

# Development of Cross-Linked Starch Microcellular Foam by Solvent Exchange and Reactive Supercritical Fluid Extrusion

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Received 28 April 2008; accepted 8 August 2008

DOI 10.1002/app.29270

Published online 5 December 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Starch microcellular foams (SMCFs) are prepared by pore preserving drying or formation processes and contain pores in the micron size range. SMCFs have high specific surface area and are useful for applications such as opacifying pigments or as adsorbent materials. The objective of this research was to determine how the processing conditions and use of a crosslinking agent would affect the foam structure and properties. SMCFs (crosslinked and uncrosslinked) were prepared from molded aquagels and carbon dioxide extrusion processes separately and then solvent exchanged. Extruded samples showed macroscopic pores whereas samples from aquagels showed a much finer micropore structure. Aquagel-based SMCF samples had lower density and higher brightness than did extruded samples. The starch foams

with micropore structure had low density and high brightness. The solvent exchange process was the most important variable in generating a microcellular structure. Micropores and not macropores contributed to increased brightness of these materials. The brightness and density of the foams were found to be linearly related. Crosslinking with epichlorohydrin imparted significant water resistance to the extruded samples as evidenced in lower water swelling and higher contact angles. Equilibrium moisture content was correlated with the microporous structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2917–2929, 2009

**Key words:** biopolymers; density; foam extrusion; gels; hydrophilic polymers

## INTRODUCTION

Starch is an important agriculture product that is primarily derived from corn, potatoes, and wheat, in the United States.<sup>1</sup> In the raw state, starch is in the form of dense granules that range in size from 2 microns in wheat to over 100 microns in potato starch.<sup>2</sup> Granular starch is utilized in many food and nonfood products and is often chemically modified to further expand its uses.<sup>3,4</sup> The low cost and availability of starch in the market attracts researchers to develop new functional starch derivatives for industrial applications.<sup>1</sup> Starch granules are generally composed primarily of two glucose polymers: amylose (linear) and amylopectin (branched), with the largest portion being amylopectin (70–85%). How-

ever, starch granules from certain plant varieties are almost entirely amylopectin (98%) whereas others may contain 45–80% amylose.<sup>5</sup> Amylose is a polymer of (1-4)-linked  $\alpha$ -D-glycopyranosyl units with a molecular weight that varies depending on the source of the starch but is generally much smaller than that of amylopectin. Amylopectin has short branches on about 4% of the D-glycosyl residues.

Starch may be dissolved in water. When heat is applied to water and starch granule slurry, the granules initially swell. The amylose material in particular extends from the starch granules and forms a gel in the water phase.<sup>6–8</sup> Eventually, the initial starch granules completely dissolve in the water. If the water is removed in a normal drying process, large capillary forces act on the starch and collapse the polymer into low porosity material.<sup>7</sup>

Starch microcellular foams (SMCFs) are generally described as a starch-based porous matrix containing pores ranging from 2  $\mu$ m to submicrometer size.<sup>9–11</sup> Glenn and Stern<sup>9</sup> have prepared SMCF from rigid starch aquagels by exchanging the water with liquids possessing lower surface tension. The SMCF can be formed by equilibrating the aquagels of wheat and corn starch with ethanol. Subsequently,

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Contract grant sponsor: National Research Initiative of the USDA Cooperative State Research, Education and Extension Service; contract grant number: 2005-35504-16264.

the ethanol/starch mixtures are air dried to remove the ethanol. As the surface tension of the air/ethanol interface is one third that of air/water, weaker capillary forces exist when drying from ethanol relative to drying from water. The result is that the foam structure is preserved.<sup>12-15</sup>

Recently at Cornell University, a new, low-temperature and low-shear extrusion technology, called supercritical fluid extrusion (SCFX), has been developed. The technology involves reactive extrusion of starch-based matrices and injection of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a blowing agent to continuously produce microcellular extrudates.<sup>16</sup> SC-CO<sub>2</sub> is an environmentally sound replacement for toxic solvents generally used in the manufacture of plastics foams. The effects of process variables and formulation on native starch foam expansion, cell size, cell density, and mechanical properties have been studied and reported.<sup>17,18</sup> However, native starch foam is readily soluble in water, preventing its use in aqueous environments. Crosslinking by reactive extrusion and subsequent expansion by SC-CO<sub>2</sub> offers a novel approach to making expanded biodegradable products using a benign and green solvent in a continuous fashion.

A number of researchers<sup>19-22</sup> have explored the possibility of using dispersed and crosslinked starch granules as an organic filler. These researchers demonstrated that paper with starch fillers had better strength properties relative to paper with traditional inorganic fillers.<sup>23-26</sup> This was presumably because of the ability of the starch to hydrogen bond with cellulosic fibers, whereas the inorganic filler could not participate in hydrogen bonding. However, the starch fillers had inferior optical properties when compared with inorganic fillers. Recently, high brightness (93%) and surface area starch microcellular foam particles were prepared by solvent exchange with ethanol from dissolved corn starch crosslinked with glutaraldehyde.<sup>14,27,28</sup> The crosslinking was found to provide some structural integrity of the foam during exposure to pressure and/or moisture.<sup>29</sup>

The current research was undertaken to explore the production of starch microcellular foam using a combination of two technologies: (1) supercritical fluid extrusion (SCFX) and (2) solvent exchange. The first technology involves the extrusion of a starch/water mixture and the injection of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a blowing agent to generate a foam. The resulting extrudates were immersed in ethanol/water solutions of varying concentration and subjected to two different protocols to successively displace the water with ethanol. For comparison, aquagel samples of starch were prepared and SMCF was generated from the aquagel using a solvent exchange technique. The brightness, particle

size, void diameter, and surface area of the SMCFs were measured for all of the samples. This research is unique in that there has been no prior research using the combination of SCFX and a postextrusion solvent exchange process to form foams, the combination of which produces new, interesting structures. Also, this is the first report in which a direct comparison of SCFX, SCFX followed by solvent exchange, and aquagel solvent exchanged materials is reported.

## EXPERIMENTAL

### Materials

Corn starch used for aquagels was supplied by Cargill, USA (Cargill Gel 03420), consisting approximately of 25% amylose and 75% amylopectin. Anhydrous ethanol Fisher product Number A405<sup>F</sup>-4) was used for solvent exchanges. Epichlorohydrin (EPI) was purchased from Sigma (45327S).

### Starch cooking procedure for aquagel samples

A cooked starch solution was prepared by adding 24 g of corn starch to 276 g of deionized water in a three-necked round-bottom flask under continuous stirring (IKA-Werk, RW 16 Basic S1) with a crescent shaped paddle, at speed setting of 10 with three different levels of cooking condition. The first two conditions involved heating the starch slurries to 90°C and 95°C over a period of about 20 min. The third cooking condition consisted of heating the starch to 95°C over a period of about 20 min and then maintaining the temperature at 95°C for an additional 20 min. The cooked starch solution was allowed to cool to room temperature over a period of 1 h in shallow metal tray. Aquagels of cooked starch solutions were prepared by refrigerating the trays containing the gelatinized starch overnight at 5°C. This aquagel was used to make SMCF by the solvent exchange technique.

