Role of Sodium Bicarbonate and Trapped Air in Extrusion¹

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ABSTRACT

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Addition of sodium bicarbonate or sodium carbonate to wheat starch improved expansion of the extrudate but weakened its structure and caused browning. The added bicarbonate or carbonate appeared to react with the acids formed from oxidation of starch during extrusion. Addition of

acidulants to bicarbonate further improved the expansion of the extrudate and eliminated the browning problem caused by the bicarbonate. Trapped air appears to provide the major nucleation sites for the bubbles formed during extrusion.

Addition of sodium bicarbonate with or without acidulants is a common practice in the high-temperature, short-time extrusion industry. However, to our knowledge, there is no literature that shows the addition of bicarbonate is beneficial. Popcorn and starch extrudate both have a honeycomb, cellular structure (Faubion and Hoseney 1982a,b; Hoseney et al 1983; Lai et al 1985a,b). Hoseney et al (1983) proposed that the starch hilum is the nucleation site for the expansion of popcorn. To our knowledge, there is no literature speculating on the nucleation sites in extrusion. Compared to popcorn, starch extrudates have much fewer but larger cells. The number and size of cells in starch extrudates were affected by the starch moisture level, the presence of proteins and lipids, and yeast cellular components (Faubion and Hoseney 1982a,b; Lai et al 1985a,b). Flow agents (silicon dioxide) were found to be effective in improving the expansion and the uniformity of the cells of the extrudate (Rosenquest et al 1975). Extruder operating conditions and the use of additives will not alter the number of starch hila; therefore, these changes in the ultrastructure of the extrudates suggest that the starch hilum may not be the nucleation site in extrusion. The first goal of this study was to study the effects of sodium bicarbonate in extrusion. The second goal was to determine the source of nucleation sites in starch extrusion.

MATERIALS AND METHODS

Materials

Starch. Wheat starch was a gift from Midwest Grain Products, Atchison, KS.

Silicon dioxide. Silicon dioxide was a gift from Degussa Company, Teterboro, NJ).

Dissolved starch. Starch was dissolved in 1N NaOH, and the alkaline starch solution was dialyzed in running tap water overnight, then in distilled water for three days. The pH of the dialyzed dissolved starch was 9.3. Dissolved starch (pH 7) was also prepared by autoclaving a starch paste (3% solid, 121°C, 60 min). The dissolved starch was dried to a powder by lyophilization.

Methods

Extrusion equipment and the operation procedure were described by Mason and Hoseney (1986), except that hand feeding was used to extrude dissolved starch. Bulk density, diameter, and breaking force were determined as described by Lai et al (1985a). The least significant differences (0.95% confidence level) for bulk density, diameter, and breaking force were 0.024 g/cm³, 1.45 cm, and 480 g, respectively. Cold and hot paste viscosity was determined on a 10% suspension of extrudate in distilled water as described by Mason and Hoseney (1986).

Starch chips were made by forming a gel and allowing the gel to air dry. Relative viscosity was determined as described by Mason and Hoseney (1986).

RESULTS AND DISCUSSION

Effect of NaHCO3 on Extrusion

Sodium bicarbonate (0.5% of starch weight, in solution) was added to wheat starch, and the mixture (17.5% moisture) was extruded using a Brabender single screw extruder. Added NaHCO3 improved the expansion but reduced textural strength of the extrudates as indicated by the reductions in bulk density and breaking force (Table I). The added NaHCO3 also caused caramelization during extrusion, as indicated by the brown color of the extruded product. Scanning electron microscopy of cross sections of extrudates showed that the added NaHCO3 increased the number of cells and decreased the average cell size (Fig. 1). Amylograph results on the extruded starch indicated that the added NaHCO₃ increased the cold paste and hot paste viscosity (Table II). This finding suggests that extruded starch with NaHCO3 swells more in cold water than the control (Ghiasi et al 1982). When NaHCO₃ was added to starch as a solution and the mixture was allowed to stand overnight, the pH of this NaHCO₃ starch mixture increased from 7.84 to 9.35. Drying that mixture (130°C, 1 hr) increased the pH to 10.02. It has been reported (Anonymous 1983) that aqueous NaHCO3 solution will slowly convert to Na₂CO₃ (2 NaHCO → Na₂CO₃ + CO₂ + H₂O). The conversion is 100% when the temperature reaches 100°C. We mixed the calculated amount of Na₂CO₃ (equivalent to 0.5% NaHCO₃) with starch and found that the pH of this mixture was 10.2. If the aqueous NaHCO3 was converted to Na2CO3, then addition of Na₂CO₃ powder should produce the same effect on extrusion as NaHCO3. Experimental results confirmed that speculation (Table I and Fig. 1).

