



## Relationship between biphasic endotherms and multi-stage gelatinization of corn starch in excess water



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### ABSTRACT

The gelatinization of corn starch was studied using differential scanning calorimetric (DSC) and rheological tests by the same heating rate (10 °C/min), temperature range (20–90 °C) and starch-to-water ratio (1 mg/10 mg). The corn starch was dually modified using acid hydrolysis (AH) followed by heat-moisture treatment (HMT) in AH-HMT sequence. The viscosity versus temperature was presented using semi-logarithmic coordinates to better demonstrate the viscosity peaks. A three-stage gelatinization of AH-HMT starches was identified through the comparative analysis of rheological and thermal properties. The first stage of gelatinization correlated with the G endotherm well ( $R^2 > 0.9$ ) and was an irreversible process; the second stage of gelatinization and concomitant disruption of the crystalline structure corresponded to the M1 endotherm, while the third-stage of gelatinization was found to be a process of water absorption without energy consumption (no endotherm). The correlation of characteristic temperature showed that the complex gelatinization process could be well explained by the multi-stage of gelatinization using comparative analysis. These findings also provided new evidence to clarify the mechanism underlying the G and M1 endotherms observed in DSC curves in excess water.

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### 1. Introduction

When heated in excess water, starch granules undergo three distinct stages associated with the gelatinization process: granule swelling, disruption of ordered structures (crystalline and molecular) and solubilization of starch molecules (Wang & Copeland, 2012c; Wang, Li, Yu, Copeland, & Wang, 2014). Gelatinization brings about irreversible changes in properties such as water uptake, granule swelling, crystal melting, birefringence, solubility and viscosity (Ratnayake & Jackson, 2009). These changes greatly affect the functional properties of starch and its digestion (Muñoz, Pedreschi, Leiva, & Aguilera, 2015). These changes also involved a sequence of thermal events that result in phase transition of starch granules.

When starches are heated in limited water, biphasic

endotherms are often observed in DSC studies and are found to be related to the gelatinization and melting of starch crystallites, identified as G and M1 endotherms, respectively (Donovan, 1979). Such biphasic endotherms are observed in starch granules of different botanical origins (Wang et al., 2014). Many literature have reviewed the theories explaining the structural changes that give rise to the G and M1 endotherms observed in DSC curves in limited or intermediate water content (Ratnayake, Otani, & Jackson, 2009; Tananuwong & Reid, 2004). However, none of these theories satisfactorily explains the detailed mechanism of the gelatinization of starch especially in excess water (Wang & Copeland, 2012c). Liu, Xie, Yu, Chen, and Li (2009) opined that the single G endotherm observed in DSC of starch gelatinized with excess water represents the gelatinization of amylopectin. However, Wang et al. (2014) attributed the G endotherm to the completion of water absorption and granule swelling. Furthermore, the well-accepted endotherms (G, M1, M2, and Z) in the DSC curves are observed mostly in limited (Donovan, 1979; Fukuoka, Ohta, & Watanabe, 2002) or intermediate (Liu, Yu, Xie, & Chen, 2006; Ratnayake & Jackson, 2007) water contents but no M1 endotherm was observed in excess water

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(Zhong & Sun, 2005).

In our recently work (Xing, Li, Wang, & Adhikari, 2017), we observed two overlapping G and M1 endotherms for the first time even in excess water (starch-to-water ratio = 1 mg/10 mg), which could be interpreted by a newly proposed polymer swelling and dissolution theory supposed by Wang and Copeland (2012a). These authors suggested that the G endotherm represents the completion of water absorption and granular swelling rather than the melting of less stable crystallites. However, the swelling process occurring during the thermal events depicted by the G and M1 endotherms was not adequately explained, especially in the presence of excess water. To the best of our knowledge, no study has been undertaken to elucidate the biphasic endotherms (G and M1) observed in excess water.

Moreover, the indirect rheological method is a better choice as it is a complementary to the thermal analysis (Kim, Yoo, Park, Shim, & Lee, 2012). During gelatinization, the starch granules increasingly swell and absorb water, which alters the viscometric, rheological or pasting properties (Xie et al., 2006). The change in viscosity characterizes important stages of the gelatinization process and can be measured by using a rheometer (RHE) (Schirmer, Zeller, Krause, Jekle, & Becker, 2014). Besides, the volume fraction and the heating rate are two important factors during the gelatinization (Steeneken, 1989) affecting both the thermal transitions and the viscosity changes of starch solution. Although the relationships between thermal and rheological characteristics of different starches have been considerably studied (Li & Yeh, 2001), the correlation between thermal and rheological properties is still limited when the two kinds of experiments are carried out under the same conditions, i.e. at the same heating rate and starch-water ratio.

