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# Modelling starch phase transitions and water uptake of rice kernels during cooking

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ABSTRACT

To model the cooking processes of rice, starch gelatinization, the level of fusion of the amylose-lipid complex, and equilibrium water uptake have to be known for any given condition. Starch phase transitions were measured by DSC in two milled Korean round rice kernels whose water contents ranged from 0.18 to 4.7 g $g^{-1}$ db. Two to three partially overlapping transitions were assessed. Starch thermal transitions were modelled using a double step approach. First, a mechanistic double sigmoid model was fitted with DSC data for any water content value. Each parameter of the mechanistic model was then modelled with conservative empirical water content functions. In this way we obtained an explicit form of phase transition levels as a function of both temperature and water content. In parallel, the water uptake kinetics of rice kernels was determined in the temperature range of 50 °C–100 °C. Equilibrium water uptake was found to be linked to starch phase transitions and a model was built to calculate equilibrium water uptake as a function of modelled starch gelatinization and amylose-lipid complex fusion levels.



## 1. Introduction

Rice (*Oryza sativa* L.) is one of the leading food crops in the world. This cereal provides a large proportion of the total nourishment of the world population.

To convert raw grains into a pleasant, agreable and digestible form, rice is boiled, the grains absorb water, and the starch gelatinizes (Briffaz et al., 2012). The end of cooking can be assessed by the swelling ratio and/or the completion of gelatinization (Vidal et al., 2007). The texture of cooked rice is strongly dependent on the cooking conditions and starch gelatinization (Billiris et al., 2012; Mestres et al., 2011; Singh et al., 2005). Modelling water transport, swelling and starch gelatinization of rice during cooking is thus of great interest to predict the properties of cooked rice such as texture. Water uptake kinetics have already been established for *Japonica* rice (Takeuchi et al., 1997) and *Tarom Mahali* long-grain varieties (Kashaninejad et al., 2007) soaked at between 25 °C and 80 °C. However, even though starch swelling power dramatically increases with gelatinization, the empirical equations used to describe grain water uptake rarely take this phenomenon into account. Aware of this problem, Ogawa et al. (2011), developed a van't Hoff type of empirical equation to predict equilibrium water content of cooking spaghetti, which also increases dramatically around gelatinization temperature. Fukuoka et al. (2002) postulated that equilibrium water content was linearly linked to the level of gelatinization, but to our knowledge, no study has established a direct relationship between the degree of gelatinization and equilibrium water content.

It is thus necessary to know the degree of starch gelatinization during cooking. In its narrowest sense, starch gelatinization is the thermal disordering of the crystalline structure of native starch granules. It is strongly dependent on water content. Gelatinization transition *sensu stricto* occurs between 60 °C and 75 °C in rice (Vandeputte et al., 2003b; Vidal et al., 2007); Mestres et al., 2011) at high water content. At intermediate water content, a melting transition appears that becomes predominant at low water content (Donovan, 1979). In addition, a fusion transition of amylose-lipid complexes occurs at around 95 °C at high water content. Beside gelatinization itself, this transition also has a major impact on the swelling behaviour of starch. It is generally accepted that amylose-lipid complexes indeed prevent starch granule swelling and rupture at relatively temperatures. Starch water uptake thus presents a bimodal figure with temperature; the first increase is linked to gelatinization and the second to the fusion of the amylose-lipid complexes (Kar et al., 2005; Vandeputte et al., 2003b).

Fukuoka et al. (2002) developed an empirical "terminal extent of starch gelatinization" (*TEG*) function which defines the upper limit

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of starch gelatinization as a function of water content and temperature. This function has been used to model the cooking process of noodles and rice (van den Doel et al., 2009; Xue et al., 2010). Unfortunately, the *TEG* function only considers the first thermal transition but not the melting one (Fukuoka et al., 2002). Using the Flory-Huggins free volume theory, Baks et al. (2007) and van der Sman and Meinders (2011) modelled the onset of gelatinization and the end of melting but obtained very different parameter values and failed to model the end of melting at high water content ($a_w > 0.8$). To date, no model has been developed to describe all the thermal starch transitions which occur during heating, including fusion of the amylose-lipid complex.

To be able to model the processes that take place when rice is cooking, starch gelatinization and fusion levels of the amylose-lipid complex and equilibrium water uptake have to be known for any given condition. In the present study, starch phase transitions were measured by DSC in rice flours with different water contents and a two-step model was built to predict the level of starch gelatinization and of the fusion of the amylose-lipid complex whatever the water content. In parallel, the water uptake kinetics of rice kernels was determined in the temperature range of 50–100 °C and a model was built to calculate equilibrium water uptake as a function of starch gelatinization and of the level of fusion of the amylose-lipid complex.

## 2. Materials & methods

### 2.1. Material

The rice cultivars used in this study were commercial milled Korean round cultivars (*Chil-bo* and *Chu-cheong*) harvested in autumn 2009. The average length and width (4.77 and 4.71 ± 0.03 mm and 2.76 and 2.94 ± 0.02 mm, respectively) of the grains were determined by image analysis, according to Vidal et al. (2007). Proximate composition was similar in the two cultivars: 13% (w/w) of water, 80% (w/w) of starch (AFNOR, 1996), 5.9% (w/w) of proteins (Kjeldahl, N × 5.7). Amylose content, determined according to Mestres et al. (1996) was 16.4 and 18.4% (dry basis) for *Chil-bo* and *Chu-cheong*, respectively.

