Structural properties of protein-stabilized starch-based supercritical fluid extrudates

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Abstract

Supercritical fluid extrusion, a low temperature and low shear process, was used to produce pre-gelatinized corn and potato starch-based extrudates, containing 4–10% thermosetting egg white (EW) or whey protein concentrate (WPC-34), and dried at 22–100°C. Addition of proteins reduced shrinkage of high-moisture extrudates, as indicated by increases in expansion ratio by up to 140 and 341% when the drying temperatures were 22 and 100°C, respectively. Products containing 7% EW or WPC-34 and dried at 85°C expanded best while maintaining an intact structure, with expansion ratio (~12) and bulk density (~0.10 g/cm³) comparable to steam extrudates. The products had a unique composite and uniform microcellular structure, with average cell sizes in the range of 50-250 μm and cell density of the order of 10⁶ cells/cm³. The classical nucleation theory and a qualitative model for cell growth and shrinkage based on glass transition temperature were used to explain the microcellular structure.

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Keywords: Supercritical fluid extrusion; Starch extrudates; Shrinkage; Microcellular structure; Classical nucleation theory

1. Introduction

Thermoplastic extrusion is a widely used industrial technology for continuous production of expanded products like breakfast cereal and snack foods. Except for a few improvements, extrusion technology for food products has remained essentially unchanged. The conventional method of steam puffing involves high temperatures (130–170°C) and shear, and low moisture contents (13–20%) (Chinnaswamy & Hanna, 1988; Harper & Tribelhorn, 1992). These extreme conditions prevalent during steam extrusion prevent utilization of heat sensitive ingredients such as whey proteins, and certain flavors and colors. Other disadvantages of high shear and temperature include costly barrel and screw wear, production of undesirable dextrins, increased losses in vitamin and amino acid availability and starch degradation which increases the water solubility of extrudates (Hauck & Huber, 1989; Kirby, Ollett, Parker & Smith, 1988). Typically, steam-expanded products have a coarse and very non-uniform cellular structure (Barrett & Peleg, 1992) with cell sizes in the range of 1–3 mm and expansion ratios in the range of 9–12 (Table 1). Moreover, there is little or no control over cell size and density. The importance of exploring new approaches, applying them effectively to overcome limitations of the present process, and producing new generations of foods with improved characteristics have been recognized in recent years and several attempts have been made in this direction.

Ferdinand, Lai-Fook, Ollet, Smith and Clark (1990) studied structure formation in maize grits, wheat starch, and dehydrated potato granules, in the absence of steam expansion, by injecting low pressure (1–5 MPa) gaseous CO₂ into the extruder. This process created somewhat porous extrudates at temperatures below 100°C, but the product did not have the highly expanded structure typical of conventional steam expansion.

Rizvi and Mulvaney (1992) patented a new extrusion technology for production of highly expanded starch foams in which carbon dioxide, above its critical pressure (7.38 MPa) and temperature (31°C), is used as a blowing agent, a nutrient carrier and, if necessary, an in-line process modifier. In this high pressure, low temperature process, the conventional roles of water as a plasticizer as well as a blowing agent are decoupled. As
supercritical fluid extrusion (SCFX) obviates the need for steam expansion, reduced shear and low product temperatures (<100°C) become attainable, which offer major advantages over steam puffing. As opposed to simple gas injection in the process described by Ferdinand et al. (1990), the SCFX process consists of the following major steps (Mulvaney & Rizvi, 1993; Rizvi, Mulvaney & Sokhey 1995): (a) development of gas holding rheological properties in the feed by gelatinization and/or mixing, and subsequent cooling to below 100°C, if necessary, (b) injection of SC-CO₂, loaded with solutes if desired, into the melt or dough, and adequate mixing to create a single phase system within the extruder barrel, (c) nucleation of cells induced and controlled by the thermodynamic instability created by a sudden pressure drop, and (d) cell growth and expansion of the extrudate at the die exit as the pressure quenches to atmospheric level, and setting of the extrudates during post-extrusion drying.

