Extruded foams prepared from high amylose starch with sodium stearate to form amylose inclusion complexes*

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ABSTRACT: Extruded starch foams were prepared from high amylose corn starch with and without sodium stearate and poly(vinyl alcohol) (PVOH) to determine how the formation of amylose–sodium stearate inclusion complexes and PVOH addition would affect foam properties. X-ray diffraction and Differential Scanning Calorimetry (DSC) showed that amylose–sodium stearate inclusion complexes were formed by low temperature extrusion and did not dissociate during foam formation by a second extrusion at higher temperatures. In the absence of PVOH, water absorption, and foam shrinkage at 95% RH were decreased because of the hydrophobicity of the complex. PVOH addition increased both the expansion ratio and the shrinkage of the foam, although shrinkage at 95% RH was still less than that observed with uncomplexed amylose. The structural integrity and some tensile properties of stearate-containing foams were improved by PVOH addition. These results provide the manufacturer of biodegradable starch foams with an inexpensive method for tailoring foam properties for specific end-use applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43251.

INTRODUCTION

Starch is a biodegradable polysaccharide composed of repeating glucose units, and is isolated from the seeds and tubers of plants as micrometer-size granules that contain both linear and branched components (amylose and amylopectin, respectively). Corn starch is the most commonly used starch of commerce, and corn starch varieties are commercially available with amylose contents varying from approximately 0–70%. Interest in using environmentally friendly natural products such as starch to replace nonbiodegradable synthetic polymers has resulted in increased interest in using starch as a replacement for polymers such as polystyrene in foamed packaging materials.[1]

Earlier research on starch-based foams has been reviewed by Glenn *et al.*,[2] and more recently by Mitrus.[3] Starch-based foams are commonly produced by the extrusion of aqueous starch dispersions. Water acts as the blowing agent in the foaming process and is released as steam when the extruded starch exits the die. This instant reduction of pressure allows the starch to expand, thus forming the foam structure. Cha and coworkers examined the effects of extrusion temperature and water content on the properties of starch-based foams.[4] Willett and Shogren prepared foams by blending corn starch, wheat starch, potato starch, and high amylose corn starch with poly(vinyl alcohol) (PVOH), cellulose acetate and several biodegradable polyesters and then extruding the mixtures using a twin-screw extruder.[5] Zhang and Sun prepared biodegradable foams from corn starch and poly(lactic acid) (PLA) using water as a blowing agent, and talc as a nucleating agent.[6] Foam cell size and distribution were affected by the extrusion temperature, die diameters, screw speed, water concentration, PLA/starch ratio, and concentration of nucleating agent. The presence of PLA

improved the water resistance of the foam and the foam recovery capacity, especially under high moisture conditions.[6] Lee and coworkers identified the effects of 10 different ingredients on the properties of extruded foams prepared from rice starch.[7] The ingredients having significant effects on foam properties were high levels of talc, citric acid, water, and fiber. Sjöqvist et al. prepared starch foams from potato starch using a two-step extrusion process and found that moisture content was the driving force for expansion during the second extrusion.[8] Two different plasticizers, urea and glycerol, were compared with regard to foaming ability in the presence of wheat gluten, which acted as a processing aid. The same authors prepared starch foams from four types of potato starch with an intermediate conditioning step at 53% relative humidity to control the moisture content.[9] Density and absorption capability were influenced by the porosity level, and foams prepared from potato amylopectin had the highest porosity, the lowest density, and the greatest water absorption. Yang and coworkers found that the density, cell structure, and rate of water penetration of extruded starch foams was affected by the feed rates of water, talc, and polyhydroxy ether, which was effective in minimizing the absorption of water.[10]

In the presence of fatty acids and their water soluble sodium salts, amylose adopts a helical conformation, in which the hydrophobic carbon chain of the fatty acid is complexed within the hydrophobic central cavity formed by the amylose helix. The properties of these complexes has been extensively studied and reviewed,[11,12] and we have recently reported the preparation and properties of amylose-fatty acid salt complexes by combining water soluble fatty acid salts with water solutions of jet cooked high amylose starch.[13] Amylose complexes have also been formed by extrusion of mixtures of amylose containing starches with complex-forming ligands,[14–23] and studies have shown that complex formation takes place near the temperature of starch gelatination.[11] The solubility of the un-foamed extrudates decreased when starch was extruded in the presence of lipids,[24,25] and increased complexation during extrusion resulted in decreased expansion, water solubility, and iodine binding capacity while increasing the bulk density.[20] Although calcium stearate[26] and magnesium stearate[27–29] have been previously added in small amounts to starch formulations used to prepare baked foams for use as disposable food containers by heating in pre-heated molds, the preparation and properties of starch-based foams for packaging materials obtained by the continuous extrusion of water dispersible amylose inclusion complexes has not been previously reported.

Economics is a major consideration in the manufacture of foam packaging. The cost of shipping the low–density final product is prohibitive, and the high cost of the extrusion equipment required to compound the formulations requires large production volumes to justify the initial investment. Thus, it is standard industry practice to compound high-density resin pellets at a central location and then ship the dense pellets to the end-use location for conversion into the low–density final product using relatively inexpensive extrusion equipment, commonly referred to as expanders.[30,31]

In this study, amylose inclusion complexes were first prepared by combining high amylose starch and sodium stearate by extrusion to form amylose inclusion complexes. Since PVOH has often been used to modify the properties of starch-based foams, PVOH was also added to some formulations to determine its effect on foam properties. Foams were then prepared by expanding the pelletized extrudates using a single-screw, short-barrel extruder designed for that purpose. The addition of sodium stearate significantly reduced both water uptake and shrinkage of the foam after incubation in a humid environment. Addition of PVOH to sodium stearate-containing foams improved the foam structure and some tensile properties.

