

Effects of Jet-Cooking Conditions upon Intrinsic Viscosity and Flow Properties of Starches

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SYNOPSIS

This work examined the sensitivity of intrinsic viscosity values of jet-cooked waxy maize starch to initial pH conditions and the effects of jet-cooker steam pressure parameters upon the intrinsic viscosity and flow viscosity values of four jet-cooked starches. Flow viscosities of the 10 wt % cooked starches and intrinsic viscosities in 90% DMSO-H₂O were the lowest when mixing and turbulence during steam jet-cooking was increased (i.e., by adjusting steam line pressure vs. pressure within the cooking chamber to allow greater amounts of steam to flow through the apparatus). The percent decreases of the intrinsic viscosity caused by the most severe cooking conditions compared to gentle cooking conditions were 52, 45, 32, and 12, respectively, for waxy maize, waxy rice, normal maize, and 70% high amylose maize starches. Initial pH values, from 3 to 10.5, of waxy maize starch had minor effects upon the intrinsic viscosity of the jet-cooked material. © 1996 John Wiley & Sons, Inc.†

INTRODUCTION

In jet-cooking of starches, a technique known for many years,¹ an aqueous slurry of granular starch is pumped to a Venturi where it is combined with high-pressure steam and forced through the Venturi within milliseconds. This action subjects the starch to a sudden increase in temperature and to high shear forces that gelatinize, disrupt, and solubilize the granules, thus producing an aqueous starch fluid. Jet cookers have been used to process starches for paper coatings,^{2,3} to disperse and cook cereal flours,⁴ and to prepare intimate mixtures and complexes of starch and poly(ethylene-co-arylic acid).⁵ However, there has been relatively little basic research reported in the literature concerning the jet-cooking of starches and even less about the effects of cooking conditions upon the mo-

lecular parameters of solubilized starches. The purpose of this report was to examine some effects of pH, starch type, and steam pressure processing conditions upon the intrinsic viscosities and other flow properties of the jet-cooked starch fluids.

The cooked starches were examined in both the dilute and concentrated states. According to the theory of uncharged polymers in dilute solution, the intrinsic viscosity, $[\eta]$, is proportional to the cube of the radius of gyration divided by the molecular weight (R_G^3/M_w) and therefore to both the hydrodynamic volume and molecular weight of the polymer in solution.⁶ Hence, measurement of $[\eta]$ as a function of processing conditions provides insight into the effects of processing upon the molecular parameters of the polymer. Viscosity measurements on the cooked starches as a function of processing conditions are of practical interest since the cooked dispersions/solutions often are used directly in applications. The amylopectin components of starches have the property of forming shear-induced structures, provided that the starch has not been treated too harshly.⁷ The effects of jet-cooking conditions upon the structure-forming ability of waxy maize starch, therefore, was also investigated.

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 USDA implies no approval of the product to the exclusion of others that may also be suitable.

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EXPERIMENTAL

Materials

Three unmodified maize starches and one waxy rice starch were used in this investigation. Amioca® (a waxy maize starch consisting of about 98% amylopectin) and Amylomaize® VII (a starch consisting of about 70% amylose) were purchased from American Maize-Products Co. (Hammond IN). Normal maize starch, Buffalo® starch 3401, consisting of about 28% amylose and 70% amylopectin, was purchased from the Corn Products Division of CPC International (Summit-Argo, IL). A low-protein waxy rice starch, StarchPlus® SPW-LP, was donated by California Natural Products (Lathrop, CA). All chemicals used in this work were reagent grade. The 90% (wt/wt) DMSO-H₂O mixed solvent was prepared by adding 10 g of distilled water to 90 g DMSO. Initial concentrations of pasted starches in 90% DMSO-H₂O were prepared by adding 10 g of hot, freshly jet-cooked starch to a 100 mL volumetric flask and then diluting to the mark with DMSO. This solvent system was chosen for intrinsic viscosity measurements because it is a good solvent for starch, and both amylose and amylopectin are stable in it.

