Reactive Supercritical Fluid Extrusion for Development of Moisture Resistant Starch-Based Foams

Ali Ayoub, Syed S. H. Rizvi

College of Agriculture and Life Sciences, Cornell University, Stocking Hall, Ithaca, New York 14853

ABSTRACT: The main objective of this work was to reduce barriers that prevent the usage of starch-based foams by understanding the effect and the sequence of dual-modification of crosslinked (XL) and acetylated (Ac) starch in one continuous supercritical fluid reactive extrusion (SCFX) process on wetting properties, physicochemical properties, and cellular structure of solid foam. The starch was reacted with epichlorohydrin (EPI) and acetic anhydride (Ac) under alkaline conditions in a twin-screw extruder in the presence of supercritical carbon dioxide (SC-CO_2). An increase in EPI concentration from 0.00 to 3.00% increased the degree of crosslinking as measured by DSC and confirmed by the quantification of the glucose units in the solution after acid hydrolysis. We observed a reduction of the glucose units from 93.07% for 0.00% EPI to 6.73% when 3.00% EPI was added. With crosslinking/acetylation processing, contact angle was higher for modified starches, indicating that chemical treatments induced dramatic changes in their surface polarity. Compared with native, the contact angle for dual modified starch increased from 43.1° to 91.7° which indicated their lower wettability. The addition of SC-CO_2, EPI, and Ac to the formulation reduced the density of the extrudates and increased the expansion ratio. The average cell size in the extrudate determined by scanning electron microscopy was also found to decrease from 150 to 34 μm by the addition of the two reagents. Moreover, the dual-modification of starches provided more hardness and adhesiveness to the extrudates than was observed for the unmodified starches. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2242–2250, 2011

**Key words:** starch; biopolymers; blowing agents; foam extrusion

INTRODUCTION

The worldwide production and consumption of plastics made from petroleum sources has increased enormously in the past 20 years.[1,2] Disposal of used plastic products has become a public concern because of their nonbiodegradability.[3–5] Much effort has been put forth to produce environmentally friendly alternatives to plastic products to alleviate widespread concerns about their long-term survival in landfills and toxic by-products from their incineration. Another challenge that by 2010, chlorofluorocarbons (CFCs) will be banned globally because of their adverse impact on the planet's protective ozone layer.[6–10] One industrial activity that has been significantly impacted by this ban is the manufacture of plastic foams-lightweight alternatives to solid plastic that are valued for their flexibility and ability to insulate, as well as their cushioning ability and (in marine applications) enhanced flotation. Plastic foams are created by combining two chemicals that would otherwise form a solid plastic, or by melting an existing solid.[4] A third substance, often a CFC, is then added as a blowing agent.[11–15] This agent vaporizes at the reaction temperature, releasing gas bubbles into the molten plastic. Today, the goal of the plastic foam industry is to make a new material that remains lighter than solid plastic but has many of the same qualities of durability and flexible rigidity as the solid version, and to do so without having to rely on ozone-depleting gases.

There is more carbohydrate on earth than all other organic material combined. Polysaccharides are the most abundant type of carbohydrate and make up ~ 75% of all organic matter.[16,17] Starch is very abundant biopolymers, utilized by plants as the major storage material for carbohydrates.[15,18,19] Starch is a high molecular weight mixture of two glucose-based polymers, amylose (linear), and amylopectin (branched). Starch-based foams have been prepared for many decades.[16] Recently, a new, low-temperature, and low-shear extrusion technology, called supercritical fluid extrusion (SCFX), has been developed in our laboratory.[20–22] The technology involves injection of supercritical carbon dioxide (SC-CO_2)
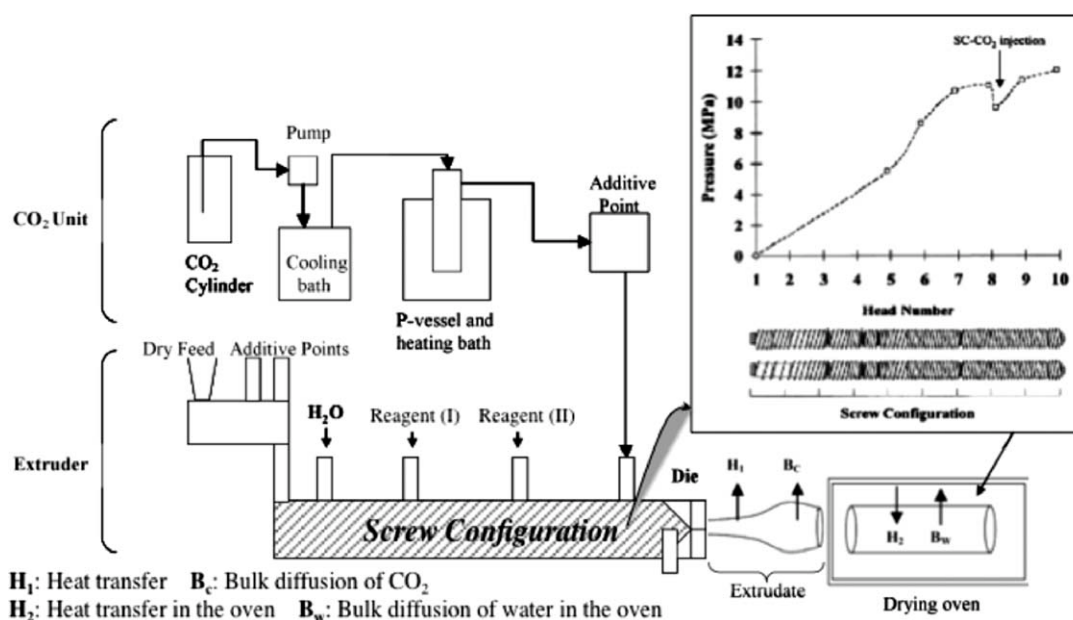
Figure 1 Schematic of dual modification of starch by (EPI) and (Ac) via reactive SCFX process with the screw configuration used in this project and the corresponding pressure profile developed along the extruder barrel.