EXPERIMENTAL

Materials

High amylose corn starch, Hylon 7 containing 70% apparent amylose, was obtained from National Starch and Chemical, Ingredion, Westchester, IL. Poly(vinyl alcohol) (PVOH) was Airvol 523S, from Air Products & Chemicals, Allentown, PA. This product is 88% hydrolyzed, has a molecular weight of 85,000–124,000, a melting temperature of 200°C, and is soluble in hot water. Magnesium silicate (talc) was purchased from Ernstrom Group, Norway. Sodium stearate was purchased from Sigma-Aldrich, St. Louis, MO.

Preparation of Pellets for Foam Production

Formulations were extruded into pellets using a 30 mm co-rotating twin-screw Werner Pfleiderer ZSK-30 extruder prior to the preparation of foams. The barrel was comprised of 14 barrel sections with a total length/diameter ratio of 44:1, and had eight zones with independent temperature control. The screw configuration was similar to a design used in a previous study in our laboratory.[5] Temperatures measured from the barrel section just after the feed throat to the die were 21/21/49/64/66/66/67/72°C, and the temperature at the die was 77°C. The screw speed was 145 rpm, and products were extruded through two rod dies 6 mm in diameter. The feed throat and barrel sections were cooled with 5°C chilled water. Dry components of the formulations were added to the feed throat with a Ktron Twin Screw Gravimetric feeder Model KCL24KT20 and a Ktron Single Screw Gravimetric feeder Model K2MLS60 (Coperion K-Tron Pitman, Sewell, NJ) at a total average rate of 190 g min^{-1}. A CORI-FLOW^{TM} series Bronkhorst Cori-Tech B.V. mass flow meter (Bronkhorst USA, Bethlehem, PA) was used to inject DI water at a steady average rate of 37 g min^{-1}. The extruded rods were allowed to cool to room temperature and were then cut into pellets with a Killion Pelletizer (Killion, Cedar Grove, NJ).

Preparation of Foams from Pellets

Foams were prepared by extruding the pellets (conditioned to a moisture content of 17–18%) through a short-barrel extruder built by Prentice Machine Works, Memphis, TN, according to a design provided by Rolla National Bio-Polymers, LLC, Rolla, Missouri. The extruder barrel was 40.6 cm long, the screw diameter was 8.26 cm, and both the barrel and screw had helical rib sections running in opposite directions to facilitate mixing of the material as it travelled the short length of the extruder barrel. Mixing was also augmented by a section in which the number of flights in the screw was unequal to the

number of grooves in the barrel. The last 10 cm of the barrel and screw were tapered down to provide a rapid increase in pressure before extruding the product through a die with an opening of 2.03 mm. The temperature in the extruder jacket was controlled by a Dynisco combination temperature thermocouple/pressure transducer, and the 44.7 kW motor was powered through an AC inverter. The following conditions were used for the production of starch-based foams: rotor speed was 380–400 rpm; temperature at the feed throat was 32–49°C; die temperature was 157–179°C; die pressure was 5.1–6.2 MPa; and the feed rate was 91–136 kg/h. This commercial scale, high throughput extruder was used in order to provide a larger, more fully expanded foam product than would be obtained with a more conventional extruder.

Foam Density

Foam density (g cm^{-3}) was calculated from the weights and volumes of 10 individual foam samples for each formulation.

Radial Expansion Ratio

The radial expansion ratio was calculated as the square of the radius of the circular cross section of the foam sample divided by the square of the radius of the die opening (2.03 mm).

Compressive Strength, Resilience, and Recovery

Compressive strength (MPa) was measured on an Instron 4201 Universal Testing Machine. Samples were conditioned at 50% RH and 23°C until equilibrated for at least 48 h. Samples were compressed by a metal probe (6.0 mm diameter) at a rate of 19 mm min^{-1}. The probe penetrated the sample to a depth of 50% of its diameter, and the compressive strength was calculated by dividing the maximum load by the cross-sectional area of the probe. Percent resilience was calculated as the force required for a second compression divided by that for the first. Percent recovery was calculated as the percentage of the penetrating distance that the foam recovered after retraction of the probe.

Water Absorption and Shrinkage

The mass and volume of foam samples were determined before being placed in a 95% RH chamber for 144 h. After this time the mass was again determined, and then the samples were dried in a 100°C oven for 24 h. After this heat treatment, the mass and volume were determined for each sample. Water uptake was calculated as the mass after the humidity treatment minus the final dry mass divided by the final dry mass. Percent shrinkage was calculated as the difference between the original volume and the final dry volume divided by the initial volume before the humidity treatment.

X-ray Diffraction

X-ray scattering patterns were provided by Texray Laboratory Services, Argyle, TX. The foam pieces were sliced into smaller pieces, and then ground into powders using a daimonite mortar and pestle. The pellets were broken up into smaller pieces using a mortar and pestle, and then pulverized in a McCrone Micronizing Mill (The McCrone Group, Westmont, IL). The samples were loaded into a zero-background sample holder for XRD analysis. Analyses were carried out with a Bruker D5000 X-ray diffractometer. The X-ray source was CuK$_{\alpha 1}$ ($\lambda = 1.5405$ Å), and samples were scanned from 2° to 35° 2θ with step size 0.05°.

Light and Scanning Electron Microscopy (SEM)

Powdered pellet and foam samples prepared for X-ray diffraction (about 0.5 mg) were dispersed in a drop of water on a microscope slide and examined by phase contrast microscopy with a Zeiss Axioskop light microscope with an Axiocam ICc 3 digital camera (Carl Zeiss, Thornwood, NY). Foam samples contained visible cell wall fragments which were stained with I$_2$KI solution to identify starch and photographed with bright field microscopy. Light micrographs depicting foam structure were obtained with hand-cut 0.5-mm thick transverse sections photographed with epi-illumination. For SEM, transverse sections about 1 mm thick were cut using a fresh razor blade with a sliding motion to prevent distortion. Sections were sputter coated with gold and examined with a JSM-6010LA SEM (JEOL USA, Peabody, MD).

