

## Heat Expanded Starch-Based Compositions

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A heat expansion process similar to that used for expanded bead polystyrene was used to expand starch-based compositions. Foam beads made by solvent extraction had the appearance of polystyrene beads but did not expand when heated due to an open-cell structure. Nonporous beads, pellets, or particles were made by extrusion or by drying and milling cooked starch slurries. The samples expanded into a low-density foam by heating 190–210 °C for more than 20 s at ambient pressures. Formulations containing starch (50–85%), sorbitol (5–15%), glycerol (4–12%), ethylene vinyl alcohol (EVAL, 5–15%), and water (10–20%) were studied. The bulk density was negatively correlated to sorbitol, glycerol, and water content. Increasing the EVAL content increased the bulk density, especially at concentrations higher than 15%. Poly(vinyl alcohol) (PVAL) increased the bulk density more than EVAL. The bulk density was lowest in samples made of wheat and potato starch as compared to corn starch. The expansion temperature for the starch pellets decreased more than 20 °C as the moisture content was increased from 10 to 25%. The addition of EVAL in the formulations decreased the equilibrium moisture content of the foam and reduced the water absorption during a 1 h soaking period.

**KEYWORDS:** Polystyrene foam; packaging; molding; biopolymer

### INTRODUCTION

The worldwide consumption of global resources has grown from 70% of regenerative capacity in 1961 to 120% in 1999 (1). This trend underscores the need for better management and conservation of global resources. Nowhere is consumption and resource depletion more apparent than in the petroleum industry where products range from fuels to chemicals and plastics. The use of valuable petroleum resources to make single-use, disposable plastic food service containers has raised concerns among environmental and consumer groups. Plastic food service containers are popular because they are attractive, sanitary, have excellent functional properties, can be formed into complex shapes, and accommodate printing requirements while being cost competitive as single-use dispensable containers. Restaurants that use disposable food service containers avoid the labor costs associated with dishwashing, and they provide consumers the option of consuming meals at locations other than the restaurant. Billions of single-use food service containers are used each year in the United States alone to dispense beverages and serve food (2). Nearly half of the 1.9 million tons of plates and cups discarded in U.S. landfills are made of plastic (2, 3). Plastic food service containers accounted for nearly 1 million tons of waste in the United States in 2005 with no significant quantities recycled (3).

The problems created by the use of plastic disposable food service containers are only becoming more acute as the list of countries increasing their use of disposable containers expands. China, for example, is fast becoming the world's largest market for disposables. It uses billions of disposable chopsticks, 10 billion disposable food containers, and 20 billion disposable cups each year (4).

One of the more popular and commercially successful plastic food service containers is made of polystyrene foam. Polystyrene foam containers may be made by either an extrusion or a steam-molding process (5, 6). The major concern about using polystyrene foam for single-use containers is that very few of the containers are recycled due to economic and food safety issues. The use of petroleum-based disposable food and beverage containers that persist in the environment and are poorly suited for recycling is not a sustainable practice and has led to an intense search for viable alternatives (7–9).

Starch-based materials have been extensively tested as replacements for polystyrene foam and other petroleum-based resins (7–12). Commercial starches are primarily from cereal or tuber crops. Starch is the lowest priced and most abundant worldwide food commodity (13). Starch biodegrades much faster than many other degradable polymers under normal composting conditions but tends to embrittle with age and has poor moisture resistance (14). Starch has been blended with other polymers to improve its moisture resistance and mechan-

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ical properties with the goal of retaining its desirable properties in terms of biodegradability and cost competitiveness (9–11).

Industrial starch-based foam products have been made using processes, such as extrusion processing, popping, and puffing, that were developed first for the food industry (15, 16). These particular processes may produce foam products that are lightweight and have an appearance similar to polystyrene foam. However, each of these processes requires the starch and water components to be heated under elevated pressures. Explosively releasing the elevated pressure causes steam to form instantaneously and act as a blowing agent that produces a starch foam. Unfortunately, the explosive foaming process that occurs is not easily controlled and adaptable to making molded foam articles.

There are alternative processes for making starch-based foams that do not require elevated pressures and are better adapted to making molded foam products. One such process involves dehydrating aqueous starch gels in ethanol and then evaporating the solvent to produce a foam (17, 18). Other starch-foaming processes have been developed for the food industry such as a baking technique used for making wafer cookies and ice cream cones (19). The baking method starts with a starch-based dough containing more than 50% moisture that is deposited in a heated mold containing steam vents. Once the mold is closed, the dough quickly heats to form a gelatinous melt that expands, fills the mold cavity, and vents the excess water as steam (20). Low-density starch foam food containers have been commercialized using this baking technology (21, 22). The containers are typically laminated with a biodegradable film to provide the moisture resistance and mechanical properties needed for food service ware (21).

Another starch-foaming technique used in the food industry is an oven-puffing process that is similar to the pre-expansion process used in making pre-expanded polystyrene foam beads (16). The technique uses much lower moisture levels than the oven-baking technology previously described. The oven-puffing process could be a useful technology for making molded foam products at ambient pressures. The process involves densifying a starch-based sample by compression, equilibrating to a desired moisture content, and then rapidly heating the sample to cause expansion (23). The present study investigated the properties of starch foam beads formed at atmospheric pressure using both solvent-exchange and oven-puffing processes.