### Supercritical fluid extrusion of crosslinked starch: processing conditions and formulation

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 was used for extruding starch/water mixtures. The extruder was configured to operate at a screw speed of 120 rpm and feed rate of 35 kg/h. The moisture content of the feed starch/water mixture was maintained at 35% w/w. The temperatures of the extrudates at the die (diameter = 4.2 mm) were controlled to 70°C to prevent evaporation of epichlorohydrin and moisture in the feed by circulating water at 35 to 60°C through the jacketed extruder

barrel. The average specific mechanical energy was 65 kJ/kg. A pilot scale supercritical fluid system was used for injection SC-CO<sub>2</sub> at a constant flow rate ( $7.6 \times 10^{-5}$  kg/s) into the starch/water mixture through four valves located around the extruder barrel at a short distance from the nozzle exit. SC-CO<sub>2</sub> injection pressure was automatically maintained higher than pressure inside the barrel for a continuous SC-CO<sub>2</sub> flow into the starch/water mixture, at the desired rate (0 and 1% SC-CO<sub>2</sub>) and pressure (1100 and 1600 psi). Samples produced at Cornell University were stored in sealed plastic bags and shipped overnight in dry ice ( $T = 0^\circ\text{C}$ ) to NCSU. The moisture content of the samples was 32, 37, and 38% for extruded starch, extruded starch crosslinked with EPI, and extruded starch crosslinked with EPI with CO<sub>2</sub> samples, respectively. Samples were then subjected to solvent exchange processes as described above.

Corn starch was supplied by Cargill, USA, and sodium hydroxide (1%) was used as control formulation. One level of 0.5% on dry basis of the crosslinking reagent epichlorohydrin (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.

### SMCF preparation process

SMCF was produced by a solvent exchange technique. In this process, the higher surface tension solvent (water) is replaced with a lower surface tension solvent (ethanol), which produces SMCF from the aquagel of starch when dried. SMCF was produced by a *slow* exchange (solvent exchange was carried out at every 48 h with 40, 70, 90, 100, 100, and 100% ethanol) and a *fast* exchange (solvent exchange was carried out at every 48 h with 100, 100, and 100% ethanol) technique. During each exchange, the previous solvent was decanted from the SMCF and then replaced with fresh solvent. Each solvent exchange was carried out using an amount of solvent equal to approximately three times the weight of the initial aquagel. Once the solvent exchanges were completed, the samples were allowed to air dry in a 23°C and 50% relative humidity atmosphere.

### Characterization of SMCF

#### Scanning electron microscopy analysis

Morphological characterization of starch microcellular foam was performed on images captured by a scanning electron microscope (SEM), Hitachi s3200-N. The samples were coated with gold-palladium of 10 nm thickness to make the samples conductive at 200 milli Torr vacuum with Denton Vacuum Desk II instrument. The digital images obtained from the

SEM were characterized using image analysis software. Random areas of the samples were taken and all of the pores (more than 30 pores were measured for each sample) in the area were measured (Revolution Software, 4pi Analysis).

#### Thermogravimetric analysis

SMCF conditioned at 23°C and 50% relative humidity was subjected to TGA, (TGA Q500, TA Instruments) at a heating 10°C/min under nitrogen purge 40/60 mL/min of nitrogen in balance and sample flow. Mass loss at 100°C is assumed to be moisture. Initial moisture content of extruded starch samples was measured by drying in a conventional oven at 105°C until a constant mass was reached.

#### Brightness measurement

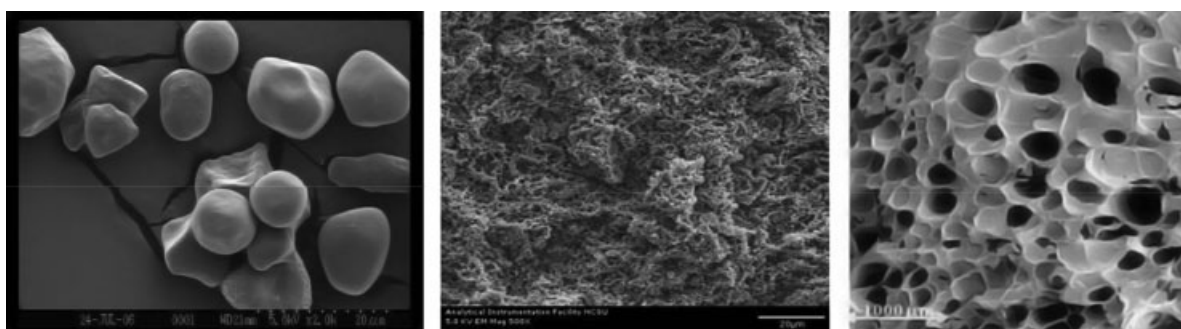
SMCF was crushed with mortar and pestle and the particles passing through a 20 mesh screen (850 micron opening) were collected and formed into a tablet. A Carver press (hydraulic unit model 3912, Carver, Wabash, IN) was used to make a 0.5 g tablet, dimensions of about 1.3–1.6 cm diameter and 0.3–0.5 cm thickness. One ton of force was applied for 1 min to make the tablet. The tablet brightness was measured with a Brightmeter Model S-5 (Technidyne, New Albany, IN). For each sample, tablet the brightness was measured twice on both sides and the average reported. The brightness is a measure of the sample reflectivity at 457 nm wavelength of light.

#### Density measurement

As all samples had irregular shapes, the densities of the samples were measured by weighing the sample alone and then weighing the sample immersed in uniform plastic beads (average diameter of 0.25 cm) in a graduated cylinder with a known total volume. The packing density of the beads was known from a plot of the volume of beads (cm<sup>3</sup>) versus mass of beads (grams), which resulted in a straight line relationship between mass and volume ( $\text{Volume} = 0.711 \times \text{Mass}$ ,  $R^2 = 0.99$ ). The slope is the inverse of the packing density of the beads, which was found to be 1.406 g/cc. The density of a sample was then determined by the following equation:

$$\begin{aligned} & \text{Volume of sample plus beads (cc)} \\ &= \frac{\text{Mass of bead (g)}}{\text{Density of bead (g/cc)}} + \frac{\text{Mass of sample (g)}}{\text{Density of sample (g/cc)}} \end{aligned} \quad (1)$$

For each sample, the measurement was taken six times (repacking the sample in beads each time) and the average and standard deviation reported.



**Figure 1** SEM images of uncooked starch (left) and SMCF by slow solvent exchange of molded starch cooked at 95°C (center) at  $\times 500$  magnification. Extruded starch with 0.5% EPI, 1% SC-CO<sub>2</sub>, 1600 psi (average cell size: 129  $\mu\text{m}$ ) (right).

