Properties of Supercritical Fluid Extrusion-Based Crosslinked Starch Extrudates

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ABSTRACT: Starch microcellular foam was produced by supercritical fluid extrusion (SCFX) using native and pregelatinized starch mixtures. The starch solution was reacted with epichlorohydrin (EPI) under alkaline conditions in a continuous twin-screw extruder in the presence of supercritical carbon dioxide. The relationship between crosslinking density and cell size and their distribution in the foamed extrudates was studied. An increase in the EPI concentration from 0 to 0.5% was accompanied by an increase in the degree of crosslinking as measured by differential scanning calorimetry and confirmed by diffusion coefficient measured by nuclear magnetic resonance. The diffusion coefficient of crosslinked sample was observed to be 12.5 times lower than that of non crosslinked control. The average cell size of the microporous structure, observed by scanning electron microscopy, showed a decrease from 147 to 61 μm as the concentration of EPI was increased. The cell size distribution of the crosslinked samples was significantly improved but the total expansion was lowered. The results obtained to date indicate, for the first time, that reactive extrusion of starch with EPI with supercritical carbon dioxide as a blowing agent offers a promising new technique to generate microporous foams for use in various applications. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3663–3671, 2008

Key words: biopolymers; blowing agents; crosslinking; foam extrusion

INTRODUCTION

Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules, each typically containing several million amylopectin molecules accompanied by a much larger number of small amylose molecules.[1,2] These polysaccharides are good candidates to alleviate environmental burden and provide alternate choices to petroleum-based polymers provided their functionalities are suitably modified.[3,4] Most industrial applications of starch derivatives depend on the type of functional group introduced to the main backbone of the starch, physical transformation it goes through, the physicochemical properties such as gelatinization, crystallization, retrogradation, gel formation it manifests, and the amylose/amylopectin ratio.[5–9]

Starch microcellular foams (SMCF) are generally described as a starch-based porous matrix containing pores.[10–13] The production of SMCF is envisioned to open up new ways to utilize starch as slow release agents for dispensing chemicals, flavor encapsulation, and as substitutes for commercial plastics. Previously SMCF have been used to develop nonmineral starch-based pigments[14,15] and pharmaceuticals[16] and several methods including freeze drying and solvent exchange have been used. Solvent exchange involves replacement of water with another solvent of lower surface tension and final drying of the low surface tension solvent with liquid or critical CO_2 or ethanol. This minimizes the large compressive forces during evaporation of high surface tension water and eliminates any collapse of the microcellular foam structure.[17] As such, SMCF have very high specific surface areas (air-solid interfaces) that can scatter light.[18] Coatings and filler particles made from microcellular foams are also recognized to be excellent in their ability to scatter light and be strong opacifying agents.[19,20] Starch-based, foam-like particles have also been proposed as an effective opacifying material for use in paper and coatings because of their large specific area and high brightness.

Microcellular foams made from starch offer the followings advantages relative to the inorganic fillers and pigments typically used in the paper industry: (1) they can contribute to hydrogen bonding and thus help strengthen the paper matrix, (2) they have low density, (3) they are made from bio-based renewable sources, and (4) they are 100% organic and biodegradable and thus recyclable.

Recently, a new, low-temperature, and low-shear extrusion technology, called supercritical fluid extrusion (SCFX), has been developed.[21] The technology involves reactive extrusion of starch-based matrices and injection of supercritical carbon dioxide (SC-

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TABLE I
Feed Formulation

Sample	Wheat native (%)	Wheat pregel (%)	EPI[a] (%)
G^1P_0[b]	100	0.00	0.00
G^1P_1[c]	100	0.00	0.00
G^1P_2	100	0.00	0.50
G^1P_3	100	0.00	1.00
G^1P_4	100	0.00	2.50
G^2P_0[b]	0.00	100	0.00
G^2P_1[c]	0.00	100	0.00
G^2P_2	0.00	100	0.50
G^2P_3	0.00	100	1.00
G^2P_4	0.00	100	2.50
G^3P_1	60.0	40.0	0.00
G^3P_2	60.0	40.0	1.00
G^4P_1	40.0	60.0	0.00
G^4P_2	40.0	60.0	1.00

[a] Added to base feed, d.b.
[b] Unextruded control.
[c] Extrudate control.