The pHs of extrudates from both starch-bicarbonate and starch-carbonate mixtures were about 8.8. This suggests that most of the carbonate was neutralized during extrusion, reducing the pH from 10 to 8.8. We titrated the extruded Na₂CO₃-starch mixture and found only a small amount of residual Na₂CO₃ (Fig. 2). This suggests that when starch was extruded with carbonate or bicarbonate, it was dehydrated and oxidized to form acids. The resultant acids may have reacted with the Na₂CO₃ or NaHCO₃ to produce CO₂, which assisted the expansion of extrudate. The dehydration and oxidation of starch apparently also caused the caramelization (brown color of extrudates).

Because the pH of the extruded control starch was neutral, the dehydration and oxidation reaction must have been catalyzed by the base or the sodium ions. Addition of an equimolar amount of NaCl (equivalent to 0.5% NaHCO₃) reduced expansion and increased the textural strength of the extrudates. The added NaCl did not cause significant browning. Therefore, we believe that the base catalyzed the caramelization.

If that hypothesis is true, then adding base to starch should cause caramelization, and the pH of the extrudates from the starch-base mixture should be about neutral. Sodium hydroxide and sodium phosphate (dibasic and tribasic) solutions were added to starch to adjust the pH to 9.3 and the mixtures were extruded. The added

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TABLE I
Effects of NaHCO₃, Na₂CO₃, Acidulants plus NaHCO₃, and pH on Extrusion

Additive	Diameter ^a (mm)	Bulk Density ^a (g/cm ³)	Mass Production Rate ^b (g/min)	Linear Production Rate ^b (cm/min)	рН		Breaking Forcea
					Before	After	(kg)
None (control)	17.36 ± 1.77	0.284 ± 0.038	51.4	75.03	5.97	6.00	2.90 ± 0.88
0.5% NaHCO3 (solution)	15.14 ± 0.58	0.248 ± 0.056	22.5	•••	9.35	8.68	1.64 ± 0.43
0.5% NaHCO ₃ (dry powder)	14.92 ± 1.19	0.233 ± 0.024	46.7	114.7	7.50	8.88	1.57 ± 0.46
Na ₂ CO ₃ (dry powder)	15.72 ± 0.85	0.257 ± 0.036	46.1	92.4	9.35	8.80	1.58 ± 0.45
NaOH (solution)	15.99 ± 2.83	0.307 ± 0.035	37.8	61.3	9.30	6.70	1.80 ± 0.43
Na ₂ HPO ₄ + Na ₃ PO ₄ (solution)	15.51 ± 1.91	0.325 ± 0.037	35.5	57.8	9.30	•••	2.24 ± 0.76
0.4% NaHCO ₃ (dry powder)	15.51 ± 1.38	0.247 ± 0.025		•••			1.75 ± 0.58
0.3% NaHCO3 (dry powder)	15.31 ± 1.45	0.204 ± 0.020	***	•••		•••	1.80 ± 0.34
0.2% NaHCO ₃ (dry powder)	15.54 ± 2.01	0.243 ± 0.020	***	****	•••	•••	1.78 ± 0.35
0.1% NaHCO ₃ (dry powder)	16.92 ± 1.96	0.297 ± 0.034	. ***	•••	•••	•••	1.99 ± 0.62
0.5% NaHCO ₃ + SAS ^c	13.51 ± 0.92	0.221 ± 0.025	41.4	130.7	•••		1.52 ± 0.08
0.5% NaHCO ₃ + SALP ^d							
(dry powder)	14.76 ± 1.70	0.201 ± 0.016	34.9	101.4		•••	1.30 ± 0.47

^aNumbers are averages of 10 observations.

^dSodium aluminum phosphate.

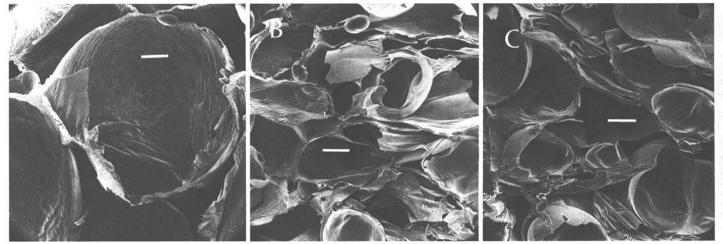


Fig. 1. Cross section of extruded starch containing A, control; B, NaHCO₃, and C, Na₂CO₃ (bar = 500 μ m).