## EXPERIMENTAL PROCEDURES

**Materials.** Native wheat starch (Midsol 50) was purchased from the MGP Ingredients, Inc. (Topeka, KS). Native potato starch (Pencook 10) was purchased from Penford Food Products (Fort Collins, CO), and native Dent cornstarch (Melojel) and waxy corn starch (Amioca) were purchased from the National Starch and Chemical Co. (Bridge-water, NJ). Poly(vinyl alcohol) (PVAL, 99% hydrolyzed, mw = 89000–98000) was purchased from Sigma-Aldrich (St. Louis, MO). Ethylene-vinyl alcohol copolymer resin powder (EVAL, E-105, and G176B, 48 mol % ethylene) was provided by Evalca (Houston, TX). Polystyrene beads were purchased from Huntsman Chemical Co. (Mansonville, QC, Canada).

**Polystyrene Bead Expansion and Molding.** Polystyrene beads were pre-expanded at approximately 105 °C using a fluidized bed dryer (Sherwood Scientific, Cambridge, United Kingdom). The pre-expanded beads were stored in a plastic bag for at least 48 h. The pre-expanded beads were molded into foam cups using a commercial cup-molding machine (model M-10, Master Machine and Tool Co., Mulberry, FL).

**Preparation of Starch Foam Beads by Solvent-Exchange Process.** A wheat starch suspension (8%, w/w) was prepared in a round-bottom flask and was constantly stirred while it was heated in a boiling water bath. Viscosity readings were taken intermittently with a viscometer (Brookfield, model RVT, Stoughton, MA). The suspension was heated

**Table 1.** Composition of Dry Formulations Used to Study the Effect of Pellet Ingredients on Expansion

formulation	starch (%)	glycerol (%)	sorbitol (%)	resin (%)
#1	100	0	0	0
#2	90	10	0	0
#3	90	0	10	0
#4	75	10	0	15
#5	60	10	0	30
#6	90	5	5	0
#7	85	5	5	5
#8	75	5	5	15
#9	60	5	5	30

until the viscosity no longer increased. The hot starch melt (90 °C) was poured into a 4 L heated pressure vessel that maintained the melt temperature at 90 °C. The gelatinized starch melt was injected under pressure (0.069–0.14 MPa) through nozzles with a 0.5 mm diameter into a stream of chilled (10 °C) vegetable cooking oil wherein it formed into small (0.5–1.5 mm) spherical gel beads. The stream of chilled oil was collected in a settling tank consisting of two liquid phases. The upper phase consisted of chilled oil approximately 15 cm in depth. The lower phase consisted of a mixture of ethanol in water (35%, w/w) approximately 15 cm in depth. The gel beads settled slowly by gravity and accumulated at the bottom of the settling tank. The beads were collected from the settling tank and dehydrated in four changes of two volumes of 100% ethanol. The beads were oven dried (80 °C) until no further decrease in weight was detected. The porous, dried foam beads were stored in plastic bags at room temperature until needed.

**Preparation of Nonporous Starch Beads.** Starch gel beads were prepared as previously described and collected from the bottom of the settling tank. The gel beads were partially dehydrated in a sufficient quantity of ethanol to produce a final moisture content of 60%. The partial dehydration step prevented the beads from congealing into large masses while oven drying (80 °C). The beads were oven dried until no further decrease in weight was detected. The moisture within the beads caused them to shrink during the oven-drying step and form a dense, nonporous, transparent product. The beads were rinsed in hexanes (Sigma-Aldrich) to remove any residual oil and stored in plastic bags at room temperature until needed.

**Preparation of Nonporous Angular Starch Particles.** Heat-expandable starch beads were laborious to make so nonporous, angular starch particles were made by first heating an aqueous wheat starch suspension (8%, w/w) in a hot water bath as previously described. The gelatinized starch melt was poured into trays (30 cm × 30 cm × 3 cm), covered, and stored at 5 °C overnight to facilitate gelation. The starch gel was cut into slices approximately 1 cm thick and dried on trays in a forced-air drier (80 °C) until no further decrease in weight could be detected. The dried starch was then milled (Wiley Mill, Arthur Thomas Co., Philadelphia, PA, and fitted with a 10 mesh screen) into particles that were angular in shape and had the appearance of coarse sand. The angular particles were stored in plastic bags at room temperature until needed.

**Preparation of Nonporous Starch Pellets.** Powders of starch and other dry ingredients including EVAL, PVAL, and sorbitol as specified in Table 1 were dry blended. The dry blend was gravimetrically fed (K tron Soder model 9475-70057, Pitman, NJ) into a Leistritz corotating twin-screw (18 mm) extruder (model MIC 18/GL 30D, Nurnberg, Germany). The extruder contained six independently set heating zones (75/95/105/110/105/100 °C) beginning in order with the feed port and ending at the die. The screw speed was maintained at 60 rpm, and the screw configuration consisted of a conveying section followed by two sections of kneading blocks separated by conveying elements. Starch or blends of starch and other powdered ingredients were fed at a constant rate of 12 g/min, and the water and glycerol were preblended and metered directly into the feeding section at a rate of 5.5 g/min. The blends were extruded through a two-strand (2 mm diameter) rod die and cut into strands approximately 50 cm in length. The strands were equilibrated overnight in plastic bags and then pelletized (~2.0 mm, micropelletizer, model 1, Wayne Machine and Die Co., Totowa,

NJ). The pellets were roughly cylindrical in shape and approximately 2 mm in length and diameter.

The moisture content of the expandable starch beads, pellets, or particles was controlled by first drying the product (50 °C) overnight and then later rehydrating to 10, 15, 20, or 25% moisture depending on the experiment. The moisture content of the hydrated samples was determined by measuring the weight loss of samples dried at 105 °C using a halogen moisture analyzer (model HR73, Mettler Toledo, Switzerland).