CO_2) as a blowing agent to produce microcellular extrudates. The SCFX process has been successfully applied to various formulations of starches and proteins for continuous generation of microcellular foam. The effects of process variables and formulation on foam expansion, cell size, cell density, and mechanical properties have been studied and reported elsewhere.[22–24]

However, native starch SMCF is readily soluble in water, preventing its use in aqueous environtments. The hydrophilic nature of starches is a major constraint that seriously limits the development of SMCF materials. Chemical derivatization has been proposed for producing water-resistant material and solving this problem. Crosslinking of starches is the most common method used in polysaccharide chemistry and occurs when a crosslinking agent introduces intermolecular bridges between polysaccharide macromolecules.[25–27] Epichlorohydrin (EPI) is one of the most common crosslinking agents. Crosslinking of starches with EPI is a well-documented reaction and a relatively easy technique for preparing polysaccharide-based derivatives.[28] Although abundant information on the crosslinking reaction between EPI and polysaccharide reaction is found in the literature of the past 80 years, some basic questions on the exact mechanisms continue to elude and interest the scientific community. Furthermore, reactive extrusion-based crosslinking of starch with EPI and its effect on SMCF materials and their properties have not been reported previously. Therefore, the current work is focused on crosslinking of starch with epichlohydrin via reactive extrusion and generation of microcellular foam (XL-SMCF) using a continuous SCFX process and characterization of product properties.

EXPERIMENTAL

Experimental design and feed formulation

A mixture of native or pregelatinized wheat starch (Cerestar, Hammond, IN) and sodium hydroxide (1%) was used as control formulation. Three levels (0.5, 1, 2.5% on dry basis) of the crosslinking reagent epichlorohydin (EPI) was added. In-barrel moisture content of the starch melt was maintained at about 45% on wet basis by injection of water in the extruder barrel. Feed formulations used in this study are divided into four groups (G) as shown in Table I

Extrusion processing conditions

A Wenger TX-52 (Wenger Manufacturing, Sabetha, KS) corotating twin-screw extruder with a barrel diameter of 52 mm, and length to diameter ratio (L/D) of 27. It was configured to operate at a screw speed of 120 rpm and feed rate of 35 Kg/h. Moisture content of the feed was adjusted to maintain the product at about 70°C at the die exit. The average specific mechanical energy was 65 kJ/kg.

Screw configuration and barrel pressure profile

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

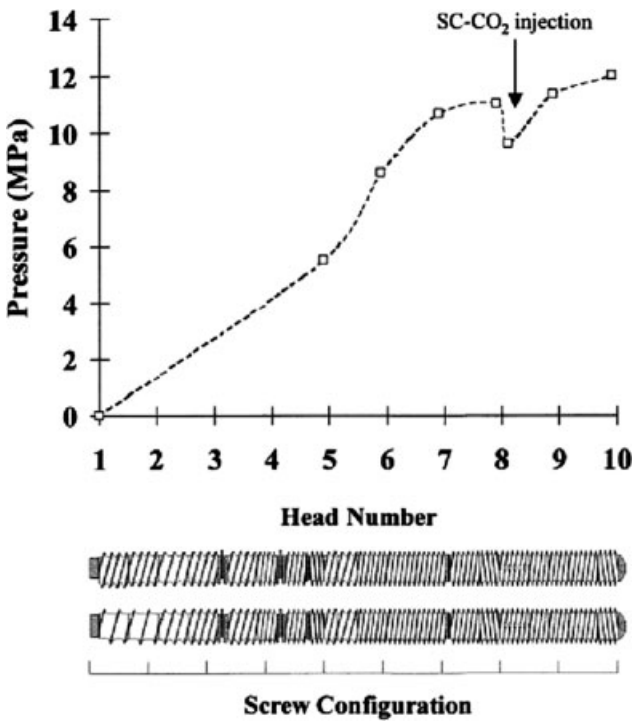

Figure 1 The screw configuration used in this study and the corresponding pressure profile developed along the extruder barrel.

element were provided for better mixing and complete hydration.

Supercritical CO_2 injection

A pilot scale supercritical fluid system was used for injection SC-CO_2 at a constant flow rate ($7.6.10^{-5}$ Kg/s) into the starch melt through four valves located around the extruder barrel at a short distance from the nozzle exit. SC-CO_2 injection pressure was automatically maintained higher than pressure inside the barrel for a continuous SC-CO_2 flow into the starch melt, at the desired rate and pressure.

Extrudate evaluation

Sample collection

Cylindrical extrudates emerging from the die were collected on metal trays and cut to a length of $\sim$ 50 cm. Trays containing the extrudates were dried in a oven at a temperature of 75°C for 3 h. Final moisture content of all extrudates was $\sim$ 8%. Moisture content was measured using the oven drying method (AOACI, 1995).

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 (13.84 and 6.6 mm^2). An average of five samples were used for measurement. The piece density (D), was determined by dividing the sample mass by its volume.

Scanning electron microscopy

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 approximately 85 representative cells on each micrograph was measured using an image processing software (Image-Pro Plus TM).