Jet-cooking

A schematic diagram of a Venturi-type jet cooker is presented in Figure 1. An aqueous starch slurry (133.3 g, dry basis, in 1 L of distilled water) was pumped into the inlet at a rate of about 1.4 L/min. Steam line inlet pressures were either 70 or 120 psig (corresponding to temperatures of about 158 or 176°C). Steam cooking conditions are designated by two pressures: *A/B*, where *A* is the steam line inlet pressure indicated by pressure gauge *A* (either 70 or 120 psig), and *B* is the pressure in the Venturi chamber of the cooker as indicated by pressure gauge *B*. Cooking pressure, defined as pressure *B*, is adjustable by opening or closing the back pressure valve. Concentrations of starch in the initial slurry were adjusted to yield a cooked starch fluid containing 10% (wt) solids. It was necessary to use somewhat higher starch concentrations in the slurry to compensate for dilution of the cooked dispersions with condensed steam. The cooked starch was collected in a stainless steel Dewar flask initially at room temperature and transported back to the laboratory.

A weighed portion of each cooked dispersion was lyophilized to determine percent solids, which were

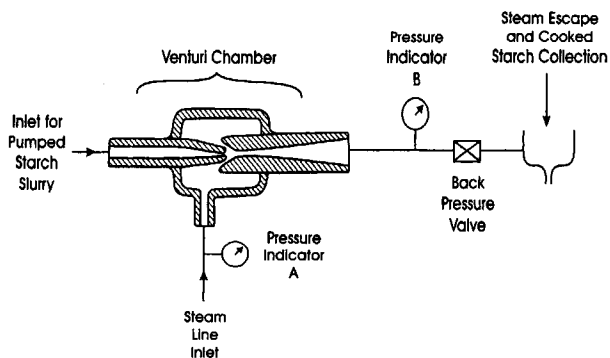


Figure 1 Schematic of jet-cooking system.

invariably within 0.3% of the desired value. Aliquots of the jet-cooked starches were diluted with distilled water to about 1% concentrations and then immediately precipitated with ethanol. These starch-ethanol complexes were critical point-dried, coated with Au-Pd, and viewed with a JEOL 6400 V scanning electron microscope. No intact starch granules or granule fragments were observed.

Viscosity

Flow measurements of the 10% jet-cooked dispersions were made in a Couette-type concentric cylinder viscometer (Haake, Rotovisco® RV20, measuring system M) at 40°C. Shear sweep measurements were made by accelerating the inner cylinder uniformly from rest to 750 S⁻¹ over a period of 2 min and then, without pause, decelerating back to a zero shear rate over a period of 2 min. This 4 min cycle was repeated immediately after completion of the first cycle.

Intrinsic viscosities were measured using Cannon-Ubbelohde shear dilution viscometers, Series 150, at the lowest obtainable shear rates (<100 S⁻¹). These measurements were made at 25.0 ± 0.1°C. Stock starch concentrations in 90% DMSO-H₂O were diluted by weight and initial concentrations used for intrinsic viscosity calculations were determined from optical rotation values by using a specific rotation of 190 at 589 nm for the maize starches.⁸ Concentrations of waxy rice starch were based on values of the lyophilized material. Concentrations of the maize starches determined by lyophilization agreed well with values determined by optical rotation.

pH Determinations and Adjustments

The pH values of both the uncooked starch slurry and the jet-cooked starch fluids were obtained at

