Effect of Eggshell on Properties of Corn Starch Extrudates[1]

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ABSTRACT

Corn starch was extruded in a single-screw laboratory extruder at 140°C barrel temperature and 140 rpm screw speed. Expansion ratio, bulk density, shear strength, percentages of closed and open pores, porosity, and molecular degradation of extruded starch were measured. Addition of up to 10% eggshell resulted in decreases in expansion ratio, bulk density, and percentage of open pores; and increases in shear strength, percentage of closed pores, and porosity of extrudates. Cross-sections became smaller with a greater number of round and uniform-sized cells for extrudates with added eggshell. Gel-permeation chromatography fractionation of starch extruded with eggshell showed extensive degradation of fraction I with increasing eggshell concentrations. The eggshell appeared to have provided nucleation sites for water vaporization as the material exited the die of the extruder.

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Many studies have been published on optimization of extrusion process conditions (Faubion and Hoseney 1982a,b; Bhattacharya and Hanna 1987; Chinnaswamy and Hanna 1987; Chinnaswamy and Hanna 1988a) and relationships between physical properties of extrudates and ingredients (Holmes and Hoseney 1987; Chinnaswamy and Hanna 1988b; Hsieh et al 1989, 1990). Other studies have examined improving the number and size of cells in the cross-section of extrudates with titanium dioxide, calcium silicate, aluminum oxide, and silicon dioxide (Rosenquest et al 1975); water, protein, and lipid (Faubion and Hoseney 1982a,b); yeast protein concentrate and yeast cellular components (Lai et al 1985a,b); sodium bicarbonate (Lai et al 1989); wheat bran and oat fiber (Lue et al 1990); bran, sucrose, and magnesium carbonate (Moore et al 1990); cellulose fiber (Chinnaswamy and Hanna 1991); citric acid (Barrett and Peleg 1992); rice bran (Grenus et al 1993); and lipid (Bhatnagar 1993). Eggshell also has been found to be effective in improving the uniformity of the cells of corn starch and flour extruded in a twin-screw extruder (Kurokawa et al 1990a,b). However, it is not known why the addition of eggshell results in improved texture of extrudates. The effects of eggshell on physical and structural properties of starches extruded in a single-screw extruder are also not known in detail. The specific objectives of this study were to 1) investigate physical, structural, and molecular properties of corn starches of different amylose contents extruded with and without eggshell in a single-screw extruder, and 2) to explain the role of eggshell in nucleation and degradation of starch extrudates.

MATERIALS AND METHODS

Materials

The corn starch used in this study was provided by American Maize-Products Co. (Hammond, IN). The powdered starch was granulated before extrusion by spraying water on the starch in an inclined rotating pan.

Glass beads and powdered $CaCO_3$ were purchased from Aldrich Chemical Co. (St. Louis, MO). Eggshells were received from a food service company in Lincoln, NE. The eggshells were washed with distilled water and dried at ambient temperature. Glass beads and eggshells were ground (Powdertec 3090, Tecator, Inc., Germany) to pass through a 150-μm sieve. Typical egg shell composition is given in Table I.

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Starch samples were blended with the eggshells, glass beads, or powdered $CaCO_3$ and distilled water in a Hobart mixer for 2 min. All samples were adjusted to moisture content of 18% (dwb). Experimental levels of eggshell were set at 0, 1, 2, 5, 7.5, and 10% (starch dwb). The glass beads and powdered $CaCO_3$ were each added at 5% of starch dry weight. The mixtures were allowed to equilibrate overnight in sealed plastic bags before extrusion.

Methods

A laboratory extruder (model 2003, C.W. Brabender) with a 1.9-cm barrel diameter and a 20:1 barrel length-to-diameter ratio was used. The extruder screw had a compression ratio of 3:1. The cylindrical die nozzle was 3 mm in diameter. The temperatures of the three barrel sections were maintained at 85, 140, and 140°C. The screw speed was maintained at 140 rpm. The extrudates were divided into two portions. One portion was used for determining expansion ratio, bulk density, shear strength, percentage of open and closed pores, and scanning electron microscopy (SEM) studies. The other portion was ground to pass through a 40-mesh sieve and used for measuring solid volume and pH, and for gel-permeation chromatography analysis of extruded starch.