A distinguishing feature of the SCFX process is that the amount of dissolved supercritical carbon dioxide (SC-CO₂) and the rate of pressure drop can be manipulated by adjusting the operating conditions and thereby the cell size, cellular density and product expansion can be varied to produce novel products having a wide range of mechanical properties. This has also been shown in the extrusion processing of microcellular polymer foams (Baldwin, Park & Suh, 1996). Moreover, a greater uniformity in the cellular structure of starch extrudates can be obtained by the SCFX process as compared to steam extrusion.

One of the ways for keeping the product temperature below 100°C and preventing formation of steam during extrusion is to increase the moisture content of the starch melt, thus reducing the viscous dissipation of heat. This approach was utilized in the past (Ferdinand, Clark & Smith, 1992; Ferdinand et al., 1990; Sokhey, Rizvi & Mulvaney, 1996), but resulted in shrinkage of the expanded extrudates due to the glass transition temperature (Tg) of the product being much lower than the product temperature at the die. This shrinkage can be reduced by addition of thermosetting proteins to the formulation that would impart rigidity to the extrudates upon gelling. Besides improving the expansion of the product, the addition of proteins would also increase its nutritive value. Sokhey et al. (1996) observed that whey protein isolate (WPI) and non-fat dry milk (NFDM) added at concentrations of 5% to a cereal formulation (90.25% corn meal, 8% sugar, 1% salt, and 0.75% soda) helped in reducing the shrinkage of high moisture SCFX extrudates.

A systematic investigation is needed to quantify the effect of different types and concentrations of proteins on the stabilization of SCFX extrudates, and this was the primary objective of this study for which egg white (EW) and whey protein concentrate (WPC) were the two chosen proteins. EW proteins consist mainly of ovalbumin, conalbumin, ovomucoid and lysozyme, which gel in the temperature range of 57.3–81.5°C (Yang & Baldwin, 1995). The WPC proteins consist of mainly α-lactalbumin and β-lactalbumin, and a smaller proportion of bovine serum albumin and immunoglobulins, and these proteins gel in the range of 59–82°C (Aguilera, 1995). During SCFX processing, if the product temperature near the die exit is maintained in the range of 60–65°C, both WPC and EW in the formulation would be only partially gelled at the die, imparting some rigidity to the extrudates. Further gelation of proteins and lowering of Tg during the drying phase would set the extrudate structure and provide a stable internal morphology. To summarize, the present study was undertaken to quantify the effect of different levels of egg white (EW) and 34% protein containing whey protein concentrate (WPC-34) on the expansion characteristics and cellular structure of starch-based SCFX extrudates. Moreover, since post-extrusion drying is an important step in the production of extrudates, the effects of different drying temperatures on expansion and cellular structure were also studied. Cellular characteristics such as cell size, uniformity of cell size distribution and cell density were quantified using scanning electron microscopy (SEM).

2. Materials and methods

2.1. Experimental design and feed formulation

A mixture of pre-gelatinized corn starch (49.5%) (Cerestar, Hammond, IN), pre-gelatinized potato starch (24%) (Resitol, Decatur, IL), sugar (24%), salt (1%) and a dough conditioner (distilled monoglyceride, 1.5%) (Davisco, New Century, KS) was used as the control formulation. EW solids (~86% proteins) (Papetti’s, Elizabeth, NJ) or WPC-34 (34% proteins) (Mid-American Dairymen, Inc., MO) were added at three levels (4, 7 and 10% on dry basis) and the extrudate drying temperature (22,
70, 85 and 100°C) was varied in a 2×4×4 factorial experimental design. In-barrel moisture content of the starch melt was maintained at about 35% on wet basis by injecting water in the extruder barrel.

2.2. Operating conditions

A Wenger TX-52 (Wenger Manufacturing, Sabetha, KS) co-rotating twin-screw extruder with 9 heads, a barrel diameter of 52 mm, and length to diameter ratio (L/D) of 27:1 was configured to operate at a screw speed of 100 rpm and feed rate of 9.88×10⁻³ kg/s (35.58 kg/h). The average specific mechanical energy (SME) was 50 kJ/kg. The extruder parameters, feed formulation, and operating conditions are summarized in Table 2.

2.2.1. Extruder barrel temperatures

Barrel temperature in all the heads, except the first, third and fourth heads (which were neither cooled nor heated), was maintained at around 40°C by circulating chilled brine (−10°C) through the barrel jackets. Since pre-gelatinized starches were used, heating to gelatinization temperatures was not necessary. The extruder parameters and moisture content of the feed was adjusted to maintain the product temperature at about 60°C at the die exit.

