Jet Cooking of Waxy Maize Starch: Solution Rheology and Molecular Weight Degradation of Amylopectin

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ABSTRACT

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The effect of processing conditions in an excess steam jet cooker on the degradation of waxy maize starch was studied. The temperature of the steam, the flow rate of the starch slurry, and the concentration of starch were determined to influence the extent of degradation. The viscosity of concentrated solutions of the jet-cooked product and the intrinsic viscosity of dilute solutions were used as measures of the extent of molecular degradation. The viscosity decreased at higher reaction temperatures, and at higher steam-to-starch ratios. Multiple passes through the jet cooker decreased the viscosity dramatically for the first two passes, but little additional change was observed for further passes. The results show that mechanical and thermal degradation effects are both important in the jet cooking of waxy maize starch, although the primary effect is due to mechanical degradation.

Steam jet cooking of starch is an effective means of rapidly forming an aqueous starch solution. A slurry of granular starch is brought into contact with high-pressure steam, leading to the gelatinization, disruption, and solubilization of the granules. Jet cookers have been used traditionally to process starch for paper coating (Klem and Brogly 1981) and more recently to form starch-lipid composites (Fanta and Eskins 1995). Previous studies have demonstrated that the processing conditions in the jet cooker will affect the viscosity and molecular weight of the cooked product. This study examines a broader range of processing conditions to relate product differences to specific processing variables.

Dintzis and Fanta (1996) studied the jet cooking of four different starches under two different cooking conditions. At low steam flow rates, all of the steam is condensed as it heats the incoming slurry; this is referred to as gentle, or thermal jet, cooking. At higher steam flow rates, or excess steam cooking, the temperature remains higher in the jet cooker and the flow is turbulent. They showed that the intrinsic viscosities for waxy maize starch, normal maize starch, and waxy rice starch were much lower for samples prepared by excess steam cooking than by gentle cooking. However, a high-amylose maize starch showed only a small difference between the two treatments. The viscosity of 10 wt% cooked starch samples also decreased with increasingly severe cooking conditions. For the most gentle cooking conditions, the viscosity showed shear thickening and flow hysteresis, as also observed for gently dispersed waxy maize starch (Dintzis et al 1995).

Dintzis and Bagley (1995) compared the effects of gentle dispersion, autoclaving, and jet cooking on the viscosity and intrinsic viscosity of waxy maize, normal maize, and high-amylose maize starches. For the conditions they studied, the jet-cooked sample had the lowest intrinsic viscosity. The intrinsic viscosity decreased with increasing temperature for the autoclaved samples, but the value at 120°C remained constant with increased holding time, whereas at 140°C, it decreased for longer holding times. Increased free radical production at 140°C was suggested as a possible cause of the lower intrinsic viscosity. They also showed that the viscosity of aqueous solutions increased sharply for samples with intrinsic viscosities >170 mL/g.

The previous studies have shown that rheological methods provide a sensitive means of measuring the extent of starch degradation during jet cooking. In this study, measurements of the viscosity and intrinsic viscosity of waxy maize starch that was jet cooked under a broad range of conditions were obtained to understand better the influence of reactor conditions on the cooked product.

MATERIALS AND METHODS

Waxy maize starch (A.E. Staley, Decatur, IL) was suspended in distilled water using a blender (Waring, East Windsor, NJ). The initial concentration of granular starch was varied from 5 wt% to 20 wt% on a dry weight basis. This slurry was passed through a jet cooker under excess steam conditions, and the cooked starch was collected and analyzed. The jet cooker was constructed at NCAUR, and its components are described below.

The slurry was delivered to the jet cooker by a progressing cavity pump (Moyno, Robbins Meyers, Springfield, OH). The pressure in the slurry was measured at the exit of the pump. Flow rates for the slurry were determined in the absence of steam, and before each cook, a measure of the steam condensation rate was made by passing water at the same flow rate through the jet cooker in the presence of steam. Slurry flow rates ranged from 400 g/min to 1,500 g/min. All flow rate and condensation rate measurements were made by collecting and weighing the product as it exited the jet cooker.