A scanning electron microscope (model JSM-6100 JEOL, Mountain View, CA) was used to observe changes in product microstructure due to extrusion cooking. A cross-section of extrudate was cut from each extrudate strand, mounted on SEM stubs using silver colloidal paste, and then coated with gold-platinum before examination (Bhatnagar 1993).

Bulk density of extrudates was determined by a displacement method using glass beads of 1.00–1.05 mm in diameter (Sokhey and Chinnaswamy 1992). Expansion ratios of extrudates were calculated by dividing the mean cross-sectional area of the extrudate by the cross-sectional area of the die nozzle. Each value obtained was a mean of 20 readings (Chinnaswamy and Hanna 1987).

Shear strength was determined on a universal testing machine (model 5566, Instron Inc., Canton, MA) and was defined as the

TABLE I
Chemical Composition of Eggshell[a]

Constituent	Percent by Weight
Water	1.66
Proteins	6.40
Lipids	0.03
Inorganic salts[b]	91.1
Total solids	97.4

[a]Burley and Vadhera (1989).

[b]Typical inorganic salts consist of 98.43% calcium carbonate, 0.84% magnesium carbonate, and 0.73% tricalcium phosphate. The powdered eggshells were off-white in color.

maximum force required to completely shear the extrudate divided by its cross-sectional area. Extrudates were dried overnight at 50°C in a vacuum oven before testing, then placed in a double-shear device as shown in Figure 1, perpendicular to the direction of the shear force. Extrudates were loaded at a rate of 1 cm/min. The shear device had several holes (not shown in figure) of different diameters. The hole most nearly equal in diameter was chosen while shearing the sample.

True volume of porous extrudates and solid volume of ground extrudates were determined using an air comparison pycnometer (Multivolume Pycnometer model 130-50000-00, Micrometrics, Norcross, GA) as described by Bhatnagar (1993). Each value obtained was a mean of five measurements. Closed pore volume was calculated as the difference between the true volume of porous extrudate and the solid volume of ground extrudate. Total pore volume was calculated as the difference between the bulk volume of porous extrudate and the solid volume of ground extrudate. Open pore volume was calculated as the difference between the total and closed pore volumes. The closed and open pore volumes were presented as percentages of total pore volumes. Porosity of extrudates was calculated as described by Bhatnagar (1993) using:

$$P = (V_s - V_b)/V_s \times 100$$

where P = porosity (%), V_s = solid density (g/cm^3), and V_b = bulk density (g/cm^3).

To study the molecular properties of extrudates, 30 mg of the extrudate was dispersed in 3 ml of 1*N* KOH and held in a refrigerator at 3°C for 30 min with occasional stirring until clear solutions were obtained. The solutions were fractionated on a Sepharose CL 2B column by ascending gel-permeation chromatography (Sokhey and Chinnaswamy 1992). The carbohydrate contents of all fractions were measured by the phenol-sulfuric acid method of Dubois et al (1956) and then calculated on a 5-mg dry starch basis.

To determine pH of extrudates, 2.0 g of ground extrudate were weighed in a 100-ml beaker and suspended in 20 ml of distilled water. The sample was agitated for 5 min and then allowed to stand until the reading on the pH meter stabilized.

All values reported here are averages of five replicates. The generalized linear model of SAS version 6 statistical package (SAS Institute, Inc., Cary, NC) was used to analyze the data and determine least significant differences.

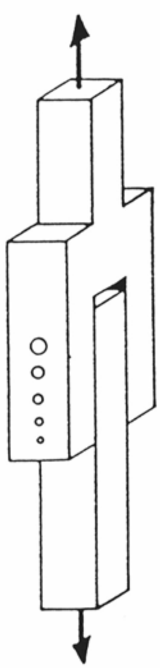

Fig. 1. Double shear cell used to determine the shear strength of extrudates.

RESULTS AND DISCUSSION

Eggshell has been reported to improve the starch extrudate texture and uniformity of cell sizes. We believe that when starch is extruded with eggshell, the eggshell serves as a nucleating agent for cell formation. This was substantiated by the structural and physical properties data of extrudates presented herein. Processed eggshell is an acceptable food ingredient. It is used as a calcium supplement.