during an extrusion process to produce microcellular extrudates. SC-CO_2, formed by putting CO_2 gas under increasing temperature and pressure, has been used as an environmentally sound replacement for other toxic chemicals, including the solvents used in the manufacture of plastics. The SCFX process has been successfully applied to various formulations of starches and proteins for continuous generation of microcellular foam.[23] The process involves introduction of SC-CO_2 into a gas-holding matrix within an extruder especially modified and configured for this purpose. The use of SC-CO_2 allows for simultaneous bubble nucleation, expansion, and reduction of matrix viscosity (due to large solubility effects). Starch can be melt-processed with water or other hydrophilic plasticizers in extruders in much the same way as conventional polymers.[24] The major drawback of using thermoplastic starch-based polymers to produce biodegradable plastics is their hydrophilic characteristic and their poor mechanical properties.[24] Thermoplastic starch will, if immersed in water, rapidly absorb moisture and lose most of its functional properties.[25] Chemical derivatization has been proposed as a way of solving this problem and of producing water-resistant materials.[13–15] For many applications, starches need to be modified to prevent degradation and to improve certain chemical and physical properties.[15,26] Crosslinking [XL] and acetylation [Ac] are widely used methods to prepare modified starches.[16–18,27] The benefits from this modification are that crosslinking will reinforce the granule of starch to be more resistant toward acidic medium, heat, and shearing while acetylation of starch was found to increase hydrophobicity and

thus is useful approach toward increasing the water resistance of starch. Derivatization of starch hydroxyl groups may also reduce the tendency of starch to form strongly hydrogen-bonded networks. The objective of this study is to eliminate barriers that prevent the usage of starch-based foams by understanding the effect of dual-modification of starch (crosslinking and acetylation), in one continuous process, on wetting properties and cellular structure of new biodegradable solid foam.

EXPERIMENTAL

Materials

Corn starch used was supplied by Cargill, USA (Cargill Gel 03420), consisting of $\sim 25\%$ amylose and 75% amylopectin. Epichlorohydrin (EPI) and acetic anhydride (Ac) were purchased from Sigma-Aldrich.

Supercritical fluid extrusion: Processing condition and formulation

Extrusion of starches was performed using a pilot-scale Wenger TX-52 Magnum (Wenger Manufacture, Sabetha, KS) corotating twin-screw extruder. This extruder was specially configured for the process with 4.5 heads, a barrel diameter of 52 mm and length to diameter ratio (L/D) of 27 was used for extruding starch/water mixture was maintained at 45% w/w on wet basis by injection of water in the extruder barrel. The temperatures of the extrudates at the die (diameter = 2.9 mm) were controlled to 70°C to prevent evaporation of the chemicals solvent and moisture in
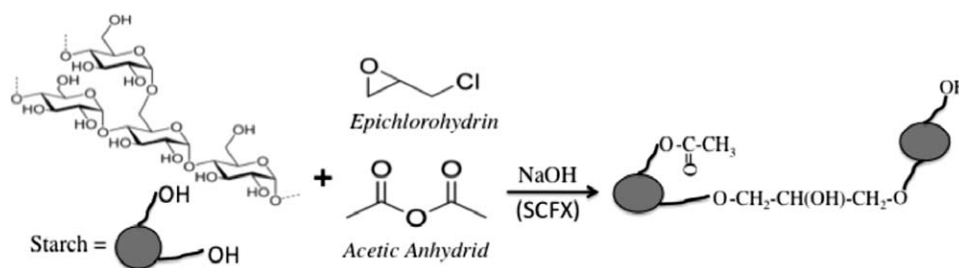
Figure 2 Schematic reaction of dual modification of starch by EPI and Ac.

the feed by circulation water of 35–60°C through the jacketed extruder barrel. The process was performed with a screw speed of 120 rpm, product temperature of 60–70°C, and feed rate of 35 kg h^{-1}. The average specific mechanical energy (SME) was 65 kJ kg^{-1}. A pilot scale supercritical fluid system was used for injection SC-CO$_2$ at a constant flow rate (7.6 × 10^{-5} kg s^{-1}) into the starch/water mixture through four valves located around the extruder barrel at a short distance from the nozzle exit. The screw configuration and a typical pressure profile in the extruder are shown in the Figure 1. The kneading paddles and the discs and reverse screw element were provided for better mixing and complete hydration. The die pressure was maintained higher than the pressure inside the barrel for continuous SC-CO$_2$ flow into the starch melt, at the desired rates (0 and 1%, dry feed basis) and pressure (4.0 Mpa). Product temperatures were monitored by a thermocouple at the end of the extruder. The cylindrical extrudates emerging from the die were collected on metal trays, dried in the convection oven at 75°C for 3h and then placed at room temperature for 24 h until the final moisture content was ∼ 8%. Moisture content was measured using the oven drying method (AOACI, 1995). The dried extrudates were stored at room temperature in sealed containers. To study the effect of the differences in properties of (Ac) and (XL) starch differing in the modification sequences on the physicochemical properties of the starch extrudates, two different reagents were injected to the extruder at the mixing zone (Fig. 1). Dual modification starches by crosslinking then acetylation (XL-Ac) and acetylation then crosslinking (Ac-XL) has been performed in this report. The schematic of dual modification of starch via reactive SCFX process is illustrated in Figure 2. Corn native starch and sodium hydroxide (1%) was used. Two levels of 0.5 and 3% of (EPI) and one level of 15% (Ac) were added. Feed formulations used in this study are shown in Table I.