2.2.2. Screw configuration and barrel pressure profile

The screw configuration and a typical pressure profile in the extruder are shown in Fig. 1. The kneading paddles in heads 3 and 4, and the discs and reverse screw element in head 4 were provided for better mixing of the water with starch to achieve complete hydration. A slight drop in pressure was achieved at the SC–CO₂ injection point by placing a reverse screw element at the end of head seven followed by a cut flight screw element. This was done to allow the SC–CO₂ to move only in the forward direction. The cut flight element provided better mixing of the SC–CO₂ into the dough. A reverse screw element at the end of head 9 provided a restriction for building up pressure for enhanced gas solubility near the die. However, the processing pressure was mainly controlled by the flow restrictors located before the die, as described by Rizvi et al. (1995). The die pressure (or pressure at the end of head 9) was maintained in the range of 10–15 MPa (1450 to 2175 psi).

2.2.3. Supercritical CO₂ injection

A pilot scale supercritical fluid system was used for injecting SC-CO₂ at a constant flow rate (7.6×10⁻⁵ kg/s) into the starch melt through four valves located around the extruder barrel at the beginning of head 8. SC-CO₂ injection pressure was automatically maintained higher than pressure inside the barrel for a continuous SC-CO₂ flow into the starch melt, at the desired rate and pressure.

2.3. Extrudate evaluation

2.3.1. Sample collection

The cylindrical extrudates emerging from the die were collected on metal trays and were cut to a length of approximately 1 m. The trays containing the extrudates were kept at room temperature (22°C) for 48 h or transferred to a 3-compartment oven (with temperatures

![Fig. 1. The screw configuration used in this study and the corresponding pressure profile developed along the extruder barrel.](image-url)
pre-set at 70, 85 and 100°C). Extrudates in the oven were dried until they had a crisp texture, and then placed at room temperature for 24 h. Final moisture content of all extrudates was approximately 5%. Moisture content of the original mix, wet extrudates and dried extrudates was measured using the oven drying method (AOACI, 1995).

2.3.2. Expansion ratio, bulk density and void fraction

Expansion ratio was calculated by dividing the cross-sectional area of the extrudate by the cross-sectional area of the die (7.07 mm² for the 3 mm die). An average diameter of 5 samples was used for calculation of the cross-sectional area. Bulk density, defined as the ratio of the mass of the sample to that of its total volume including the voids, was measured using the sand displacement method (Park, 1976). Void fraction ($V_f$), defined as the ratio of pore volume to that of the total volume of the sample, was calculated from the following equation.

$$V_f = 1 - \frac{\rho_b}{\rho_s}$$  \hspace{1cm} (1)

where $\rho_b$ = bulk density of expanded sample (g/cm³), $\rho_s$ = density of unexpanded material (g/cm³).

2.3.3. 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 stripe 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 microscope (Leica 440 SEM).

Average diameters of approximately 80 representative cells on each micrograph were measured using an image processing software (Image-Pro Plus™). The percentage of closed and open cells was also found out. Based on the assumption that the extrudates comprised entirely of spherical cells, cell density for each sample was calculated from the average cell diameter and bulk density using the equation given by Shimbo, Baldwin and Suh, 1995

$$N = \frac{(\rho_s/\rho_b) - 1}{\pi D^2/6}$$  \hspace{1cm} (2)

where $N$ = number of cells/cm³ of unexpanded material, $\rho_s$ = density of unexpanded material (g/cm³), $\rho_b$ = bulk density of expanded sample (g/cm³), $D$ = average cell diameter (cm).

The spread of cell size distributions of various samples was quantified by calculating the polydispersity index (PDI), as detailed by Goel and Beckman (1994). A value of PDI close to unity indicated a very uniform distribution.

$$\text{PDI} = \frac{\bar{D}_n}{\bar{D}_w}$$

Where $\bar{D}_n$ = number average of cell sizes $= \Sigma (D_i n_i)/\Sigma n_i$ and $\bar{D}_w$ = weighted average of cell sizes $= \Sigma (D_i^2 n_i)/\Sigma (D_i n_i)$

2.3.4. Statistical methods. The MINITAB statistical program was used to test the normality of the cell size distributions using the Kolmogorov-Smirnov test at a significance level of $p < 0.05$.