Structural Properties of Extrudates

The structural properties, exemplified by scanning electron micrographs, percentage of open and closed pores, and porosity, gave an indication of the number and size of the cells and their uniformity of distribution in the starch extrudates. Scanning electron micrographs of starch extruded with and without eggshell are shown in Figure 2. The starch extruded without eggshell had very large size cells, some as big as the extrudate diameter. As the eggshell concentration was increased from 1 to 10%, the number of cells increased and the diameter of cells decreased.

The percentages of closed and open pores, and the porosity of the starch extruded with and without eggshell, are shown in Table II. The percentages of closed pores and porosity increased from 3.8 and 86.0 to 12.8 and 92.3%, respectively, as the eggshell concentration increased from 0 to 5%. However, further increasing eggshell concentration to 10% decreased the percentage of closed pores and porosity to 7.9 and 90.6%, respectively. The percentage of open pores decreased from 96.2 to 87.2% as eggshell concentration increased from 0 to 5%.

Adding eggshell to starch reduced the overall expansion of the extrudates. The smaller and more uniform cell sizes, and the thinner cell walls of the extrudates, resulted in lower bulk densities at lower eggshell concentrations. The higher density of eggshell as compared to starch overwhelmed that effect at higher eggshell concentrations, resulting in small increases in bulk density at 7.5

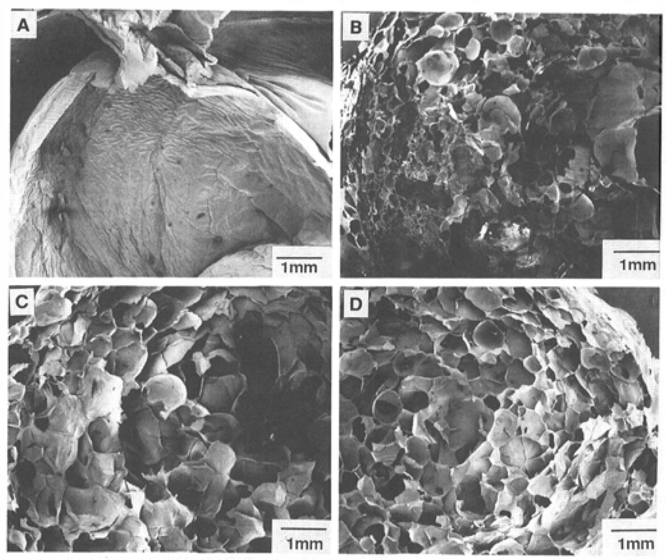

Fig. 2. Scanning electron micrographs of extrudate containing 0% **(A)**, 1% **(B)**, 5% **(C)**, and 10% **(D)** eggshell.

TABLE II
Effect of Eggshell Concentration on Properties of Extruded Corn Starch

	Eggshell Concentration, %					
Property	**0**	**1**	**2**	**5**	**7.5**	**10**
Closed pores, %[a]	3.8	10.7	10.6	12.8	10.3	7.9
Open pores, %[b]	96.2	89.3	89.4	87.2	89.7	92.1
Porosity, %[c]	86.0	90.5	91.5	92.3	92.2	90.6

[a] Least significant difference = 0.489.
[b] Least significant difference = 0.0582.
[c] Least significant difference = 0.229.

and 10% concentrations. The inverse relationships between bulk density and porosity accounts for the trends observed in Table II and Figure 3.

Physical Properties of Extrudates

Physical properties such as expansion ratio, bulk density, and shear strength are important because they affect product texture directly or indirectly. The relationships between these properties and eggshell concentration are shown in Figure 3. The expansion ratio of extrudates decreased from 12.8 to 9.1 as eggshell concentration increased from 0 to 10%. The bulk density of extrudates initially decreased from 213 to 118 kg/m^3 as the concentration of the eggshell increased from 0 to 5% and then increased with further increase in eggshell concentration. The minimum bulk density was observed for 95% starch and 5% eggshell, while the maximum bulk density was observed for starch without eggshell. Kurokawa et al (1990a,b) reported a similar effect of eggshell on bulk density of corn starch extruded in a twin-screw extruder. One would normally expect an inverse relationship between shear strength and expansion ratios. In this case, the shear strength was not significantly affected by eggshell concentration.