Sugar content

The measurement of the reducing sugars with phenol after acidic hydrolysis, as described by Dubois

et al.[28] was used for the determination of the amount of glucose in the unmodified and modified starches. A sample of 5.5 mg was hydrolyzed with 10 mL of 2M trifluoroacetic acid for 8 h at 120°C. After filtration, the solution was neutralized by several washing with water with a rotavapor until the solution became neutral. Once again the soluble part was washed, and exactly 10 mL of distilled water was added. Several fractions of the aqueous solution containing the sugar were placed into tubes. In some cases, an insoluble part was obtained and weighed. A 5% phenol solution (0.5 mL) and 5 mL of 96% sulfuric acid were added to each tube. The sulfuric acid induced convection currents at the surface of the liquid, leading to good mixing and even heat distribution. Each tube was then agitated with a vortex. After 10 min, the tubes were reshaken and placed in a water bath at 25°C for 20 min. A yellow-orange color appeared that was stable for several hours. The absorbance was measured with a spectrophotometer at 480 nm, which corresponded to the characteristic wavelength of the colored complex. The amount of sugar was determined with a standard curve as a reference previously prepared for the particular sugar assayed.

Expansion ratio and piece density

Expansion ratio (ER) was calculated by dividing the cross-sectional area of extrudate by the cross-sectional area of the die. An average of five samples was used for measurement. The density (D), was determined by dividing the mass by its volume.

TABLE I
Formulations of the Samples Prepared

Extrudate (E)	Name	SC-CO$_2$[a] (%)	EPI[a] (%)	Ac[a] (%)
1	Unmodified-1	0.00	0.00	0.00
2	Unmodified-2	1.00	0.00	0.00
3	0.5EPI-15Ac	1.00	0.50	15.0
3′	15Ac-0.5EPI	1.00	0.50	15.0
4	3.0EPI-15Ac	1.00	3.00	15.0
4′	15Ac-3.0EPI	1.00	3.00	15.0

[a] Added to base feed, dry basis.

Scanning electron microscopy analysis

Samples were cut into 5-mm thick slices perpendicular to the longitudinal axis and mounted on aluminum stubs with double-side conductive carbon tape. A thin strip of conductive carbon paint was brushed on the side of each sample for electrical conductivity from the coated specimen surface to the stub to reduce the possibility of charging the coated surface during scanning. Samples mounted on the stubs were sputter-coated with gold and imaged in a scanning electron microscopy. Average diameter of ~ 85 representative cells on each micrograph was measured using an image processing software (Image-Pro Plus TM).

Pasting and gelling properties

Pasting characteristics of extrudate starch sample E-1, and dual modified of starch (E-4, E-4') with the pH adjusted to 7.5 or 3.5 were measured using a Brabender Viscograph-E (C.W. Brabender Instruments, South Hackensack, NJ) equipped with a pen recorder (Brabender, Model 3021) and 700 cm g^{-1} (a torque of 700 cmgequals 1000 Bu) cartridge at a speed of 75 rpm. The temperature was raised from 50° to 95°C at a rate of 1.5°C min^{-1}, maintained at 95°C for 20 min, and lowered to 50°C at the same rate. Duplicate measurements were performed on each modified sample.

The starch paste prepared by Brabender Viscograph-E was used to determine the gelling property of modified starches after storing for one month at 5°C using a TA.XT2 Texture Analyzer (Texture Technologies, Scarsdale, NY). The paste was poured into three aluminum dishes (75 mm diameter × 20 mm height). The rims and of the dishes were extended with aluminum foil to increase the height of the gel 1 cm above the rim. The gel was compressed at a speed of pretest 2.0 mm s^{-1}, and post-test 0.2 mm s^{-1}, to a distance of 5.0 mm with a cylindrical probe (2.54 mm diameter × 2.54 mm height) under the texture profiles analysis (TPA) test mode. The peak force of the first penetration was termed hardness and the negative force after the first penetration was reported as adhesiveness.[29]

Differential scanning calorimetry

About 2 mg of polymer was weighed and transferred to a preweighed standard aluminum pan, distilled water (10 μL) was added and the pan was hermetically sealed. The standard pan was heated from 20 to 120°C at 5°C min^{-1} and cooled back at the same rate. The endothermic melting transition of amylopectin was observed. An empty pan was used as the reference and the DSC was calibrated using indium. All measurements were carried out at least in duplicate. The onset (T_0), peak (T_p), and conclusion (T_c) temperatures and the melting enthalpy (ΔH) were calculated.

Contact angle measurements

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart (model 100-00). A drop of deionized water (mass ~ 35 mg) was placed on the outer skin of the starch. The contact angle on two sides of the drop was measured immediately and the average reported. The contact angle was then monitored.