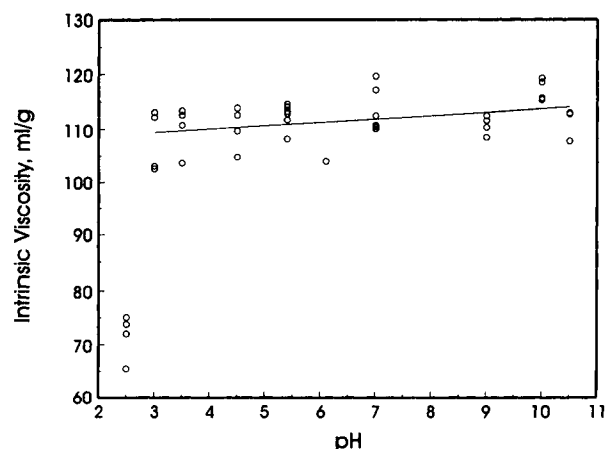


Figure 2 Intrinsic viscosity of 10% (wt) jet-cooked waxy maize starch vs. pH of initial slurry. 70/40 steam pressures.

room temperature with a Ag/AgCl electrode (Orion, Model 19-02). A small portion of the cooked starch was placed in a beaker to cool for several hours prior to measurement. Dilute concentrations of either NaOH or HCl were used to adjust the uncooked starch slurry to a desired pH.

RESULTS AND DISCUSSION

Slurries of waxy maize starch were prepared, adjusted to a specific pH value, and jet-cooked at approximately 70/40 steam pressures. The intrinsic viscosities of the cooked starches (in 90% DMSO-H₂O) are presented in Figure 2 as a function of the initial pH of the slurry. A best-fit regression line was included for pH values from 3 to 10.5. A minimum of two samples were jet-cooked and measured in duplicate at all pH values except 6.1, where the result of a single cook and measurement is presented. As discussed later, there was little change in pH values caused by cooking the starches (Table I).

An obvious point of Figure 2 is that the intrinsic viscosity of the jet-cooked waxy maize starch is practically independent of slurry pH between pH values of 3 to 10.5. (Because of the known sensitivity of starch to acid hydrolysis, we were initially surprised by this result until we considered the short residence time of starch in the jet cooker.) Only at the pH value of 2.5 was the intrinsic viscosity of the cooked starch significantly lowered because of initial pH conditions. We did not test slurries at pH values > 10.5 because the starch granules would begin to dissolve. A range of approximately 12 mL/g is indicated for the intrinsic viscosity values of the cooked starch (pH values 3–10.5). Duplicate intrinsic

Table I pH Values of Initial Starch Slurries and Cooked Pastes

Starch Type	Uncooked Slurry	Jet-cooked Paste
pH of slurry not adjusted^a		
Waxy maize	6.1	6.2 NS
Normal maize	4.2	4.9*
Amylomaize VII	4.2	4.3 NS
Waxy rice	7.1	7.4*
pH of slurry adjusted^b		
Waxy maize	2.5 ^c	2.2
	3.0	3.3
	3.5	3.8
	4.5	5.0
	5.4	5.6
	7.0	8.1
	9.1	9.4
	10.0	10.0
	11.0 ^d	10.4

ANOVA: * $P < .01$, NS = difference not significant.

^a Average of $n = 4$, 70/65 and 120/40 steam conditions.

^b Average of $n = 2$, 70/65 steam conditions.

^c Approximately 30 mL of 0.5N HCl needed to adjust pH.

^d Approximately 20 mL of 0.7N NaOH needed to adjust pH.

viscosity measurements on the same cook were within 6% of each other.

The intrinsic viscosity behavior of different starches jet-cooked at 70/65 or 120/40 steam conditions is displayed in Figure 3. All samples were cooked in duplicate and the intrinsic viscosity of at

