



Effect of damaged starch on the rheological properties of wheat starch suspensions

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ABSTRACT

The influence of damaged starch content on particle size distribution and rheological properties of unheated starch suspensions and pasting properties were investigated. Four samples containing different amounts of damaged starch were studied. Particle size distribution curves shifted toward higher diameters, and a greater overlap of both populations of particles (A- and B-type granules) and a decrease of both peak heights were produced. The flow curves of unheated starch suspensions were fitted using the power law model. The flow behavior indexes were higher than the unit. The consistency coefficient increased with the increment of damaged starch content. Unheated starch suspensions showed time-dependent rheological behavior and were described by the Weltman model. The unheated suspensions exhibited a thixotropic behavior. With regard to the pasting process, the increment of damaged starch content produced gradual reductions in peak viscosity, final paste viscosity, breakdown and setback. Results demonstrated the importance of the presence of physically damaged granules in wheat starch rheological characteristics.

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1. Introduction

Starch is one of the most common biopolymers and is deposited as discrete granules in the amyloplasts of plant storage organs. In foods, one major use of starch is as a thickening/gelling agent. During processing, starch dispersions are subjected to combined high heating and shear rates that affect their rheological change as well as the final characteristics of the product.

Much information about starch suspensions gelatinized in different conditions has been published; the effect of temperature, time and shear rates on the rheology of gelatinized starch suspensions has been informed (Rao and Tattiyakul, 1999; Abu-Jdayil et al., 2001; Al-Malah et al., 2000; Nguyen et al., 1998). However, few studies have dealt with the flow behavior of starch suspensions without heating. (Frith and Lips, 1995) investigated the rheology of the dilatant behavior, using concentrated waxy maize starch suspensions, and reported that the dilatant transition does appear to be strongly affected by the deformability of the starch granules.

From an engineering point of view, the viscosity difference due to the raw material has to be carefully considered, since it may change flow regimes, processing variables and final product quality. The composition of the starting material can also cause changes in the rheological profile of starch dispersions.

Granular integrity can be affected by the mechanical action of the wheat milling process, since this operation may damage granular structure, thus producing what is called damaged starch. The level of the damage depends on wheat hardness and the conditions and technique at the milling process. The composition and architecture of starch granules regulate their susceptibility to physical damage as a function of milling time and, probably, of the magnitude of applied force (Tester, 1997). Starch damage profoundly changes starch granular structure and it influences rheological and functional properties of the starch systems (Faridi, 1990). Several studies have shown that damage induced by ball milling generates a range of fractions, which have quite different roles in starch gelatinization and swelling properties. These fractions include native granules, two forms of granule fragments and low-molecular weight soluble material (Karkalas et al., 1992; Morrison et al., 1994; Tester et al., 1994; Morrison and Tester, 1994; Tester and Morrison, 1994).

Damage facilitates swelling of starch granules, due to destruction of the forces which prevent granules from swelling in water (Tester, 1997). Therefore, damaged starch has the ability to absorb

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more water than native granules, native wheat starch can absorb between 39% and 87% its weight in water, while damaged starch between 200% and 430% (Berton et al., 2002). Some studies have reported that, unlike native starch, mechanically damaged starch spontaneously gelatinizes in cold water and this process is similar to gelatinization caused by heating. This spontaneous gelatinization produces a reduction on the gelatinization endotherm up to partial or complete disappearance, during heating (Morrison et al., 1994; Tester, 1997; Barrera et al., 2012). On the other hand, the higher water absorption capacity of damaged starch compared to native starch, may affect the viscosity of starch suspensions even without heating. The aim of this work was evaluated the effect of damaged starch content on particle size distribution and rheological properties of unheated starch suspensions and on starch pasting properties.

2. Materials and methods

2.1. Samples

Unmodified (native) wheat starch (S5127 Sigma–Aldrich CAS Number 9005-25-8) was used for samples preparation. It has 10.7 g moisture/100 g and 0.18 g protein/100 g, 3.8% damaged starch (DS) and 31.1% amylose, according to AACC 44-19, 46-13, 76-30A (AACC 2000) and Megazyme amylose/amylopectin assay kit (Megazyme International, Ireland), respectively. Damaged starch was produced as described by Barrera et al. (2012). Unmodified wheat starch was milled in a Whisper Series Bench Top disk mill (Rocklabs, Auckland, New Zealand) to cause a rupture of starch granules. Temperature was monitored during the milling; it was kept under 40 °C. Four starch samples with different damaged starch contents were obtained after milling and mixing: 3.8% DS (native wheat starch from SIGMA, unmilled in mill disk), 8.4, 12.9 and 23.8% DS. The values of damaged starch were chosen according to the range of damaged starch (6.10–26.90%) generated by roller milling (Ghodke et al., 2009).