Steam was supplied at pressures between 60 and 78 psig. The steam inlet line was equipped with a flowmeter (7700 series, King Instrument Co., Huntington Beach, CA), although when the jet cooker was operated with excess steam, it was very difficult to obtain a steady reading due to the pulsating flow. The steam flow rate for a steam pressure of 78 psig was estimated to be 380 g/min.

The starch slurry and steam were combined in a hydroheater (M103, Hydro-Thermal, Waukesha, WI), which combines the streams with the slurry introduced as an annular flow around the steam. The width of the annulus, and therefore the slurry velocity for a given flow rate, could be adjusted by means of a sliding combining tube. Downstream of the hydroheater, the combined fluid passed through a volume of ≈ 35 cm^3 before being flashed to atmospheric pressure. A diaphragm valve was used to control the back pressure and the temperature was also measured shortly before the exit.

The cooked starch was collected and the solids content was determined either by drum drying or using a moisture analyzer (Mettler-Toledo HG53, Greifensee, Switzerland). A portion of the cooked starch was diluted in distilled water to 5 wt% and mixed on a roller to disperse starch fully. The viscosity of these samples was measured in stress sweep experiments on a controlled-stress rheometer (CarriMed CSL^2 500, Dorking, UK) using a 60-mm diameter, 4°

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cone. The bottom plate contained a Peltier temperature-control system to maintain the temperature at 25.0 ± 0.1°C. Another portion was diluted with dimethyl sulfoxide (DMSO) to yield a solvent composition of 90% DMSO/H_2O (w/w). The concentration of these samples was determined from measurements of the optical rotation (Dintzis and Tobin 1969) with a polarimeter (Perkin-Elmer 341, Wellesley, MA). The intrinsic viscosity of these samples was measured using an automated viscosity system (Schott AVS 360, Hofheim, Germany). For the runs that started with 5wt% solids, the cooked product was concentrated to ≈7wt% solids by drying in a rotary evaporator under vacuum at 40°C and then proceeding as above.

RESULTS AND DISCUSSION

The effect of steam inlet pressure on the viscosity of 5 wt% aqueous starch solutions is shown in Fig. 1. The initial slurry in each case consisted of 10 wt% waxy maize starch, and the same flow rate of ≈1,000 g/min was used in each case. The back pressure was 40 psig in each case. The lower steam pressure results in a much higher viscosity, consistent with previous results. For the 70 and 78 psig cooks, the downstream temperature remained at 140°C, as expected for steam at 40 psig. However, for the 60 psig cook, the temperature fell to 107°C, indicating that this was a thermal jet condition, whereas the cooks with higher inlet steam pressure operated under excess steam conditions. The viscosity of each sample is a function of the shear rate, $\dot{\gamma}$. The simplest way to compare samples cooked under different conditions is in terms of the zero-shear-rate viscosity, η_0 which is the shear-rate-independent value of the viscosity at low shear rates. For solutions at the same concentration, η_0 increases with molecular weight, and the lower the shear rate at which the viscosity begins to decrease is a further indication of a high molecular weight.

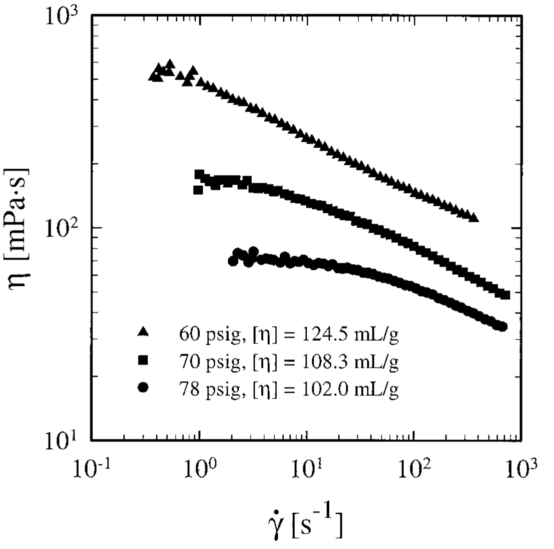

Fig. 1. Effect of steam temperature on viscosity of 5 wt% aqueous solutions of jet-cooked waxy maize starch. Initial slurry concentration 10 wt% and slurry flow rate 1,000 g/min.