FTIR analysis

The FTIR analysis was performed using a Bruker Vertex 70 FTIR spectrometer (Rheinstetten, Germany). The unmodified (E-1) and modified starch sample (E-3) were collected using the KBr pellet method. FTIR spectra were recorded at a resolution of 4 cm^{-1} and with a total of 32 scans, and wave number range between 400 and 4000 cm^{-1}. The native and modified starch samples were equilibrated at 50°C for 24 h prior to analysis.

Beta-amylolysis limit and water solubility

One gram of starch was added to 100 mL of distilled water in a test tube and heated to 60°C for 10 min in water bath. The dispersion was subsequently centrifuged at 1800 rpm for 20 min. A measured quantity of the supernatant was dried to a constant weight to determine the amount of dissolved starch.

The β-amylolsis limit was determined by hydrolyzing the starch samples (0.9 mg) with b-amylase (150 U) at 30°C in 50 mM acetate buffer (pH 4.8) for 180 min. Maltose produced was determined by the methods of Park and Johnson.[30] β-limit dextrin was recovered by precipitation with the sevenfold volume of ethanol for further characterization.

RESULTS AND DISCUSSION

Determination of the amount of glucose

The results show that for the unmodified extrudate starch, the whole sample fraction was soluble after acid hydrolysis. Therefore, this step could be used to evaluate the fraction impurities of the industrial starches, which were estimated to be 5.33%. For extrudate E-3, which was synthesized with low amounts of EPI (0.5%), about 50% of the entire fraction was soluble after acid hydrolysis. This indicates a low degree of crosslinking for the polymer. Moreover, we observed a reduction of the glucose

TABLE II
Influence of the Amount of EPI Added to the Synthesis on the Amount of Glucose Present in the Soluble Part of the Materials

Extrudate (E)	% Glucose
1	93.00
2	94.58
3	55.01
3′	54.89
4	6.80
4′	6.73

with an increase in the amount of the crosslinking agent used during the synthesis. Indeed, EPI could react with the glucose molecules (crosslinked step) and/or itself (polymerization step), and this led to a decreasing amount of glucose in polymer. The extrudate E-4, synthesized with larger amounts of EPI (3%), had insoluble parts, which became larger. As expected, the overall trend was an increase in the substitution reactions as the amount of EPI increased. Thus, a more important crosslinking step inducing a rigid structure with a higher degree of crosslinking could be expected. The results showed (Table II) that the amount of glucose decreased, because the high extent of crosslink formation.

Cellular structure of extrudates

The average density (d_{av}) of the SCFX extrudates shows that the values depend on the concentration of SC-CO_2 used, the degree of chemical modification achieved by the addition of (EPI) and (Ac).

The addition of small concentration of (EPI) and (Ac) to the formulation reduced the density of the extrudates and increased the expansion ratio (ER). According to the classical nucleation theory, which has been successfully used to describe the kinetics of nucleation in polymer melts, a higher nucleation rate and a small density is associated with a greater amount of SC-CO_2 dissolved in the polymer melt, lower interfacial tension and viscosity of the mixture, and a high degree of supersaturation achieved during the pressure quench. Addition of EPI/Ac to the starch during extrusion would tend to increase the viscosity of the melt due to the chemical reaction, and this would in turn lead to a lowering of the nucleation rate of the extrudate. On the other hand, increased crosslinking because of the presence of EPI would tend to increase the degree of supersaturation of SC-CO_2, and thus increases the density of the cell. The average cell size of various extrudates, shown in Table III, ranged from 34 to 150 μm. The control sample had a larger spread than extrudates with 3% EPI and 15% Ac which indicated that dual modification increased the uniformity of cellular structure (Fig. 3). The more uniform cellular

structure of SCFX extrudates with chemical modification can be explained on the basis of the rate of cell nucleation. Nucleation of cells usually takes place over a period of time, and competes with diffusion of gas into the cells, which leads to cell growth. The relative rates of nucleation and gas diffusion determine the cell size distribution of the extrudates. If nucleation is rapid and the number of nucleation sites large, cells will develop so fast that the diffusion effects will be negligible, and the resultant structure will have a uniform cell size distribution. On the other hand, if nucleation is very slow, the cells nucleated first will be significantly larger than others due to greater diffusion of gas to cell from the surrounding matrix, and the resultant structure would have wide dispersion in cell size. It is hypothesized that the first regime was more dominant in SCFX processing and thus produced numerous cells with a uniform cell size distribution. A uniform cellular structure is important for developing a product with isotropic mechanical properties and provides greater control over its texture. SCFX extrudates also exhibited the unique characteristic of a nonporous skin surrounding the internal cellular morphology. This skin comprised of unexpanded starch, and very small cells. Rapid diffusion of CO_2 out of the sample creates a depletion layer near the edges in which the gas concentration is too low to contribute significantly to cell growth. A combination of these factors caused the formation of a nonporous skin. The skin reduces water penetration and delays onset of water-related changes, which may be a desirable characteristic.

Pasting and gelling properties

The effects of dual modification sequence of crosslinked (XL) and acetylated (Ac) extruded corn starch on the properties physicochemical including pasting and gelling were investigated on this part.