TABLE II
Effects of NaHCO₃, NaOH, and NaHCO₃ + SAS^a
on the Pasting Properties of Extruded Starch

Additives	Cold Paste Viscosity (BU) ^b	Swell Peak Area (BU·min)	Hot Paste Viscosity (BU)
None (control)	385	84.8	65
NaHCO ₃	515	77.3	105
NaHCO3 + SASa	418	85.0	70
NaOH	487	83.9	100

Sodium aluminum sulfate.

base did cause caramelization and also reduced both expansion and textural strength of extrudates (Table I). The pHs of both extruded starches were about neutral (Table I). Apparently, the base was neutralized during extrusion.

Sodium bicarbonate powder (0.5%) was added to starch, and the mixture was allowed to stand overnight before it was extruded. The pH of the mixture did not change significantly during standing. However, the dry NaHCO₃ had essentially the same effect on extrusion as the aqueous form (Table I). Added bicarbonate reduced the mass production rate slightly but increased the linear production rate of extrudates (Table I). These findings suggest that the melt containing bicarbonate expanded more in an axial direction than in a radial direction. One possible

explanation is that the melt started to expand while it was still in the die. Because of the limitation of the die, the melt could only expand axially. These results indicated that the diameter of extrudates is a function of melt rheology and degree of expansion, and, thus, may not be a good indicator of expansion for extrudates.

Various amounts of NaHCO₃ were added to starch to determine the minimum effective level that would change extrudate properties. We found that 0.1% of NaHCO₃ was sufficient to affect the textural strength. Addition of 0.2% NaHCO₃ improved expansion and decreased the textural strength of extrudates. The effects diminished when the addition levels exceeded 0.2% (Table I).

Role of Acidulants

Equivalent amounts of sodium aluminum phosphate and sodium aluminum sulfate were added separately to NaHCO₃-starch mixtures to neutralize the added NaHCO₃. We found that the added acidulants improved expansion and eliminated the browning problem. Presumably, the acids neutralized the NaHCO₃ before it induced the caramelization reaction. Sodium aluminum phosphate was more effective than sodium aluminum sulfate in improving extrudate expansion (Table I).

Addition of sodium bicarbonate or NaOH increased the cold paste viscosity of the extruded starch, and this effect was eliminated by acidulants (Table II). This finding suggests that a base caused starch oxidation during extrusion and changed the water absorption capacity of the extruded starch. The acid released from acidulants during extrusion neutralized the bicarbonate

^bNumbers are averages of three observations. Because of the caking problem in the rotary feeder, the production rate varied from 51.4 to 33.6 g/min. However, this degree of variation did not affect the extrudate's properties.

^cSodium aluminum sulfate.

^bBrabender units.

before it induced the starch oxidation. Therefore, the acidulants eliminated the effects of bicarbonate on caramelization and cold paste viscosity.

Effect of Screw Speed

According to bubble mechanics (Handleman et al 1961), the pressure needed to create a bubble in a continuous mobile phase is infinitely large. Thus, the most likely nucleation site of extrudates is the air trapped in the melted starch or in the starch hila.

Wheat starch was extruded at low temperatures (at or below 160°C) and at various screw speeds. The degree of expansion increased with screw speed (Table III). One possible explanation for this finding is that air was trapped in the melt because of the action of the screw. At higher screw speeds, more air bubbles were trapped.

Another theory explaining the effect of screw speed on extrudate expansion is that the melt inside the die was cooled significantly when slow screw speed (160° C, 50 rpm) was used. The reduction in melt temperature caused an increase in viscosity and reduced the expansion of the extrudate.

To further test the effect of screw speed, starch was extruded using a die extension (about 8.89 cm) and a small die cap (0.318 cm opening). The die extension was wrapped with a heat tape to prevent the melt from cooling. We found that the expansion of extrudates was still improved by using higher screw speeds (Table III). Presumably, that improvement was the result of a reduction in melt viscosity (higher back pressure causing a reduction in molecular weight) and an increase in nucleation caused by the high shear (screw speed). Starch molecular size is also reduced during extrusion (Mercier et al 1979). Data in Table III demonstrate that the effect of cooling on expansion was much more significant when low screw speed was used. Apparently, the high shear produced more frictional heat and more reduction in molecular size, and,