3. Results and discussion

3.1. Expansion ratio, bulk density and void fraction

As shown in Table 2, the moisture content of the extrudate was 35% and its temperature at the die was 60°C. The glass transition temperature ($T_g$) of such high moisture containing SCFX extrudates was around −30°C, as determined by preliminary studies. This prevented the structure from setting and caused shrinkage as the gas inside the cells contracted due to cooling. Addition of EW or WPC-34 helped in imparting rigidity to the structure and reducing shrinkage because of their forming a gel-like network in the starch matrix. At the same time, presence of EW or WPC-34 did not inhibit the expansion of the extrudates, as the product temperature at the die was just high enough to cause only partial gelation of the proteins. The extrudates expanded further on oven drying at 70, 85 or 100°C until their structure was finally set due to reduction in moisture content. The effect of protein content and drying temperature on the expansion ratio and bulk density data for samples with EW are shown in Fig. 2(a) and (b), and that for samples with WPC-34 in Fig. 2(c) and (d), respectively. Bulk density of the unexpanded product obtained without injection of SC-CO₂ was 1.31 g/cm³. Depending on the protein content and the drying temperature, the bulk density of the expanded extrudates ranged between 0.09 and 0.58 g/cm³, while their expansion ratio varied between 2.33 and 15.78. The void fraction of the extrudates ranged from 0.56 to 0.93 (Table 3).

3.1.1. Effect of room temperature drying

Samples dried at room temperature (22°C) were used to study the effect of SCFX processing alone on formation of expanded cellular structure, while eliminating
the effect of oven drying which substantially altered the structure. The control sample (no added protein) dried at 22°C had the highest bulk density and lowest expansion ratio, which indicated that its shrinkage on emergence from the die was most pronounced. This was confirmed by the SEM micrograph of this sample, which showed a considerably shrunk cellular structure [Fig. 3(a)]. Extrudates with 4, 7 or 10% protein level (WPC-34 or EW) and dried at 22°C, had higher expansion ratio (20–140%) and lower bulk density (33–70%) as compared to the control sample dried at that temperature. Moreover, the microstructure of the extrudates dried at 22°C and containing 4–10% EW or WPC-34 exhibited regular polygonal cells with little signs of shrinkage and cell sizes 80–160% higher than that for the control sample [Figs. 3(b) and (c)], indicating that addition of either of EW and WPC-34 helped reduce shrinkage of the extrudates. For the room dried samples, the highest expansion and least bulk density was observed for extrudates with 7% EW or WPC-34.

3.1.2. Effect of oven drying

Depending on their protein content, the expansion ratio of extrudates dried in the oven at 70, 85 or 100°C increased by 48–341% and bulk density decreased by 27–74%, as compared to the room-dried product (Fig. 2). This indicated that the extrudates further expanded during oven drying until the structure was set due to the raising of \( T_g \) caused by drying and gelation of the yet undenatured portion of EW or WPC-34. In general, the higher the drying temperature, the greater was the expansion ratio and lower the bulk density. Similar to the room dried extrudates, maximum expansion and minimum bulk density at all other drying temperatures was observed at 7% EW or WPC-34.

### Table 3
Void fraction \( \left( V_f \right) \) of the extrudates

<table>
<thead>
<tr>
<th>Protein level</th>
<th>EW 4%</th>
<th>EW 7%</th>
<th>EW 10%</th>
<th>WPC 4%</th>
<th>WPC 7%</th>
<th>WPC 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>22°C</td>
<td>0.74</td>
<td>0.86</td>
<td>0.80</td>
<td>0.74</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>70°C</td>
<td>0.85</td>
<td>0.91</td>
<td>0.86</td>
<td>0.85</td>
<td>0.85</td>
<td>0.84</td>
</tr>
<tr>
<td>85°C</td>
<td>0.87</td>
<td>0.92</td>
<td>0.85</td>
<td>0.85</td>
<td>0.92</td>
<td>0.87</td>
</tr>
<tr>
<td>100°C</td>
<td>0.88</td>
<td>0.93</td>
<td>0.91</td>
<td>0.87</td>
<td>0.92</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Fig. 2. Expansion ratio and bulk density at different drying temperatures, and varying levels of egg white (a and b) and whey protein concentrate (c and d).
Extrudates dried at 70 or 85°C exhibited a more uniform and intact cellular structure (Fig. 4), and these were the best products in terms of both expansion and structure. The cells in the interior of the extrudates dried at 100°C were found to expand and stretch to the point of rupture, resulting in a damaged cellular structure. The cells at the edges of these extrudates, however, grew to a large size and remained intact, as their structure

Fig. 3. Scanning electron micrographs of SCFX extrudates dried at room temperature (22°C): (a) control (no EW or WPC-34), (b) 7% EW, (c) 7% WPC-34.