Differential scanning calorimetry

Two milligram of starch 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 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.

Nuclear magnetic resonance

A Bruker machine operating at a resonance frequency of 20 MHz (^1H) was used. The pulsed field gradient spin-echo (PFGSE) sequences were used to measure the diffusion coefficient. The gels were prepared directly in the nuclear magnetic resonance (NMR) 8 mm diameter tube by heating to 70°C for 10 min. The samples were dissolved in D_2O (10 mg in 500 μL D_2O + 100 μL of a 10 m*M* NaOD solution).

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 a 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.

α-Amylase degradation

Twenty-five milligram of sample was dispersed in 10 mL of pH 4.8, 50 m*M* sodium acetate buffer stabilized with 0.01% (w/v) NaN_3. Ten units of powdered α-amylase were added and the mixture was incubated at 20°C for 24 h. The enzyme was then inactivated by heating the samples at 100°C for 15 min. According to the Park-Johnson method[29] a 10-μL aliquot of the solution containing the reducing sugar was added to 10 μL of 1*N* NaOH and 380 μL of distilled water. Two hundred microliter of a 0.1% (w/v) potassium ferricyanide solution and 200 μL of a (0.065% w/v) potassium cyanide, (0.92% w/v) sodium bicarbonate, and (0.48% w/v) Sodium Carbonate solution were added to this mixture. The resulting mixtures were incubated at 100°C for 15 min, then were left for 10 min at room temperature before adding 1000 μL of (0.3% w/v) ammonium ferric sulfate in a 50 m*M* sulfuric acid solution. Fifteen minutes after the addition of this last solution; the absorption was recorded at 715 nm with a spectrophotometer. The results were obtained with 5% accuracy.

TABLE II
Gelatinization Temperature and Enthalpy of Crosslinked and Control Starch Samples Made by SCFX

Sample	T_0 (°C)	T_P (°C)	ΔH (J/g)
G^1P_0	65.17 ± 0.08	69.37 ± 0.16	1.29 ± 0.22
G^1P_1	35.77 ± 0.02	69.29 ± 0.11	0.23 ± 0.06
G^1P_2	68.96 ± 0.06	77.12 ± 0.23	0.46 ± 0.03
G^1P_3	70.32 ± 0.09	78.01 ± 0.18	0.63 ± 0.11
G^1P_4	70.01 ± 0.11	79.12 ± 0.19	0.91 ± 0.07
G^2P_0	64.07 ± 0.13	69.37 ± 0.16	0.03 ± 0.005
G^2P_1	65.17 ± 0.08	68.37 ± 0.27	0.04 ± 0.007
G^2P_2	68.06 ± 0.19	76.12 ± 0.24	0.27 ± 0.031
G^2P_3	69.01 ± 0.21	77.12 ± 0.49	0.34 ± 0.084
G^2P_4	68.79 ± 0.17	78.02 ± 0.51	0.57 ± 0.072
G^3P_1	63.35 ± 0.08	70.07 ± 0.23	0.21 ± 0.08
G^3P_2	72.02 ± 0.06	76.01 ± 0.22	0.58 ± 0.13
G^4P_1	64.15 ± 0.12	69.35 ± 0.19	0.16 ± 0.04
G^4P_2	68.78 ± 0.35	78.12 ± 0.63	0.48 ± 0.07

RESULTS AND DISCUSSION

Thermal property by differential scanning calorimetry

Table II presents the gelatinization enthalpy of native, pregelatinized control, and 0.5–2.5% EPI crosslinked starches. Gelatinization temperatures were found to be significantly increased (by up to 5°C) with increasing degree of crosslinking. The results confirmed that the introduction of EPI to starch tightened the molecular organization in the starch molecules, thus gelatinization occurred at a higher temperature. The gelatinization enthalpy was also positively enhanced by crosslinking. 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 part of the ordered structure. The amylose-lipid complex endoderm (90–110°C) was also observed but found to be more prominent in the native and the control samples. It is possible that the chemical modification treatment might have interfered with the molecular structure of amylose-lipid complex, resulting in a small or unstable complex that is not detectable by DSC.

Yeh and Li[30] reported that crosslinking increases the heat of gelatinization of rice starch. The crosslinked wheat starches were reported to have virtually changed the onset (T_0) and peak (T_p) temperatures values compared with unmodified starch, (T_p) was slightly increased. The increases in (T_p) were observed to be small, which may be due to an increase in the rigidity of the crosslinked starches. On the basis of DSC studies, Woo and Seib[31] reported that the crosslinked starches showed higher gelatinization temperatures than their parent starches. Therefore, it has been reported that the effect of crosslinking on gelatinization properties depends on the starch sources.

