Effect of Processing Conditions on Intrinsic Viscosity of Extruded Cornstarch

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SYNOPSIS

Unmodified cornstarch from dent corn was used in this study to determine the effect of twin-screw extrusion conditions on the intrinsic viscosity of this polysaccharide and water. The study focused on the intrinsic viscosity of the cornstarch as a function of the key variables. Primary variables examined were temperature (75, 100, and 125°C), starch concentration or consistency (35, 50, and 65%), and screw speed (100, 200, and 300 rpm) during the extrusion processing. The most favorable conditions examined were the extrusion of the cornstarch at 35% consistency, 100°C, and 200 rpm. Two-thirds of the original intrinsic viscosity of the unmodified starch was retained upon extrusion at 35% consistency at all temperatures and the screw speeds (200 and 300 rpm) examined. Also, similar values were observed at 50% consistency for 75°C at 100 and 200 rpm and for 100°C at all three screw speeds. © 1996 John Wiley & Sons, Inc.†

INTRODUCTION

A mixture of two glucose polymers (amylose and amylopectin) comprises the starch molecule, the predominant component in cereal grains,[1] with about 25–30% being amylose.[2] Extrusion cooking of starch has been studied extensively during the last decade.[3] The process of extrusion is vital to food, feed, plastics, and other polymer processing. Prior studies have considered the effect of extrusion variables upon the molecular degradation, gelatinization, melting, expansion volume, and other physicochemical changes in starches.[4–16] More information is needed on the effect of twin-screw extrusion variables on the degradation of the starch. This study focused on the intrinsic viscosity of the dehydrated cornstarch extrudates as a function of processing variables, including extrusion temperature, solids, and screw speed.

EXPERIMENTAL

Extrusion

Buffalo 3401 cornstarch, a food-grade starch supplied by CPC International (Englewood Cliffs, NJ) with an amylose/amylopectin content of dent corn, was processed with distilled water in a Werner & Pfleiderer (Ramsey, NJ) intermeshing, corotating, ZSK 30 twin-screw extruder under varying conditions. These variables included solids content, screw speed, and barrel section temperature settings. Pressure on the melt varied according to these conditions, but it was not evaluated as an independent variable. Extruder runs were made such that sets of samples could be compared based on one variable. The extruder consisted of 14 barrel sections (divided into seven independently controlled temperature zones) used in previous and subsequent studies as a reactor for converting starch to chemical derivatives.[17] These experiments were primarily for studying the effect on starch in reactive extrusion re-

* Names are necessary to report factually on available data. However, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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quiring a long barrel for increasing residence time. The temperature was computer controlled in the zones with electrical resistance heaters and the circulation of an ethylene glycol/water mixture (50/50, v/v) through special cooling channels inside the barrel sections. Cornstarch in its air-equilibrated state with a moisture content of about 10% was fed into the first barrel section of the extruder (25°C) by a K-TRON (Pitman, NJ) model T20, F-1 feeder. Barrel sections 2 and 3 of the extruder were maintained at 70°C for all runs. Distilled water was injected directly into the extrusion channel at the third section by a high-pressure piston pump (EK 1, American Lewa Inc., Holliston, MA) at a rate sufficient to give the desired moisture level when combined with the starch's inherent moisture content.

The range of the variables used was as follows. The temperature settings along zones 1 through 7 were, respectively: 70, 75, 75, 75, 75, 75, 75°C; 70, 100, 100, 100, 100, 100, 70°C; and 70, 125, 125, 125, 125, 110, 50°C. These settings will be referred to as 75, 100, and 125, respectively. Actual material temperatures remained reasonably close to these settings. Starch solids levels were 35, 50, and 65% (dry basis). Screw speeds were 100, 200, and 300 rpm. Starch was fed at the rate of 84 g/min (as is moisture). The mixing screw contained a variety of conveying, kneading, reverse pitch, and compression screws. With the kneading blocks followed by reverse pitch screw sections, this configuration provides higher shear (see Fig. 1). Selected combinations of variables led to separate extruder runs.