Role of Eggshell

As discussed above, the addition of eggshell improved the texture of the starch extrudates. The eggshell was assumed to act as a nucleating agent. Eggshell is primarily $CaCO_3$. $NaHCO_3$ has been reported to improve the cell size and cross-section of the extrudate due to evolution of CO_2 (Lai et al 1989). $NaHCO_3$ begins to lose CO_2 at about 50°C, while $CaCO_3$ decomposes into CaO and CO_2 at 825°C. However, it was not clear whether texture improvement on addition of eggshell was due to evolution of CO_2 or to its acting as a nucleating site for formation of water vapor bubbles. To confirm this, we extruded starch with powdered $CaCO_3$ and glass beads (Table III). Powdered $CaCO_3$ should serve the same purpose as eggshell, while glass beads, being inert material, should act as a true nucleating agent. Addition of $CaCO_3$ and glass beads resulted in decreases in bulk density and percentage of open pores, and increases in percentage of closed pores and porosity of extrudate, as compared to the starch extruded without $CaCO_3$ and glass beads. This response was probably a result of the $CaCO_3$ having small particle size distribution and, therefore, better dispersal throughout the starch.

Furthermore, we monitored the pH of the extrudates. If the $CaCO_3$ or eggshell in the previous experiments decomposed inside the extruder, the result should be the formation of CaO and CO_2. The CaO should then form $Ca(OH)_2$ to increase the pH of the extrudates. Table IV shows that the pH of starches before and after extrusion did not differ significantly. $Ca(OH)_2$ was added to 2.0 g of starch extruded without eggshell to achieve a $Ca(OH)_2$ content of 0, 1.0, 2.0, and 4.8 mg, and the pH of the mixtures were 6.23, 8.92, 9.94, and 10.45, respectively. Therefore, we believe that improvement of texture on addition of eggshell was due to its nucleating capability, because it was not decomposed at the heat and pressure experienced inside the extruder. It should, however, be noted that pH of extrudates increased with added egg shells, which may affect odor and flavor in a cereal product.

TABLE III
Effects of $CaCO_3$ and Glass Beads on Properties of Corn Starch Extrudate

Property	Starch	$CaCO_3$	Ground Glass Beads
Expansion ratio	12.8	10.3	11.1
Bulk density, kg/m^3	211	122	144
Closed pores, %	3.7	13.1	10.3
Open pores, %	96.3	86.9	89.7
Porosity, %	85.9	92.7	90.5

TABLE IV
pH of Samples Before and After Extrusion Cooking with Different Eggshell Concentrations

Eggshell Concentration, %	pH Before Extrusion	pH After Extrusion
0	5.29	6.23
1	7.81	8.07
2	8.26	8.44
5	8.60	8.72
10	8.62	8.81

Molecular Properties of Extrudates

It was suspected that the addition of eggshell induced molecular degradation of starch extrudates. Previous studies by Chinnaswamy and Hanna (1988a–c, 1990, 1991) clearly indicated that starch degraded during extrusion cooking. Depending on the processing conditions, the starch degradation patterns changed drastically, affecting expansion properties. Therefore, the status of starch degradation in the starch-eggshell extrudates was studied to better understand the functional property changes. The extrudates, with different eggshell concentrations, were used for this analysis, along with native and extruded starch without eggshell as control samples. The results are shown in Figure 4 and Table IV. Generally, starch fractionation on a gel-permeation chromatography column gives two major peaks, fractions I and II. Unextruded 25% amylose starch and 25% amylose starch extruded without eggshell gave two peaks. Fraction I corresponded to materials that eluted between K_{av} of −0.06 to 0.38, and fraction II corresponded to materials that eluted after K_{av} 0.38. K_{av} is a chromato-

