig. 8. Effect of relative humidity on compressive strength of starch foams with 10% PHEE. (normal corn starch ■; wheat starch ●; potato starch ▼; high amylose corn starch ▲).

foam density and thinner cell walls as contributing to the greater flexibility of the foam structure.

### 3.7. Compressive strength

Compressive strength is a measure of a foam's ability to deform under load. 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.

Compressive strength data for starch/polymer foams conditioned at 50% RH before testing are shown in Fig. 7. A strong correlation exists between foam density and compressive strength, regardless of the type of resin blended with the corn starch. Similar correlations are observed when the foams are conditioned at lower or higher humidities, although the magnitude of the compressive strength is a function of RH. At higher humidities, there is more scatter in the density–strength plot, and the values of compressive strength are generally lower compared to higher humidities. The regression line in Fig. 7 is drawn using all the data displayed, and has a slope of 0.92 (±0.12). This value is somewhat less than the value of 1.5 predicted for open-cell foams. Smith and coworkers [20,21] report exponents of approximately 1.5–1.6 for compressive strengths of extruded foams prepared using maize grits.

The effect of relative humidity during conditioning is shown in Fig. 8. The addition of 10% PHEE significantly

Table 7  
Water absorption and solubility data for selected corn starch–resin foams

Material	Water absorbed (%)	Weight loss (%)	pH
Starch control	415 (89)	33 (10)	5.5
PLA (5%)	300 (113)	37 (16)	4.5
PLA (10%)	320 (127)	25 (15)	4.1
PLA (20%)	220 (28)	6.0 (0.1)	3.7
PHEE (5%)	265 (49)	28 (7)	5.1
PHEE (10%)	230 (14)	15 (1)	4.7
PHEE (20%)	155 (21)	6.0 (0.2)	4.4
PHB-HV12 (10%)	330 (0)	16 (0)	5.5
CA (low MW)	420 (0)	16 (0)	5.6
PBAT	555 (64)	16 (2)	4.8
PEA	895 (7)	6.0 (0)	5.1
PBSA	770 (113)	11 (2)	4.2
PCL	420 (42)	8.0 (0.3)	4.3
PVOH	460 (0)	51 (0.4)	5.6

1% (w/v) foam dispersed in deionized water. Standard deviations are in parentheses.

reduces the foam density and hence the compressive strength. Increasing relative humidity from 20 to 50% has little effect on compressive strength. As RH increases to 85%, compressive strength is reduced by approximately 20–25% for all foams regardless of density. This reduction is due to the plasticizing effect of sorbed water on the starch matrix. Although water is also a plasticizer for PHEE [19,42], the compressive strength is dominated by the starch matrix in these blends.

### 3.8. Water absorption and solubility

One of the advantages of using extruded starch foams for loose-fill packaging applications is their water solubility. In certain applications, some degree of water resistance may be desirable. Therefore, the absorption and solubility characteristics were determined.

Table 7 gives water absorption and solubility data for most of the corn starch formulations. All foams tested absorbed significant amounts of water; the starch control absorbed 415% of its original weight. The PHEE significantly reduced water absorption, with the effect increasing as the PHEE increased. PLA also reduced water absorption, although the reduction was not as great as with PHEE. Note that the resins which gave the densest foams—PBAT, PEA, PBSA, PCL, and CA—had water absorption values equal to or greater than the control starch. On the other hand, resins which gave the lowest density foams tended to absorb less water than the starch control. In general, the water absorption decreased as the polymer surface concentration increased.

Weight loss of the control starch was 33%. All resins at 10% except PLA and PVOH significantly reduced the weight loss. Weight loss was greater for the starch/PVOH foam, consistent with the water solubility of PVOH. Foams

with the lowest weight loss had the greatest water absorption. Weight loss also decreased with increasing polymer surface concentration.

Also shown in Table 7 are pH data for solutions in which 1% foam was dispersed. In all cases, the resin reduced the pH below the level of 5.5 measured for the control starch. The pH was lowest with 20% PLA. The reduced pH values relative to the starch control suggest some degradation of the resins occurred during extrusion, as carboxylic acid endgroups would be generated by depolymerization of polyesters.

## 4. Conclusions

Various starches were blended with biodegradable polymers and extruded into foams. The addition of PLA, PHEE, and PHBV significantly increased radial expansion and gave low density foams. Other polymers studied either decreased foam density to a lesser extent or, in one case, increased density. Friability at 50% RH was reduced when polymer was present in the foams. Compressive strength depended primarily on foam density, and not on starch type or polymer structure. Several formulations gave foams with densities comparable to commercially available starch-based materials. Foams made from extrusion of starch and polyesters have a phase separated morphology in which most of the polymer occupies spherical to elongated inclusions inside the starch phase and some migrates to the surface. Surface migration is probably enhanced by low molecular weight and/or low melt viscosity polymers. Foam expansion and resistance to fragmentation increases with increasing polymer surface concentration. Polymers which are amorphous or slowly crystallizing and have moderate glass transition temperatures tend to give more highly expanded, less friable starch foams.

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