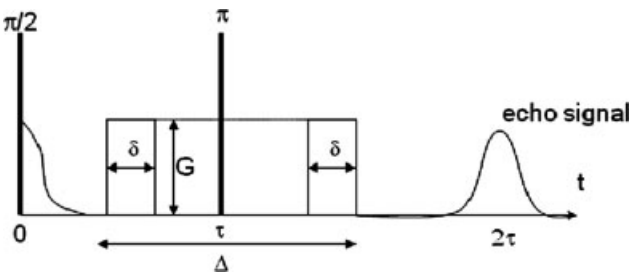

Figure 2 Pulsed field gradient for measurement of diffusion coefficient *D*.

Water self-diffusion in different starch solutions

Behavior of starch in aqueous environment is of major interest in different areas of application. Also, diffusion of water has a direct impact on the shelf-life of the starchy products. It has been demonstrated that NMR spectroscopy gives useful information about the structure and dynamics of polymer gel system. The spin-lattice relaxation time (T_1) and spin–spin relaxation time (T_2) give information about the microscopic molecular motion of solvent and probe polymer in polymer network. Additionally, the pulsed field-gradient spin-echo (PGSE) ^{1}H-NMR method has become a powerful technique for studying self-diffusion. For molecules with a very small diffusion coefficient in a polymer network, the pulse with a large magnetic-field gradient must be used. To quantify the diffusion behavior of water in modified and unmodified starches, these new techniques were employed.

In the PGSE[32–34] method, the ($\pi/2-\tau-\pi$) pulse sequence and the two gradient pulses were used as shown in Figure 2, where τ is the pulse interval, δ is the gradient pulse length, Δ is the gradient pulse

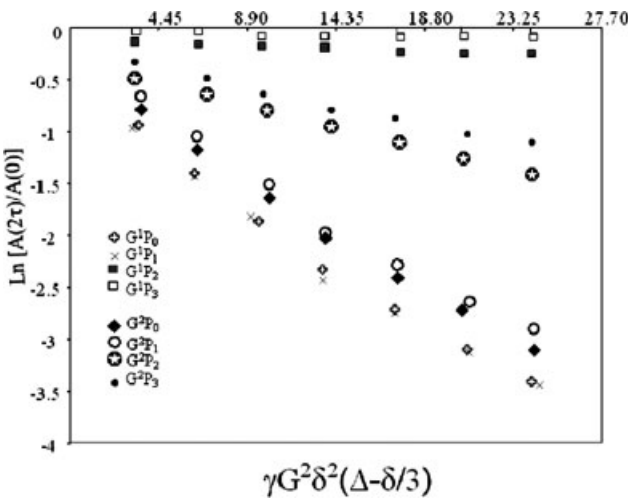

Figure 3 A log plot of the echo reduction during pulsed field gradient NMR experiments carried out on different starch-based formulations.