#### Water swelling and mass loss measurement

Water swelling and mass loss of the SMCF was measured. In a sealed glass beaker, a known sample mass was placed into 25 mL of deionized water for 24 h at 23°C. After 24 h, the sample was filtered through preweighed wet qualitative Whatman filter paper (Product number 1004070) under conventional house vacuum for 60 s. The weight of the wet filter paper and sample was determined. The wet filter paper with sample was placed into an oven at 105°C for 1 h and then weighed again. The water swelling and mass loss of the SMCF was calculated as:

Water swelling of SMCF (g water absorbed

$$/\text{g of sample}) = \frac{d - (b \times a) - a - x}{x} \quad (2)$$

where:

*a*, Dry mass of filter paper (OD mass of filter paper);

*b*, Water retention value of filter paper (g/g)  
 $= \frac{\text{Weight of wet filter paper} - \text{Weight of oven dried filter paper}}{\text{Weight of oven dried filter paper}}$ ;

*c*, Initial mass of sample;

*d*, Wet mass of filter paper with sample;

*e*, Dry mass of filter paper with sample (OD mass of filter paper with sample); and

*x*, Mass of starch retained =  $e - a$

$$\% \text{ Mass loss} = \frac{c - x}{c} \times 100\% \quad (3)$$

#### Contact angle measurement

Contact angle measurements were performed with a NRL Contact Angle Goniometer by Rame Hart (model 100-00). A drop of deionized water (mass of approximately 35 mg) was placed on the surface of the starch rod or molded starch sample. The contact angle on two sides of the drop was measured immediately and the average reported. The contact angle

was then monitored every minute for 4 min. Two tests (drops) were conducted on each sample.

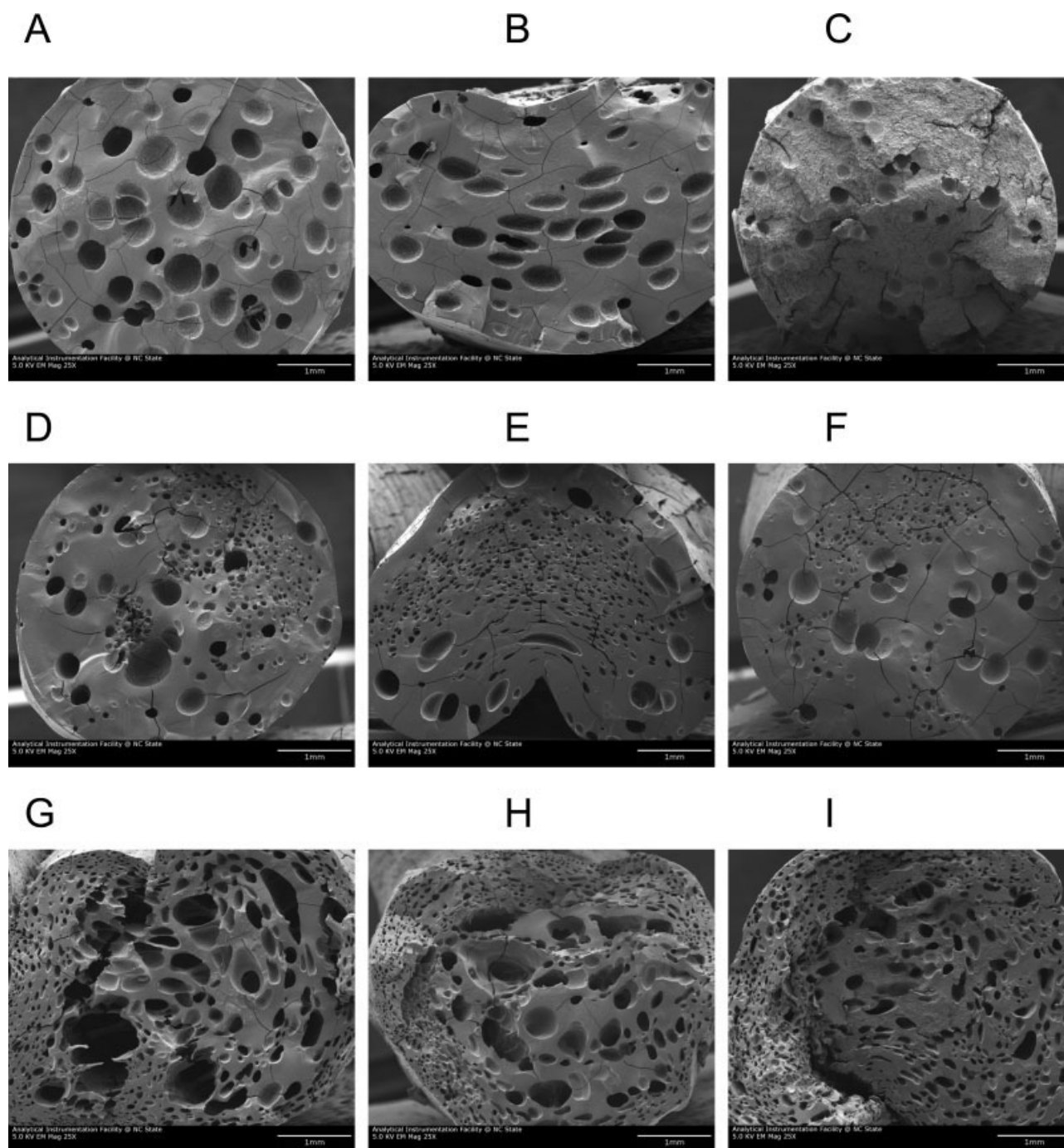
## RESULTS AND DISCUSSION

### SMCF morphology

The main purpose of this study was to investigate methods to create a low density SMCF with micropores less than 10  $\mu\text{m}$  in diameter. These materials typically have excellent light scattering properties. The SMCFs were produced by taking aquagels or extruded (never-dried) samples of the starch and exchanging the water with ethanol. SEM images of the uncooked starch and an example of the SMCF produced from an aquagel clearly show the increased porosity of the solvent exchanged materials, Figure 1. Also included is an image of CO<sub>2</sub> extruded starch material (not solvent exchanged) for comparison.

SMCFs were produced by solvent exchange of extruded starch, extruded starch crosslinked with EPI, and starch crosslinked with EPI extruded in presence of CO<sub>2</sub>. The extruded samples were solvent exchanged by a slow and a fast solvent exchange procedure, cf. Figure 2.