Differential Scanning Calorimetry

Thermal properties were determined using a TA Instruments (New Castle, DE) model Q2000 Differential Scanning Calorimeter (DSC) calibrated against an indium standard (156.68°C, 28.86 J g^{-1}). Data were collected and analyzed with TA Universal Analysis 2000 V3.9A software. Freeze-dried samples for DSC were prepared at 20–25 wt % (dry weight basis) of sample (approximately 10–12 mg) in water using high-volume stainless steel DSC pans. The pans were hermetically sealed and allowed to equilibrate at least 4 h before analysis. Samples were referenced against an identical DSC pan containing water and analyzed using modulation ($\pm$ 0.40° C every 40 s) at a heating rate (β) of 5.0°C min^{-1}. Samples were analyzed by first heating from 0°C to 190°C, immediately cooling back to 0°C at 5.0°C min^{-1}, and then reheating from 0°C to 190°C. The melting points (T_M) were taken at the peaks of the DSC curves. Exothermic signals are reported in the upward direction.

RESULTS AND DISCUSSION

### Preparation and Analysis of Foams

Table I shows the four formulations used for foam preparation. Sodium stearate was added to formulations 3 and 4 to form inclusion complexes with amylose. PVOH was also added in formulations 2 and 4 to determine its effect on foam properties. Water was included in these formulations in amounts equal to 30 g per 100 g of starch or starch-PVOH, and 2% talc (based on total solids) was also added as a nucleating agent for foam

Table I. Formulations of Extruded Foams

Formulation number	High amylose starch	PVOH	Sodium stearate	Water	Talc
1	100	0	0	30	2
2	90	10	0	30	2
3	100	0	5.25[a]	30	2
4	90	10	4.73[a]	30	2

[a] 7.5% based on amylose content.
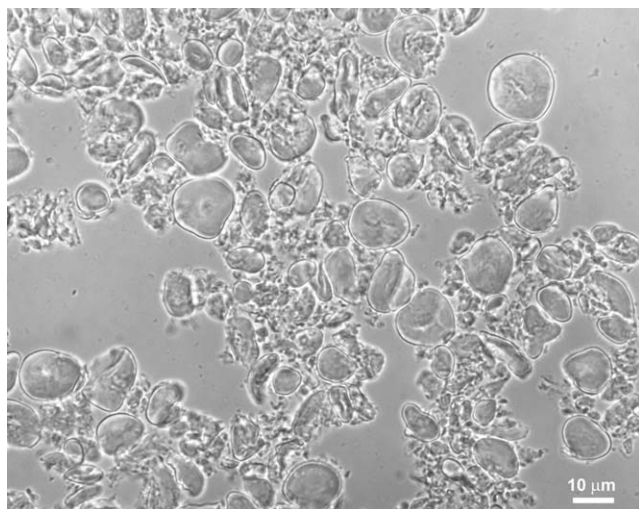
Figure 1. Phase contrast light micrograph of a water dispersion of ground pelletized extrudate prepared using Formulation 3 (high amylose starch with sodium stearate).

formation with water as the blowing agent. The formulations in Table I were first compounded and pelletized by extrusion through a twin-screw ZSK extruder. Light micrographs of the four pelletized formulations dispersed in water at room temperature were similar in appearance, and a representative micrograph for the pellets obtained from formulation 3 (Table I) is shown in Figure 1. Because of the low extrusion temperature, starch granules and granule fragments were still observed in the extruded and pelletized materials, although the absence of birefringence showed that complete gelatinization of starch had taken place.

X-ray scattering patterns for the extruded pellets prepared from high amylose starch and sodium stearate without PVOH [Formulation 3, Figure 2(A)] and with PVOH [Formulation 4, Figure 2(B)] showed major reflections at 13° and 19.8° 2θ, indicating that V_6 amylose inclusion complexes were formed during the extrusion process despite the low extrusion temperatures used.[32,33] Although amylose inclusion complexes have been prepared by others by continuous extrusion under a variety of different conditions, our results show that these complexes can be prepared at lower temperatures than those previously reported.[18–20,25] The broader reflections at 13° and 19.8° 2θ for the PVOH-containing formulation [Figure 2(B)] could result from the formation of smaller crystallites from the amylose–sodium stearate complex when PVOH was added to the formulation. The sharp reflections at 9.5° and 28.6° 2θ in both patterns are because of the presence of talc, added to these formulations as a nucleating agent for foam formation.

Foams were prepared by expanding the pre-formed pellets by passing through a short-barrel extruder. X-ray scattering patterns of the foams prepared with sodium stearate (Formulations 3 and 4) showed reflections indicating the presence of amylose complexes at scattering angles similar to those observed for the pre-formed pellets (Figures 2C and 2D), although broader reflections were observed for the foamed formulations suggesting the presence of smaller crystallites in the foamed products.

Differential scanning calorimetry (DSC) is a well-known technique used to examine the thermal interactions of starch with lipids, and a considerable amount of research has been directed toward the use of DSC to analyze amylose-fatty acid inclusion complexes.[34–40] Samples were therefore analyzed by DSC to better understand the interactions between high amylose starch and sodium stearate during the extrusion of pellets and the preparation of foam samples. Representative thermal curves are shown in Figure 3 and summarized in Table II.