Figure 4 present the Brabender profiles of unmodified (extrudate E-1), sequence Ac-XL (15% Ac, 3% EPI), and sequence XL-Ac (3% EPI, 15% Ac) extruded starches at pH 7.5 and 3.5, respectively. The polymer E-1 broke down brusquely after it

TABLE III
Average Density and Expansion Ratio of Unmodified and Dual Modified Extrudate Foam Starches

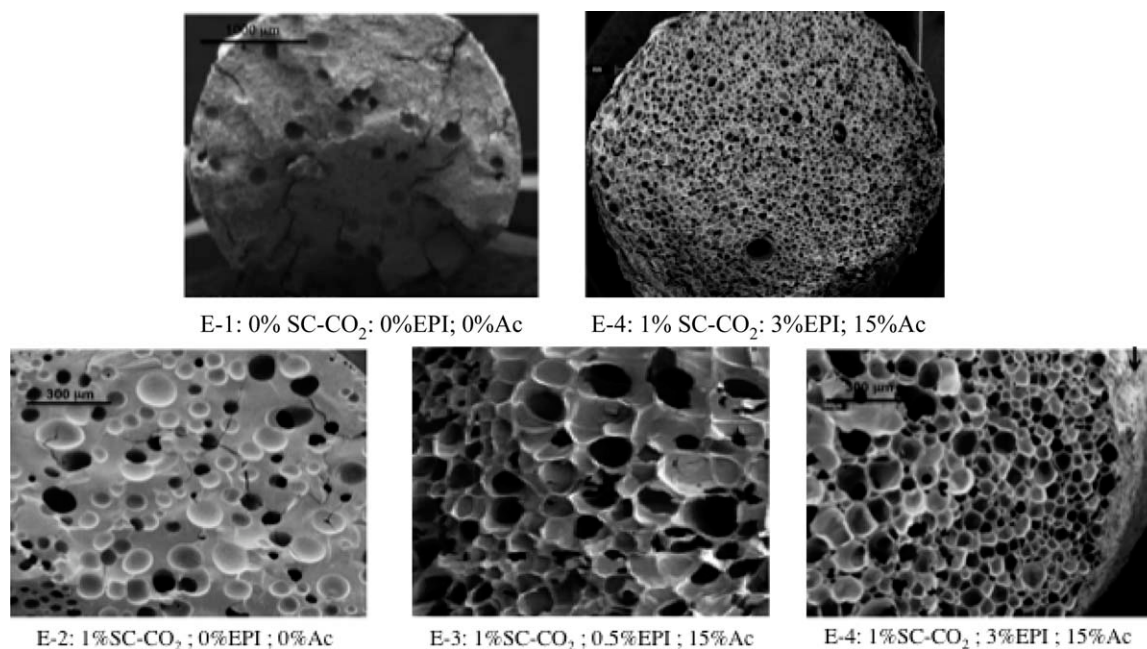| Extrudate (E)	Expansion ratio	Density (g cm^{-3})	Aver. pore diameter (μm)
1	1.65	1.352	ND
2	2.04	0.889	124
3	2.78	0.528	78
3′	2.85	0.524	76
4	2.35	0.632	34
4′	2.38	0.653	36

Figure 3 SEM micrographs of unmodified and modified extrudates with EPI and Ac.

reached the peak viscosity and little delay was noted at both pH 3.5 and 7.5. Moreover, extrudate E-1 displayed lower pasting temperature and more breakdowns at pH 3.5 than at pH 7.5. Regarding the dual-modified starches exhibited significantly lower

pasting temperatures, higher viscosities, and fewer breakdowns. Between the two modified starches, the XL-Ac exhibited lower pasting temperature and viscosity at both pHs. On the other hand, the Ac-XL showed similar viscosity at both pHs, but the XL-Ac produced higher viscosity at pH 3.5 than at pH 7.5, suggesting the locations of the crosslinks in the sequence XL-Ac starch might be different from those of the Ac-XL starch and the crosslinks in the XL-Ac starch were more inhibited to be attacked by enzymes and chemicals. The difference in acid stability of dual modified starches was proposed to be caused by different modification sequences, assuming the same level of crosslinking for both dual-modified starches. Table IV summarizes the gelling properties of unmodified and dual-modified starches. The dual-modified starches exhibited greater hardness and adhesiveness than did the extrudate 1 and 2 as a result of the chemical reaction. Because of the crosslinking reinforcement, most of the starch granules in the dual-modified starch pastes were still intact, and the swollen starch granules behaved as soft gels with permanent junctions resulting in stronger gel structure as well as greater adhesiveness. However, no difference was observed between the two dual-modified starches in gelling properties, suggesting the network structures of the two modified starch pastes were similar.
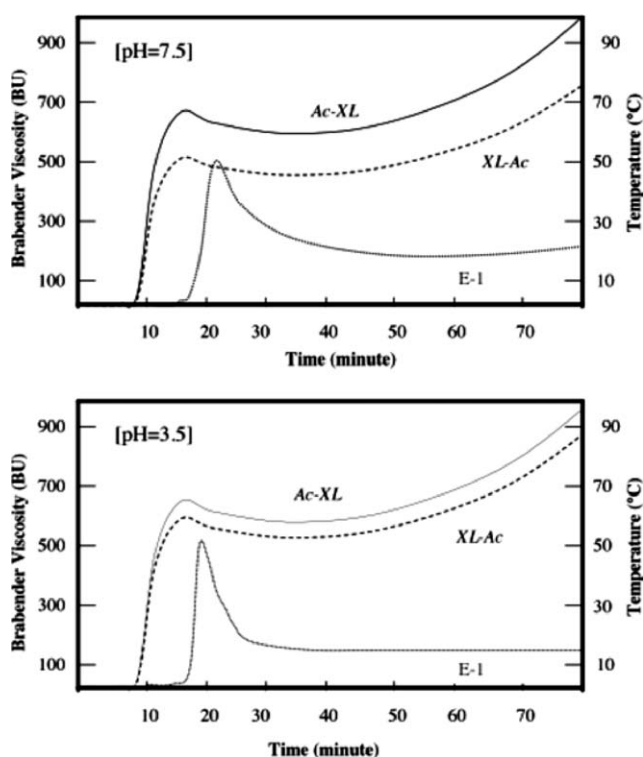
Thermal properties by differential scanning calorimetry