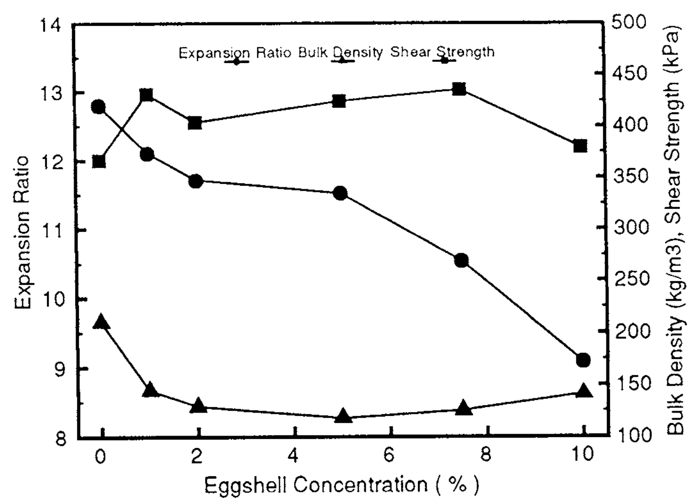

Fig. 3. Effect of eggshell concentration on properties of extruded corn starch.

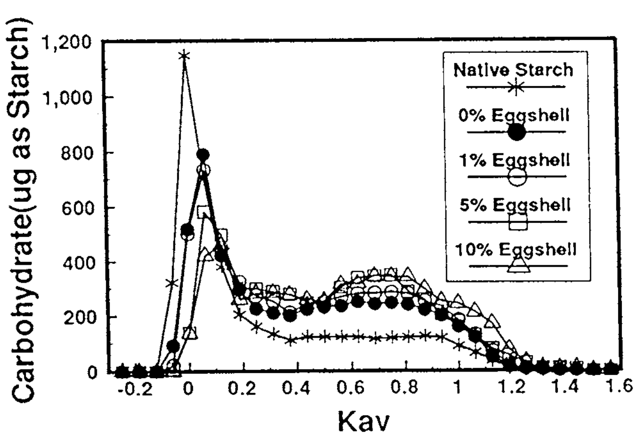

Fig. 4. Gel-permeation chromatographic fractionation patterns for native and extruded corn starch with and without eggshell. K_{av} = chromatographic partition coefficient.

graphic partition coefficient that relates the void and total volumes of the chromatograph column and the elution volume, or actual volume, passed through the column when the peak appears. However, for 25% amylose starch extruded with eggshell, a fraction III (K_{av} of 0.19 to 0.50) was observed between fractions I and II. Chinnaswamy and Hanna (1990) suggested that fraction III was most likely a degradation product of fraction I after extrusion cooking. The starches extruded with and without 1% eggshell had lower fraction I percentages (51.5 and 49.7%, respectively) than did native starch (78.5%), while fraction II increased from 21.5 to 48.5 and 50.3% after extrusion cooking for the same starch samples. With the addition of eggshell at concentrations of 5 and 10%, the fraction I content further decreased, and fraction III appeared between K_{av} 0.19 and 0.50. The percentages of fractions I, II, and III of starches extruded with 5 and 10% eggshell were 22.2, 47.2, and 30.6 and 18.3, 52.9 and 28.8%, respectively. It is clear that eggshell altered the degradation patterns of the molecules in fraction I during extrusion cooking. Maximum starch degradation occurred when 10% eggshell was added. The increased degradation of starch with increasing eggshell concentration appears to be due to the abrasiveness of eggshell. This is supported by the fact that bulk density reached a limiting value at an eggshell concentration of 5%. It appears that, up to this concentration, the eggshell served as a nucleating agent. Further increases in eggshell concentration did not contribute further to nucleation phenomena.

CONCLUSIONS

The addition of eggshell to starch influenced the physical properties and structural properties of the extrudates. The cross-section of the extrudates became smaller with a greater number of round and uniform-sized cells. Addition of eggshell also resulted in decreased expansion ratio and bulk density, and increased shear strength and percentage of closed pores and porosity of extrudates. Gel-permeation chromatography fractionation of starch extruded with eggshell showed extensive degradation of fraction I starch with increasing eggshell concentrations. The eggshell provided nucleation sites for water vaporization as material exited the die of the extruder.

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