



# Viscosity and hydrodynamic radius relationship of high-power ultrasound depolymerised starch pastes with different amylose content



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## ABSTRACT

Corn starch pastes (5 or 10 w%) with different amylose content (~2.7%, ~5.1%, ~29.6%, or ~52.7%) were treated using high-power ultrasound (frequency 20 kHz, power 13.5 or 29.9 W) for up to 20 min. Changes in the physical properties were determined using viscosity measurements and dynamic light scattering. Results show that both the viscosity ( $\eta$ ) and hydrodynamic radius ( $R_H$ ) decreased markedly with the increase in ultrasound treatment time. FT-IR showed that the molecular scission occurred at the C–O–C bond of  $\alpha$ -1,6 glycosidic linkage, and that the extent of breakage was inversely correlated with amylose content. Further, high-amylose starch pastes were found to be more resistant to ultrasound treatment due to their aggregation. A master curve for the behaviour of  $\eta$  and  $R_H$  is proposed, which is also confirmed by a similar study carried out on the ultrasound treatment of rice starch pastes with different amylose contents. The findings of this work can be used to tailor starch solutions with different viscosities using high-power ultrasound.

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## 1. Introduction

The degradation or depolymerisation of macromolecules by high power ultrasound (HPUS) is known since a long time (Schmid & Rommel, 1939). However, in recent years the use of HPUS to reduce the size of large biomacromolecules has been revisited since this method offers an alternative to the conventional enzymatic and chemical methods. Another advantage of the HPUS is that it tends to breakup macromolecules in the middle of the chain, generating monodispersed fragments (Price, West, & Smith, 1994; Van der hoff & Gall, 1977). Of particular interest is the use of HPUS for starch based systems, which range from starch granules with different size and shape depending of their botanical origin to their individual polysaccharide components (Jane et al., 1999; Pérez, Baldwin, & Gallant, 2009). When starch granules in aqueous solutions are pasted, that is when heated under shear in the presence of excess water, the starch granules dissociate into their main

polysaccharide components, amylose and amylopectin. The ratio of amylose to amylopectin vary for different starches, with waxy starches having a low amylose content (typically less than 5%) and normal or native starches having higher amylose content (>10%).

Amylose is essentially a linear macromolecule consisting of a  $\alpha$ -D-glucan chain which is linked through  $\alpha$ -D-(1–4) linkage (Bergthaller, 2005; Liu, 2005) with a degree of polymerization (DP) between 1000 and 10,000. A small portion (0.1%) of amylose molecules are branched via (1–6)- $\alpha$  linkages (Bergthaller & Hollmann, 2007; Takeda, Hizukuri, Takeda, & Suzuki, 1978) and approximately 500–6000 glucose units are distributed among 1–20 chains. The length of these branch chains varies from 4 to 100 DP (Hizukuri, 1996; Takeda et al., 1978). The molecular weight ( $M_w$ ) of amylose is dependent on the botanical source, and is normally around  $0.15\text{--}0.4 \times 10^6 \text{ g} \times \text{mol}^{-1}$  (Hizukuri, Abe, & Hanashiro, 2006, 1996). Because of the presence of hydroxyl groups and its linear structure, amylose molecules have a tendency to approach each other and to bond together. This may cause the reduction of affinity of amylose molecules for water, which affects its solubility (Jane & Chen, 1992; Liu, 2005). Compared to amylose, amylopectin has much larger  $M_w$ , ranging from  $10^6$  to  $10^9 \text{ g} \times \text{mol}^{-1}$ , depending on the botanical

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origin of the starch (Hermansson & Svegmarm, 1996; Liu, 2005). Amylopectin is a highly branched molecule which is composed mainly of  $\alpha$ -(1–4) linked D-glucopyranose (as in amylose) but also has a greater proportion of non-random  $\alpha$ -(1 → 6)-linkages at the branching (Jane & Chen, 1992; Liu, 2005; Nikuni, 1978).

In recent years, many studies on starch degradation by HPUS have been published, although the first study reporting the effect of power ultrasound on starch molecules has been published by Szent-györgyi, in 1933 (Szent-györgyi, 1933). The degradation of high molecular weight polysaccharides is associated with the marked reduction in viscosity and molecular weight. Huang, Li, and Fu (2007) observed a decrease in the viscosity of corn starch pastes after sonication (ultrasound power at 500 W for 3–15 min) which was related to a breakage of glycosidic linkages and weakening of the biopolymer network. The effects of 360 kHz ultrasound (output power at 100 W for 22 min) on an aqueous solution of chitosan and corn starch have been studied by Czechowska-Biskup, Rokita, Lotfy, Ulanski, and Rosiak (2005). They also observed a reduction in viscosity of starch dispersion and in the molecular weight of amylopectin, and suggested that hydroxyl radicals and the mechanical effects due to ultrasound cavitation are responsible for the depolymerisation of the polysaccharide solutions. Similar observation was also reported by Luo et al. (2008) where they sonicated different corn starch samples (various in amylose content) at 100 W power for 30 min. They suggested that hydroxyl radicals produced from acoustic cavitation could react with linear amylose and the side chains amylopectin. Iida, Tuziuti, Yasui, Towata, and Kozuka (2008) reported the reduction of viscosity of sonicated (power of 120 W, up to 30 min) waxy maize, tapioca, potato and sweet potato starch pastes which decreased dramatically at initial period and then tended slowly to a limiting value.

