Functional, physicochemical properties and structure of cross-linked oxidized maize starch

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ABSTRACT

Cross-linked, oxidized and cross-linked oxidized maize starches were prepared with hydrogen peroxide and sodium trimetaphosphate (STMP), respectively. The physicochemical properties, determined by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), confirmed that the native maize starch was successfully modified. The functional properties (solubility, light transmittance, retrogradation rate and freeze–thaw stability) of native and modified starches demonstrated that cross-linked starch displayed the best freeze–thaw stability. The light transmittance and retrogradation properties of cross-linked oxidized starch were highly improved compared to the native starch. This work suggested that both cross-linking and oxidation firstly happened in amorphous regions of the starch, and a possible structure of cross-linked oxidized maize starch and reaction mechanisms were hypothesized.

1. Introduction

Starch is a kind of low-costly renewable and biodegradable polymer and has been applied in academic research and industry for the past few decades. Native starches are widely used in food industry as thickener, colloidal stabilizer, gelling agent, bulking agent and water retention agent. However, the modern food processing of native starches was limited by their low thermal stability, susceptibility to extreme pH conditions, as well as strong retrogradation rate and low light transmittance (Singh, Kaur, & McCarthy, 2007; Witczak, Juszczak, Ziobro, & Korus, 2012; Xiao, Lin, Liu, & Yu, 2012). For example, gelatinized starches in chilled foods require strong hydrophilic property and low retrogradation rate. However, native starches exhibit high tendency to retrogradation and syneresis, leading to the texture and taste damage, which shorten the shelf life. Therefore, most native starches employed in practical food applications are required to be modified to improve their functional properties. Chemical modification is a classical way to effectively improve the functionalities of starch. Typically, modified starches can be obtained through acetylated, hydroxypropylated, cross-linked, oxidized and etherified starches

(Carmona-Garcia, Sanchez-Rivera, Mendez-Montealvo, Garza-Montoya, & Bello-Perez, 2009; Jayakody & Hoover, 2002). Chemical modification alters the structure of starch, affects the physicochemical properties of the starch to various degrees and makes it appropriate for various industrial uses (Karim, Sufha, & Zaidul, 2008; Singh et al., 2007). However, compared to the single modified starch, composite modified starch exhibits better properties and more extensive applications.

Maize is a main crop in China and maize starch accounts for 80% of all starches. To date, most studies about maize starch focused on the single modified starch, such as oxidized maize starch and cross-linked maize starch. In general, oxidized starch has unique functional properties such as low viscosity at high solid concentration, clarity, film forming and binding properties, etc. (Chang, Park, Shin, Suh, & Kim, 2008; Kuakpetoon & Wang, 2006; Zhang, Wang, Zhao, & Wang, 2012). Besides, cross-linking can stabilize the granules and strengthen the tender starch, leading to higher viscous, better resistant to acid, heat and shearing and less likely to breakdown than native starch (Jyothi, Moorthy, & Rajasekharan, 2006; Kaur, Singh, & Singh, 2006; Mao, Wang, Meng, Zhang, & Zheng, 2006; Prochaska, Konowal, Sulej-Chojnacka, & Lewandowicz, 2009). However, few researches paid attention to the composite modified starch with two or more methods, especially oxidation and cross-linking, using maize starch. Although Chen and Wang (2006) have studied the synthesis of cross-linked oxidized corns starch,

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they mainly focused on its adsorption behavior for calcium ion but not its properties.

Thus, the aim of this study was to prepare the dual-modified maize starches (cross-linked oxidized starch). The physicochemical properties of native, cross-linked, oxidized and cross-linked oxidized starch were determined using DSC, FTIR and XRD. Besides, the functional properties including light transmittance, retrogradation rate and freeze–thaw stability of these starch were investigated. A possible structure of modified starch and the reaction mechanism was further studied.

2. Materials and methods

2.1. Materials

Native maize starch was obtained from Hengren Trade & Industry Co., Ltd., Shandong, China. Sodium trimetaphosphate (STMP) and hydrogen peroxide were purchased from Puxiu Biotechnology Co., Ltd, Hangzhou, China. All chemicals and reagents used in the study were of analytical grade.

2.2. Preparation of cross-linked maize starch

Cross-linked starch with STMP was prepared using the method of Kittipongpatana and Kittipongpatana (2011) with some modifications, as shown in Fig. 1 (a). In brief, maize starch (30 g), distilled water (45 mL) and STMP (0.60 g) were mixed in a reactor. The mixture was adjusted to pH 10.0 with a few drops of 1 M NaOH (with slow manual stirring using a glass rod). The slurry was stirred

(a)   **(b)**

Fig. 1. Process flow chart of preparation of (a) cross-linked maize starch and (b) oxidized maize starch.

continuously, warmed up to 45 °C, and held at this temperature for 30 min. The slurry was neutralized to pH 6.5 with 1 M hydrochloric acid, and then washed thoroughly. The obtained starch was dried at 40 °C for 24 h, pulverized, and passed through a sieve with 80-mesh.