**Thermogravimetric Analysis (TGA).** Samples were prepared from nonporous pellets by cutting the pellets into small pieces and weighing 10 mg into a sample pan. TGA was performed on each sample using a TGA (model 2950, TA Instruments, New Castle, DE). The samples were first equilibrated for 1 min at 20 °C and then heated at a rate of 10 °C/min up to 800 °C. The percent weight change as a function of temperature was monitored for each sample.

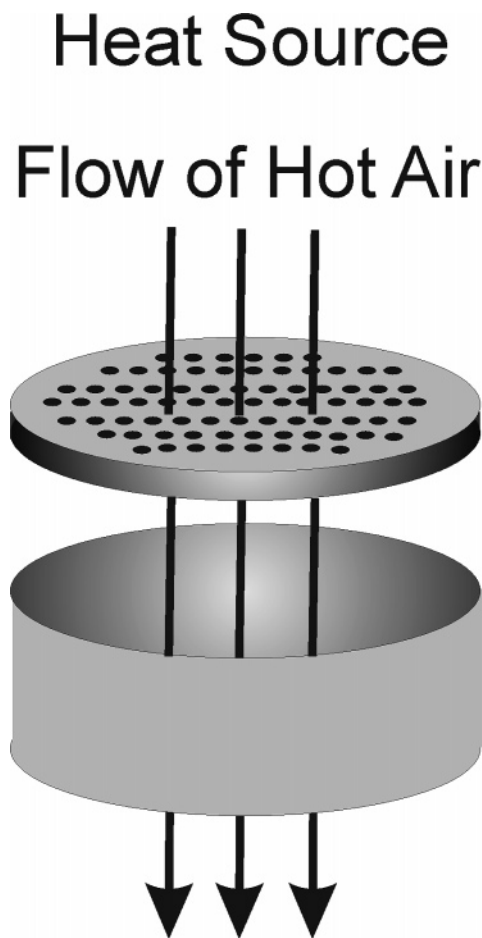
**Expansion Onset Temperature.** The minimum temperature needed to puff samples was determined using a Thermal Mechanical Analyzer TMA (model 2920, TA, Instruments). The heating rate was 10 °C/min. The samples were preloaded with a force (0.01 g) large enough to ensure adequate surface contact but small enough to not affect the degree of expansion while heating. Data were collected until the samples were fully expanded. Sample expansion as a function of temperature was monitored and graphed.

**Heat Expansion Process.** A commercial hot-air popper (Cretors Flo-thru, C. Cretors & Co., Chicago, IL) was used to test the degree of puffing through a temperature range (170–240 °C) based on TGA and TMA data. The residence time was approximately 60 s. The optimal puffing temperature range was approximately 190–210 °C. Processing temperatures lower than 190 °C did not expand fully while temperatures over 210 °C caused some discoloration in the expanded samples. A benchtop popper (Hamilton Beach, Proctor Silex, Washington, NC) that operated within the desired temperature range (~200 °C) was used to expand samples for all subsequent tests. A test was initiated by pouring 20 g of sample into the preheated popper. A standard residence time of 60 s was used for all samples. The expanded sample was collected, cooled to room temperature, and either tested or stored in plastic Ziploc bags. The bulk density of the expanded sample was determined from weight (ca. 10 g) and volume measurements using a 250 mL graduated cylinder.

**Water Absorption.** Puffed samples (1 g) were submerged for 60 min in 200 mL of water and then blotted with a paper towel for 3 min. The weight increase for each sample was recorded. A second moisture sensitivity test was performed by equilibrating puffed pellets for 72 h in chambers held at 51 and 81% relative humidity. The humidity was maintained using saturated salt solutions [ $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (51% RH) and  $\text{NH}_4\text{Cl}$  (81% RH)]. The moisture content of the hydrated samples was determined by measuring weight loss of samples dried at 105 °C for 2 h.

**Scanning Electron Microscopy (SEM).** SEMs were prepared of sample beads and particles. Cross-sectional views were made of samples that were cryofractured in ethanol as per Humphreys et al. (24). Briefly, samples were soaked in two exchanges of 100% ethanol for 1 h. The samples were removed from ethanol using a tweezers and dropped immediately into liquid nitrogen and fractured with a razor blade held in a clamp. The razor blade and clamp were equilibrated to liquid nitrogen temperatures prior to the fracture. The fractured samples were then collected using a liquid nitrogen-chilled tweezers and dropped back into ethanol. All samples were critical point dried (Tousimis Autosamdri 815, Tousimis Research Corp., Rockville, MD) and mounted onto aluminum specimen stubs using double adhesive-coated carbon tabs (Ted Pella, Inc., Redding, CA). The samples were then coated with gold-palladium in a Denton Desk II sputter-coating unit (Denton Vacuum, Inc., Moorestown, NJ), viewed, and photographed in a Hitachi S4700 field emission SEM (Hitachi, Japan).