Before a sample was collected, the extruder was given sufficient time to equilibrate at the imposed run conditions (judged by the stabilization of torque, pressure, and temperature). Then a sample was collected in a plastic bag for 2 min while the actual melt conditions were measured along eight of the extruder barrel sections equipped with thermocouple sensors. After each sample was allowed to air cool, the resulting solid extrudate was divided into smaller pieces and sealed inside bags.

Drying

To prepare the samples for intrinsic viscosity study, they were spread out on metal trays and placed in a VirTis (Garginer, NY) 100-SRC freeze drier for a week. This was necessary to minimize the possible detrimental effects of grinding.[12] When the samples were removed, they were allowed to equilibrate in moisture content at room conditions and then sealed in glass jars.

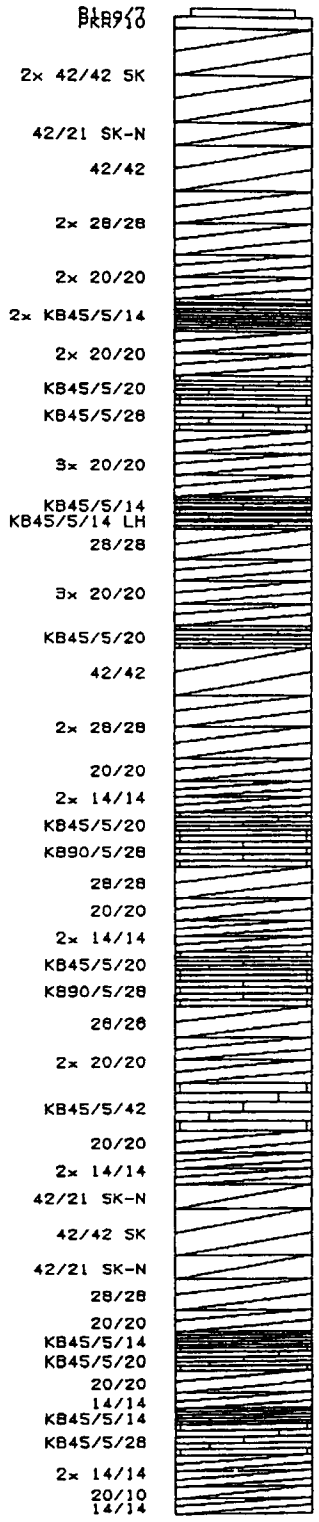

Figure 1 Screw profile of the twin-screw extruder.

Grinding

To facilitate the solvation process necessary for determining intrinsic viscosity, the dried samples were ground in an Arthur H. Thomas Company (Philadelphia, PA) ED-5 Wiley mill using a 1-mm screen. Care was taken to avoid excessive heating during the grinding process, and dry ice was added in the grinding of the more arduous samples. This undesirable heating effect also limited the mill size screen to 1 mm.

Sample Preparation

To accurately determine the starch concentrations used in the intrinsic viscosity solutions, ground samples were dried in a forced-air oven at 105°C overnight. Samples were rapidly removed from the oven and placed in a desiccator, under vacuum for 30 min, containing anhydrous calcium sulfate with 3% cobalt chloride as the desiccant. Dry containers were weighed using a Sartorius (Brinkmann Instruments, Westbury, NY) model A200S analytical pan balance with digital readout, and between 1 and 3 g starch was added. The dry container/wet sample weight was recorded, and the containers were returned to the oven where they remained for 4 h. The dry weight of the container and sample was measured after cooling in the desiccator. After at least one repetition, the average dry weight percentage of the ground sample was determined.

Next, the solutions to be used in a Cannon (State College, PA) CUSDU-11 series 100 Ubbelohde, uncalibrated, four-bulb, shear dilution viscometer were prepared. Each sample of around 0.209 g was weighed directly into a Pyrex, 50-mL volumetric flask (±0.05 mL). The sample was dissolved in sufficient 1*N* KOH solvent (Fisher Scientific, Pittsburgh, PA) certified 1.005–0.995*N* to prepare 50 mL of solution at ambient temperature. This heterogeneous solution was shaken on a LabLine Instruments (Melrose Park, IL) model 3589 multi-wrist-action shaker (set at 7.5) for 24 h (±4 h). By visual observation, it was determined that this shaking action (combined with more vigorous hand shaking and mixing in a beaker just before pipetting for viscometry work) provided homogeneous solutions.