2.3. Preparation of oxidized maize starch

Hydrogen peroxide oxidation of starch was carried out as described by Sangseethong, Termvejsayanon, and Sriroth (2010), with some modifications. A maize starch slurry containing 40% dry solid was prepared and the pH was adjusted to 8.0 with NaOH solution. The temperature of the slurry was maintained at 45 °C. Ferrous sulfate (0.07% based on starch) was added as catalyst and hydrogen peroxide solution was added dropwise to the reaction mixture over a period of 15 min to obtain a final concentration of 12% (based on starch). The reaction continued for 3 h at the same temperature. Then the slurry was neutralized to pH 6.5 with 1 M hydrochloric acid. The samples were then filtered and thoroughly washed with water until the filtrate gave negative response to silver nitrate solution. Then the collected sample was treated in the same way as described in Section 2.2. The whole process was shown in Fig. 1 (b).

2.4. Preparation of cross-linked oxidized maize starch

The collected cross-linked maize starch was oxidized using the method as described in Section 2.3.

2.5. Determination of carboxyl group content

The carboxyl group content of starch was determined following the method of Sangseethong et al. (2010). Starch sample (5 g) was stirred in 25 mL of 0.1 M HCl for 30 min. The slurry was then filtered and washed with distilled water until it was free of chloride ions. The filtered cake was then transferred to a 600 mL beaker and adjusted to 300 mL with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure completed gelatinization. The hot sample was immediately titrated with 0.1 M NaOH using phenolphthalein as an indicator. A blank determination was run on the native starch in the same manner but being stirred in 25 mL of distilled water instead of 0.1 M HCl.

2.6. Solubility

Solubility was measured according to the method of Lee and Yoo (2011) with a slight modification. A 0.4 g (dry basis) ground sample was mixed with 40 mL of water. The starch dispersion was moderately stirred for 1 h at room temperature, and then heated at 80 °C in a water bath for 30 min. The hot starch paste was cooled to room temperature in an iced water bath and centrifuged at 3000 r/min for 10 min.

$$\text{Solubility } (\%) = (\text{weight of dissolved solids in supernatant}/$$
$$\text{weight of starch sample in dry basis}) \times 100\%$$

2.7. Light transmittance

Paste clarity was determined using the method of Lawal (2004), and Bhandari and Singhal (2002). 50 mg (on dry weight basis) of native and modified starch was suspended in 5 mL of distilled water, using 10 mL cotton-plugged test tubes. The suspensions were then heated in a boiling water bath for 30 min (with constant shaking for the fir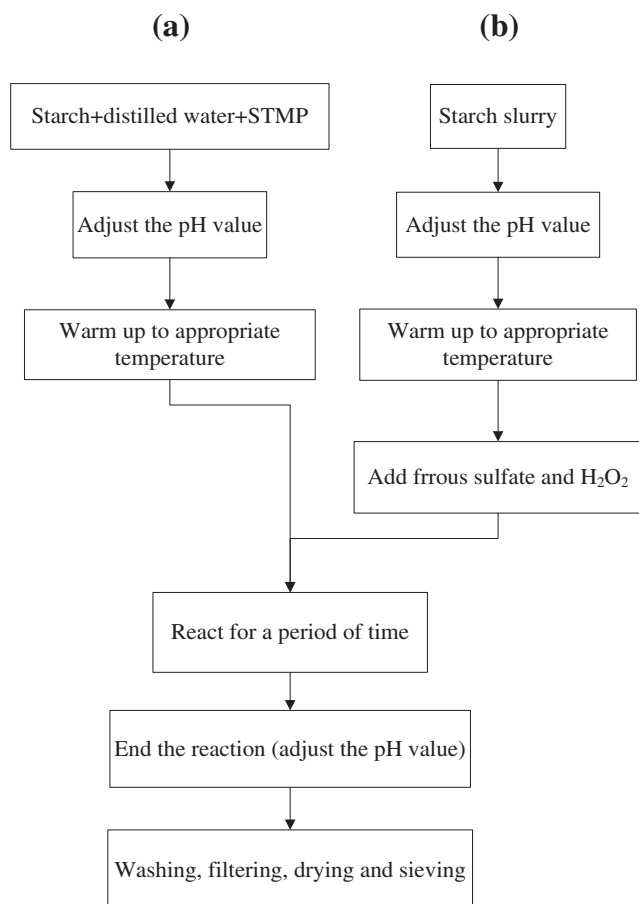st 5 min and occasional shaking afterward). After