**Mold Prototype.** A small aluminum mold was made of a specimen dish perforated with small holes (1 mm) to allow hot air to be drawn through the mold (Figure 1). The mold was filled with starch pellets (20 g) and mounted to a heat source at one side and a vacuum source at the other to facilitate the flow of hot air through the sample. Hot air



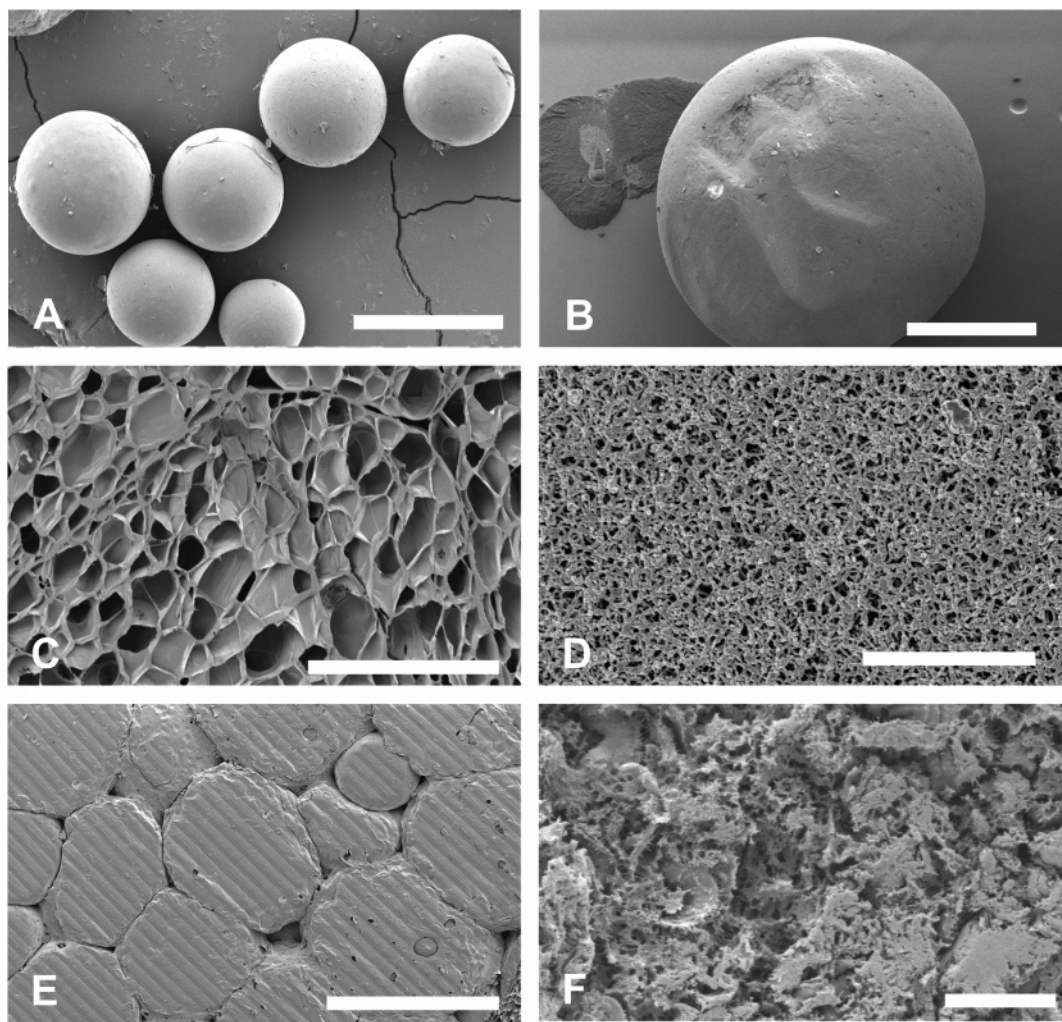
**Figure 1.** Schematic of simple cylindrical mold used to mold starch foam made by heat expansion. The mold was loaded with 20 g of sample, and the lid was affixed. The sample was expanded into foam by a flow of hot air through the sample. The rate of heat transfer was maximized by using a vacuum source to draw hot air through the sample.

(~200 °C) was drawn through the mold for 60 s to heat the sample and maximize expansion.

**Experimental Design.** All experiments were performed in triplicate. Statistical differences between mean values were determined using standard methods (SigmaStat, SPSS Inc., Chicago, IL). The effect of different ingredients on expansion of the pellets was determined from a set of 15 formulations containing various ranges of glycerol (4–12%), sorbitol (5–15.5%), starch (52–86%), EVAL (E-105A, 5–15%), and water (10–25%). Data analysis and model fitting were performed using JMP statistical software (JMP, SAS Institute, Cary, NC). On the basis of data analysis, nine formulations were chosen and tested (Table 1).

## RESULTS AND DISCUSSION

**Polystyrene Bead Expansion and Molding.** Polystyrene foam containers may be made by either extrusion or a steam-molding process (5). The steam-molding process uses very small beads (0.4–1.6 mm diameter) that contain 3–8% blowing agent (5, 25). The beads are pre-expanded by heating beyond the glass transition temperature ( $T_g$ ) of polystyrene using steam. The beads soften at a temperature (~90 °C) that is much higher than the boiling temperature (36.1 °C) of pentane (5, 25, 26). The vapor pressure of the pentane acts as a blowing agent that expands the softened polystyrene forming a homogeneous cellular structure with polyhedral-shaped closed cells (27). The cell size can be controlled in the range of 50–750  $\mu\text{m}$  by varying the amount of pentane and nucleating agents and adjusting the



**Figure 2.** Scanning electron micrographs of pre-expanded polystyrene foam beads (A, C, E) and starch foam beads made by a solvent exchange process (B, D, F). (A) Pre-expanded polystyrene foam beads (scale bar = 500  $\mu\text{m}$ ). (B) Starch foam bead made from the solvent exchange process (scale bar = 500  $\mu\text{m}$ ). (C) Cross-sectional view of the cut surface of a pre-expanded polystyrene foam bead (scale bar = 300  $\mu\text{m}$ ). (D) Surface view of starch foam bead (scale bar = 5  $\mu\text{m}$ ). Note the porous structure. (E) Surface view of a polystyrene foam cup made by heat expansion and adhesion of individual pre-expanded foam beads (scale bar = 1 mm). (F) Cross-sectional view of the cut surface of a foam bead made from the solvent exchange process (scale bar = 25  $\mu\text{m}$ ).

expansion processing parameters (25, 28, 29). The beads are cooled, dried, and conditioned for up to 2 days to allow the internal vacuum that formed during expansion to dissipate. The conditioning process also allows the remaining pentane to condense and surface moisture to evaporate (5, 25). The polystyrene foam beads used in the present investigation were quite uniform in size and were less than 0.5 mm in diameter (Figure 2A). The pre-expanded, conditioned beads were fed into a molding machine and successfully molded into cups.