One of the difficulties in understanding the mechanism of amylopectin degradation in a jet cooker is that for saturated steam, the temperature and pressure cannot be independently varied. Previous discussions of jet cooking have focused on the inlet steam pressure and the resulting shear as the explanation for changes in the cooked product, but the autoclave experiments of Dintzis and Bagley (1995) showed that increased temperature is also important. The aim of this work was to determine the relative importance of thermal and mechanical degradation effects in a jet cooker. Unless otherwise noted, all other results presented here are for an inlet steam pressure of 78 psig. The downstream pressure was also generally maintained at 40 psig. Decreasing the back pressure such that the temperature at the exit decreased from 140 to 125°C led to a 60% increase in the viscosity, and the shear rate dependence of the viscosity was nearly the same in each case. This is a small effect compared with the eightfold difference in zero-shear-rate viscosities shown in Fig. 1, but it further suggests that the rate of degradation depends on temperature.

To compare cooking conditions, each sample was characterized in terms of its zero-shear-rate viscosity, η_0, and its intrinsic viscosity, [η]. Each of these measures scales with molecular weight were used as measures of molecular weight degradation. However, there is expected to be a broad range of molecular weights present both in the native starch and the cooked product, and these measures do not provide any information about that distribution or changes in it. The value of the intrinsic viscosity in 90% DMSO for each experiment is listed in Fig. 1, and it also decreases with increasing steam inlet pressure.

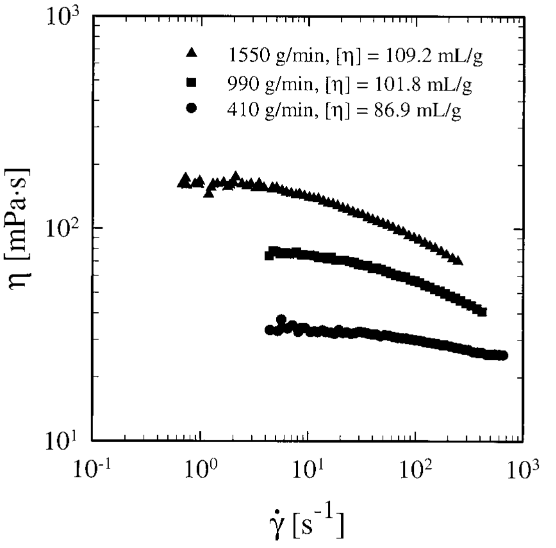

Fig. 2. Effect of slurry flow rate on viscosity of 5 wt% aqueous solutions of jet-cooked waxy maize starch. Initial slurry concentration 10 wt% and steam pressure 78 psig.

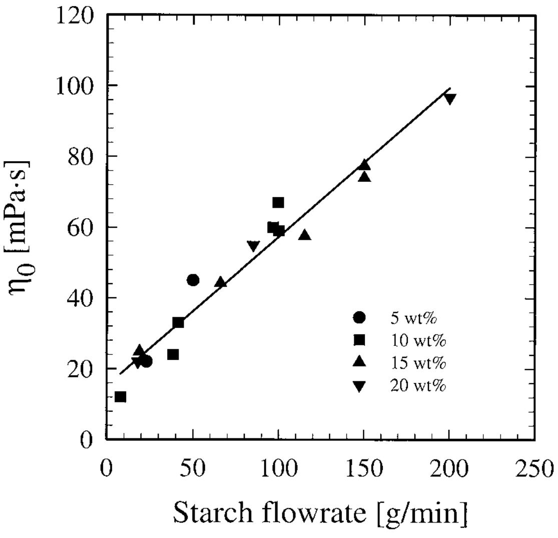

Fig. 3. Effect of slurry concentration and flow rate on the zero-shear-rate viscosity of 5 wt% aqueous solutions of jet-cooked waxy maize starch (r^2 = 0.96). Steam pressure 78 psig.