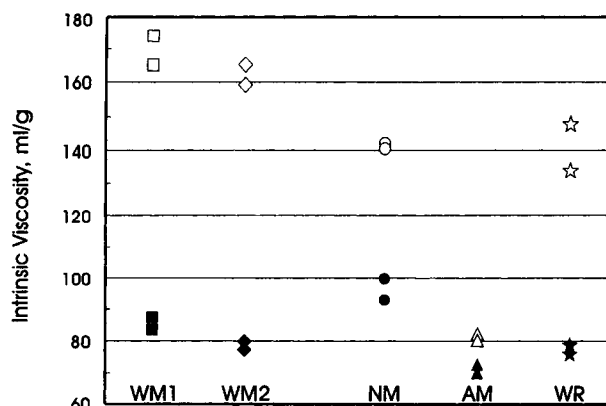


Figure 3 Effect of steam pressures and starch type upon intrinsic viscosity of 10% (wt) jet-cooked starches. Open symbols: 70/65 steam; filled symbols: 120/40 steam. WM1: waxy maize starch, pH initially adjusted to 7.0. WM2: waxy maize starch, as is (i.e., pH not adjusted). NM: normal maize starch, as is. AM: amylo maize VII starch, as is. WR: waxy rice starch, as is.

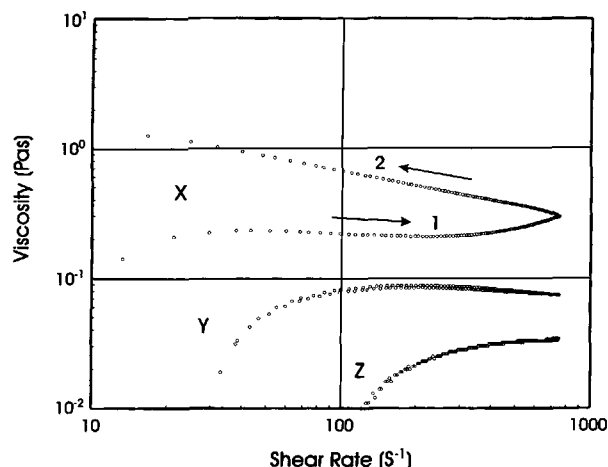


Figure 4 Effect of steam pressure conditions on flow properties of 10% (wt) jet-cooked waxy maize starch; first cycle of shear sweep measurement: (X) 70/65 steam, flow induced structure in state 2; (Y) 70/40 steam; (Z) 120/40 steam.

least one of the two samples was measured in duplicate. We note that only for high amylose starch (AM) is there little difference between the intrinsic viscosity of the “gently” cooked material, 70/65 steam, and the “severely” cooked material, 120/40 steam. The intrinsic viscosities of the other three starches were greatly affected by the difference in cooking conditions. Also, the intrinsic viscosities of waxy maize starches whose slurries were adjusted to pH 7 (WM1) apparently were slightly higher than those from the “as is” slurries at pH 6.1 (WM2). Starches dispersed by gentle stirring in 90% DMSO–H₂O at 85°C for 2 h had intrinsic viscosities approximately 20% greater than those starches jet-cooked at 70/65 steam.

In Table I are presented comparisons of pH values of the uncooked slurries with the corresponding jet-cooked dispersions. Generally, there was less than one pH unit change between the uncooked and the cooked materials, and except for the pH extremes of slurries with adjusted values, the pH of the cooked dispersion was slightly higher.

The responses to the first cycle of a 4 min shear sweep experiment are presented in Figure 4 for 10% (wt) jet-cooked waxy maize starch dispersions prepared at different steam pressure conditions. The sample cooked at 70/65 steam (X) shows the two-state viscosity behavior of amylopectin that has been dispersed with sufficient gentleness to maintain the property of being able to form a shear-induced structure.⁷ At 300 S⁻¹, $\eta = 0.21$ Pa s in state 1 and 0.44 Pa s in state 2; $[\eta] \sim 163$ mL/g in 90% DMSO, 25°C. The arrows and numbers indicate the order