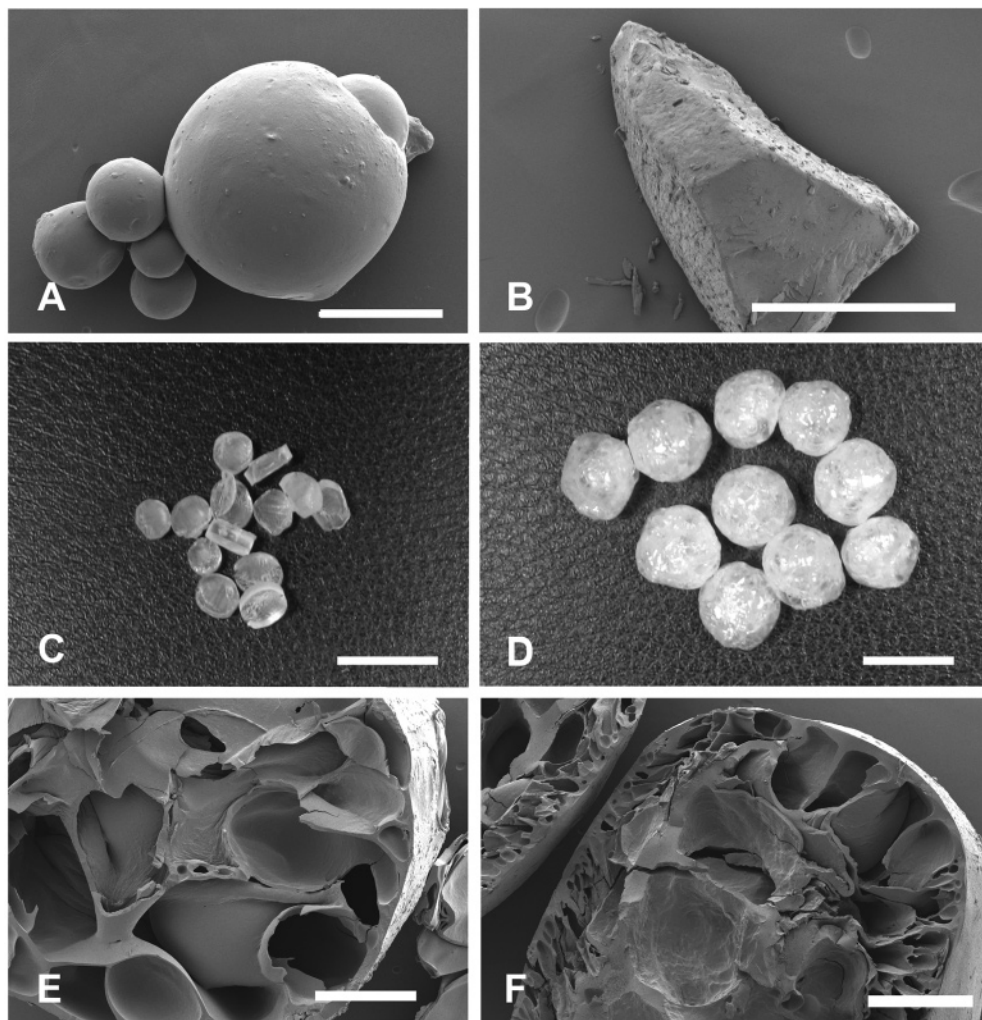
#### Starch Foam Beads Formed by Solvent-Exchange Process.

Starch beads made by the solvent exchange process were white and opaque and were very similar in appearance to the polystyrene foam beads. The starch beads ranged in diameter from 0.25 to 1.5 mm (Figure 2B). Although the polystyrene and starch foam beads had a similar appearance, their microstructure was very different (compare Figure 2C,E and D,F). Polystyrene foam beads consisted of thin-walled, closed cells (Figure 2C). The closed cell structure is essential for entrapping blowing agent and building internal pressure during the foaming and molding process (5, 26, 27). Once the pre-expanded foam beads are loaded into a mold and heated, they expand, fill in voids, and adhere to each other to form a molded part (Figure 2E).

In contrast to the polystyrene foam beads, the starch foam bead made by the solvent exchange process consisted of a network of open pores both internally and on the bead surface (Figure 2D). The microstructure of the starch bead interior consisted of a network of open cells and starch granule remnants that were very distinct from the interior structure of the polystyrene foam (compare Figure 2C and F). Efforts to expand the starch foam by heating were unsuccessful, most likely because of the difficulty in building up any significant internal pressure within the open pore microstructure.

**Nonporous Starch Beads.** Spherical, nonporous, transparent beads of starch were made in the same size range as the polystyrene foam beads (Figure 3A). It was difficult to prepare the beads due to their tendency to adhere to each other and fuse during the final drying step. The adhesion problems were minimized by first partially dehydrating the gel beads in ethanol before air drying. There was still some adhesion during the final drying step that resulted in some clumping (Figure 3A). However, the clumps were easily reduced to individual beads by gentle agitation and sieving.