For comparison with our extruded foam samples, a freeze-dried sample of a high amylose starch–sodium stearate inclusion complex was prepared by jet-cooking high amylose starch and then adding a water solution of sodium stearate to the hot aqueous starch solution in a manner similar to that reported previously (Fanta 2010).[13] A thermogram of this material, shown in Figure 3 (curve A), showed a single endothermic melting transition at $T_m = 108.5°C$ having an enthalpy (ΔH_m) of 9.8 J g^{-1}. The T_m at 108.5°C falls within the wide temperature range of 99–130°C for amylose-stearic acid complexes reported by others,[35, 40–42] and attributed to the melting and dissociation of various polymorphic forms of the amylose-lipid complex.[38] To confirm that the transition was because of an amylose–sodium stearate complex, a rescan of the sample after cooling (data not shown) showed the disappearance of the complex peak at 108.5°C and the appearance of a new endothermic transition at approximately 69°C corresponding to free stearic acid.
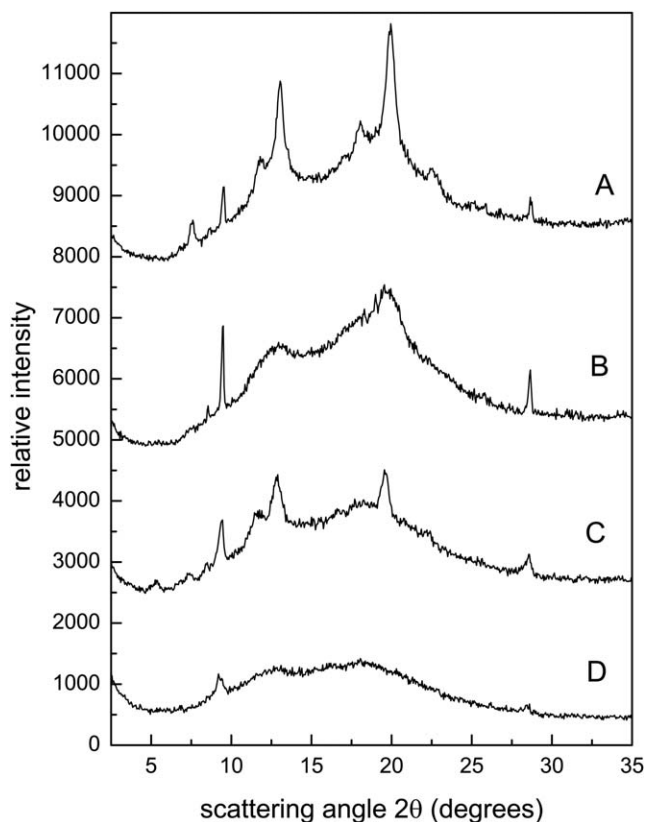
Figure 2. X-ray diffraction patterns of extruded pellets (A,B) and foams (C,D) prepared from high amylose starch and sodium stearate. B and D represent pellets and foams, respectively, prepared with PVOH.
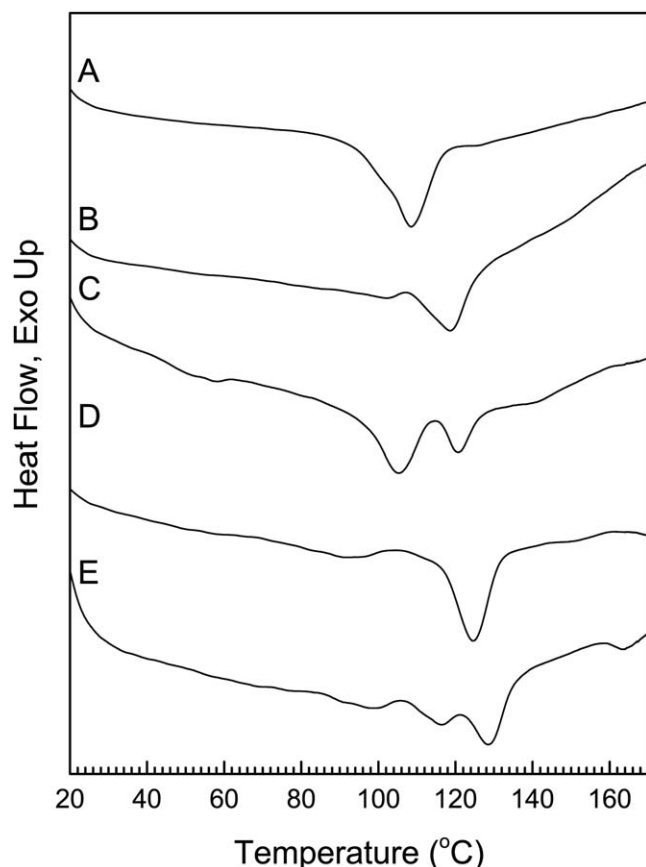
Figure 3. DSC thermograms of: (A) Freeze-dried high amylose corn starch-sodium stearate inclusion complex prepared by jet-cooking; (B) Pelletized extrudate containing high amylose corn starch, sodium stearate, and talc (Formulation 3) from the ZSK-30 extruder; (C) Pelletized extrudate containing high amylose corn starch, sodium stearate, talc, and PVOH (Formulation 4) from the ZSK-30 extruder; (D) Foam prepared by extrusion of pelletized of high amylose corn starch, sodium stearate, and talc (Formulation 3); (E) Foam prepared by extrusion of pelletized high amylose corn starch, sodium stearate, talc, and PVOH (Formulation 4). All samples were run at 20–25% w/w in water using a scan rate of 5°C min^{-1}.