Damaged starch content was determined according to AACC 76-30A method (AACC 2000). A fungal enzyme from *Aspergillus oryzae* (A6211, Sigma Chemical Co., St. Louis, MO, USA) was used in this analysis. Analyses were performed in triplicate.

2.2. Particle size analysis

Granular size distribution of starch samples was determined by laser light scattering (Mastersizer 2000E ver. 5.20, Malvern, Worcestershire, UK). The assay was performed in two different ways. In the first case, the starch samples were transferred to the particle size analyzer dispersion tank, containing Micropore filtered water; this measure was defined as time zero (not swelled). In the second case, starch–water suspensions (6.25% w/w) were first mixed during 3 h (swelled) at room temperature. The starch suspension was transferred into the particle size analyzer dispersion tank containing Micropore filtered water, and the measure was then carried out. The instrument provides size distribution information parameters, such as volume distribution, d_{10} , d_{50} and d_{90} , De Brouckere mean diameter ($D_{4.3}$) and Sauter mean diameter ($D_{3.2}$). Size values designated as d_{10} , d_{50} , and d_{90} indicate that 10%, 50%, and 90% of particles are smaller than such values. De Brouckere mean diameter is the volume mean diameter of the particles, and Sauter mean diameter is the surface area weighted mean diameter of the particles. All these parameters were calculated assuming that the granules are spherical particles (Malvern Instruments, 1999).

2.3. Evaluation of leached amylose from granules

Starch suspensions (11.8% w/w) were prepared and gently agitated for 40 min at room temperature. After this time, the suspensions were centrifuged at 10,000g for 5 min and the supernatants were held at 50–55 °C for 5 min. An aliquot of 1.5 ml was used to determine the percentage of amylose and amylopectin contents leached out as consequence of spontaneous gelatinization. The amylose content was determined using the Megazyme amylose/amylopectin assay kit (Megazyme International, Ireland), according to the procedure described by Gibson et al. (1997) but the gelatinization step was avoided. Results were expressed as grams of leached amylose per 100 g of available starch.

2.4. Rheological measurements

Flow properties of the unheated starch suspensions were determined with a rheometer (AR 1000-TA Instrument, New Castle, DE 19720). Steel plate geometry (40 mm diameter) and 0.5 mm gap were used for the determinations. The starch suspensions (20% w/w) were agitated during 3 h at a fixed stirring rate which was just enough to keep the starch granules suspended. An aliquot (~1 ml) of the starch suspension was poured on the rheometer bottom plate and equilibrated to 25 °C.

The geometry was accelerated uniformly from 0 to 300 s⁻¹ in 3 min and the shear rate was kept constant for 10 min. After this time, the shear rate was decelerated uniformly to the rest in 3 min and immediately accelerated from 0 to 300 s⁻¹ in 3 min. The starch suspensions were monitored during the shear cycle. The shear rate used for the rheological determinations did not affect measurement conditions.

In order to characterize the rheological behavior of the unheated starch suspensions the flow curves were modeled using the power-law model, which describes the data of shear-thinning and shear-thickening fluids (Rao, 1999). The model was applied to the descending segment, which starts at the higher shear rate, to minimize the starch granules sedimentation:

$$\tau = K * \left(\dot{\gamma} \right)^n$$

where K is the consistency coefficient (Pa) and n is the flow behavior index (dimensionless).

Weltman (1943) model was used to describe the thixotropic behavior of unheated starch dispersions. The experimental shear stress versus shearing time data were fitted to Weltman equation:

$$\tau = A + B * (\ln t)$$

where τ is shear stress (Pa), t is shearing time (s) and A (value of stress at $t = 1$ s) and B are constant parameters, which characterize the time-dependent behavior (Rao, 1999).

2.5. Pasting profile

Pasting properties of starch samples were determined with a Rapid Visco Analyser (RVA-4), using the RVA General Pasting Method (Newport Scientific Pty. Ltd., Warriewood, Australia). The RVA parameters were obtained from starch–water suspensions. Starch samples (3.5 g) were transferred into a canister and approximately 25 ± 0.1 ml distilled water were added. The slurry was heated to 50 °C, while stirring at 160 rpm for 10 s for thorough dispersion of batter ingredients. The slurry was held at 50 °C for 1 min, and then heated up to 95 °C at a heating rate of 9.4 °C/min and a stirring rate of 960 rpm. It was held at 95 °C for 2.5 min, and finally cooled to 50 °C at a cooling rate of 11.8 °C/min. Initial pasting temperature (PT), peak viscosity (PV), final or cool paste

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