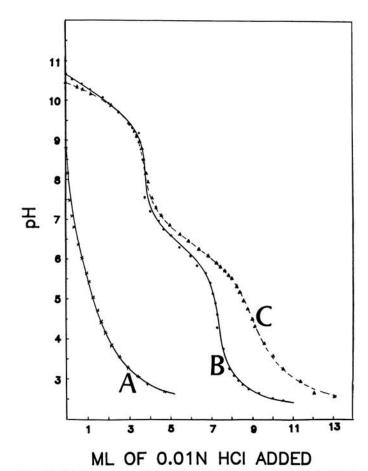


Fig. 2. Titration curves of Na₂CO₃: extruded without added internal standard (A), unextruded (B), extruded with added internal standard (C).

thus, was less sensitive to cooling. Therefore, the effect of screw speed cannot be attributed only to an increase in nucleation.

Despite longer cooling time, starch extruded using a die extension (without heat tape) at 160°C and 100 rpm had better expansion than the control (regular die, 160°C, 100 rpm) (Table III). Apparently, the die extension plus the small opening increased the back pressure inside the barrel, and thus, the melt had longer barrel residence time and more shear. That shear reduced viscosity and increased the number of air bubbles trapped. More study is needed to understand the effects on extrusion and the interactions between operating conditions such as die length and size, screw speed, and barrel temperature.

Effect of a Flow Agent on Extrusion

According to Rosenquest et al (1975), addition of flow agents such as silicon dioxide improved the ultrastructure and expansion of extrudates. The improvement might have been caused by increased nucleation (air bubbles trapped in silicon dioxide). If this is true, inclusion of a flow agent should be beneficial (more cells and better expansion) when there are few air bubbles trapped. Addition of 0.5% silicon dioxide to the starch substantially improved expansion and increased the number of cells in the cross section (Table III and Fig. 3).

Role of Trapped Air Bubbles in Extrusion

When starch was extruded using a screw speed of 50 rpm and a die extension described by Yost (1985) but without a heat tape, a glassy rod was obtained. There were few visible air bubbles in the glassy rod. Deep fat frying of that glassy rod produced a puffed product with a fine, honeycomb, cellular structure. Visual examination showed that there were a few big cells scattered throughout the expanded product (Fig. 4B). Presumably, those big cells resulted from the air bubbles trapped in the extrudates. Many of these trapped air bubbles may not be visible with the naked eye; thus, we did not see them in the glassy rod. Fine cells were presumed to be nucleated by the starch hila. When the melt left the

TABLE III
Effects of Aerosol, Screw Speed, and Barrel Temperature
on Starch Extrudates

Barrel Temp. (°C)	Screw Speed (rpm)	Aerosol Level (%)	Bulk Density (g/cm ³)	Specific Energy Consumption (Watts/g)	Die Extension
160	50	0.1	0.638 ± 0.132	***	
160	50	0.5	0.467 ± 0.034		***
160	100	0.1	0.399 ± 0.047	***	***
175	100	0.1	0.308 ± 0.022	***	***
175	50	0	0.364 ± 0.017	24.35	***
175	100	0	0.294 ± 0.023	16.09	•••
175	150	0	0.242 ± 0.020	9.64	***
160	50	0	0.480 ± 0.057	•••	no heat tape
160	100	0	0.416 ± 0.04	***	no heat tape
160	100	0	0.292 ± 0.026	***	with heat tape
160	100	0	0.442 ± 0.028	•••	•••

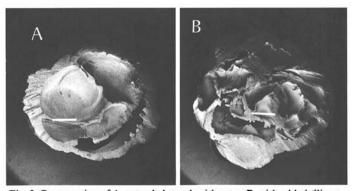


Fig. 3. Cross section of A, extruded starch without or B, with added silicon dioxide (bar = 1,000 μ m).

barrel and entered the die, it was subjected to a pressure gradient. As the melt moved toward the end of the die, some of the trapped air bubbles began to expand. Occurring simultaneously was a cooling of the melt as heat was lost to environment, causing the melt to become more viscous. When the melt exited the die, few of the trapped air cells expanded and became visible. However, when the glassy rod was deep-fat fried, there was ample and continuous heat. The starch melt was not cooled when water started to evaporate and sufficient internal pressure could be generated to expand the small trapped air bubbles as well as the starch hila. Thus, the deep-fat fried glassy rod had some big cells scattered through the uniform, honeycomb structure. In extrusion, the evaporation of superheated water created internal pressure to expand some of the trapped air bubbles. At the same time an increase in melt viscosity occurred because of the loss of plasticizer and a reduction in temperature resulting from evaporation of water. That increase in viscosity prevented the starch hila from expanding but still allowed the big cells, which had already expanded inside the die, to expand further. Therefore, the extrudates had fewer but bigger cells than the same sample deep-fat fried.