Thermograms of pelletized formulations prepared with sodium stearate prior to foam formation (Formulation 3) are also shown in Figure 3. The pellets prepared without PVOH (Formulation 3, curve B) had an endothermic transition at $T_m = 119.0$°C ($\Delta H_m = 10.2$ J g^{-1}) that can be attributed to the amylose–sodium stearate complex. An endothermic transition corresponding to free stearic acid derived from neutralized sodium stearate was absent, indicating that the added sodium stearate was fully complexed during the pelletizing process. The transition for the complex derived from the pelletized extrudate was shifted 10.5°C higher than the complex obtained by jet-cooking shown in curve A. Different polymorphic forms of the amylose-lipid complex are known, and the thermal behavior of amylose-lipid inclusion complexes can be influenced not only by the properties of the complexing agent but also by the conditions under which the complexes are formed and how they are analyzed.[36–38,43] Biliaderis and coworkers and Eliasson have demonstrated that formation and melting properties of the structural forms of amylose-fatty acid complexes are highly dependent on annealing treatments and water content, and that these factors can influence the formation of polymorphic forms with various melting temperatures.[36–38,44] It is conceivable that under dilute conditions, such as those used in the jet cooking process, a single low temperature melting transition would be observed, since interactions between the polymers is minimal in dilute solutions, and the conditions favoring the formation of various polymorphic complexes would not be ideal.[44,45] In contrast, at low moisture contents (< 70%), such as those used in extrusion processing, it is possible that some annealing of the inclusion complex structures could take place leading to crystalline states with higher temperature melting transitions.

In contrast to the pellets prepared in the absence of PVOH, the pellets containing PVOH [Formulation 4, Figure 3(C)] showed a mixture of two endothermic transitions at $T_m = 105.4$°C and 120.9°C related to the amylose–sodium stearate complex. The presence of PVOH in these formulations apparently influenced the polymorphic forms obtained during the pelletizing process. Although the X-ray diffraction pattern supports the formation of the a V_6 amylose inclusion complex (Figure 2), the broader diffraction pattern relative to the pattern obtained for the pelletized sample prepared in the absence of PVOH suggests a modification of the complex, possibly because of the formation of smaller crystallites.

Table II. Thermal Properties for Jet-Cooked High Amylose Starch-Sodium Stearate Complex, Pelletized Extrudate formulations and their Corresponding Foam Extrudates.

Sample	Peak 1		Peak 2	
	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
Starch/Na stearate complex	108.5	9.8	–	–
Pelletized extrudate from starch/Na stearate (Formulation 3)	119.0	10.2	–	–
Pelletized extrudate from starch/Na stearate/ PVOH (Formulation 4)	105.4	8.1	120.9	7.6
Foam from starch/Na stearate (Formulation 3)	124.6	18.3	–	–
Foam from starch/Na stearate/ PVOH (Formulation 4)	116.5	6.1	128.4	7.4
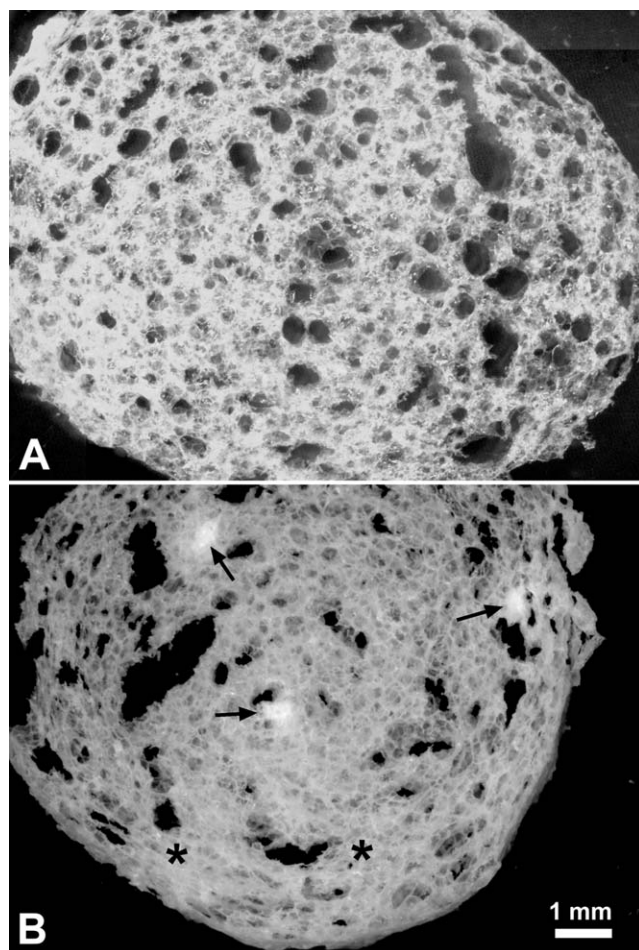
Figure 4. Photographs of sections of foams containing (A) PVOH but no sodium stearate (formulation 2) showing cellular structure of uniform density with some tears; (B) sodium stearate but no PVOH (formulation 3) showing unexpanded diffuse (asterisks) and discrete (arrows) areas having much higher density than the surrounding cellular structure. Sections were 0.5 mm thick and photographed with epi-illumination.

DSC thermograms for the extruded foams prepared are also shown in Figure 3. The foam prepared without PVOH (Formulation 3, Curve D) showed an endothermic melting transition at $T_m = 124.6°C$ corresponding to the amylose–sodium stearate complex and is shifted 5.6°C higher than that observed for the pelletized extrudate prior to foam formation [Figure 3(B)]. Foams prepared from the pelletized extrudate containing PVOH [Formulation 4, Figure 3(E)] showed endothermic melting transitions at $T_m = 116.5°C$ and 128.4°C.