of data collection. The initial state 1 shows the first half of the first cycle and state 2, which now has shear-induced “structures,” shows the second half of the first cycle. At shear rates < 50 S⁻¹ in state 1, the limits of instrument response were exceeded and therefore we consider the initial four data points to be unreliable. The two other samples, cooked at 70/40 (Y, $\eta = 0.086$ Pa s at 300 S⁻¹, $[\eta] \sim 105$ mL/g) or 120/40 (Z, $\eta = 0.028$ Pa s at 300 S⁻¹, $[\eta] \sim 78$ mL/g) steam pressures, no longer exhibit the formation of a shear-induced structure. The shear sweep tests of these samples indicated only one viscosity state. The increased severity of cooking conditions within the jet cooker has reduced the flow (shear) viscosities of samples Y and Z as shown in the figure. The dispersions Y and Z are so reduced in viscosity compared to X that at low shear rates the viscosity is well below the sensitivity of the measuring instrument. Thus, we consider that approximately the initial half of curves Y and Z are artifacts of the measuring system.

The viscosity of the cooked 10% starch fluid decreased as the severity of the jet-cooking conditions increased. This expected behavior is indicated in Table II. Viscosity values for the high amylose starch were uncertain because the dispersions gelled rapidly at 40°C and, at higher temperatures, the viscosities were below the limit of instrument sensitivity.

This work has revealed some interesting aspects of the jet-cooking of starches. The lack of sensitivity to the initial slurry pH conditions (Fig. 2) is most likely a result of the rapid cooking aspect of the steam jet, wherein the starch granule was subjected to high shear forces and high-temperature gradients within milliseconds. Our terminology of “gentle” (70/65 steam) and “severe” (120/40 steam) jet-cooking corresponds to the Klem and Brogley² (1981) discussion of “thermal-jet” and “excess-steam-jet” cooking. We agree with the concept of these workers that the combination of higher steam

Table II Viscosity of Jet-Cooked Starches

Starch Type	Viscosity ^a (Pa s)	
	70/65 Steam	120/40 Steam
Waxy maize	0.68 ^a	0.035
Waxy rice	0.84	0.048
Normal maize	0.30	0.055
Amylomaize VII ^b	—	—

10% (wt) starch pastes, 40°C flow, 130 S⁻¹.

^a State 2 viscosity, upper curve.

^b Paste gelled at 40°C.

line pressures and pressure differences in the Venturi chamber cause greater turbulence and higher shear forces that result in greater degradation of starches during severe jet-cooking.

The influence of gentle versus severe cooking conditions upon intrinsic viscosity as a function of starch variety is demonstrated in Figure 3. The decreases of intrinsic viscosity, $100 \times \{[\eta]_{70/65 \text{ steam}} - [\eta]_{120/40 \text{ steam}}\} / [\eta]_{70/65 \text{ steam}}$, were approximately 52, 45, 32, and 12%, respectively, for waxy maize, waxy rice, normal maize, and Amylomaize VII starches. We speculate that the relatively low percentage decrease for Amylomaize VII is a result of the following possible factors: (a) the low concentration of amylopectin, which is more sensitive to shearing because of its greater hydrodynamic volume; (b) the amylopectin could be less easily degraded than amylopectins from waxy starches; and (c) granules of high amylose maize are more difficult to disrupt by thermomechanical means than are the granules of waxy maize or normal maize starches.⁹ Because of the short residence time in the Venturi chamber and the probable greater difficulty in disrupting granules of high amylose starch versus the other starches, the granule contents have been exposed less effectively to the cooking conditions. Thus, waxy starches suffered the greatest decrease and the high amylose starch the least decrease in hydrodynamic volume when subjected to severe cooking conditions. This result is compatible with previous works that show both amylose and amylopectin components degrade when starch undergoes extrusion cooking and that the more highly branched, high molecular weight amylopectin is degraded to a greater extent.^{10,11}

Dispersion viscosity can be controlled over wide limits by adjustment of steam pressures (compare

state 2 of X with Y and Z, Fig. 4, and refer to Table II). Although our steam-jet cooker is a simple device, it offers the operator the ability to prepare starch dispersions with a wide range of properties suitable for a variety of practical applications.

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