**Nonporous Angular Starch Particles.** Angularly shaped starch particles made by drying and milling a gelatinized starch melt resulted in a wide range of particle sizes (Figure 3B). The

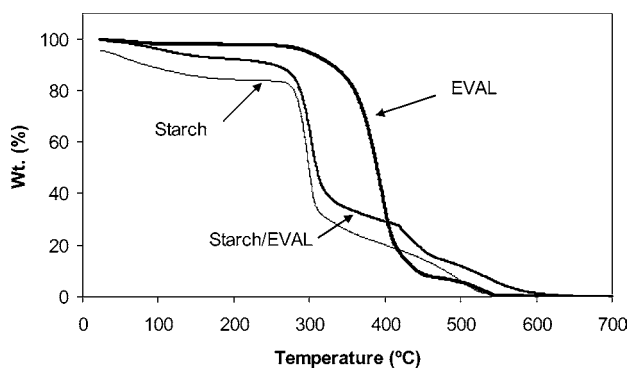


**Figure 3.** (A) SEM of solid beads of starch (scale bar = 500  $\mu\text{m}$ ). (B) SEM of a starch particle made from milled dried starch gels (scale bar = 300  $\mu\text{m}$ ). (C) Photograph of a pelletized starch extrudate (scale bar = 10 mm). (D) Photograph of a pelletized starch extrudate after heat expansion (scale bar = 10 mm). (E) SEM of a cross-sectional view of a cut surface of a puffed starch bead (bar = 1 mm). (F) SEM of a cross-sectional view of a cut surface of a puffed starch bead containing talc (bar = 1 mm).

range in particle size was narrowed by sieving the product into different size ranges. A wide range in starch particle sizes could be prepared using this technique, but a fraction of the material is lost in the form of fines during the milling operation.

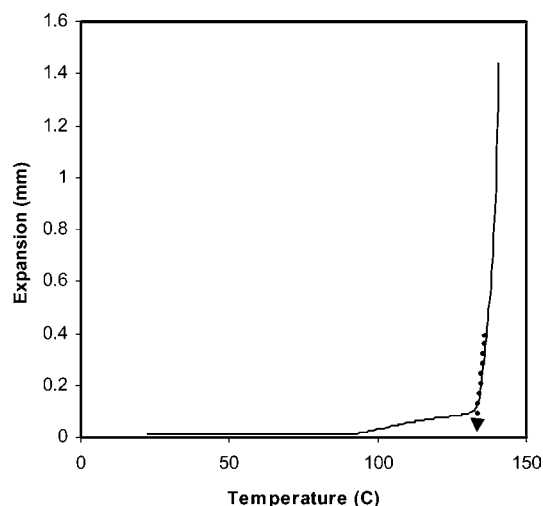
**Nonporous Starch Pellets.** Extrusion was an effective process for compounding starch with other ingredients and forming an extrudate 2–3 mm in diameter. The extrudate was pelletized (**Figure 3C**) and puffed ( $\sim 200\text{ }^\circ\text{C}$ ) into a foam bead. The puffed foam bead was much larger than the expanded polystyrene beads (compare **Figures 2A** and **3D**) and, therefore, not compatible with commercial cup-molding equipment. Smaller puffed beads made from smaller diameter pellets would be necessary if the beads were to be tested in commercial cup-molding equipment. Smaller diameter pellets could be made using smaller diameter extruder dies, but the viscosity of the melt and the melt pressure may preclude the use of dies much smaller than 1 mm. A better option may be to reduce the diameter of extrudate by drawing the hot extrudate upon leaving the die as is done with fibers. Another option would be to mill the extrudate to obtain angular particles of the proper size range as described earlier with the angular starch particles.

**TGA.** TGA was useful in establishing the temperature range at which weight loss due to thermal degradation occurred. The TGA curves for pure starch showed an initial 16–18% weight loss probably due to moisture loss (**Figure 4**). Weight loss due



**Figure 4.** Thermogravimetric curves for potato starch (starch), EVAL, and a blend of starch and 30% EVAL (starch/EVAL).

to thermal degradation began at about 270  $^\circ\text{C}$  and accelerated quickly with higher temperatures until about 30% of the original weight remained. Weight loss of the starch sample occurred at a much slower rate at temperatures greater than 320  $^\circ\text{C}$ . In contrast to the starch, the EVAL sample initially had very little weight loss. The weight loss increased slowly as temperatures surpassed 270  $^\circ\text{C}$  but accelerated at temperatures approaching 360  $^\circ\text{C}$  (**Figure 4**). The sample consisting of a blend of starch and 30% EVAL had an intermediate curve. There was an initial



**Figure 5.** Typical thermal expansion response of a starch pellet heated at 10 °C/min. The expansion onset temperature was taken as the intercept of a line parallel with the initial slope of the expansion curve.

**Table 2.** Expansion Onset Temperature for Different Mixtures at Moisture Levels Ranging from 10 to 25%<sup>a</sup>

water content	10%	15%	20%	25%
control (#1)	163 b <sup>b</sup>			140 a
glycerol (#2)	171 a			135 b
sorbitol (#3)	162 b			136 ab
Gly/sorb mixture (#6)	173 ab	156 a	144 a	137 ab
15% EVAL (G176B)	153 c	140 b	132 b	126 c
5% EVAL (E-105A, #7)	170 ab	153 a	143 a	137 ab
15% EVAL (E-105A, #8)	164 b			131 b
30% EVAL (E-105A, #9)	156 c			128 c
30% EVAL (E-105A, #9), waxy corn	133 d	132 c		

<sup>a</sup> The number shown within parentheses corresponds to dry formulation ingredients given in **Table 1**. <sup>b</sup> Values within columns followed by a different letter are significantly different (0.05 level).

weight loss of about 10% followed by an accelerated weight loss beyond 260 °C. The results indicate that samples could be heated to 260 °C without significant weight loss due to thermal degradation. However, as mentioned earlier, samples discolored at temperatures far below 260 °C so an upper temperature limit of 210 °C was used.