### 2.2. Steeping experiments

The steeping system was a thermo-regulated water bath (WB22, Memmert, Hannover, Germany) whose temperature was set to a fixed value ranging from 50 °C to 95 °C. Three grams of *Chil-bo* milled rice were placed in a tea ball, which was immersed in a 250 ml aluminium pot filled with 150 ml distilled water and previously equilibrated at the steeping temperature. Steeping time ranged from 5 min to 4 h. The temperature inside the tea ball was checked to make sure it reached the fixed value in less than 1 min.

After steeping, the tea ball was taken out of the water and centrifuged at 100 g for 5 min. The grains were then recovered and weighed. The water content ($X$) was calculated on a dry basis after weighing the dried steeped grains (100 ± 1 °C for 48 h).

### 2.3. Characterization of the thermal transition phases

Rice grains were ground into fine flour using a laboratory hammer mill (Mill 3100, Perten Instruments AB, Huddinge, Sweden) equipped with a 500 μm sieve. The resulting rice flour was weighed in stainless steel pans. Deionized water was then added to each pan using a micropipette and the pan was hermetically sealed. The amount of water was adjusted to obtain a water content (dry basis) ranging from 0.18 to 4.7 g g$^{-1}$db. The total mass of the sample inside the pan was around 40 mg. The pans were allowed to stabilize at room temperature for 8–24 h before analysis.

Thermograms were recorded using a DSC 8500 instrument (Perkin–Elmer, Norwalk, USA). The samples were heated from 20 °C to 160 °C at 10  C min$^{-1}$. The area under the endothermic peaks was integrated and partial integration values were calculated at 5 °C intervals, using the same baseline. Measurements were made in duplicate or triplicate. The coefficient of variation of total enthalpy change was 14%.

## 3. Results and discussion

### 3.1. Thermophysical effects on starch during cooking

Fig. 1 shows normalized and baseline subtracted DSC thermograms for the *Chil-bo* cv at different water contents ($X$). In excess water ($X > 1.5$ g g$^{-1}$ db), two main phenomena were observed: gelatinization (G endotherm as named by Donovan and Mapes, 1980) with a peak temperature of 67.9 °C ± 0.7 °C,, an enthalpy change of 11.9 ± 1.2 J g$^{-1}$, and fusion of the amylose-lipid complex (Cx) which displayed one main peak (at 100 °C), occasionally followed by a small shoulder, with a total enthalpy change of 2.6 ± 0.6 J g$^{-1}$. With decreasing water content, the intensity of the G endotherm decreased whereas its temperature was stable. In the meantime, a starch fusion peak, named M1 by Donovan and Mapes (1980), appeared; its intensity and its transition temperature gradually increased with a decrease in $X$. At intermediate water content, the three phenomena partly overlapped; G and M1 at $X$ between 0.6 and 1.2 g g$^{-1}$db and M1 and Cx at lower $X$. At low water content ($X \leq 0.4$ g g$^{-1}$db), the G endotherm disappeared; starch and Cx fusion peaks were more or less superposed, the last one only appearing as a shoulder at high temperature. Very similar features were recorded for the *Chu-cheong* cv, which displayed an enthalpy change of 10.4 J g$^{-1}$ and a peak gelatinization temperature of 68.5 °C ± 0.1 °C in excess water.

The measured enthalpy changes and peak temperatures of starch gelatinization in excess water were in the same range as those cited in the literature i.e. 8.2–19.6 J g$^{-1}$ and 56.9–80.0 °C, respectively (Vandeputte et al., 2003b; Vidal et al., 2007; Wani et al., 2012). The enthalpy we attributed to amylose-lipid fusion was almost twice as high as values reported by Vidal et al. (2007) for rice flour and by Vandeputte et al. (2003b) and Kar et al. (2005) for rice starch. During storage, triglycerides in the flour are indeed degraded to free fatty acids which are able to complex amylose. The Cx endotherm thus increases with an increase in the storage period (Mestres et al., 1997). The rice grains used in the present study were harvested and milled in autumn 2009 and

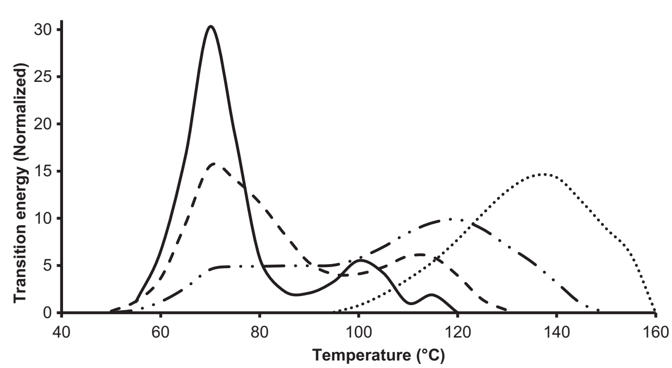


**Fig. 1.** Endotherms recorded for *Chil-bo* rice flour mixtures with excess or limited amounts of water. Water contents of 0.3 (• •), 0.6 (– • • –), 1.15 (– –), and 2.88 (–) g g$^{-1}$db.