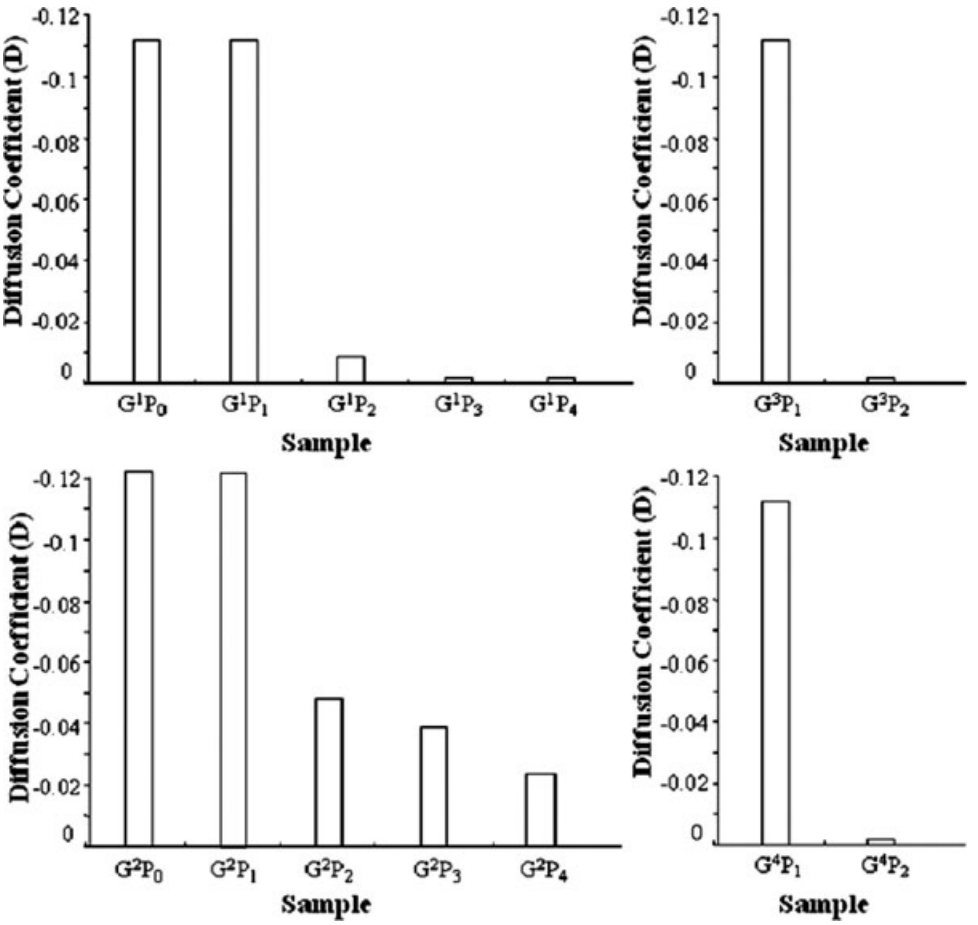

Figure 4 Diffusion coefficient (D) of crosslinked and control starch samples.

interval, and G ($= \partial H/\partial z$; where H is the magnetic field in the z direction) is the field gradient strength. A combination of the $\pi/2$ and π pulses, in a homogeneous static field, a spin-echo signal is observed at time $t = 2\tau$. The echo intensity $A(2\tau)$ decays exponentially with the variation of 2τ by T_2 effect and is expressed as:

$$A(2\tau) = A_0 \exp(-2\tau/T_2) \quad (1)$$

where A_0 is the intensity of the free induction decay at $t = 0$. Diffusion of given molecules in an inhomogeneous static field with the field gradient causes a spin-echo to decay as the time between the $\pi/2$ and π pulses is increased. For diffusion, following Fick's second law, the magnetization density M_z (r,t) corresponding to the signal intensity is expressed by:

$$\partial M_z/\partial t = D\partial^2 M_z/\partial^2 r \quad (2)$$

where D, r, and t are diffusion coefficient, displacement, and time, respectively. On the basis of this equation, in the inhomogeneous filed with the two gradient pulses, the spin-echo intensity A is given as:

$$A(\delta) = A(0) \exp[-\gamma^2 G^2 D\delta^2(\Delta - \delta/3) \quad (3)$$

$$\mathrm{Ln}[A(\delta)/A(0)] = -\gamma^2 G^2 D\delta^2(\Delta - \delta/3) \quad (4)$$

where $A(\delta)$ and $A(0)$ are the echo signal intensities at $t = 2\tau$ with the field gradient and without the field gradient, respectively, and γ is the magnetogyric ratio. As seen from eq. (4), plots of $\mathrm{Ln}[A(\delta)/A(0)]$ against $-\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ give straight lines with a slope of D. In these experiments, the τ, Δ, and δ values employed are 0.0008, 0.5, 0.005 s respectively. For convenience, the spin-echo signal in the time domain was Fourier-transformed to obtain the conventional spectrum in the frequency domain.

The self-diffusion coefficient measurements using the PFGSE method based on varying the gradient amplitude were undertaken for native (G^1P_0), pregel (G^2P_0), extruded native (G^1P_1), extruded pregel (G^2P_1), and their derivatives (G^1P_2, G^1P_3, G^2P_2, and G^2P_3). The results are shown in Figure 3. As seen in the figure, the log plot profiles for both native and nonmodified pregel starches were strikingly similar to their extruded counterparts, indicating no effect due to extrusion.

TABLE III
Average Density and Expansion Ratio of Crosslinked and Control Extrudates Containing Native and Pregel Starch

Sample	EPI (%)	SC-CO_2 (%)	ER	d_{av} (g/cm^3)
[Native starch (N): 100%]				
G^1P_1	0.00	0.00	1.65	1.352
	0.00	0.50	1.84	1.219
	0.00	1.00	2.04	0.589
G^1P_2	0.50	0.00	2.10	1.003
	0.50	0.50	2.39	0.885
	0.50	1.00	2.78	0.773
G^1P_3	1.00	0.00	1.58	1.110
	1.00	0.50	1.38	0.936
	1.00	1.00	1.28	1.177
G^1P_4	2.50	0.00	1.46	1.279
	2.50	0.50	1.31	1.392
	2.50	1.00	1.19	1.428
[Pregel starch (P): 100%]				
G^2P_1	0.00	0.00	2.93	0.422
	0.00	0.50	4.69	0.348
	0.00	1.00	6.49	0.226
G^2P_2	0.50	0.00	3.36	0.369
	0.50	0.50	6.61	0.307
	0.50	1.00	9.00	0.190
G^2P_3	1.00	0.00	3.71	0.294
	1.00	0.50	7.11	0.276
	1.00	1.00	9.58	0.158
G^2P_4	2.50	0.00	3.62	0.301
	2.50	0.50	8.32	0.265
	2.50	1.00	8.92	0.172
[Mix starch: 60% N + 40% P]				
G^2P_1	0.00	0.00	2.30	0.45
	0.00	1.00	3.21	0.33
G^2P_2	1.00	0.00	1.64	0.72
	1.00	1.00	1.58	0.44
[Mix starch: 40% N + 60% P]				
G^2P_1	0.00	0.00	2.69	0.89
	0.00	1.00	3.67	0.39
G^2P_2	1.00	0.00	2.11	1.20
	1.00	1.00	3.07	0.73

