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Effect of high-speed jet on flow behavior, retrogradation, and molecular weight of rice starch

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ABSTRACT

Effects of high-speed jet (HSJ) treatment on flow behavior, retrogradation, and degradation of the molecular structure of indica rice starch were investigated. Decreasing with the number of HSJ treatment passes were the turbidity of pastes (degree of retrogradation), the enthalpy of melting of retrograded rice starch, weight-average molecular weights and weight-average root-mean square radii of gyration of the starch polysaccharides, and the amylopectin peak areas of SEC profiles. The areas of lower-molecular-weight polymers increased. The chain-length distribution was not significantly changed. Pastes of all starch samples exhibited pseudoplastic, shear-thinning behavior. HSJ treatment increased the flow behavior index and decreased the consistency coefficient and viscosity. The data suggested that degradation of amylopectin was mainly involved and that breakdown preferentially occurred in chains between clusters.

1. Introduction

Starches are major ingredients in various food products; even greater quantities are used in non-food applications. The use of starches as additives in food products is limited because of their instability under the conditions of temperature, shear, and pH experienced during processing, preparation, and/or storage. Chemical and physical modifications are used to overcome these deficiencies. Owing to a desire for a clean label, physical modifications are desired. The viscosities and rheological properties of starch pastes and gels are most important since starch is generally used to provide bulk and body structure to food products. Being composed of large polymers, starches often develop high viscosity, which causes practical problems in their application.

Degradation of polymer molecules, including natural polymers, which reduces the viscosity they generate, by application of mechanical stress is a known phenomenon (see, e.g., Arisawa & Porter, 1970; Bucholz, Zhan, Kenward, Slater, & Barron, 2004; Harrington & Zimm, 1965; Ying, Yong, & Yong, 1991). Evidence of depolymerization is generally based on reductions in solution viscosities; actual reductions in average molecular weights are reported in a few cases. Evidence that mechanical stress results in depolymerization of starch polymer, especially amylopectin, molecules, with molecules in solution being most susceptible, has accumulated (BeMiller & Huber, 2015).

An interesting and unique characteristic of the effect of high shear on polymer molecules is that shear forces seem to effect cleavage of the molecules near their mid-points (because that is where maximum stress occurs), with a definite minimum chain length limiting the process (Basedow & Ebert, 1977; Harrington & Zimm, 1965; Henglein & Gutierrez, 1988; Malhorta, 1982, 1986; Odell, Keller, & Muller, 1992; Price & Smith, 1993; Price, West, & Smith, 1994), making the process much less random than depolymerization via chemical reactions.

High-speed jet is a novel ultra-high velocity jet homogenizing technology (Soon, Harbridge, Titchener-Hooker, & Shamlou, 2001). Xia et al. (2015) observed that high-speed jet treatment resulted in decreased crystallinity and severe destruction of tapioca starch granules. The degree of gelatinization increased with an increase in treatment pressure. During high-speed jet treatment, cavitations, shear, and turbulence are produced. The high-speed jet equipment uses a hydraulic mechanism that acts on a piston within a cylinder to force the sample through a fixed orifice to a chamber of lower pressure. The principle of operation consists of a downward stroke during which the crude suspension is drawn into a piston chamber. During the upward stroke, the suspension is forced through a small orifice producing a high-velocity jet. The jet travels through a pipe of varying cross-sectional area before impinging a target. The disrupted material is cooled by contact with the walls of the disruption chamber, which are held at a low temperature by a recirculation flow of coolant. The electronically controlled hydraulic

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system and fixed orifice ensure that the disruption environment is repeatable.

Our previous study (Fu, Luo, BeMiller, Liu, & Liu, 2015) demonstrated that HSJ treatment of indica rice starch led to an alteration in starch granule morphology and crystalline structure and influenced the characteristics of starch, indicating that the HSJ treatment effectively modified the starch in an environmentally friendly way. In this work, HSJ treatment on retrogradation properties, flow behavior, and changes in molecular structure are further investigated.

2. Materials and methods

2.1. Materials

Indica rice starch (22.9% amylose, 0.34% protein, 0.2% fat) was purchased from Gold Agricultural Biotechnology Co., Ltd. (Shanggao, Jiangxi, China). Isoamylase from *Pseudomonas* sp. was purchase from Sigma-Aldrich Co., USA. All other chemicals were of analytical reagent grade.

2.2. HSJ treatment

Native indica rice starch (100 g) was added to 1000 mL distilled water and the suspension was stirred at room temperature until the starch was completely dispersed. The slurry was then treated by high-speed jet (HSJ) in a TS Series Benchtop Cell Disruptor (Constant Systems Ltd., UK) at a pressure of 200 MPa for 0, 2, 4, 6, 8, 10, and 20 passes—differentiated by the subscript used, viz., H_0, H_2, H_4, H_6, H_8, H_{10}, H_{20}. During HSJ treatment, the temperatures of the slurries did not change significantly. After HSJ treatment, the samples were freeze-dried and ground for analysis.