Foam Structure
Figure 4(A) shows the typical interior structure of the foams as revealed by sections approximately 0.5 mm thick. Areas of intact cellular structure were separated by voids presumably formed by tearing of the structure during expansion. These voids could often be seen on or near the exterior surface of the foam pieces and likely resulted from steam rupturing the cell walls because of the poor melt strength of starch.[3] The random direction of the tears and the presence of the same void patterns in successive slices indicate that they formed during expansion of the

foam and not during slicing of the specimens. The sample depicted in Figure 4(A) was prepared from starch and PVOH (formulation 2) for which the expansion ratio was 26.80 and the foam density was 25.04 kg m^{-3}. Foams made with formulation 3 (prepared from starch and sodium stearate) had a similar expansion ratio of 24.48 but a significantly higher foam density of 58.84 kg m^{-3}. One structural feature observed in the sodium stearate-containing foam (formulation 3) that might explain the higher density observed was the presence of regions of poorly expanded or unexpanded material dispersed randomly throughout the samples [Figure 4(B)]. Both diffuse areas, indicated by asterisks, and smaller discrete areas, indicated by arrows, having much higher density than the surrounding open cellular structure were observed.

SEM images of the four formulations are shown in Figure 5. Open cell structures were observed for the foams and the broad distribution of cell sizes was similar among the four formulations. The only difference observed was that both formulations containing PVOH [Figure 5(B,D)] had fewer tears and discontinuities and larger areas of intact, continuous cellular network than those formulations without PVOH [Figure 5(A,C)]. This likely resulted from strengthening of the cellular structures by PVOH addition. A light micrograph of cell wall fragments stained with iodine (Figure 6) revealed a continuous phase with mottled staining in which were embedded many darkly stained domains of diverse sizes and shapes indicating uncomplexed amylose [Figure 6(A)]. The more lightly stained areas are interpreted as being areas rich in amylopectin, PVOH, and amylose–sodium stearate complexes, since those materials would not stain blue with iodine. Even though the foams were produced with die temperatures ranging from 157°C to179°C, the feed rate was very high and therefore the length of time at the high temperature was very short. Also, the water content was low, so even though the shear rate was high and the granules were reduced to small fragments, some discrete amylose-rich granule fragments were still present in the melted extrudate. In many cases the darkly stained domains had an elongated or striated appearance presumably resulting from the high shear conditions during extrusion and the stretching of the thermoplastic material during foam expansion [Figure 6(B)]. No difference in the appearance of the cell wall fragments among the four formulations could be discerned at the light microscope level.

Foam Properties
The properties of foams prepared from high amylose starch, with and without the addition of sodium stearate and PVOH, are shown in Table III. Addition of sodium stearate caused a significant reduction of the expansion ratio from 50.72 to 24.48, and nearly doubled the foam density from 30.06 to 58.84 kg m^{-3}. Similar effects on expansion ratio and density were observed by Bhatnagar and Hannah with un-foamed extrudates of starch supplemented with stearic acid.[19,20] Addition of sodium stearate to starch in our study significantly reduced the compressive strength, percent resilience, and percent recovery from 0.336 to 0.291 MPa, 66.6% to 60.4%, and 68.1% to 41.9%, respectively. These results could be related to areas of unexpanded material seen within the foam structure in the micrograph [Figure 4(B)]. The reduction of percent recovery,
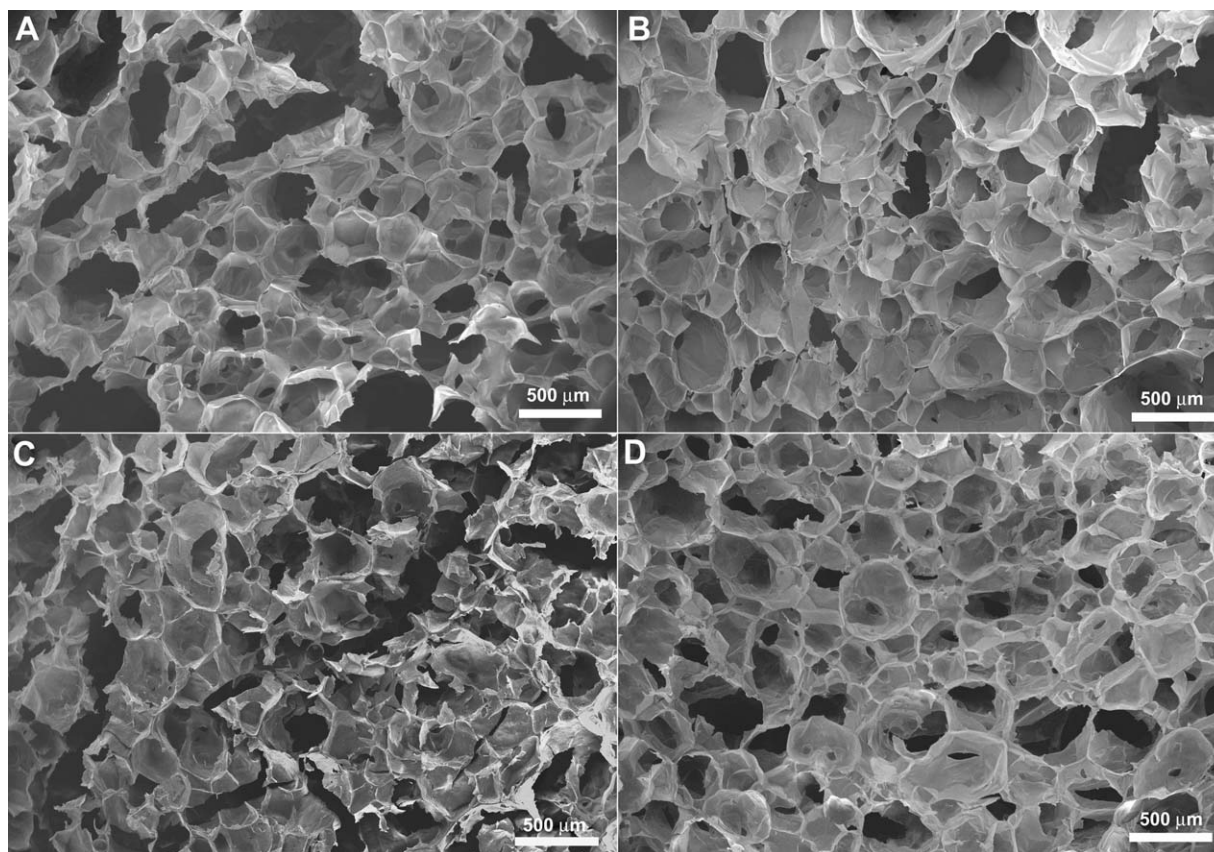
Figure 5. SEM images of foams made with (A) high amylose starch; (B) high amylose starch with PVOH; (C) high amylose starch with sodium stearate; (D) high amylose starch, sodium stearate, and PVOH.