As the concentration of EPI was increased, the relative self-diffusion coefficient (D) decreased -rapidly, reaching a negligible value at EPI concentration higher than 0.5% in native starch, confirming good crosslinking. As the concentration of crosslinking agent was increased from 0.0% to 0.5% in the native starch, a 12.5 times drop of the diffusion coefficient value was observed. The D value of sample G^2P_4 was observed to be 2.5 times lower than that of G^2P_3. Since the pregelatinization starch is a soluble product than the native starch due to the physical destruction of its crystalline structure during manufacture, these values tend to confirm the results obtained by differential scanning calorimetry. It was found that (D) varies as function of the structure crystallinity of biopolymers and is lower with higher crosslinked biopolymers (Figure 4).

Using NMR to study the diffusion showed that the technique readily permits, within the limitations of the relaxation properties, the variation of the time scale over which the diffusion process in observed (D). This led to the conclusion that in the time scale considered by the experiment, the starch crosslinked acted as barrier restricting the diffusion process by means of specific molecular interactions (hydrogen bonding, ^1H exchange, etc.) and also by physical, steric obstructions hindering the translational mobility of the diffusion molecule.

Cellular structure of the extrudates

The average density (d_{av}) of the SCFX extrudates (Table III) 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 the nature of the starch (native or pregelatinized).

The addition of small concentration of EPI to the formulation reduced the density of the extrudates and increased the ER. According to the classical nucleation theory,[35] which has been successfully used to describe the kinetics of nucleation in polymer melts,[36] 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 to the native starch as well as pregelatinized starch during extrusion would tend to increase the viscosity of the melt due to crosslinking, and this would in turn lead to a lowering of the nucleation rate and the higher density 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. This effect might not very significant through, since most of the SC-CO_2 is dissolved in water.

The average cell size of various extrudates, shown in Table IV, ranged from 61 to 147 μm. In general, extrudates of pregelatinized (G^2P_1) without any EPI had larger average cell size indicating that crosslinking suppressed expansion.

TABLE IV
Enzyme Digestibility and Water Solubility of Native and Crosslinked Starches

Sample	α-Amylase degradation (D.O.)	Solubility (%)
G^1P_0	0.543 ± 0.11	37.98 ± 1.62
G^1P_1	0.689 ± 0.07	37.11 ± 2.09
G^1P_3	ND[a]	14.58 ± 3.11
G^2P_1	0.663 ± 0.11	78.01 ± 1.55
G^2P_3	0.216 ± 0.14	35.00 ± 3.01
G^3P_1	0.701 ± 0.13	41.99 ± 1.29
G^3P_2	ND[a]	16.80 ± 2.44
G^4P_1	0.653 ± 0.09	49.65 ± 2.71
G^4P_2	ND[a]	18.73 ± 1.98

[a] Not detectable.