Table V presents the gelatinization enthalpy and the retrogradation of unmodified and dual-modified

Figure 4 Branbender profile of 5% (dry basis) unmodified (E-1), acetylated-crosslinked (15%Ac-3%XL), and the crosslinked-acetylated (3%XL-15%Ac) starches. (a) at pH 7.5 and (b) at pH 3.5.

TABLE IV
Hardness and Adhesiveness of Unmodified and Dual Modified Starches

	E1	E2	E3	E3′	E4	E4′
Hardness (g)	13.41	10.02	27.47	26.09	43.40	43.50
Adhesiveness (g)	0.00	0.00	4.12	3.86	12.00	11.80

extrudates starches. The gelatinization of starch corresponds to the dissociation of the amylose and amylopectin with granules and leaching out of amylose to the continuous phase. A significant change in onset and peak temperature, and enthalpy was observed in all extruded starch dual-modified samples as compared with unmodified (Fig. 5). The $SC-CO_2$ did not significantly change the gelatinization pattern of extruded modified starch. The gelatinization enthalpy decreased by crosslinking. Enthalpy provides an overall measure of crystallinity and indicates the loss of molecular order within the granules. The lower enthalpy suggests a disorganized arrangements or lower solubility of the crystals. The results suggest that complete melting of crystalline regions occurred in the native feed materials during extrusion processing, but the crosslinked samples showed restoration of the ordered structure. The crosslinked starches were reported to have virtually changed the onset (T_0) and peak (T_p) temperature values compared with unmodified starch. Our DSC finding indicates the disorganization of starch granules and completed melting of crystalline regions in the crosslinked starch during reactive extrusion and chemically modified. The gelatinization combined with the solubility results suggests that the introduction of new chemical bonds to starch altered the starch functionalities, possibly by tightening the organization in starch molecules and producing low molecular mobility. In term of comparison, the E-4 had significantly lower gelatinization temperature compared with that of the E-4′ (15%Ac, 3%EPI), confirming the previous assumption that the locations of crosslinks were different in both modified starches. The polymer E-1 retrograded rapidly after being gelatinized, whereas dual-modified starches (E4 and E4′) showed no sign of retrogradation after 1 week of storage. It is noted

that the E-4′ had slightly but significantly less retrogradation than did the E-4 after 2 and 4 weeks of storage, suggesting the locations of acetylated groups were also different, and the acetylated groups in the E-4′ provided better storage stability. Our finding is consistent with the research conducted by Liu et al.[31] who reported that after crosslinking the gelatinization enthalpy of all starches greatly decreased. It is believed that reduces stability of the starch structure and, consequently, reduces energy required for the structural transitions in gelatinization. However, some studies reported that crosslinking had little effects on the gelatinization parameters, in contrast to its marked effect on pasting properties. Chang and Lii[32] speculated that the extruded starch crosslinked exhibited slightly lower gelatinization temperature, lower enthalpies, and lower paste viscosities than starch crosslinked produced by the conventional method. The authors concluded that such behavior could be attributed to the high percentage of damaged starch induced by extrusion process. It suggests that the type and concentration of crosslinking agent, amylose/amylopectin ratio of starch, and modification process significantly affects the extent of change in thermal properties.

Contact angle measurements

Contact angles of water on starch samples were determined as a function of time for all extruded as shown in Table VI. The contact angle of unmodified extruded starch, dual modified extruded starch (3% EPI, 15% Ac) with CO_2 for air-dried samples were 43.7° and 91.7° respectively, at the beginning of measurement. Unmodified extruded starch had rapid water drop absorption indication that the microporous structure accelerates the absorption of water into the materials. The chemical modification caused the water drop to not absorb into the starch; the contact angle was observed to be approximately constant with respect to time for modified samples. This is an agreement with previous research showing a decrease in water diffusion with increased EPI of starch foams.[33]

The most prominent feature of the esterified starches was their increased hydrophobicity as determined by contact angle measurement. The reduced

TABLE V
Gelatinization and Retrogradation of Unmodified and Dual Modified Extrudate Starches

		E1	E2	E3	E3′	E4	E4′
Gelatinization	Onset temperature (°C)	67.50	67.35	64.89	64.17	61.40	62.00
	Peak temperature (°C)	72.50	72.46	70.01	70.57	66.20	66.80
	Enthalpy (J g^{-1})	15.60	15.47	13.65	14.07	10.40	13.10
Retrogradation (%)	Week 1	55.00	55.02	15.25	12.07	0.00	0.00
	Week 2	62.00	61.88	25.01	22.98	11.00	10.00
	Week 3	68.00	68.17	37.02	34.74	22.00	18.00

Figure 5 Comparison of DSC curves of modified starches.