Intrinsic Viscosity Measurement and Extrapolation

To make viscosity measurements, the viscometer was placed vertically in a Cannon CT-1000 constant temperature water bath maintained at 25°C (±0.2°C). Three or six dilutions for a good curve fit were made with two to three runs (for checking purposes) at each dilution. Flow times on each of the four bulbs were visually measured with the aid of two calibrated digital stopwatches. Seven milliliters of sample solution was added to the viscometer using a Gilson Brand, Pipetman precision microliter pipette (Rainin Instrument Company, Woburn, MA). Four milliliters of 1*N* KOH was added and the two liquids were vigorously mixed by bubbling air through them. Each successive run for a given dilution was performed after remixing the solution to avoid error due to the repeated shear of the same starch molecules.

The viscometer was cleaned between samples by the following steps. First, the starch solution was poured out, and the viscometer was filled with distilled water. The water was removed, and the viscometer was filled with concentrated sulfuric acid. After 0.5 h, the acid was drained and then flushed with water. Next, the viscometer was completely filled with acetone and allowed to stand for a few minutes before applying a vacuum. Finally, the cleaned viscometer was dried at 105°C for 1 h and was allowed to air cool before being used again.

The points (mL/g) obtained for each dilution were then plotted against the concentrations (g/mL), and the best linear fit with corresponding y intercept was obtained using Jandel Scientific's TableCurve program. Data from bulb two of the viscometer were used primarily for comparisons because relative viscosities were generally less than 1.5, as recommended,[5] the standard error in each curve fit was the most acceptable, and the chance of error due to additive shearing degradation effects from the viscometer bulbs was reduced.

Statistical Analyses

Least squares multiple linear regression was done using Microsoft (Redmond, WA) Excel 5.0 for Windows to develop quantitative expressions for the relation of specific mechanical energy (SME), moisture content, and temperature to intrinsic viscosity.

RESULTS AND DISCUSSION

General

The intrinsic viscosity of the cornstarch before extrusion was determined to be 243 mL/g using the 1*N* KOH solvent method described above. The effect

Table I Cornstarch Extrusion Conditions and Effect on Intrinsic Viscosity

Consistency (%)	Temperature (°C)			rpm			Torque (%)	Pressure (kPa)	Intrinsic Viscosity (mL/g)
	75	100	125	100	200	300			
35	X				X		19	414	162
	X					X	21	414	160
		X			X		15	379	211
		X				X	18	379	190
			X		X		15	310	172
50	X			X			30	345	181
	X				X		28	414	165
	X					X	29	414	149
		X		X			21	345	162
		X			X		22	310	164
		X				X	24	276	179
			X		X		22	241	147
			X			X	25	207	152
65	X			X			67	414	152
	X				X		60	414	138
	X					X	47	345	133
		X		X			49	276	154
		X			X		48	276	139
		X				X	47	345	152
			X	X			41	138	144
			X		X		44	206	123
			X			X	45	276	120

of three primary variables on the extrusion of the cornstarch was measured by their intrinsic viscosity values. Table I shows the accompanying extruder conditions during the experiments.

The solutions could not be used more than 1 day after their preparation due to the time degradation effect of the solvent as determined by side experiments. This observation seems to be supported by the gelatinization procedure involving the addition of alkali.[18] It was determined also that filtration of the solution affects the intrinsic viscosity to a small degree (may lower the viscosity value obtained by as much as 3 where a typical value is 180 mL/g), by reducing the sample concentration. Therefore, the samples were not filtered.