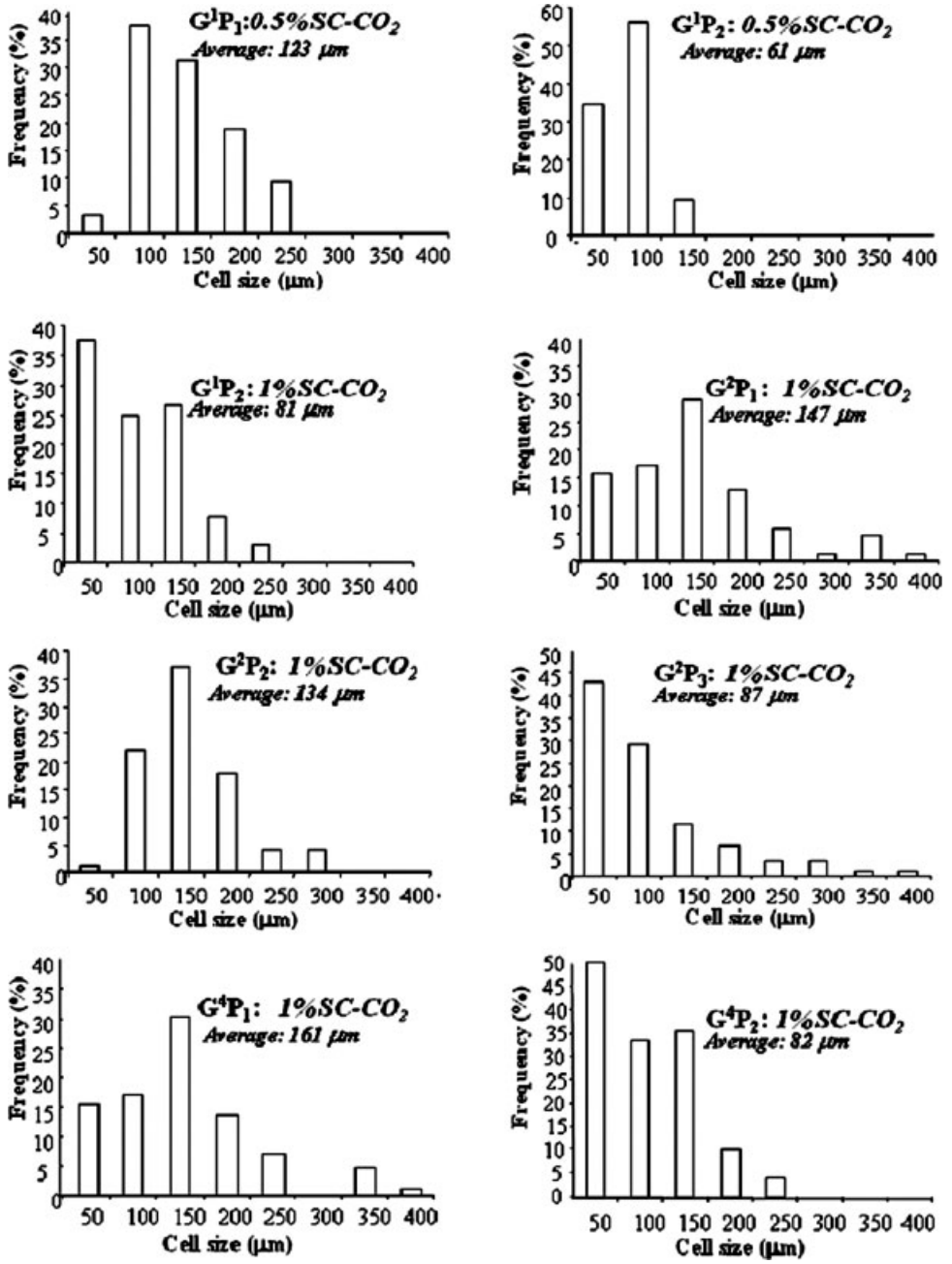

Figure 5 The cell distribution size of SCFX at different concentration of CO_2 and EPI.

For example, for sample (G^2P_3) the average cell size is 87 μm while for the sample (G^2P_1) with 0% of (EPI) the average cell size was 147 μm at the same SC-CO_2 level. Cells of SCFX extrudates modified with EPI were $\sim$ 2 times smaller than nonmodified, native, or pregelatinized. The cell size distribution index values of dried samples are shown in Figure 5. The control sample had a larger spread than extrudates with 1% EPI which indicated that crosslinking increased the uniformity of cellular structure. The cell size distribution of SCFX extrudates with EPI had a much narrower spread. The more uniform cellular structure of SCFX extrudates with EPI 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.[37] 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 sur-