Starch granules were heated (50% solid) to 80° C and sliced into 0.2-cm thick chips and air-dried. The starch was dispersed in water; therefore, there should have been no trapped air bubbles. Frying that air-dried starch gel produced a fine-celled honeycomb structure with no big cells (Fig. 4A). We also prepared starch chips from dissolved starch. The glassy chip from dissolved starch did not puff when it was deep fat fried. Because the dissolved starch has no hila, this suggests that the starch hilum was the nucleation site in the starch chip. The fact that the starch hilum was essential for the starch chip to puff indicated that the nucleation site could not be created during heating.

If the starch hilum is the nucleation site for extrusion, then

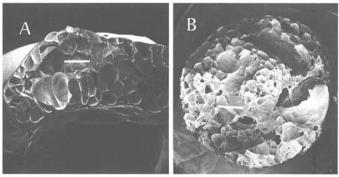


Fig. 4. Cross section of A, expanded (fried) dried starch chip and B, expanded (fried) starch glassy rod captured by the die extension (bar = $1,000 \mu m$).

extruding the dissolved starch should produce a glassy rod. If the trapped air is the major nucleation site, then the extrudates should expand. Extrusion of the dissolved starch gave a melt that expanded and then collapsed after it exited the die. The excessive shrinkage of the extrudates caused a wrinkled surface. Scanning electron microscopy showed that the extrudates from dissolved starch had many small cells (Fig. 5B). Apparently, air bubbles were trapped and were the major nucleation sites for extrudates.

The melt from dissolved starch must have had lower viscosity (more mobility) than the control; thus, the extrudates collapsed upon cooling. Measurement of relative viscosity of the extruded control and dissolved starch indicated that the molecular size of the extruded, dissolved starch was much smaller than that of the control (Table IV).

CONCLUSIONS

Addition of sodium bicarbonate or sodium carbonate alone to starch increased expansion but reduced the structural strength of extrudate. These beneficial effects are caused by the CO2 produced from neutralization of the bicarbonate or carbonate by the acids generated from oxidation of starch. Extrusion of starch with base induced starch oxidation; therefore, bicarbonate and NaOH both caused caramelization and increased the cold paste viscosity of the extruded starch. Acidulants neutralized the NaHCO3 before it induced starch oxidation and, therefore, further improved the expansion and eliminated the caramelization problem. It appeared that the starch hila were the nucleation sites in the puffed starch chips, and trapped air bubbles were the major nucleation sites for extrusion. Experimental data indicated that the amount of shear and effectiveness of the plasticizer significantly influenced the degradation of starch molecules in extrusion. More study is needed to understand the effects of operating conditions, such as screw speed, die length, die size, temperature, and moisture, on extrusion.

TABLE IV
Properties of Extrudates from Control Starch, Dissolved Starch, and Dissolved Starch plus Silicon Dioxide

Type of Starches	Bulk Density (g/cm ³)	Moisture (%)	Relative Viscosity
Control (pH 9.3)	0.307 ± 0.035	10.59	0.283
Dissolved starch ^b (pH 9.3)	0.648 ± 0.117	9.18	0.159
Control (pH 7)	0.280 ± 0.047	•••	0.263
Dissolved starch ^c (pH 7)	0.387 ± 0.120		0.129
Dissolved starch (prior to extrusion)		***	0.296

^aOf extrudate.

^cDissolved by autoclaving.

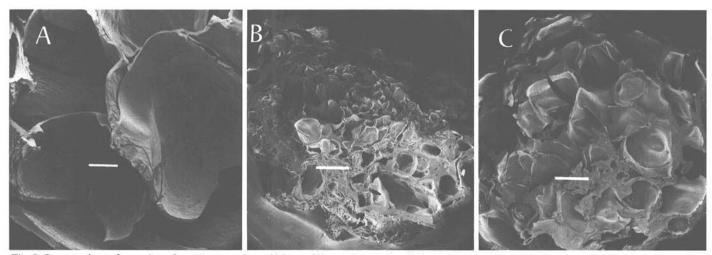


Fig. 5. Cross sections of extrudates from: A, control starch (bar = $500 \mu m$); B, autoclaved dissolved starch (bar = $1,000 \mu m$); and C, autoclaved dissolved starch plus 0.5% silicon dioxide (bar = $1,000 \mu m$).

^bDissolved with base.

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