Temperature

Extrusion temperature has the greatest effect on the starch extrudate viscosity because it affects the slurry viscosity inside the extruder, contributing to both thermal and mechanical degradation of the starch. Of the three temperature settings, the 100°C setting was generally the gentlest, as judged by the highest intrinsic values (Table I). Apparently, this result is a compromise between excessive shear from the higher viscosity of low temperatures and excessive thermal degradation effects of higher temperatures; consequently, it is less degrading than the other two temperature settings. The lower intrinsic viscosity values for the 75°C setting can be attributed to a higher slurry viscosity that in turn allows the shearing effect of the screw to transfer more mechanical energy to the starch. The 125°C temperature setting shows definite degradation from the 100°C. This can be attributed to thermal-induced gelatinization discussed by Gomez and Aguilera,[11] but a lower slurry viscosity reduces the effect of shear. Wang[16] showed that shear energy is more effective than thermal energy in the gelatinization of starch.

Water Concentration

As a general trend, the 65% starch solids extrusion processing resulted in lower extrudate viscosity values than at 50% solids. Of the 22 experiments, all samples extruded at 65% solids exhibited intrinsic viscosity values under 160 mL/g. This can be attributed to the higher slurry viscosity, which allows

shear to have a greater effect upon the starch. Ten samples of extruded starch had intrinsic viscosity values of 160 mL/g and above, equal to at least two-thirds of the original value. Only one sample extruded at 125°C retained an intrinsic viscosity above 160 mL/g (172 mL/g), but the starch consistency of this sample in the extruder was 35%. It must be noted that starch appears to undergo two distinct cooking mechanisms, demarcated by the 39% starch solids (61% moisture level) reported by Wang.[16] This needs to be considered whenever comparisons are made across this moisture level boundary. Also, there is less water available to act as a coolant, so the starch absorbs more thermal energy. This latter effect may be minimal, due to the temperature control design of this extruder.

Screw Speed

Screw speed, as well as screw configuration, is directly responsible for both shear rate and residence time of the material in the extruder. As concluded by Bhattacharya and Hanna,[4] these effects oppose one another because under certain conditions, reduced retention time may cause less granule swelling, due to lower mechanical shearing. Also, the extent of degradation is a factor of residence time multiplied by shear rate. Screw speed influences the viscosity of the melt in the extruder and is interrelated to temperature, shear, moisture, and residence time conditions. The lower viscosity reduces the ability of the extruder to effectively transfer mechanical energy via shear. However, at 75°C the viscosity is high enough that the higher screw speeds result in some starch degradation, but the high water concentration appears to minimize this effect. More research is needed to evaluate the effect of screw speed at 125°C and 35% solids.

The effect of screw speed at 50% moisture is more complex and more dependent upon temperature. The general trend of temperatures has the effect elucidated earlier, but screw speed changes have varying effects. At 100°C, similar degradation occurred at 100 and 200 rpm, and less degradation occurred at the lowest consistency. At 75°C, the intrinsic viscosity of the extrudate decreased with an increase in screw speed.

The effect of screw speed when related to temperature is even more intricate when considered at the relatively high solids mass flow (65% solids). Both the 75 and 125°C settings show the combined effect of shear rate and retention time. At 75°C, shear can have a very significant effect on the starch, so the retention time of the slurry inversely affects the intrinsic viscosity of the extrudate. At 100 rpm, the extruded starch was less degraded than at 200 rpm, but the longer retention time at 100 rpm caused the starch to be less degraded than with the 300 rpm setting. On the other hand, the starch from the 100 rpm/125°C condition was less degraded than the starch from the 300 rpm setting. Samples from the 200 and 300 rpm screw speeds at this temperature (125°C) and moisture are relatively indistinguishable using this method of analysis, showing the important affects of both shear rate and residence time of screw speed upon extrudate viscosity values.

The following curve fit was obtained for the extrudates: intrinsic viscosity (mL/g) = 227 − 0.828 (SME) − 0.721 (solids) − 0.162 (°C) $r^2 = 0.626$. The SME and moisture content (solids) were the most important factors affecting conversion during the twin-screw extrusion. The highest temperature (125°C) had a thermal degrading effect on the starch in the extruder.

CONCLUSIONS

Two-thirds of the original intrinsic viscosity of the starch was retained upon extrusion at 35% consistency at 75, 100, and 125°C at 200 and 300 rpm. However, the least degradation of cornstarch occurred at 100°C and 200 rpm (35% starch solids). The most important factors affecting conversion during twin-screw extrusion were SME and moisture content (solids).

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