2.3. Turbidity measurement

The method of determining turbidity (as absorbance) was based on that of Jacobson, Obanni, and BeMiller (1997); 0.125% starch pastes were used. Starch slurries (0.05 g starch (dry basis (db)) + 40 mL double-distilled water) were prepared in 50-mL centrifuge tubes. Centrifuge tubes were sealed and immersed for 60 min in a boiling water bath with continuous gentle stirring, then cooled for 20 min in a 25 ± 2 °C water bath with continuous stirring. Initial turbidity was determined by absorbance at 640 nm (Miles, Morris, Orford, & Ring, 1985) using a Thermo/Milton Roy Spectronic Genesys 5 spectrophotometer equipped with a programmable cell changer and Citizen MSP-10 printer (Thermo Fisher Scientific, Waltham, MA USA). The centrifuge tubes containing the remaining starch pastes were stored in a refrigerator at 4 °C. After 0, 1, 2, 4, 7, and 8 days at 4 °C, the centrifuge tubes were vortex mixed, and A_{640} was measured.

2.4. DSC analysis

A differential scanning calorimeter (Q2000 DSC; TA Instruments, New Castle, DE, USA) was used to determine the retrogradation characteristics of starch. A portion (10 ± 1 mg) of starch was weighed into an aluminum DSC pan and double-distilled water (30 μL) was added. Samples were heated from 25 to 110 °C at a rate of 10 °C/min. The gelatinized samples were stored at 4 °C for 7 days, and analyzed by heating from 25 to 110 °C at a rate of 10 °C/min. A sealed empty pan was used as a reference, and indium was used for temperature calibration. Duplicate analyses were performed on each sample. The onset (T_o) and peak (T_p) temperatures, and the enthalpy of melting (ΔH_r) of retrograded amylopectin were recorded.

2.5. Steady shear analysis

For steady shear analysis (Discovery Hybrid Rheometer (TA Instruments, New Castle, DE, USA) using parallel metal plates with diameters of 40 mm and a gap of 1000 μm), a starch suspension (60 mg starch (db) + 1.2 mL H_2O), was conditioned at 25 °C for 1 min. At a shear stress of 5 Pa, the temperature was ramped from 25 to 95 °C, then from 95 to 25 °C, with a ramp rate of 10 °C/min. Thereafter, the sample was sheared from 0.1 to 200 s^{-1}, and then from 200 to 0.1 s^{-1} at 25 °C to determine steady state flow behavior. Data were modeled by the power law equation:

$$\delta = K\gamma^n \quad (1)$$

where δ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the flow behavior index (dimensionless).

2.6. SEC/MALLS-DRI

Determination of molecular weights was done by SEC as described by Chen and Bergman (2007) and Bultosa, Hamaker, and BeMiller (2008) with slight modification. Slurries of starch samples (2 mg/mL water) were heated in boiling water for 60 min with occasional vortexing. After cooking, the hot samples were filtered through a nylon membrane filter (5.0 μm) and then immediately injected into a SEC column (Sephacryl™ S-500 HR; Amersham Biosciences AB, Uppsala, Sweden) through a 200-mL loop injector (Rheodyne 7125, Cotati, CA, USA). Water with 0.02% sodium azide was passed through a 0.45-μm Millipore filter, degassed, and pumped (Shimadzu, LC-10ATVP, Kyoto, Japan) isocratically to the column at a flow rate of 1.3 mL/min. Data collected from the response of an on-line MALLS photometer (DAWN DSP-F, wavelength 632.8.0 nm with a K-5 flow cell) and DRI (Wyatt/Optilab 903; Wyatt Technology Corp., Santa Barbara, CA, USA) was used to determine weight-average molecular weight (M_w); number-average molecular weight (M_n); polydispersity index (PI), and weight-average radius of gyration (R_w) using Astra for Windows software (version5.3.4.14, 1994–2002) (Wyatt Technology Corp.).

2.7. Starch debranching with isoamylase

Starch debranching was conducted as described by Hizukuri (1985) and Bultosa et al. (2008) with modification. Slurries of starch samples (10 mg db) in water (0.9 mL), after addition of a stir bar, were vortex mixed and heated in a water bath (100 °C) for 60 min, then cooled to room temperature. Sodium acetate buffer (0.1 mL; 1 M, pH 3.5), 0.02% sodium azide (1 mL), and isoamylase (3 μL, 1000 U/mL) were added, and the mixture was incubated at 50 °C in a shaking (120 rpm) water bath for 24 h. After 24 h, 0.5 mL of water was added, and the mixture was heated at 100 °C for 10 min with occasional vortexing to stop enzymic activity.

2.8. Statistical analyses

At least two replicate data results were analyzed by one-way analysis of variance (ANOVA), and means were compared at $p < 0.05$ using Fisher's least significant difference (LSD) via SPSS 16.0.1 (SPSS Inc., 1989 21999, Chicago, IL, USA).

3. Results and discussion

3.1. Retrogradation properties

3.1.1. Turbidity analysis

Changes in turbidity of pastes of native and HSJ-treated indica rice starch are shown in Fig. 1. The turbidity values of starch