Fig. 4. Scanning electron micrographs of SCFX extrudates oven-dried at 70 and 85°C.
was set due to faster moisture loss. This effect was most pronounced for the control extrudates (Fig. 5). Addition of 4–10% EW or WPC-34 in the formulation enabled the structure to set faster, and reduced damage to the cellular structure, during drying at 100°C.

Among all extrudates, the maximum expansion ratio (15.8) and minimum bulk density (~0.1 g/cm³) was observed for those with 7% EW or WPC-34 and dried at 100°C. These products, however, had broken cellular structure. Among samples having unbroken, uniform microstructure, the maximum expansion ratio (12.9) and minimum bulk density (0.10 g/cm³) was observed for extrudates with 7% EW and dried at 85°C. Extrudates with 7% WPC-34 and dried at 85°C, had similar bulk density (0.11 g/cm³) but lower expansion ratio (11.6). The expansion of the last two SCFX extrudates was comparable to conventional steam expanded products reported in literature (Table 1). In general, extrudates with EW exhibited higher expansion ratio (up to 1.6 times) and lower bulk density (up to 0.46 times) as compared to those with the same amount of WPC-34, and dried at the same temperature. A possible reason for this could be that EW contained much more protein (86%) than WPC-34 (34%), and the increase in $T_g$ of extrudates was up to 3.5 times more when EW was added to the formulation as compared to WPC-34 (as determined by preliminary investigations), and thus the former was more effective in stabilizing the structure and reducing the shrinkage of extrudates.

3.2. Cellular structure of extrudates

The average cell densities of SCFX extrudates (Table 4) were of the order of $10^6$ cells/cm³. Addition of 4–10% EW or WPC-34 to the formulation reduced the cell density of the extrudates by up to three times. According to the classical nucleation theory (Blander & Katz, 1975), which has been successfully used to describe the kinetics of nucleation in polymer melts (Goel & Beckman, 1994), a higher nucleation rate and cell density is associated with a greater amount of CO₂ dissolved in the polymer melt, lower interfacial tension and viscosity of the mixture, and a high degree of supersaturation achieved during the pressure quench. The partial gelation of EW or WPC-34 proteins in the extruder would tend to increase the viscosity of the dough, and this would lead to a lowering of the nucleation rate and the cell density. On the other hand, increased cross-linking due to gelation of proteins would tend to increase the degree of supersaturation of SC-CO₂, and thus

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Fig. 5. Scanning electron micrograph of SCFX extrudate (without any WPC-34 or EW) oven-dried at 100°C, showing damaged cells in the interior and intact cells near the edges.
increase the cell density. The latter effect might not be very significant though, since most of the SC-CO₂ is dissolved in water. This could be the reason for the lowering of cell density on addition of EW or WPC-34 to the formulation.

As SCFX samples dried at 85°C had expansion comparable to steam expanded products and an intact cellular structure, the average cell sizes for only these samples are shown in Table 4, along with the cell sizes of samples dried at room temperature for comparison. Cellular structure of control samples dried at 85°C was extensively damaged for the same reason as discussed in the previous section, and average cell size obtained from the intact cells was not representative of the whole extrudate. The average cell size of the various extrudates ranged from 56 to 244 µm. In general, the higher the drying temperature, the greater was the average cell size of extrudates, irrespective of the protein level. For example, for samples with 4% EW, the average cell size increased from 102 to 174 µm as the drying temperature was raised from 22 to 100°C, while for samples with 4% WPC-34, the average cell size increased from 118 to 183 µm, in the same temperature range. In general, maximum average cell size at all drying temperatures was observed at 7% EW or WPC-34. Cells of SCFX extrudates were 5–15 times smaller than that of steam expanded products (Table 1).