It is observed that the porous structure is impacted by the extrusion conditions and the solvent exchange conditions. The materials in Figure 2 all display large macro pores. Foams can be designated as either micro- or macrocellular foam according to the cell diameter or size, generally, macrocellular foams have low density and have large (around 100 to 1000  $\mu\text{m}$ ) cells with cell wall thickness ranging from 10 to 100  $\mu\text{m}$ , whereas microcellular foams have cell diameters or size less than 10  $\mu\text{m}$ . The pore diameter and the cell wall thickness for both the extruded and aquagel foams are listed in Table I. The extruded starch has a lower pore number concentration of macropores compared with the extruded starch crosslinked with EPI without and with CO<sub>2</sub>. The presence of CO<sub>2</sub> during extrusion of starch crosslinked with EPI caused an increase in the pore number concentration of the materials and



**Figure 2** SEM images of extruded starch – air dry (A), fast exchange (B), and slow exchange (C). Extruded starch crosslinked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch crosslinked with EPI with CO<sub>2</sub> – air dry (G), fast exchange (H), and slow exchange (I).

also the appearance of a bimodal pore size distribution. For the CO<sub>2</sub> assisted extrusion of starch crosslinked with EPI the larger pores were found to be mostly in the center of the extrudate whereas smaller pores tended to be toward the exterior of the extrudate. These macropores were not significantly altered by solvent exchange. However, the solvent exchange process produced micropores in only the slow exchanged extruded noncrosslinked starch

with an average pore diameter and cell wall thickness of about 300 nm [Fig. 3(C) and Table I] but not with any of the crosslinked starches, Figure 3(F,I) and Table I. It was expected that the slow exchange process was the most effective method to preserve pores in the structure when dried and the results in this study are in agreement. These extruded starch samples have macropores of similar diameter but a lower pore number density to Ayoub<sup>30</sup> in which

TABLE I  
Average Pore Diameter and Cell Wall Thickness

Sample	Ave. pore diameter (micrometer)		Ave. cell thickness (micrometer)	
	I	II	I	II
Extruded starch – Air dry	325		153	
Extruded starch – Fast exchange	293		151	
Extruded starch – Slow exchange	190	0.379	219	0.398
Extruded starch cross-linked with EPI – Air dry	132		103	
Extruded starch cross-linked with EPI – Fast exchange	85		69	
Extruded starch cross-linked with EPI – Slow exchange	77		57	
Extruded starch cross-linked with EPI with CO <sub>2</sub> – Air dry	127		66	
Extruded starch cross-linked with EPI with CO <sub>2</sub> – Fast exchange	125		41	
Extruded starch cross-linked with EPI with CO <sub>2</sub> – Slow exchange	82		3.9	
Aquagel – Starch cooked at 95°C – Fast exchange	2.7	0.172	2	0.163
Aquagel – Starch cooked at 95°C – Slow exchange	2.8	0.153	1.9	0.119
Aquagel – Starch cooked at 95°C for 20 min – Fast exchange	1.8	0.138	1.7	0.092
Aquagel – Starch cooked at 95°C for 20 min – Slow exchange	2	0.133	2	0.122

Note that, in some cases there is a bi-modal distribution of pores and thus the averages of both sizes of pores (labeled I and II) are listed.

wheat starch samples were extruded under similar conditions but air dried. This study shows that for extruded samples, that by using an ethanol exchange prior to air drying that the pore size and cell wall thickness can be decreased. Other researchers Xu and Hanna<sup>31</sup> have also shown that extruding in ethanol rather than water produces starch-based foams that have smaller pore and pore wall sizes and increased uniformity, in agreement with our observations on the effects of ethanol exchange on structure.

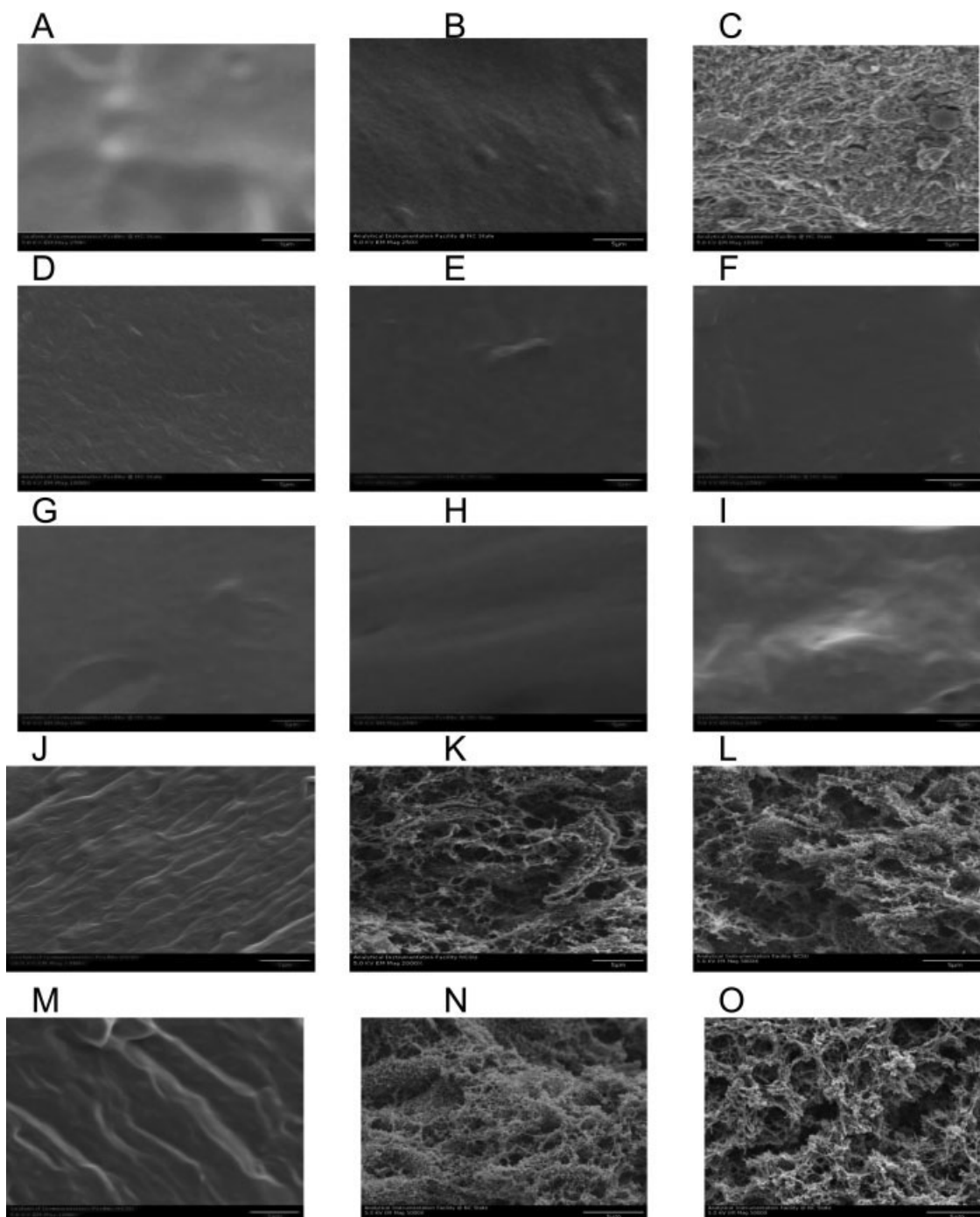
SMCFs formed from corn starch aquagels only exhibited a micropore structure, Figure 3(K,L,N,O). Listed in Table I are the average pore diameters and pore wall thickness for both the fast and slow solvent exchange processes. A bi-modal pore structure was observed for these samples. The average pore diameter and cell wall thickness for the finer pores was similar for both exchange processes,  $\sim 0.15$  and  $\sim 0.12$  microns, respectively. The larger pore distribution of these samples was independent of exchange processes, with pores in the range of approximately 2–3 microns.