**Expansion Onset Temperature.** The expansion onset temperature was taken as the *x*-intercept of a line tangent with the initial slope of the temperature/expansion curve (**Figure 5**). The thermal expansion onset temperature was measured for various starch pellet samples to determine the minimum temperatures necessary to expand the starch particles. Typical expansion curves show only a small increase in expansion as a function of temperature before the expansion onset temperature (**Figure 5**). A sharp increase in expansion as a function of temperature at or beyond the expansion onset temperature was typical for starch pellets tested (**Figure 5**).

The expansion onset temperature was much higher for the starch samples than for expanded bead polystyrene (**Table 2**). Variations in starch formulation and moisture content were investigated to determine whether the thermal expansion temperature could be lowered to the range of the polystyrene. The results show that the expansion onset temperature was decreased by increasing the moisture content from 10 to 25% (**Table 2**). The addition of plasticizers had only a minor effect on the expansion onset temperature, whereas EVAL, especially at the 30% level, lowered the expansion onset temperature (**Table 2**).

**Table 3.** Effect of Water Content on the Bulk Density of Puffed Samples Containing Different Levels of Plasticizers or EVAL

water content	10%	15%	20%	25%
control (#1) <sup>a</sup>	0.16 b <sup>b</sup>	0.17 c	0.18 c	0.18 d
glycerol (#2)	0.13 a	0.12 a	0.11 b	0.10 b
sorbitol (#3)	0.15 b	0.12 b	0.098 a	0.071 a
EVAL (E-105A, #4)	0.22 d	0.16 c	0.13 b	0.13 c
EVAL (G176B, #4)	0.18 c	0.14 bc	0.12 b	0.13 c
EVAL (E-105A, #5)	0.32 e	0.28 d	0.26 d	0.26 e

<sup>a</sup> The number corresponds to the formulations listed in **Table 1**. <sup>b</sup> Values within columns followed by a different letter are significantly different (0.05 level).

The lowest expansion onset temperature was reached using a waxy corn starch.

**Heat Expansion Process.** Pelletized starch samples were equilibrated to a moisture content ranging from 10 to 25% and then rapidly heated at ambient pressure using the laboratory hot air popper. The starch pellets began to puff after about 20 s of heat treatment. Puffed samples that were removed from the popper after 25 s quickly collapsed, probably due to the vacuum formed within the cells when water vapor within the expanded sample condensed. Heating the samples for a total of 1 min removed sufficient moisture to keep the sample from collapsing (**Figure 3D**). Cross-sectional views of the expanded foam beads revealed that the interior structure was composed of closed cells that were very large as compared to the cell size of pre-expanded polystyrene (compare **Figures 2C** and **3E,F**). Talc was added as a nucleating agent to some starch formulations to determine its effect on cell size as compared to puffed samples without talc (compare **Figure 3E** and **F**). Samples containing the talc had a greater number of small cells as compared to the sample without talc. Further work with nucleating materials could result in more uniform cells and small cell sizes.

The bulk density of the expanded starch pellets varied depending on the formulation (**Table 3**). For most formulations, the bulk density decreased as the moisture content increased. The exception was a formulation containing only starch (**Table 3**, control). The addition of plasticizers (10% w/w glycerol, sorbitol) decreased the bulk density of the expanded product, especially at moisture levels higher than 10% (w/w). The bulk density was generally higher in formulations containing EVAL as compared to formulations containing only starch and plasticizers (**Table 3**). The bulk density increased significantly as EVAL levels were increased to 30% of the formulation. There was no consistent difference in the bulk density of samples made with two different grades of EVAL (**Table 3**).

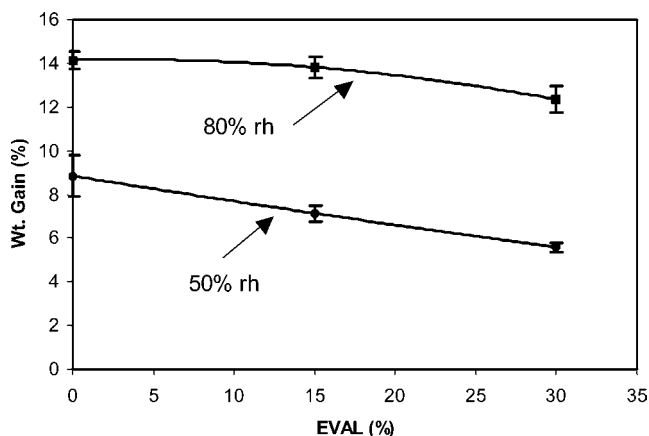
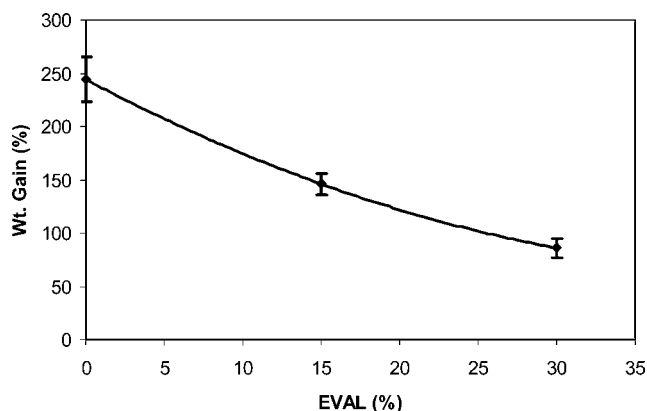
Starch products typically are moisture sensitive and embrittle as they age. Blending starch with other polymers is one way to improve properties such as mechanical strength or moisture resistance. However, replacing the starch component of a blend may reduce the expansion and increase bulk density. Starches from three sources were blended with EVAL (5%) and PVAL (5%) to compare the effect of the polymers on the bulk density of the heat-expanded blend. There was no significant effect on bulk density by incorporating EVAL into the formulation at low concentrations. The PVAL, however, had a marked effect on the foam expansion resulting in a bulk density nearly double that of the control (**Table 4**). The starch source affected the bulk density of the expanded product (**Table 4**). Foam made of potato or wheat starch had a lower bulk density as compared to foam samples made of Dent corn.