### Table 4

Average cell size (diameter) of extrudates dried at room temperature (22°C), and those oven dried at 85°C, and the average cell density

<table>
<thead>
<tr>
<th>Protein level</th>
<th>Average cell size (µm)</th>
<th>Average cell density (10⁶ cells/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>56 µm</td>
<td>22°C: 6.8</td>
</tr>
<tr>
<td>EW 4%</td>
<td>102 µm 148 µm</td>
<td>85°C: 4.0</td>
</tr>
<tr>
<td>7%</td>
<td>110 244</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>134 180</td>
<td></td>
</tr>
<tr>
<td>WPC 4%</td>
<td>118 µm 180 µm</td>
<td></td>
</tr>
<tr>
<td>7%</td>
<td>146 216</td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>110 173</td>
<td></td>
</tr>
</tbody>
</table>

a Damaged cellular structure.

b Number of cells in the expanded product per unit volume of unexpanded material.

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Fig. 6. Cell size distribution of SCFX samples dried at 85°C, and containing different levels of egg white (EW) ($D_{av}$ = average cell size, PDI = polydispersity index).
The cell size distributions and polydispersity index (PDI) values of samples dried at 85°C are shown in Figs. 6 and 7. The results of the Kolmogorov–Smirnov test for normality, and the normal probability plot of a typical SCFX extrudate cell size distribution are shown in Table 5 and Fig. 8, respectively. In general, the cell sizes of the SCFX extrudates were normally distributed. There were a few exceptions where the distribution was closer to the log normal distribution (indicating skewness to the right). This finding was in contrast with the findings of Barrett and Peleg (1992) for conventional steam puffed corn meal extrudates whose cell size distribution

![Fig. 7. Cell size distribution of SCFX samples dried at 85°C, and containing different levels of whey protein concentrate (WPC) (D_{av} = average cell size, PDI = polydispersity index).](image)

![Fig. 8. Normal probability plot for the cell size distribution of a typical SCFX extrudate (no added protein and dried at 70°C). (Cell size = 137.5 ± 35.5 µm, p-value > 0.15 for the Kolmogorov-Smirnov normality test).](image)

**Table 5**

*p*-values for the Kolmogorov–Smirnov test for normality of cell size distributions (a *p*-value ≥ 0.05 indicates that the distribution is normal at 0.05 significance level)

<table>
<thead>
<tr>
<th>Protein level</th>
<th>Drying temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22</td>
</tr>
<tr>
<td>Control</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>EW 4%</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>7%</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>10%</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>WPC 4%</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>7%</td>
<td>&gt; 0.15</td>
</tr>
<tr>
<td>10%</td>
<td>&gt; 0.15</td>
</tr>
</tbody>
</table>
mostly followed the log normal distribution. PDI of control sample was 0.9, but increased on addition of protein to the formulation. PDI was 0.96 and 0.97 for samples with 10% EW and 10% WPC, respectively. Thus, the cell size distribution of the control sample dried at 85°C had a larger spread than extrudates with 4, 7 or 10% EW or WPC-34, which indicated that addition of protein increased the uniformity of cellular structure. The cell size distribution of SCFX extrudates had a much narrower spread than that of steam puffed extrudates. The PDI value of cell size distribution of steam extrudates calculated from the data of Barrett and Peleg (1992) was 0.29. The more uniform cellular structure of SCFX extrudates as compared to steam extrudates 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 (Martini, Waldman & Suh, 1982). The relative rates of nucleation and gas diffusion determine the cell size distribution of the extrudate. 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 homogenous or uniform cell size distribution. On the other, 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 (in contrast with steam-based extrusion), 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.

The number of closed cells was much higher as compared to open cells in all the samples, although the number of closed cells decreased as the oven-drying temperature was raised. For example, in samples with 4% WPC the proportion of closed cells decreased from 85 to 64% as the drying temperature was raised from 22 to 85°C, while in samples with 4% EW this proportion decreased from 79 to 72% over the same temperature range.

