Carbohydrate Polymers 101 (2014) 727–732

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Studies on the starch–water interactions between partially gelatinized corn starch and water during gelatinization

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ARTICLE INFO

*Article history:*
Received 21 May 2013
Received in revised form 4 September 2013
Accepted 28 September 2013
Available online 9 October 2013

*Keywords:*
Partially gelatinized starch
Gelatinization
Unfreezable water
Moisture content
Interactions

ABSTRACT

The effect of moisture content on the interactions between water and partially gelatinized starch during gelatinization process was investigated. The interactions were probed using differential scanning calorimetry (DSC). The starch samples were partially gelatinized at 25 °C (*S25*), 64 °C (*S64*), 68 °C (*S68*) and 70 °C (*S70*) and the moisture contents were varied from 25% to 78% (w/w). The G endotherm was not observed and only the M1 endotherm was observed in *S64*, *S68* and *S70* in the entire moisture content range. The G endotherm was not observed and only the M1 endotherm was observed at higher peak temperature in *S25* when the moisture content was below 30% (w/w). The melting temperature of M2 endotherm in *S70* was the highest among all the samples tested in the entire moisture content range. At water content > 30% (w/w), *S68* and *S70* had lower amount of unfreezable water, while *S64* had higher amount of unfreezable water.



## 1. Introduction

Starch is a renewable biomass and it has been commonly used in food, chemical, textile, papermaking, medicine and many other industries (Hoover, Hughes, Chung, & Liu, 2010). Partial gelatinization of starch commonly occurs due to high hydrostatic pressure, parboiling of rice, and drying of moist cereals because of exposure to heat, high humidity and mechanical stress in production processes. Because of very poor solubility of native starch in water at ambient temperature, gelatinization of starch is essential in most production processes. The moisture content within the starch granules, the ease or difficulty with which the moisture diffuses within the starch granules and temperature of the starch–water suspension or treatment temperature determine the gelatinization behavior of starch (Hoover, 2001). Hence, a proper understanding of the role of water and its interplay with starch during thermal treatment is essential in the industrial processing and subsequent application of starch and starch-containing materials (Rolée, Chiotelli, & Meste, 2002).

Heating of an aqueous starch suspension induces a number of structural changes in the starch granules during gelatinization (Orlowska & Randzio, 2010). Differential scanning calorimetry (DSC) is now commonly regarded as one of the most suitable methods for quantifying the endothermic behavior of starch during gelatinization (Campanha & Franco, 2011; Patel and Seetharaman, 2010; Thirathumthavorn & Trisuth, 2008). When starch is heated in the presence of excess water, a single symmetric endotherm, usually denoted as G, is observed in the lower temperature region. As the amount of available water decreases, a biphasic endotherm with a tailing shoulder (M1) is observed. When water content is reduced further, the first endotherm (G) fades out and it is only possible to observe the second endotherm (M1) and the temperature shifts toward a higher region. Yet another endotherm appears at higher temperatures (M2) induced by the melting of the amylose–lipid complex (Svensson & Eliasson, 1995). Several theories have been proposed in order to explain the mechanism of starch gelatinization; however, no model has been generally or universally accepted until now (Karapantsios, Sakonidou, & Raphaelides, 2002). Starch samples having different crystalline patterns and granular structures exhibit different gelatinization behavior (Crochet and Beauxis, 2005; Jyothi, Sajeev, & Sreekumar, 2011; Tran, Piyachomkwan, & Sriroth, 2007). The understanding of the influence of the amorphous and crystalline structures and the overall granular form on the gelatinization of starch granule is a complex problem. The complexity is induced by many factors such as the interaction of water both at the interior and exterior of the granule and the role of the amorphous and crystalline domains

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0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.09.098

within the granule (Crochet and Beauxis, 2005). Hence, it would be of practical importance to study the gelatinization of starch samples having different microstructure and which have undergone partial gelatinization. Such study can also provide better understanding of the mechanism involved in the gelatinization of starch.

Interaction between starch and water is one of the most important factors that determines the physicochemical properties of starch. The interaction between starch and water can be monitored by following the change in physical state of water within the starch (Tananuwong & Reid, 2004). The physical state of water in starch can be described as unfreezable and freezable water (Li, Dickinson, & Chinachoti, 1998). The unfreezable water is strongly bound to starch molecules and it is responsible for the stability of a starch-based product (Charles, Kao, & Huang, 2003). The water binding capacity has an important relationship with the microstructure of starch granules. Chung, Lee, & Lim (2002) studied the difference in the water binding capacity between native and gelatinized rice starch. They found that the freezable water was reduced by gelatinization due to a greater proportion of amorphous chains to interact with water. Many researchers have detected the freezable water content (Brouillet-Fourmann, Carrot, Lacabanne, Mignard, & Samouillan, 2002; Li et al., 1998; Zhong & Sun, 2005). However, there is still little insight on the interactions between water and partially gelatinized starch having different microstructure.

In these contexts, the main objective of this work was to study the effect of partial gelatinization of starch on starch–water interactions during gelatinization. The DSC was used to probe these interactions. The gelatinization thermograms were determined and the amount of unfreezable water was calculated. Information obtained from this study would provide better understanding of the mechanism of starch gelatinization, especially when it is partially gelatinized.