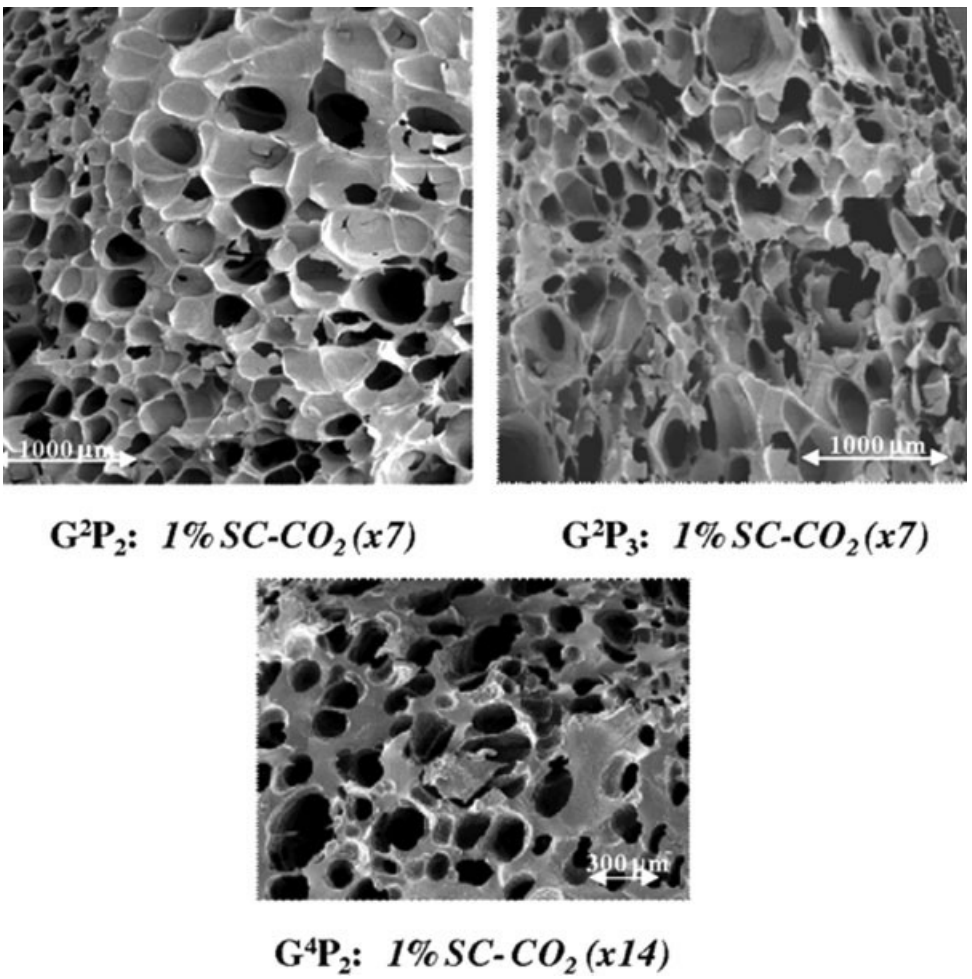

Figure 6 SEM micrographs of SCFX extrudates at different concentration of CO_2 and EPI.

rounding 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 (Figure 6). 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 non porous 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 non porous skin. The skin reduces water penetration and delays onset of water-related changes, which may be a desirable characteristic.

Enzyme digestibility and water solubility

The modified pregel-starches with low degree of crosslinking exhibited lower digestibilities when compared with native starch and their extrudates. However, there was a gradual decrease in the enzyme susceptibility of crosslinked starches with increase in degree of crosslinking (Table IV). The samples G^1P_3, G^3P_2, and G^4P_2 showed no-detectable enzyme digestibilities. The decrease in enzyme susceptibility of these samples could be attributed to the stabilization of starch granules through crosslinks which inhibits the action of α-amylase.

According to Huber and BeMiller,[38] the crosslinking of starch restricts the entrance of α-amylase through the channels that lead to the interior of cereal starches and therefore there was a decrease in the enzyme digestibility. The crosslinking has been reported to interfere with the formation of the α-amylase and starch complex and also restricts swelling and thus difficult to be hydrolyze by α-amylase.

However, the modified starches were insoluble in water at room temperature and as a result, solubility was determined at 60°C. In percentage, the G^1P_3, G^3P_2, and G^4P_2 having the considerable lower solubility index. The pregel show much greater solubility index than the native starch. The pregel has a more open structure which allows rapid water penetra-

tion. The solubility was considerably reduced by crosslinking. Crosslinking restricts of the granule swelling and will also lower solubility by increasing chain binding.

CONCLUSION

The starch microcellular foam is achieved by SCFX and crosslinker reagent EPI. The results indicate that the structure/chemistry of the starch material and the processing conditions can be controlled to produce particles with morphology and properties useful for light scattering applications.

Low shear and low temperature processing, and formation of products having a nonporous skin and a high degree of uniformity in their cell size distribution are some characteristics of SCFX. Morever, the SCFX process showed a high degree of control over the extrudate expansion and microstructure can be achieved by varying the rate of injection of SC-CO_2.

The addition of pregel starch and EPI have been found to enhance the uniform foam formation. The results indicates that the EPI proportion on the formulation significantly influence the physicochemical properties, the size, density, and morphology of the cells in the foam. In addition, the EPI is very beneficial for the increment of crosslinking degree and offers a means for reinforcing the granules to the extent where intact granules can be used as such under condition would swell granules of the native starch. The NMR results confirmed that a more important crosslinked step inducing a rigid structure could be expected when the amount of EPI used during the synthesis was more important.

These results indicate that the formation of the porous structure is a complicated function of starting material composition and processing conditions.

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