In our previous studies,<sup>14,25</sup> SMCF particles were produced by introducing cooked starch solutions into a bath of ethanol under shear and pore sizes were determined from SEM images of the particle surfaces. Average pore diameters from 0.2 to about 1 micron were determined in that study. The pore size could be adjusted via changes in crosslink concentration and starch molecular weight. In comparison with those studies, the pore diameters generated in these aquagel molded samples were generally smaller and qualitatively more uniform, similar to SMCF molded materials generated by Glenn and Irving.<sup>11</sup>

## Density

The density of the starch materials was measured as another way to characterize the foam materials, Table II. For the extruded samples, in general, the density decreased significantly with the use of the slow solvent exchange processes relative to the air dried samples. The samples subjected to the fast solvent exchange did not show a consistent density decrease relative to the air dried samples. Visual observations also indicated a significant difference in the materials' structures. The extruded fast exchange samples had a similar clarity and yellowish-gray color as the air dried samples. In contrast, the slow exchanged samples were whiter and more opaque compared with the air dried samples, Figure 4(a,b). The densities determined in this study are similar to those in a previous study with carbon dioxide assisted extruded wheat starches air dried.<sup>30</sup> Neither crosslinking nor extrusion with carbon dioxide significantly affected the density relative to the extruded samples in this study under the extrusion conditions studied.

For the samples formed from aquagels, the air dried samples had a density of about 1 g/cm<sup>3</sup>, cf. Table II. These samples were solid and translucent compared with the solvent dried samples. The fast and slow solvent exchange materials showed a  $\sim 40$ – $60\%$  decrease in density relative to the air dried samples, cf. Table II. Both the fast and slow exchanged materials displayed an opaque white appearance in contrast to the yellowish, somewhat clear air dried materials, Figure 4. The effect of the extent of cooking on the density of the resulting materials was much less important than if the samples were air dried or solvent exchanged before



**Figure 3** SEM images of extruded starch – air dry (A), fast exchange (B), and slow exchange (C). Extruded starch cross-linked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch crosslinked with EPI with CO<sub>2</sub> – air dry (G), fast exchange (H), and slow exchange (I). Starch cooked at 95°C – air dry (J), fast exchange (K), and slow exchange (L). Starch cooked at 95°C for 20 min – air dry (M), fast exchange (N), and slow exchange (O), respectively, on 5 μm length scale.

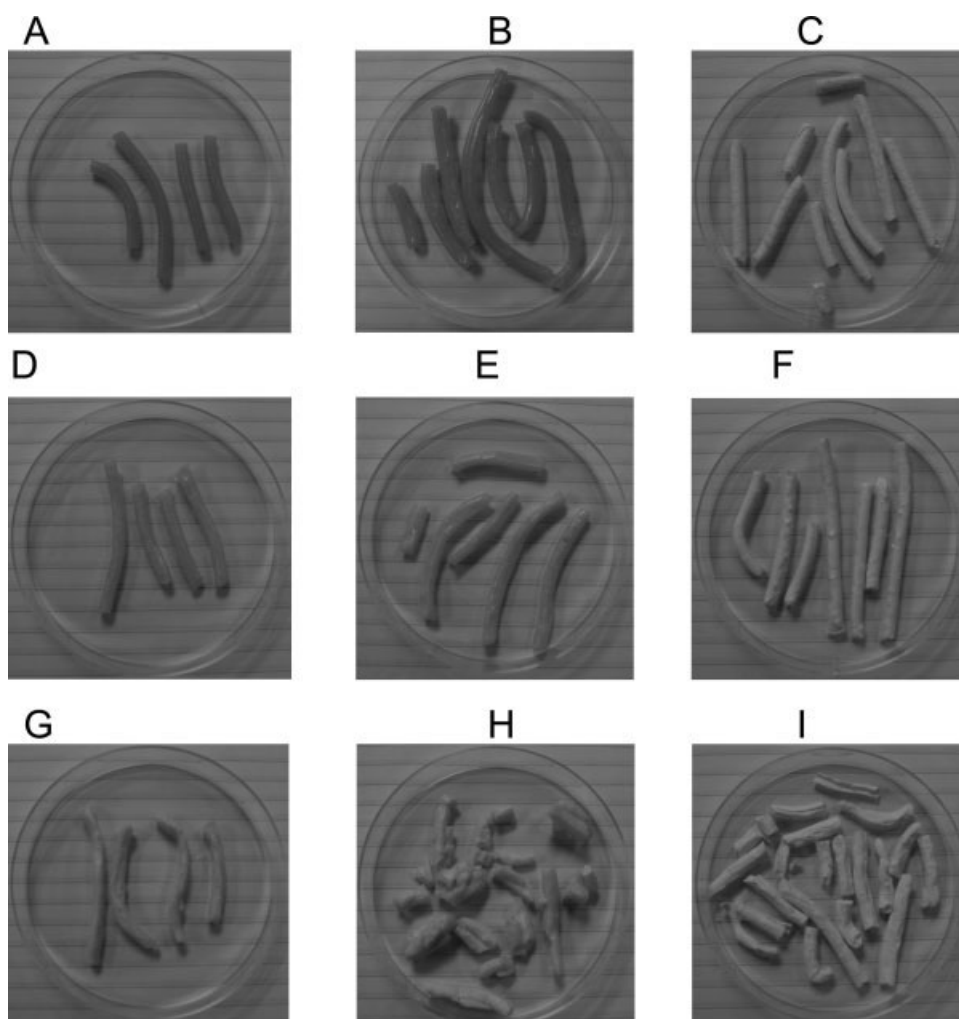
drying. The densities for ethanol exchanged aquagel samples were around 0.39 g/cc, which is slightly higher than those found by Glenn,<sup>11</sup> and for ethanol exchanged corn starch aquagel samples with minimum density of 0.25 g/cc.

#### Brightness

It was expected that the brightness of the SMCF samples will be related to the pore volume of the materials. Most specifically, there should be a strong

**TABLE II**  
**Density and Calculated Pore Volume Fraction of Starch Samples**

Sample	Type of exchange	Average density (g/cc)	Standard deviation	Pore volume fraction (%)
Extruded starch	Air dry	0.71	0.02	34
Extruded starch	Fast exchange	0.85	0.03	20
Extruded starch	Slow exchange	0.56	0.01	48
Extruded starch cross linked with EPI	Air dry	0.93	0.04	13
Extruded starch cross linked with EPI	Fast exchange	0.92	0.01	14
Extruded starch cross linked with EPI	Slow exchange	0.59	0.01	45
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Air dry	0.91	0.01	16
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Fast exchange	0.67	0.004	37
Extruded starch cross linked with EPI in presence of CO <sub>2</sub>	Slow exchange	0.58	0.003	46
Aquagel – Starch cooked at 90°C	Air dry	1.07	0.09	0
Aquagel – Starch cooked at 90°C	Fast exchange	0.39	0.02	64
Aquagel – Starch cooked at 90°C	Slow exchange	0.53	0.02	50
Aquagel – Starch cooked at 95°C	Air dry	1.05	0.06	2
Aquagel – Starch cooked at 95°C	Fast exchange	0.45	0.02	58
Aquagel – Starch cooked at 95°C	Slow exchange	0.53	0.008	51
Aquagel – Starch cooked at 95°C for 20 min	Air dry	1.06	0.03	2
Aquagel – Starch cooked at 95°C for 20 minutes	Fast exchange	0.59	0.02	45
Aquagel – Starch cooked at 95°C for 20 min	Slow exchange	0.51	0.005	52



**Figure 4** (a) Extruded starch – air dry (A), fast exchange (B), and slow exchange (C). Extruded starch crosslinked with EPI – air dry (D), fast exchange (E), and slow exchange (F). Extruded starch crosslinked with EPI with CO<sub>2</sub> – air dry (G), fast exchange (H), and slow exchange (I), respectively. (b) Starch cooked at 90°C – air dry (J), fast exchange (K), and slow exchange (L). Starch cooked at 95°C – air dry (M), fast exchange (N), and slow exchange (O). Starch cooked at 95°C for 20 min – air dry (P), Fast exchange (Q), and slow exchange (R), respectively.