3.3. Role of $T_g$ and proteins in reducing extrudate shrinkage and damage

A possible mechanism of product expansion in terms of the variation in average cell size ($D_{av}$) is illustrated in Fig. 9. When the product temperature ($T_p$) is above $T_g + 30°C$ (or the bubble temperature) (Della Valle, Vergnes, Colonna & Patria, 1997; Fan, Mitchell & Blanshard, 1994), the cell wall viscosity is low enough for bubble growth or shrinkage. Differential scanning
calorimetry (DSC) experiments indicated that $T_g$ of the control formulation (with 35% moisture), as it exited the die, was about $-30^\circ$C while the product temperature was $60^\circ$C. This caused the extrudates to shrink as the gas inside the cells cooled down and contracted. Subsequently, in the drying oven, $T_p$ increased steadily but so did $T_g$ because of continuous loss of moisture. The cells increased in size as long as $T_p$ remained greater than $T_g + 30^\circ$C, but at a certain critical cell size, the cell walls reached their maximum extensibility (especially when oven temperature was $100^\circ$C), beyond which they ruptured and the extrudate structure was damaged. When the oven temperature was 70 or 85°C, the structure was set before this critical cell size could be attained, thus no rupture of cells was observed. Addition of EW or WPC-34, and their partial gelation at the die raised the $T_g$ of the product, and thus reduced shrinkage before the oven drying phase. During drying, the combined effect of continued gelation of proteins and loss of moisture increased the $T_g$ at a much faster rate, and a greater proportion of cells were set before the critical cell size was reached, and thus damage to the cellular structure due to rupture of cell walls was reduced.

### 3.4. Formation of non-porous skin

SCFX extrudates also exhibited the unique characteristic of a non-porous skin surrounding the internal cellular morphology (Fig. 10). 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. Moreover, rapid drying and gelation of the proteins near the edges sets the material quickly and inhibits growth of any nucleated sites. A combination of these factors caused the formation of a non-porous skin. The “skin effect” was not observed for extrudates dried at $100^\circ$C because of rupture of any skin that might have developed initially. The skin reduces water penetration and delays onset of sogginess, which is a desirable characteristic for ready-to-eat breakfast cereal. Moreover, the skin provides a composite structure to the extrudates and variation of its thickness can provide another means for manipulating extrudate mechanical properties and texture.

### 4. Conclusions

The effects of protein content and drying temperature on the expansion and cellular structure of SCFX extrudates were established. Shrinkage of extrudates before oven drying was reduced (expansion ratio increased by up to 140% and bulk density decreased by up to 70%) when 4–10% of EW or WPC-34 was added to the formulation, because the partial gelation of pro-
proteins inside the extruder barrel. Expansion ratio of extrudates increased up to 341% and bulk density decreased up to 74% as the drying temperature was raised from 22 to 100°C, although drying of extrudates at 100°C caused damage to the cellular structure. In general, maximum expansion ratio and minimum bulk density was observed at 7% EW or WPC-34 for all drying temperatures. The products with the best expansion, while maintaining an intact cellular structure, were those dried at 85°C and containing 7% EW or 7% WPC (expansion ratio of around 12 and bulk density of 0.10 g/cm³). These extrudates were comparable to steam puffed products in terms of degree of expansion. Cell size of the extrudates ranged between 56 and 244 μm. The PDI of cell size distribution of SCFX extrudates ranged from 0.90 to 0.97 as compared to a value of 0.29 for steam extrudates (Barrett & Peleg, 1992) indicating that the cell size distribution of SCFX extrudates much more uniform. The cell density of the extrudates, which was of the order of 10⁶ cell/cm³, decreased by up to three times on addition of 4–10% EW or WPC-34, which was explained on the basis of the classical nucleation theory.

Low shear and low temperature processing, and formation of products having a non-porous skin and a high degree of uniformity in their cell size distribution while having expansion comparable to steam expanded products, are some characteristics of SCFX process that make it superior to steam-based expansion. Moreover, in the SCFX process a high degree of control over the extrudate expansion and microstructure can be achieved by varying the rate of injection of SC-CO₂, the operating pressure and the die dimensions. This provides greater control over mechanical properties like compressive strength, which are greatly dependent on bulk density of the expanded extrudates and their micro-structural characteristics like the cell size, proportion of closed cells to open cells, and the cell density.

Acknowledgements

The authors are grateful to Wenger Manufacturing, Inc. for their assistance through the Cornell-Wenger Extrusion Program.

References