Because the steam temperature and pressure cannot be varied independently, a range of cooking conditions was achieved by varying the solids content of the starch slurry and the slurry flow rate. The effect of the slurry flow rate on the viscosity of 5 wt% aqueous solutions from cooks that began with 10 wt% starch is shown in Fig. 2. Each of these cooks was under excess steam conditions, yet the zero-shear-rate viscosity increased by almost a factor of five as the slurry flow rate was increased. For a cook with a higher slurry flow rate, it is necessary for more steam to condense to heat the slurry and gelatinize the starch. This decreases the total volumetric flow rate through the jet cooker, and therefore decreases the average shear rate. However, even for the almost four times higher slurry flow rate in Fig. 2, this is only expected to result in a 20% lower average shear rate. This is a small effect, and it will be at least partially offset by the higher viscosity of the cook with the higher flow rate. The mechanical degradation of polymers increases with the shear stress (Basedow et al 1979; Yu et al 1979), which is the product of the shear rate and the viscosity. Although details of the internal flow in the jet cooker are not accessible, differences in the flow field would not seem to account for the large differences in the cooked starch.

A similar series of experiments was also performed for initial slurry concentrations of 5, 15, and 20 wt% starch. The zero-shear-rate viscosity of aqueous solutions at a concentration of 5 wt% for all slurry concentrations and flow rates is shown in Fig. 3 to scale with the starch flow rate, which is simply the slurry flow rate multiplied the starch concentration. Although the viscosity of a cooked slurry depends on the solids concentration, when different products are compared on the same solids basis as in Fig. 3, the zero-shear-rate viscosity depends only on the starch flow rate. Although the results in Fig. 2 for a single slurry concentration of 10 wt% at different flow rates are not conclusive due to changes in the average shear rate, experiments at a single flow rate but different slurry concentrations should have the same flow field within the jet cooker. The energy input required for the gelatinization of the starch component of the dispersions (Krueger et al 1987) is negligible compared with that required to heat the different amounts of water at the different slurry flow rates. Because the total volumetric flow rate is expected to be the same for experiments at the same slurry flow rate, these experiments are expected to have the same average shear rate, and only the ratio of starch to steam is different.

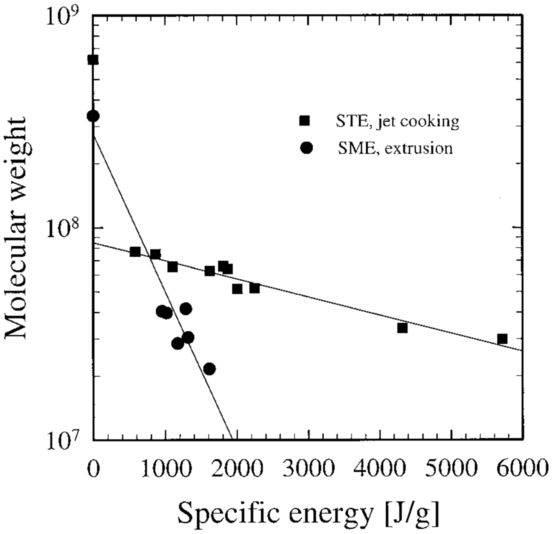

Fig. 4. Molecular weight of amylopectin as a function of energy input: specific thermal energy (STE) for jet cooking (r^2 = 0.95) and specific mechanical energy (SME) for extrusion (r^2 = 0.93). Extrusion data from Willett et al (1997).