percent resilience, and compressive strength could also be explained by discontinuities in the foam structure as evidenced by the microscopic observations (Figures 4 and 5). It is known that thermoplastic starch has relatively low melt strength and elasticity,[3,5] so apparently the inclusion of sodium stearate further reduces the melt strength, since the expansion was arrested resulting in much higher foam density. However, the foams took up substantially less water in a humid environment (12.33% vs. 28.45%) and exhibited greatly reduced shrinkage (31.12% vs. 81.86%) with sodium stearate added. The increased hydrophobicity of amylose–sodium stearate complexes relative to uncomplexed starch is consistent with the substantial reduction of water uptake and shrinkage observed.[24,25]

Addition of PVOH to starch (formulation 2) caused a similar reduction of expansion ratio, from 50.72 to 26.80, but did not significantly affect foam density (Table III). This suggests that the marked increase in foam density observed in starch/sodium stearate foams is related to the frequently observed areas of unexpanded material seen in micrographs (Figure 5), which were not characteristic of starch/PVOH foams. The reduced expansion ratio seen with PVOH addition may have been caused by contraction of the foam after exiting the die, because of the presence of PVOH. Both compressive strength and percent resilience were significantly reduced (from 0.336 to 0.202 MPa and from 66.6% to 64.8%, respectively), and percent recovery was significantly increased from 68.1% to 79.1%. These

results indicate that PVOH may plasticize the foam and impart increased elasticity, as suggested by Shogren et al.[27] PVOH did impart substantial resistance to water uptake (7.91% vs. 28.45%) but only slightly reduced the percent shrinkage from 81.86% to 71.33%. It is well known that materials made from starch suffer from brittleness and increased water absorption, and that these undesirable properties can be improved by the addition of PVOH.[27] PVOH is one of the few synthetic polymers that is biodegradable and exhibits good strength and flexibility, low water absorption, and good film forming properties.[46,47] Accordingly, when stored at 95% RH for 144 h, the foam containing PVOH (formulation 2, Table III) absorbed only 7.9% water. However, despite this low water content, the foams exhibited 71.33% shrinkage in volume, because of the combined plasticizing effects of PVOH and water.

The combined effects of sodium stearate and PVOH addition are shown by the properties of formulation 4 in Table III. The expansion ratio of 39.07 was significantly higher than that observed with either starch/sodium stearate or starch/PVOH. Apparently the inclusion of PVOH reduced the tendency of the starch–sodium stearate complex to inhibit foam expansion by imparting additional flexibility and elasticity to the resulting foam. Moreover, complex formation with sodium stearate reduced the contraction of the expanded foam after exiting the die that was observed with starch/PVOH. The foam density of formulation 4 was the same as that observed with starch itself
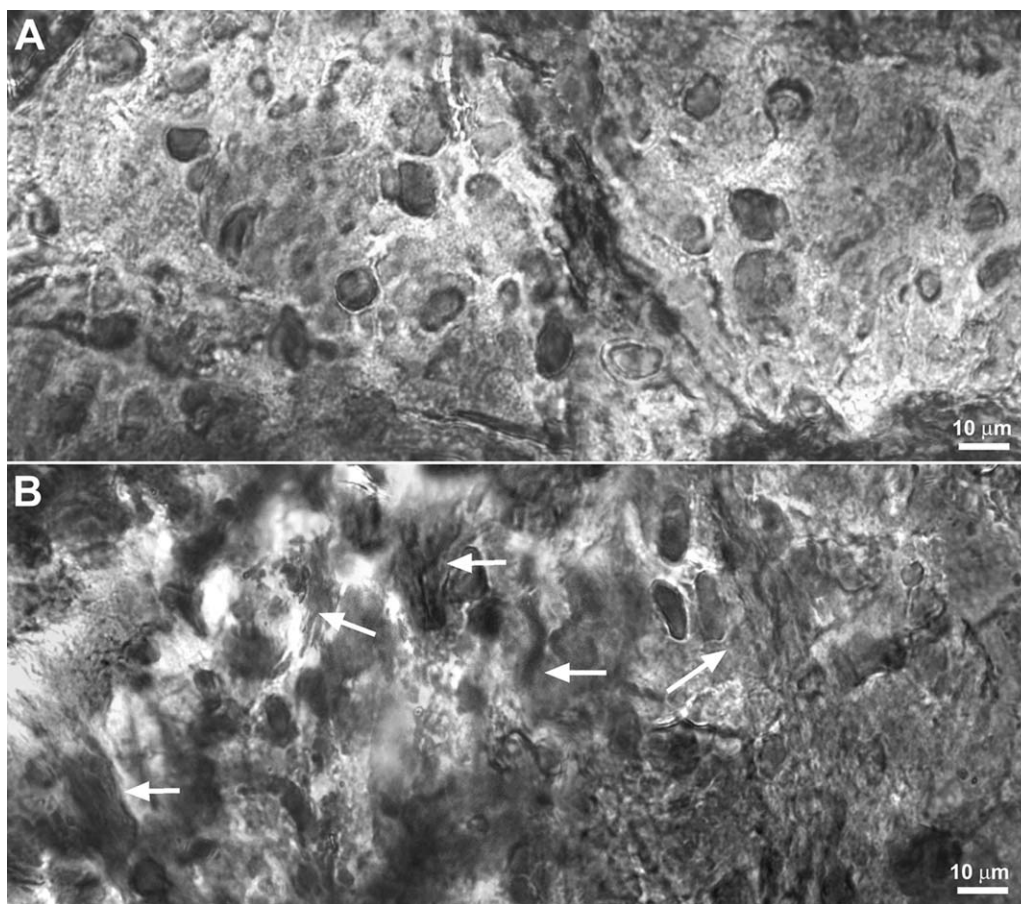
Figure 6. Light micrograph of foam cell wall fragments (formulation 1, high amylose starch) stained with I_2KI. A, area showing embedded starch granule fragments; B, area showing elongated and striated starch domains (arrows).