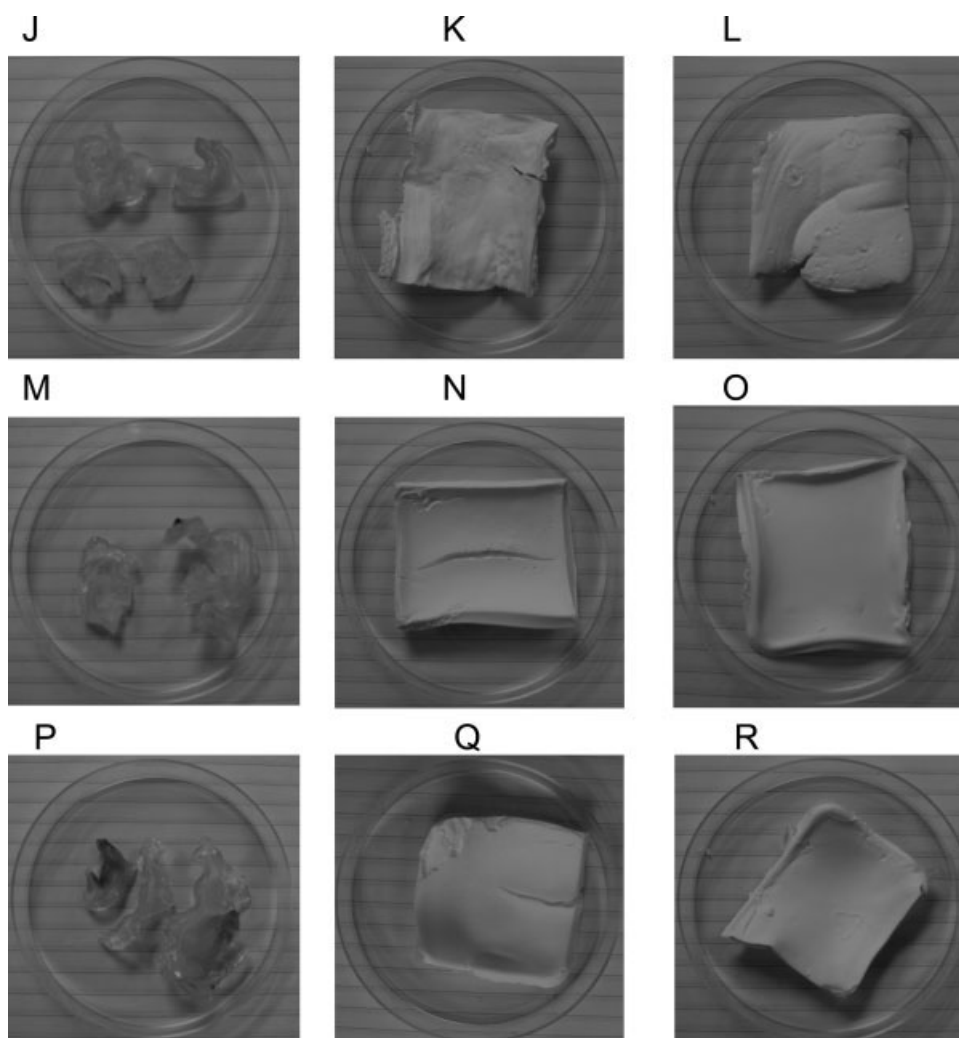


Figure 4 (Continued from the previous page)

relationship between micropore volume and the brightness. In general, structures with high micropore volume visually had higher brightness, see Figures 3 and 4. The brightness measurements of particles ground from the samples and pressed into pellets are presented in Figure 5. The standard deviation for the brightness measurements on a single sample pellet was 0.973%. For the extruded samples, slow exchange samples had a significantly higher brightness than did fast exchange samples. For aquagel samples, fast versus slow exchange did not alter the brightness significantly. A somewhat linear correlation exists between the brightness and the density of the materials, Figure 6. As expected, the solvent exchanged materials that have highly porous microstructure display the highest brightness. The existence of crosslinker or CO<sub>2</sub> during extrusion or the different cooking levels during preparation of aquagel samples is not as significant as the sample density. Data from both aquagel and extruded samples all fall on the same brightness versus density line in Figure 6, indicating the processing method is

not as important as the final density in determining brightness. In previous research, a maximum brightness for fine precipitated SMCF particles of around 96% ISO was determined,<sup>14,23</sup> whereas in this study with molded aquagel samples a maximum

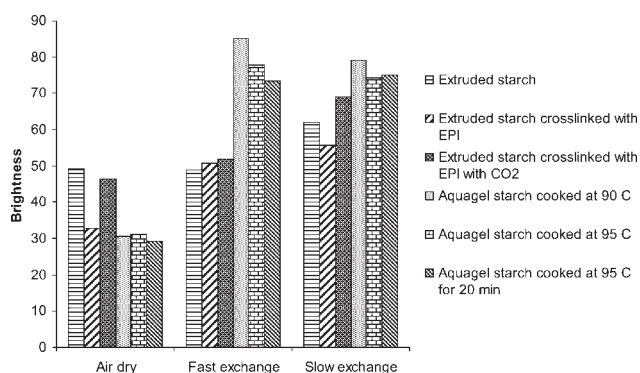
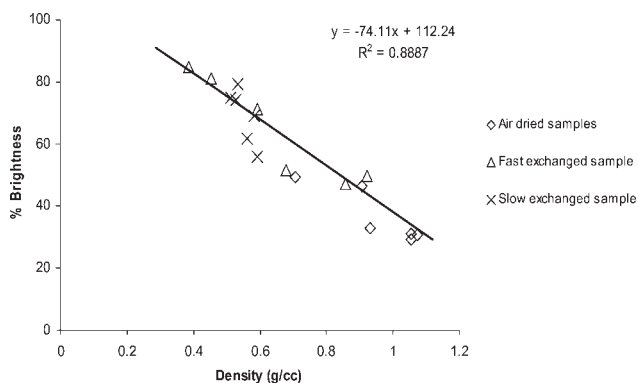


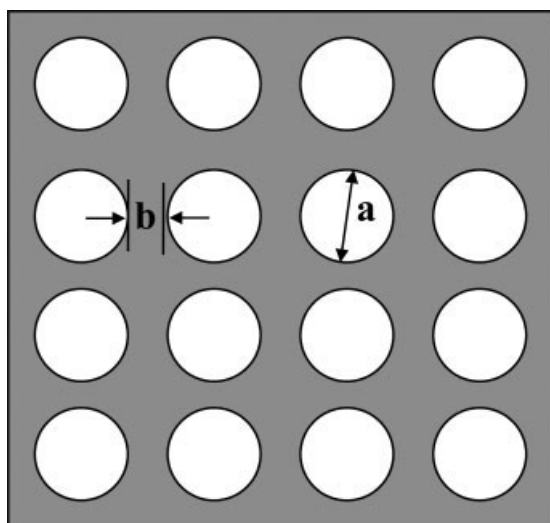
Figure 5 Percent brightness of starch materials. Note that in general solvent exchange samples exhibited higher brightness.