The main objectives of the current study are, firstly to determine the importance of the amylose content on the extent of starch degradation by HPUS. Secondly, to develop a relationship between the viscosity of the starch pastes and the hydrodynamic radius of the starch molecules. For these reasons, pastes obtained from corn starches having different amylose content were subjected to HPUS under different power and sonication time conditions. The viscosity of the HPUS treated starches were measured, and the size of the starch molecules was determined through their hydrodynamic radius, measured by dynamic light scattering. To validate the relationship between the viscosity and particle size, additional data obtained on waxy and normal rice starches are also used. These experimental data are also obtained using dynamic light scattering and rotational viscometry.

## 2. Materials and methods

### 2.1. Materials and starch pastes samples preparation

The four starches used in this study were kindly supplied by

**Table 1**  
Composition (%) of the corn starches used in this study.

	Amylose <sup>a</sup>	Moisture <sup>b</sup>	Lipid <sup>c</sup>	Protein <sup>d</sup>	Ash <sup>e</sup>
Amioca	2.72 ± 0.35	9.13 ± 0.33	0.23 ± 0.06	0.11 ± 0.02	0.07 ± 0.01
Mazaca	3.59 ± 0.29	10.40 ± 0.17	0.15 ± 0.02	0.14 ± 0.01	0.06 ± 0.01
Melojel	29.64 ± 0.67	8.32 ± 0.01	0.11 ± 0.02	0.16 ± 0.03	0.11 ± 0.01
Gelose	52.71 ± 0.41	10.31 ± 0.06	0.35 ± 0.09	0.46 ± 0.11	0.12 ± 0.04

Compositions are obtained using.

<sup>a</sup> Amylose/amylopectin assay kit (Megazyme Int, Ireland).

<sup>b</sup> AACC International Method 44–15.02 (1999).

<sup>c</sup> AACC International Method 30–10.01 (1999).

<sup>d</sup> AACC International Method 46–16.01 (1999).

<sup>e</sup> AACC International Method 08–17.01 (1999).

National Starch Food Innovation, New Zealand. Their chemical compositions are reported in Table 1. Two of the starches were waxy (AMIOCA and MAZACA), one was normal (Melojel) and the fourth starch had a high-amylose content (Gelose50).

Starch dispersions were made by stirring the required amount of starch powder in milliQ water containing 0.02% sodium azide, using a magnetic stirrer at room temperature for at least 5 min. Sodium azide was added as a preservative. Starch pastes were obtained by heating the starch dispersions either at 10% for AMIOCA and MAZACA or 5% in the case of Melojel and Gelose 50. For these latter starches, lower concentrations were used as the resulting starch pastes formed after cooling were gelled. The starch dispersions (20 g) were pasted using the Paar-Physica MCR301 stress-controlled rheometer fitted with the Smart Starch Geometry system (C-ETD 160/ST cup with a specially-designed stirrer with 3 pairs of blades ST24-2D/2V/2V-30). The heating procedure consisted of equilibrating the starch dispersion at 45 °C for 2 min, heating to 95 °C in 3 min, then holding at 95 °C for 15 min, then cooling back to 45 °C in 5 min. The heated starch dispersions were taken out of the cell and left to cool to room temperature. Note that all concentrations of starch dispersions correspond to the weight of starch divided by the total weight of sample.

### 2.2. High-power ultrasound treatment

Starch pastes dispersions were treated by a high-power ultrasound using a 20 kHz VCX-750 Watt Ultrasonic Processors (Sonics & Materials, Inc, USA). The ultrasound equipment was fitted with a horn with a 13 mm tip diameter. The volume of the sonicated sample was 20 ml and they were sonicated for different times (up to 30 min). The ultrasound power used was calculated using a calorimetric method (Koda, Kimura, Kondo, & Mitome, 2003):

$$P = m \cdot C_p \cdot \left( \frac{\Delta T}{\Delta t} \right) \quad (1)$$

Where  $m$  is the mass of sonicated liquid,  $C_p$  is the specific heat capacity at constant pressure (water heat capacity is 4.18 J/(g K)), and  $\Delta T/\Delta t$  is the changes in temperature over time. The values of the two ultrasound powers (13.5 and 29.9 W) used in this study are calculated using equation (1).

### 2.3. Experimental methods

Viscosity measurements were carried out using Paar-Physica MCR301 stress-controlled rheometer fitted with the Double Gap geometry. This geometry was chosen as it is adequate for low-viscosity measurements. The dimensions of this geometry were: Bob (diameter 26.7 mm, length 45 mm) and cup ((diameter  $D_1 = 27.6$  mm,  $D_2 = 23.5$  mm), (length  $L = 14.3$  mm,  $L_1 = 27.5$  mm)). The viscosity was obtained by applying a shear rate from 0.1 to 1000  $s^{-1}$  (up measurement) then by decreasing the shear rate from 1000 to 0.1  $s^{-1}$  (down measurement). Measurements were performed at a constant temperature of 25 °C, and each measurement point was obtained in 20 s.

Particle size measurements were performed in a Nano-Zetasizer ZS (zen3600 Nano series, Malvern instruments, UK) with the scattering angle of 173° and a light source (He–Ne laser) of fixed wavelength of 633 nm. The hydrodynamic radius  $R_h$  is calculated using a refractive index of 1.330 for water and 1.476 for DMSO; and viscosity of 0.8877 mPa s for water and DMSO. Before measurement the starch dispersion made from AMIOCA and MAZACA starches were first diluted to a concentration of 0.1% in milliQ water. In the case of the high-amylose starch (Melojel and Gelose 50) the starch samples were dissolved to a final concentration of 0.1% in 90%

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