**Water Absorption.** The two moisture sensitivity tests were conducted to determine the effect of the EVAL on moisture

**Table 4.** Effect of Starch Source, PVOH (5%), and EVOH (5%) on the Bulk Density of Foam Beads<sup>a</sup>

	potato (g/cm <sup>3</sup> )	wheat (g/cm <sup>3</sup> )	corn (g/cm <sup>3</sup> )
control (#6) <sup>b</sup>	0.13 a <sup>c</sup>	0.12 a	0.21 a
PVAL (#7)	0.285 b	0.37 b	0.42 b
EVAL (#7)	0.14 a	0.17 a	0.25 a

<sup>a</sup> The moisture content ranged from 10 to 25% and was combined into one mean value for each treatment. <sup>b</sup> Formulation used for test (see **Table 1**). <sup>c</sup> Values within columns followed by a different letter are significantly different (0.05 level).

**Figure 6.** Equilibrium moisture content at 50 and 80% relative humidity of samples containing up to 30% EVAL. Error bars represent standard deviations.**Figure 7.** Percent weight gain of samples containing EVAL (0–30%) after immersion in water for 1 h. Error bars represent standard deviations.

uptake over time. The first test was a measure of moisture content of samples with different amounts of EVAL equilibrated at two different levels of relative humidity. The results indicate that the equilibrium moisture content of the samples decreased about 2% by increasing EVAL levels up to 30% (**Figure 6**). The second test was a measure of weight increase after immersing the sample in water for 1 h. The results show that EVAL reduced the amount of water absorption from 250% to about 100% during a 1 h soaking period (**Figure 7**). While the samples remained relatively sensitive to moisture, the results show that EVAL reduces the moisture sensitivity of starch-based foams as compared to the control.

Blending starch with other polymer additives offers an effective way to improve the physical and mechanical properties of starch-based products while still exploiting the cost benefit and biodegradability associated with starch. An important property of the starch component is its ability to produce a low-

density foam product. Displacing the starch component in a blend with a polymer additive may result in lower foaming capacity and a more dense foam product. When added at low concentrations, polymer additives such as EVAL confer some moisture resistance to a starch blend without significantly increasing the foam density. In contrast, other polymer additives such as PVAL markedly affect foam density, even in small amounts. Further work with blends of starch and other polymer additives such as biodegradable polyesters could be effective in developing starch-based foam products with improved properties.

The technology for molding pre-expanded polystyrene beads into food and beverage containers relies largely on proper temperatures and heat transfer rates. The expansion onset temperature for the polystyrene beads as measured by TMA is 90 °C. In commercial manufacturing facilities, polystyrene beads are first pre-expanded to the desired density (5) and subsequently molded into containers using temperatures higher (~135 °C) than the expansion onset temperature (90 °C). Mold temperatures in excess of the expansion onset temperature ensure rapid heat transfer and shorten cycle times (5, 26, 27). Mold temperatures for processing starch-based samples must be much higher than for expanded bead polystyrene since the expansion onset temperatures for starch samples ranges from 126 to 173 °C. Depending on the starch formulation used, mold temperatures in the range of 173 to 218 °C should be sufficient to foam starch provided that the heat transfer rate is also high. Unfortunately, the upper temperature range of the commercial cup molding machine used in this study was far below the range needed for the starch samples.

A small aluminum mold was used with an external heat source (190–200 °C) to test whether a starch sample (pellets) could be foamed and molded into a shape at ambient pressure by providing sufficient heat (**Figure 1**). A vacuum was effective in drawing hot air through the sample to improve the heat transfer rate to the starch pellets within the mold. The starch expanded as it was heated and became a foam product. The individual foam pellets adhered to each other to make a molded foam article. On the basis of these results, a successful commercial process for molding starch-based pellets or beads into a foam product could be designed. However, it may be necessary to laminate the starch product with a moisture resistant film as is currently done with other starch-based packaging materials (21).

In conclusion, the results of this study show that dense beads comprised of starch can be expanded into a foam at ambient pressures. Furthermore, when processed in the proper temperature range, the individual beads can fuse and form a molded foam product. The bulk density of the foam is affected by the source of starch, plasticizers, moisture content, and polymer additives. Small amounts of EVAL can be added to starch formulations to improve moisture resistance without markedly affecting bulk density. However, moisture resistant films or coatings would likely be necessary if the technology were further developed for food service packaging applications.

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