Figure 6 FTIR spectra for unmodified starch (E-1) and dual modified starch (E-3).
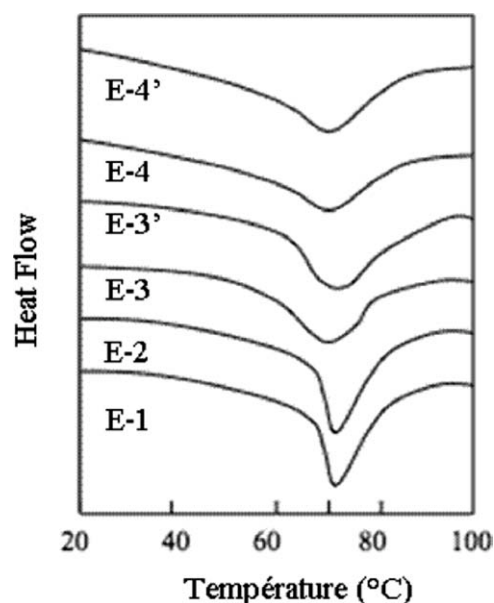
hydrophilicity of esters was attributed to the replacement of hydrophilic hydroxyls by the relatively hydrophobic ester groups. When adding a drop of distilled water, it was quickly spread on the starch surface and gave the lowest contact angle value. Because there are many OH groups on the surface of native starch macromolecule, the hydrogen bond can be formed in water. With acetylation processing, contact angle was higher for modified substance, indicating that chemical treatments induced dramatic changes in surface polarity of starch.

Compared with polymer E-1 (unmodified) and polymer E-4, contact angle was increased from 43.1° to 91.7° indicating that lower wettabilities between two phases. The modified starches improved hydrophobicity performance of starch materials, having good applied prospect.

Water solubility and β-amylosis limit

During reactive extrusion of starch with EPI and Ac under alkaline conditions the hydroxyl groups (—OH) of starch were functionalized as indicated by

FTIR spectrum (Fig. 6) and NMR results from our previous published report.[33] However, justification of degree of crosslinking by an increase in total incorporated chemical bonds content can be difficult. For this reason, crosslinking of starch is often evaluated by changes in physical properties such as pasting consistency, thermal properties, swelling, and water solubility stated that a small number of crosslinks can drastically alter the functional behaviors of starches. The introduction of covalent bonds causes the structural change in starch granules, reflecting a change in the functional properties of extruded starch such as water solubility and pasting behaviors. Crosslinking reinforces the structure of starch granules and limits water absorption and solubility of starch, thereby restricting the mobility of the starch chain in the amorphous region. Our preliminary study showed that the extruded starch samples were insoluble in water at room temperature. Therefore, the water solubility of starch samples was determined at 60°C and the results are shown in Tables VII. Crosslinked starches exhibit lower solubility than their native equivalents, and solubility further decreases with an increase in crosslink density. However, the modified starches were totally insoluble in water at room temperature and as a result, solubility was determined at 60°C. In percentage, the polymer E-4′ has the lower solubility index. The solubility was considerably reduced by

TABLE VI
Contact Angle of Water on Starch Foam Materials

Extrudate	Contact angle (°), at 5 s	Contact angle (°), at 1 min	Contact angle (°), at 3 min	Contact angle (°), at 5 min
1	43.70	40.10	37.00	36.00
2	43.70	40.10	37.00	36.01
3	72.50	71.90	72.00	72.30
3′	72.48	71.90	72.06	72.28
4	91.70	92.00	91.80	91.70
4′	91.72	92.03	91.80	91.67

TABLE VII
Enzyme Digestibility and Water Solubility of Starch Materials

Extrudate	β-amolysis limit (%)	Solubility (%)
1	62.80	37.98
2	63.15	39.99
3	32.14	10.87
3′	36.45	12.40
4	9.22	3.21
4′	10.70	2.99

crosslinking and acetylated. The dual modification restricts of the granule swelling and will also lower solubility by increasing chain binding and reduce the amount of hydroxyl free groups on the starch macromolecules. However, The results of β-amylolysis limit analysis are: unmodified starch E-1 had the highest β-amylolysis limit (62.8%), followed by the E-4′ (10.7%) and the E-4 (9.22%), respectively, (Table VII). These results again confirm previous observation in which the sequence XL-Ac was more inhibited in nature and less accessible to enzymatic attack, resulting in less degistibility. The crosslinking of starch restricts the entrance of enzyme through the channels that lead to the interior of starches and therefore there was a decrease in the enzyme digestibility. The crosslinking has been reported to interfere with the formation of the enzyme and starch complex and also restricts swelling and thus difficult to be hydrolyze by enzymatic reaction.

FTIR of acetylated starches

To detect the structure of acetylated starches, FTIR spectra are recorded, and the spectra of the polymer E-3 are shown in Figure 6. In the spectra of native starch polymer E-1, there are several discernible absorbencies at 1159, 1082, 1014 cm^{-1}, which were attributed to C—O bond stretching. Additional characteristic absorption bands appeared at 929, 861, 765, 575 cm^{-1} due to the entire anhydroglucose ring stretching vibrations. An extremely broad band due to hydrogen bonded hydroxyl groups appeared at 3421 cm$^{-1.}$

FTIR spectra of acetylated starch showed some new absorption bands at 1754, 1435, 1375, 1240 cm^{-1} assigned to carbonyl C=O, CH$_3$ antisymmetry deformation vibration, and CH$_3$ symmetry deformation vibration and carbonyl C—O stretch vibration, respectively. These new absorptions suggest that the acetylated starch products were formed during the esterification process. In addition, the spectra of acetylated starch showed that the anhydroglucose unit moved towards a high wave number.