In these experiments, the solids content of the cooked products was lower for the runs with low starch flow rates. This effect was present even after accounting for the condensation due to ambient heat losses, which would result in greater dilution of runs at low flow rates. Thermal scission degrades polymers at high temperatures (Odell et al 1992), so it was assumed that steam condensation beyond that required to heat the slurry and lost to ambient heat was the result of an input of thermal energy toward degradation of the starch. For each slurry flow rate, the jet cooker was operated without starch, and the amount of condensate was determined. The rate of condensation during a cook was calculated based on the solids content of the starch product and the starch flow rate. A specific thermal energy (STE) input was then calculated as

$$\mathrm{STE} = \Delta H_{vap}\,(\dot{m}_{XScond}/\dot{m}_{starch}) \qquad (1)$$

where ΔH_{vap} is specific enthalpy of vaporization of steam, $\dot{m}_{XScond}$ is the mass rate of condensation during the cook minus mass rate of condensation for the same flow rate with water alone, and $\dot{m}_{starch}$ is the starch flow rate. The molecular weight of the cooked starch

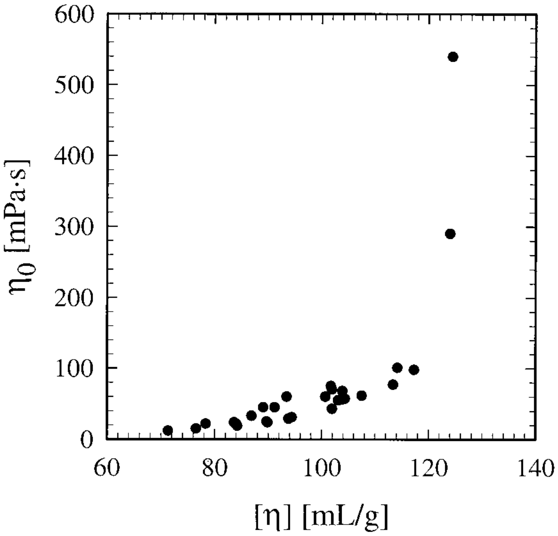

Fig. 5. Zero-shear-rate viscosity of 5 wt% aqueous solutions of jet-cooked waxy maize starch as a function of intrinsic viscosity in 90% DMSO/H_2O.

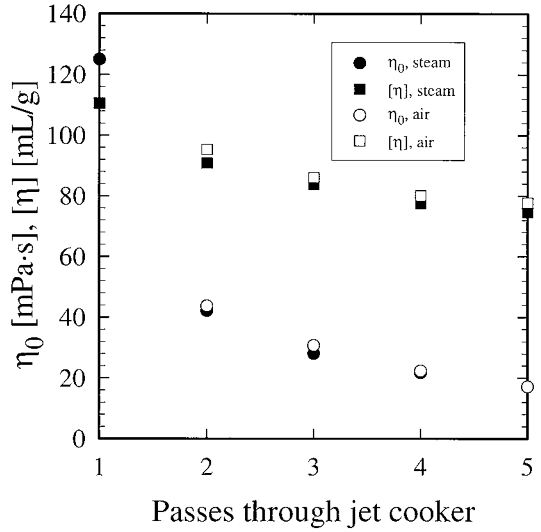

Fig. 6. Effect of multiple passes through the jet cooker on viscosity and intrinsic viscosity.

is shown as a function of specific thermal energy in Fig. 4, where the molecular weight (MW) is calculated as (Millard et al 1997)

$$[\eta] = 0.59MW^{0.29} \quad (2)$$

Although the linear regression fit to the data implies that the thermal energy input can account for the degradation observed in the jet cooker, the intercept at STE = 0 is far below the molecular weight for uncooked starch (MW = 6.2×10^8, based on $[\eta]$ = 209 mL/g from Carriere [1998]). For the results in Fig. 3, each sample experienced nearly the same shear flow, which accounts for a large fraction of the reduction in molecular weight relative to native amylopectin. However, because of the difference in the starch flow rate and the differences in the starch to steam ratio experienced, Fig. 4 shows that additional thermal degradation can account for the further differences between samples. The molecular weight data obtained by light scattering for samples extruded at different specific mechanical energy (SME) values by Willett et al (1997) are also shown in Fig. 4. The mechanical degradation of amylopectin in an extruder results in a much greater decrease in molecular weight per unit energy input.