**Figure 6** Correlation between brightness and density of starch materials. Note the near linear relation between brightness and density of starch materials.

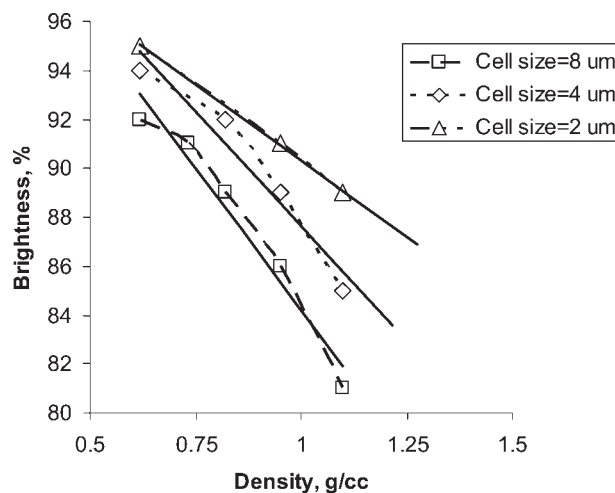
brightness of only 86% ISO was determined. This may be due to the differences in the particle diameters, as shown to be important in determining the brightness.<sup>14</sup> Also, differences in sample preparation for the brightness measurement could affect the measured brightness.

If one assumes that starch foam is essentially air voids within a continuous matrix, a simple model can be generated for the foam structure, cf. Figure 7. In this model, the air voids are considered round pores within a continuous matrix of starch. Considering the three dimensional nature of the material and assuming the density of the cell wall remains constant, then the density of the starch foam can be simply calculated by accounting for the voids within the starch matrix. The result is that a foam structure is specified by its cell wall thickness and void diameter. Using this model, the minimum possible den-



$a$  = cell diameter  
 $b$  = minimum cell wall thickness

**Figure 7** Model of the foam structure.

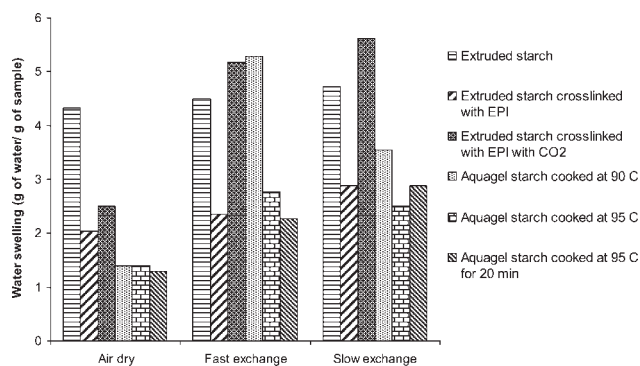


**Figure 8** Correlation between density and brightness from Kubelka-Munk theory. Note that the existence of relationship for a given pore cell size, when the density is varied by changing the cell wall thickness. Solid lines are best-fit straight lines of the simulation results.

sity for a starch foam would be when the wall thickness goes to zero. The resulting minimum density, assuming the cell wall density is 1.3 g/cc, is 0.62 g/cc for this packing geometry. The overall minimum packing density of monodispersed spherical pores in the starch matrix is 0.338 g/cc with the pores arranged in a closed packing geometry. The relationship between density and brightness can be modeled using known optical theories. Using these inputs into a Mie theory<sup>32</sup> computational program, the specific scattering coefficient of the Kubelka-Munk<sup>33</sup> theory can be determined. This can then be used in the Kubelka-Munk theory to determine the brightness of the material. The end result is a relationship between density and brightness as shown in Figure 8. It is worth noting the relationship exists for a given pore cell size, when the density is varied by changing the cell wall thickness. As the density of the material approaches the density of the cell wall material, the relationship between the density and brightness becomes nonlinear. This model is in agreement with our findings that the brightness and the density are somewhat linearly related.

#### Water swelling and mass loss

The dry structure of the starch microcellular foam is desired to be maintained when immersed in water or subjected to high humidity environments. To investigate, the foams were soaked in for 24 h (no stirring). After this soaking, the water swelling and mass loss were measured. The solvent exchanged aquagel samples all initially floated on the surface of the water, but settled to the bottom of the container after a time period of approximately 5–6 h. Air dried



**Figure 9** Water swelling (g of water/g of sample) of starch samples after 24 h of immersion. Note in general increase in water swelling of starch materials with solvent exchange processes.

aquagel samples settled to the bottom immediately. Solvent exchanged extruded samples settled after 0–20 min except for the extruded starch crosslinked with EPI with CO<sub>2</sub> (fast and slow) solvent exchanged, which took almost 8 h to settle. Air dried EPI with CO<sub>2</sub> samples took approximately 2 h to settle, in contrast to all other air dried samples, which settled in approximately 1 min. These settling times indicate that crosslinking of the starch prevented water penetration through the thick pore walls of the extruded samples. Generally, it is expected that SMCF microporous structures with higher pore volume and thinner pore walls should increase water swelling. If the starch material is soluble, then a higher specific surface area would be expected to increase the rate of mass loss.

The swelling of extruded starch was about 4.5 g of water per gram of starch and this was not significantly affected by solvent exchange, Figure 9. The extruded crosslinked samples showed a significantly lower swelling than for the extruded starch alone. This is in agreement with previous work showing that increased crosslinking of starch with EPI decreases the water diffusion in the starch.<sup>30</sup> The crosslinked and CO<sub>2</sub> extruded samples were the only extruded samples that showed a significant increase in the water swelling for solvent exchanged extruded samples relative to the corresponding air dried sample.