CONCLUSIONS

New starch-based microcellular foam with porous structure was produced with supercritical fluid reactive extrusion, low shear, and low temperature processing and formation of products having a nonporous skin and a high degree of uniformity in their cell size. The starch foams which showed existence of microstructure had low density and high expansion. The dual modification imparted significant water resistance to the extruded samples. The results indicate that the structure/chemistry of the starch material and the processing conditions can be con-

trolled to produces particles with morphology and properties useful for green plastics industry.

This study has demonstrated that modification sequence has a significant impact on the structures and properties of dual-modified starches. Reaction conditions employed in modification process determine the distribution and location of modifying groups, which in turn determine the properties of the modified starch. Retrogradation of the samples E-3 and E-4 (XL-Ac) is higher than of the samples E-3′ and E-4′ (Ac-XL), and the hardness difference between the XL-Ac and Ac-XL samples are not remarkable.

References

1. Jobling, S. Curr Opin Plant Biol 2004, 7, 1.
2. Felix, H. O.; Richard, P. W. U.S. Pat.4,337,181, 1980.
3. Sawson, C. L.; Shogren, R. L.; Fanta, G. F.; Imam, S. H. J Polym Environ 1993, 1, 155.
4. Baga, M.; Repellin, A.; Demeke, T.; Caswell, K.; Leung, N.; Abdel-AAl, E. S.; Hucl, P.; Chibbar, R. N. Starch/Starke 1999, 51, 111.
5. Harland, L.; Wetztein, L. V.; Priscilla, L. U.S. Pat. 2,754,232, 1956.
6. Heidi, J.; Jan, A. D. J Agric Food Chem 1998, 46, 2895.
7. Jane, J.-L.; Jen-Fang, C. Cereal Chem 1992, 69, 60.
8. Lai, L. S.; Kokini, J. L. Biotechnol Prog 1991, 7, 251.
9. Glenn, G. M.; Stern, D. J. U.S. Pat. 5,958,589, 1999.
10. Gregory, M. G.; Arthur, P. K.; Gary, T.; William, J. O.; Delilah, W.; Robert, W. J Agric Food Chem 2002, 50, 7100.
11. Glenn, G. M.; Klamczynski, A. P.; Takeoka, G.; Orts, W. J.; Wood, D.; Widmaier, R. J Agric Food Chem 2002, 50, 7100.
12. Dujidao, P.; Manisara, P.; Pitt, S.; Ratana, R. Carbohydr Polym 2005, 59, 329.
13. Griesbach, H. L. U.S. Pat. 5,506,277, 1994.
14. Anderson, T. E. U.S. Pat. 459,783, 1986.
15. Buttery, R. G.; Glenn, G. M.; Stern, D. J. J Agric Food Chem 1999, 47, 5206.
16. El-Tahlawy, K.; Venditti, R. A.; Pawlak, J. J Carbohydr Polym 2007, 67, 319.
17. Wendy, A.; Allan, A.; Brian, T. Polym Int 1999, 47, 89.
18. Shogren, A. L.; Lawton, J. W. U.S. Pat. 5,756,194, 1996.
19. Saari, J.; Kataja, K.; Qvintus-Leino, P.; Kuuti, L.; Peltonen, S.; Mikkonen, H. Proceedings of the Fillers and Pigments for Papermakers; Pira International: Atlanta, 2005.
20. Rizvi, S. S. H.; Mulvaney, S. J.; Shokhey, A. S. Trends Food Sci Technol 1995, 6, 232.
21. Alavi, S. H.; Rizvi, S. S. H. Int J Food Properties 2005, 8, 23.
22. Alavi, S. H.; Rizvi, S. S. H.; Harriot, P. Food Res Int 2003, 36, 309.
23. Alavi, S. H.; Rizvi, S. S. H.; Harriot, P. Food Res Int 2003, 36, 321.
24. Wurzburg, O. B. In Modified Starches: Properties and Uses; Wurzburg, O. B., Ed.; CRC Press: Florida, 1986, 56.
25. Yeh, A.; Li, J. Y. Starch/Starke 1996, 48, 17.
26. Chen, L.; Imam, S. H.; Gordon, S. H.; Greene, R. V. J Environ Polym Degrad 1992, 5, 111.
27. Kyungsoo, W.; Seib, P. A. Carbohydr Polym 1997, 33, 263.
28. Dubois, M.; Gilles, K. A.; Hamilton, J. K.; Rebers, P. A.; Smith, F. Anal Chem 1956, 28, 350.
29. Takahashi, S.; Maningatand, C. C.; Seib, P. A. Cereal Chem 1989, 66, 499.
30. Park, J. T.; Johnson, M. J. J Biol Chem 1949, 149, 181.
31. Liu, H.; Ramsden, L.; Corke, H. Cereal Chem 1999, 76, 938.
32. Chang, Y. H.; Lii, C. Y. J Food Sci 1992, 57, 203.
33. Ayoub, A.; Rizvi, S. S. H. J Appl Polym Sci 2008, 107, 3663.