The intrinsic viscosity was also measured for each sample, and these results are shown in Fig. 5. For $[\eta] < 120$ mL/g, the zero-shear-rate viscosity increases with the intrinsic viscosity. This is expected, because each should depend on the molecular weight of the cooked product. The two results shown for $[\eta] > 120$ mL/g were prepared under thermal jet cooking conditions. The intrinsic viscosity is measured in the limit of infinite dilution, so it should be a better indication of the actual molecular weight of the sample. Although the product from the thermal jet experiments may have an only slightly higher molecular weight, the much higher viscosity of the aqueous solutions indicates that there is an additional intermolecular interaction in those solutions that is not present in the samples cooked under excess steam conditions. The additional turbulence in the flow for the excess steam conditions apparently was sufficient to break these intermolecular associations without necessarily resulting in a large additional decrease of molecular weight. Dintzis and Fanta (1996) also showed a large difference in the intrinsic viscosity between samples cooked under thermal jet and excess steam conditions. The sharp increase in viscosity over a narrow range of intrinsic viscosity is similar to the results presented by Dintzis and Bagley (1995). For autoclaved samples, the viscosity increased sharply for $[\eta] > 170$ mL/g. There was, therefore, a much smaller decrease in molecular weight for samples before the intermolecular associations were broken. This is probably due to the fact that the stirring in the autoclave was a mild shearing relative to the conditions in the jet cooker.

As a final measure of the relative importance of mechanical and thermal degradation effects, a cooked starch slurry was passed through the jet cooker for multiple passes. Steam was used as in a regular cook in one set of experiments, and in another, the steam was replaced with air at the same inlet pressure. These air-based cooks will generate nearly the same shear field as the steam cooks, but without any additional thermal energy input. The first pass obviously requires steam to gelatinize the granule, so passes 2 through 5 in Fig. 6 demonstrate the differences between the two conditions. Although the viscosity and intrinsic viscosity remain slightly higher for multiple passes with air, multiple passes for both conditions result in further decreases that approach a constant value after five passes. These results are consistent with those in Fig. 4 in showing that mechanical degradation is the primary mechanism for amylopectin degradation in jet cooking, but they also show that thermal degradation is most important on the first pass through the jet cooker.

CONCLUSIONS

This work addresses the relative importance of mechanical and thermal degradation mechanisms in the jet cooking of waxy maize starch. The susceptibility of amylopectin to degradation in shear is well known and care must be taken to measure the properties of amylopectin by chromatography (Klavons et al 1997). However, the molecular weight decrease in an autoclave depended on temperature (Dintzis and Bagley 1995). Previous studies of jet cooking are not conclusive because reaction conditions were controlled by the steam pressure, which simultaneously affects the shear field and the temperature. Experiments with the same steam inlet pressure were conducted with different starch slurry flow rates and concentrations. This resulted in similar shear fields in each case, but because the starch-to-steam ratio changed, the specific thermal energy input varied. Mechanical degradation was the primary cause of molecular weight decrease, with the intrinsic viscosity decreasing from 209 mL/g for native amylopectin to 120 mL/g or lower for all samples processed under excess steam conditions. Differences in the thermal energy input led to further decreases in the intrinsic viscosity to as low as 77 mL/g for the most severe conditions studied. A comparison of samples passed through the jet cooker multiple times with and without steam showed that mechanical degradation alone is sufficient to reduce the viscosity and intrinsic viscosity to nearly constant values after five passes.

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