In this study, the corn starch will be modified using acid hydrolysis (AH) and heat-moisture treatment (HMT) with the AH-HMT sequence according to the method in our last study (Xing, Liu, Li, Wang, & Adhikari, 2017). The thermal and rheological analyses will be carried out using a DSC and a rheometer (RHE) under the same heating rate (10 °C/min) and starch-to-water ratio (1:10, excess water). The relationship between the phase transition and rheological behavior of the AH-HMT starch granules will be further studied. The characteristic temperatures associated with the thermal and rheological studies will also be correlated with each other. The results will be compared and interpreted using the multi-stage swelling theory to elucidate the mechanism of the biphasic endotherms in DSC curves. We believe that this comparative study of biphasic endotherms observed in DSC curves and multi-stage swelling observed in rheological curves both in excess water will provide a new insight into the gelatinization of starch granules.

## 2. Materials and methods

### 2.1. Materials

Corn starch was obtained from Hebei Zhangjiakou Yujing Food Co., Ltd. (Hebei, China). Native corn starch sample was modified using acid hydrolysis (AH) and heat-moisture treatment (HMT) in AH-HMT sequence according to our previous work (Xing, Liu, et al., 2017; Xing, Li, et al., 2017). The starch samples were prepared as follows. Native starch sample was dispersed in 1 mol/L hydrochloric acid and slurry samples with 300 g/L starch concentration were prepared. These slurry samples were incubated at 40 °C for 6, 12, 24, 48, 72 h. Each slurry sample was centrifuged first, neutralized with NaOH and centrifuged once again. The insoluble starch granules were re-suspended in distilled water and washed three times. These acid-treated granules were then air-dried at 40 °C and the moisture of which were measured and adjusted to 0.3 g/g before heat-moisture treatment. These starch-water mixtures were sealed

and equilibrated in Duran glass containers for 24 h at ambient temperature. These sealed containers were then placed in a forced air oven maintained at 120 °C for 30 min. After incubation, the samples were cooled to ambient temperature. These samples were air dried at 40 °C and then grounded to pass through a 120 µm sieve. Finally, the AH-HMT samples were packed in zipper bags and kept in desiccators until used. These starches samples were abbreviated as AH<sub>6, 12, 24, 48, 72</sub>-HMT<sub>30</sub> in this study.

### 2.2. Methods

#### 2.2.1. Differential scanning calorimetric analysis

The gelatinization characteristics of AH<sub>0, 6, 12, 24, 48, 72</sub>-HMT<sub>30</sub> starch samples were studied using a differential scanning calorimeter (DSC-Q10, TA Instruments, New Castle, USA). About 3–4 mg starches were weighed in an aluminum pan and distilled water was added to the starch using a microsyringe to obtain a starch-to-water ratio of 1 mg/10 mg which provided excess water. The hermetically sealed pan was equilibrated for 24 h at room temperature before heating from 20 to 120 °C at a rate of 10 °C/min.

#### 2.2.2. Rheological analysis

The gelatinization of starches was also studied by using AR2000ex Rheometer (TA Instruments Ltd., New Castle, USA) with aluminum parallel plate geometry (40 mm diameter, 1 mm gap). A platinum resistance thermometer (PRT) and an embedded Peltier system were used to control the temperature of samples. It is well known that most of experiments studying starch gelatinization are carried out using Rapid Visco-analyzer (RVA) to produce “pasting profiles” (Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009). These measurements are generally processed under constant stirring and followed by a programmed heating and/or cooling cycle. The variation of viscosity in RVA tests is recorded as a function of temperature. The major pasting parameters, such as peak viscosity, breakdown viscosity, final viscosity, and pasting temperature are obtained from the RVA data (Pukkahuta, Suwannawat, Shobsngob, & Varavinit, 2008). It is worth mentioning that the viscosity does not increase noticeably at the initial stage of swelling and it can be lower than the peak viscosity by an order of magnitude, thus the viscosity at the initial swelling stage is generally neglected in RVA analysis. However, one cannot overlook the significance of the characteristic properties of starch at and around initial stage of swelling.

In this paper, the viscosity data were demonstrated against temperature using semi-logarithmic coordinates. Viscometer was operated at a constant shear rate of 300 s<sup>-1</sup> and the viscosity data were collected in 1 s interval. Previously, a thin layer of silicone oil was commonly applied on the edges of sample in order to prevent the evaporation water. However, this study did not follow this procedure since the presence of oil in the sample interfered seriously with viscosity of the AH starch samples. The evaporation is considered to be negligible as the total time in these experiments was quite short (about 7 min). In this study, the rheological tests were carried out at the same scanning rate (10 °C/min) and starch-to-water ratio (1 mg/10 mg) with the DSC tests.

#### 2.2.3. Sample treatment and scanning steps

The heating (thermal scan) and cooling protocols applied to the DSC and Rheometer (RHE) are illustrated in Fig. 1 and are briefly presented below.

**2.2.3.1. Test 1. full scan.** Starch samples (described in Section 2.1) were scanned from 20 to 120 °C at 10 °C/min by using the DSC (Section 2.2.1) and/or RHE (Section 2.2.2).

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