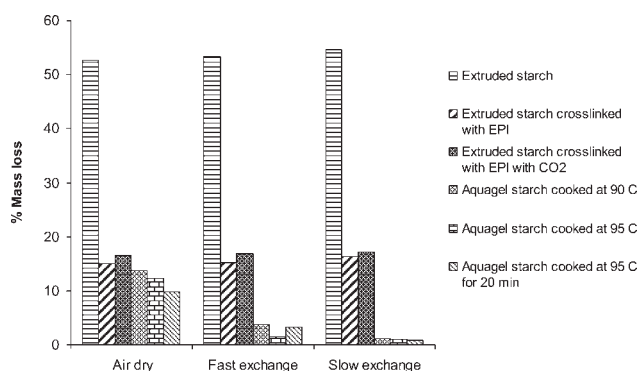
For the aquagel samples, the air dried samples showed the lowest swelling of about 1.2 g/g. The slow and fast solvent exchanged aquagel samples showed about twice the swelling as the corresponding air dried sample. There seems to be an approximate trend that increased cooking decreases the swelling, although more data is required to confirm this relationship. The swelling of the samples was plotted versus density but displayed no correlation, data not shown.

Mass loss of the crosslinked extruded samples during the swelling experiments were approximately 15%, which is much less than the over 50% mass loss for the uncrosslinked extruded samples, Figure 10. This indicates that the crosslinking inhibited the dissolution of the starch in extruded samples as would be expected. Unexpectedly, for the aquagel samples, the air dried materials showed approximately 10% mass loss whereas the solvent exchanged materials showed about 1% mass loss. It was expected that higher pore volume would promote more dissolution of the starch foams, but this was not the case.

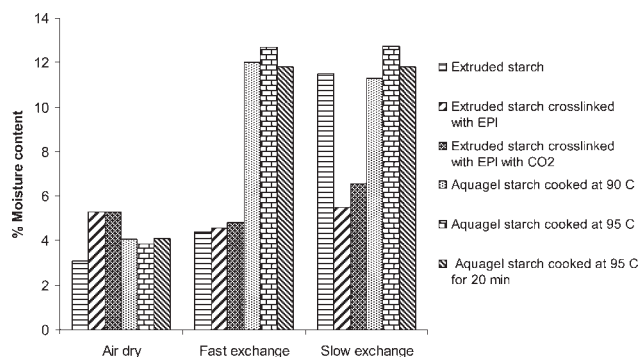
### Moisture content and thermal degradation

Thermal degradation and adsorbed moisture were observed by TGA, on samples that were conditioned at 23°C and 50% relative humidity. All samples showed similar trends of thermal degradation, data not shown. The indication is that the extent of crosslinking occurring in the EPI containing samples does not affect measurably the thermal degradation process.

Mass loss at 100°C was considered mainly due to the removal of water associated with the sample, which was considered as the moisture content of the sample, Figure 11. The solvent exchanged aquagel samples showed significantly higher moisture content compared with air dried samples, which can be attributed to the microporous structure of the solvent exchanged materials. The solvent exchanged aquagel samples showed a similar moisture content as SMCF particles produced with or without crosslinking in previous research.<sup>14,23</sup> Of the extruded starch samples, the extruded slow exchanged sample showed significantly higher moisture content, 11.5%,



**Figure 10** Percent mass loss of starch samples after immersion in water for 24 h. Note that there was no significance difference in mass loss of extruded samples for solvent exchange processes; however, aquagel samples showed decrease in mass loss with solvent exchange processes.



**Figure 11** Percent moisture content of starch samples. Note in general the increase in moisture content with solvent exchange.

relative to all other extruded samples. This is in agreement with the observations that this sample was the only extruded one that demonstrated a well formed microporous structure. This sample also had the lowest density and the highest brightness among the extruded samples. These results indicate that moisture content is sensitive to the microporous structure of the materials.

### Water contact angle

Contact angles of water on starch samples were determined as a function of time for all extruded

and aquagel samples, Table III. The contact angle of extruded starch, extruded starch crosslinked with EPI with, and without CO<sub>2</sub> for air dried samples were 51, 60, and 72° respectively, at the beginning of measurement. For the aquagel samples, the contact angle values of the air dried samples were all around 45°, independent of cooking conditions.

All samples, except for crosslinked samples, had a decreasing contact angle with time. Crosslinking caused the water drop to not absorb into the starch; the contact angle was observed to be approximately constant with respect to time for crosslinked samples. This is in agreement with previous research showing a decrease in water diffusion with increased EPI crosslinking of starch foams.<sup>30</sup> The aquagel samples showed a rapid decrease in contact angle compared with extruded samples. At 4 min of contact time, the water drop was completely absorbed into the aquagel samples. The slow exchanged extruded starch (the only extruded starch with microporous structure) also had rapid water drop absorption similar to the solvent exchanged aquagel samples, indicating that the microporous structure accelerates the absorption of water into the material. In previous work, the addition of a reactive wax (Alkyl Ketene Dimer) with the starch demonstrated that small amounts of the wax could increase the contact angle to approximately 90 degrees.<sup>14,23</sup> This indicates that the combination of crosslinking and blending or coating with a hydrophobic

**TABLE III**  
Contact Angle of Water on Starch Materials

Sample	Contact angle (°), at start	Contact angle (°), at 1 min	Contact angle (°), at 2 min	Contact angle (°), at 3 min	Contact angle (°), at 4 min	% Decrease in contact angle
Extruded starch – Air dry	51	48	45	45	45	12
Extruded starch – Fast exchange	46	45	44	36	35	24
Extruded starch – Slow exchange	31	17	0	0	0	100
Extruded starch cross-linked with EPI – Air dry	60	58	58	57	57	5
Extruded starch cross-linked with EPI – Fast exchange	63	63	61	60	60	4
Extruded starch cross-linked with EPI – Slow exchange	82	80	80	80	80	2
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Air dry	72	71	71	71	71	1
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Fast exchange	71	70	69	69	68	4
Extruded starch cross-linked with EPI in presence of CO <sub>2</sub> – Slow exchange	72	72	70	70	69	4
Aquagel starch cooked at 90°C – Air dry	45	35	20	0	0	100
Aquagel starch cooked at 90°C – Fast exchange	26	16	0	0	0	100
Aquagel starch cooked at 90°C – Slow exchange	26	15	0	0	0	100
Aquagel starch cooked at 95°C – Air dry	47	33	23	8	0	100
Aquagel starch cooked at 95°C – Fast exchange	39	29	21	10	0	100
Aquagel starch cooked at 95°C – Slow exchange	42	30	17	10	0	100
Aquagel starch cooked at 95°C for 20 minute-Air dry	47	35	28	10	0	100
Aquagel starch cooked at 95°C for 20 minutes – Fast exchange	30	25	14	0	0	100
Aquagel starch cooked at 95°C for 20 minutes – Slow exchange	30	19	8	0	0	100

component would be a strong method to improve water resistance in SMCF materials.

### CONCLUSIONS

Starch-based microcellular foam with porous structure were produced with a solvent exchange process. The starch foams which showed existence of micro pore structure had low density and high brightness. The solvent exchange was much more important in generating a microcellular structure than extrusion versus aquagel, existence of crosslinking, existence of CO<sub>2</sub> during extrusion, and cooking extent. Micropores and not macropores contributed to increased brightness of these materials. Brightness and density of the foams were found to be linearly related. The crosslinking with EPI imparted significant water resistance to the extruded samples. Moisture content was a better predictor of microporous structure than water swelling.

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