(formulation 1), since the expansion was not as inhibited as it was with starch/sodium stearate (formulation 3). Compressive strength was highest with starch alone (0.336 MPa) and was reduced by both PVOH and sodium stearate addition to 0.202 and 0.291 MPa, respectively. Evidently the effect of PVOH and sodium stearate was additive for formulation 4, since this formulation had the lowest compressive strength of only 0.117 MPa, a value within the range observed in other studies.[5,48] The

addition of PVOH to the starch/sodium stearate formulation avoided the reduction of percent resilience and percent recovery that was observed with starch/stearate without PVOH (formulation 3). The water uptake of formulation 4 (7.99%) was significantly lower than that of starch by itself (28.45%) and starch/sodium stearate (12.33%), but was similar to that of starch/PVOH (7.91%). Both formulations containing sodium stearate exhibited significantly less shrinkage than the formulations

Table III. Properties of Foams Prepared by Pelletizing Formulations through ZSK Extruder and then Preparing Foams by Extrusion through Short-Barrel Extruder[a]

Formulation number	Content[b]	Radial expansion ratio	Foam density, kg m^{-3}	Compressive strength, mpa	% Resilience	% Recovery	% Water uptake[c]	% Shrinkage[c]
1	starch only	50.72[a]	30.06[bc]	0.336[a]	66.6[a]	68.1[b]	28.45[a]	81.86[a]
2	starch PVOH	26.80[c]	25.04[c]	0.202[c]	64.8[b]	79.1[a]	7.91[c]	71.33[b]
3	starch stearate	24.48[c]	58.84[a]	0.291[b]	60.4[c]	41.9[c]	12.33[b]	31.12[d]
4	starch stearate PVOH	39.07[b]	30.82[b]	0.117[d]	64.5[b]	69.7[b]	7.99[c]	58.32[c]

[a] Values with different letters within columns are significantly different ($P < 0.05$) using Duncan's multiple range test.
[b] Starch = high amylose cornstarch, stearate = sodium stearate, PVOH = poly(vinyl alcohol).
[c] After 144 h incubation at 95% relative humidity.

without sodium stearate. Whereas the least shrinkage (31.12%) was obtained with starch/sodium stearate, addition of PVOH resulted in 58.32% shrinkage, which was significantly lower than the 81.86% and 71.33% shrinkage observed with starch and starch/PVOH, respectively.

It can be seen from the results in Table III that although the hydrophobicity conferred to the foams by sodium stearate complexation with the amylose component of the starch causes some deterioration of certain physical properties, the addition of PVOH overcomes many of these effects while preserving much of the advantages in lower water uptake and shrinkage resistance. In light of the lower compressive strength observed with formulation 4, starch foams prepared using both sodium stearate and PVOH may be particularly useful as low-density loose-fill foam for cavity filling in packaging for light weight goods under low compressive stress situations.

SUMMARY AND CONCLUSIONS

Starch foams containing amylose inclusion complexes were prepared by a two-step extrusion process whereby the components were first compounded by low temperature extrusion and the resulting pellets were then expanded into foam by passing through a short-barrel extruder at high temperature. X-ray diffraction and DSC of the extruded pellets showed that amylose–sodium stearate complexes were formed despite the low extrusion temperatures used. When foams were then prepared by expanding the pelletized extrudates with a second extrusion using an extruder designed to maximize compression during the foaming process. X-ray diffraction and DSC demonstrated that the amylose–sodium stearate complexes did not dissociate during the high temperature foaming process and were still present in the resulting foams. Although starch was gelatinized during extrusion, light microscopy showed that both starch granule fragments and thermoplastic starch were present in the extruded foams. Microscopy of foam sections showed intact areas of cellular structure separated by voids presumably formed by tearing of the structure during expansion. Fewer tears and discontinuities were observed in the foams when PVOH was included in the formulations. Water absorption and foam shrinkage at 95% RH were reduced in formulations containing sodium stearate because of the increased hydrophobicity of the amylose–sodium stearate complex. When PVOH was added to the amylose–sodium stearate formulation, the expansion ratio of the foam was increased because of the plasticizing effect of PVOH on the starch extrudate. Although the shrinkage of the foam at 95% RH was also increased by PVOH addition, the shrinkage was less than that observed for the foams prepared in the absence of sodium stearate. This investigation has shown that the properties of starch-based foams can be modified by the simple and inexpensive process of adding sodium stearate to the formulations to form helical inclusion complexes with the amylose component of starch. This technique provides the manufacturer of biodegradable starch foams with an inexpensive method for tailoring the properties of these foams for specific end-use applications.

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