## 2. Materials and methods

### 2.1. Materials

Native corn starch was purchased from Hebei Zhangjiakou Yujin Food Co., Ltd. (Hebei, China). Its moisture content was 10% (w/w). The lipid content in this corn starch varied between 0.15% (w/w) and 0.20% (w/w) (as per the certificate of analysis provided by the supplier, Hebei Zhangjiakou Yujin Food Co., Ltd. (Hebei, China)).

Partially gelatinized starch *S64*, *S68* and *S70* were prepared by using the method proposed by Fu, Wang, Li, & Adhikari (2012). Corn starch dispersions (10.0%, w/w) were prepared by adding 20.0 g of pre-dried corn starch into deionized water at 24 ± 1 °C. Each batch of corn starch dispersion was thoroughly stirred at 300 rpm (in beakers) for 15 min using a thermostated water bath at 64 °C, 68 °C and 70 °C. After being preheated these partially gelatinized starch dispersions were spray dried using a bench-top spray drier (GPW120-II, Shandong Tianli Drying Equipment Inc., China). The feed rate, inlet temperature, flow rate of the air and exhaust aspiration level used in the spray drying process were maintained at 7.2 ml/min, 200 °C, 0.375 $m^3$/h and 95%, respectively. Partially gelatinized starch *S25* was used as a control and it was prepared by stirring corn starch dispersion for 15 min at room temperature followed by spray drying.

The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was determined as previously reported (Fu et al., 2012). Distilled water (7.5 μl) was added with a microsyringe into partially gelatinized starch sample (2.5 mg) in an aluminum pan. This mixture of water and starch sample was then immediately hermetically sealed with an aluminum lid. Each sealed sample was equilibrated for about 3 h at ambient temperature before thermally scanning using a differential scanning calorimeter (DSC-Q10, TA Instruments, New Castle, USA). In these DSC tests, these samples were heated from 20 °C to 120 °C with a heating rate of 10 °C/min. The gelatinization enthalpy ($\Delta H_{gel}$) was calculated. The degree of gelatinization (GD) was determined using Eq. (1) given below (Błaszczak et al., 2007).

$$GD = \{(\Delta H_{ns} - \Delta H_{it})\Delta H_{ns}^{-1}\} \times 100\% \quad (1)$$

where $\Delta H_{ns}$ and $\Delta H_{ts}$ are the melting enthalpies of native and modified starches, respectively.

### 2.2. The differential scanning calorimetry (DSC) analysis

The DSC measurements were performed using the same instrument as mentioned in Section 2.1 above. The DSC analyzer was calibrated using indium (melting point = 156.6 °C, melting enthalpy = 26.59 J/g) and an empty aluminum pan was used as a reference. Samples for DSC analysis were prepared using procedures similar to those described by Jang and Pyun (1996) and Maaruf, Che Man, Asbi, Junainah, and Kennedy (2001). Partially gelatinized starch samples (2.0–3.0 mg) were prepared in aluminum pans. Distilled water was added with a microsyringe into starch until all the granules were wetted and uniformly settled at the bottom of the pan. Filled pans were left to air dry until the contents reached the desired moisture level (25, 30, 40, 50, 60 and 78%, w/w) and then immediately sealed with an aluminum lid. Each sealed sample was equilibrated for 1 h at ambient temperature before thermally scanning in the DSC. The samples were then heated from −60 °C to 200 °C at 10 °C/min. The peak ($T_p$) of the gelatinization temperature and melting temperature of amylose–lipid complexes were quantified. The enthalpy of the frozen water of the samples was recorded.

Unfreezable water was determined using the DSC data following the method described by Ross (1978) and Zhong and Sun (2000). The same calorimetric measurements were carried out for pure water. The melting enthalpy of pure water was obtained and used as the reference enthalpy. The amount of unfreezable water was calculated using Eq. (2) given below:

$$M = \frac{m_m}{m_s} - \frac{\Delta H_1}{\Delta H_2} \quad (2)$$

where $M$ (g water/g dry starch) is the amount of unfreezable water, $m_m$ (g water) and $m_s$ (g dry starch) are the amounts of moisture content and dry starch in samples, respectively. $\Delta H_1$ (J/g dry starch) and $\Delta H_2$ (J/g water) are the ice melting enthalpies of moisture in starch samples and pure water, respectively.

### 2.3. Statistical analyses

All the tests were carried out at least in triplicate and results are reported as the mean and standard derivation of these measurements. Duncan's multiple comparison tests were carried out to determine the significant effect of heating processes on the properties of starch samples at 95% ($P < 0.05$) confidence level using the SPSS statistical package (LEAD Technologies, US).

## 3. Results and discussion

### 3.1. Thermal endotherms of starch at different moisture contents

The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was calculated and was found to be 32.30%, 47.75%, 69.40% and 96.78%, respectively. The DSC thermograms of *S25*, *S64*, *S68* and *S70* starch samples having moisture contents between 25% and 78% (w/w) are presented in Fig. 1. As can be seen in Fig. 1A, the G endotherm is observed in the case of *S25* starch sample at moisture contents higher than 40% (w/w) and this disappeared at moisture contents lower than 30% (w/w). However, G endotherm