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Potato starch oxidation induced by sodium hypochlorite and its effect on functional properties and digestibility

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ABSTRACT

The effects of different concentrations of sodium hypochlorite (active chlorine content at 0.1, 0.2, 1.0, 2.0, 3.0, and 4.0 g/100 g) on the properties of potato starch (PS) were investigated by determining the morphological, physicochemical, crystallinity, pasting, gel texture and digestive properties. The starch granules of PS oxidized with high oxidant concentrations caused cracks and pores, and oxidation mainly acts on the amorphous regions of the starch granules. As the sodium hypochlorite concentration increases, the carbonyl content, carboxyl content, solubility, and pasting temperature of PS increased, as measured using a Rapid Visco Analyser (RVA). The swelling power, breakdown, setback, and peak and final viscosities decreased according to the RVA ($P < 0.05$). The gel strength increased under low-intensity oxidative treatments and decreased under high-intensity oxidative treatments. Oxidative treatment decreased the digestibility of gelatinized potato starch. The slowly digestible starch and resistant starch contents increased significantly, while the rapidly digestible starch content decreased after the oxidation modification ($P < 0.05$). Overall, PS oxidation with sodium hypochlorite improved the functional characteristics of starch and decreased starch digestibility.

1. Introduction

Starch is an important component in many foods and a major energy source in human diets. As a food ingredient, starch has been used in various food preparations primarily based on its thickening or binding properties and has great value in food industry [1]. Natural starch has some defects, such as poor thermal stability, poor shear resistance and susceptibility to retrogradation. These characteristics limit the application of natural starch in food processing [2]. Many chemical methods have been used to modify natural starch to improve its function in the food industry, for instance, hydroxypropylation [3], carboxymethylation [4], cross-linking [5], acetylation [6], and oxidization with sodium hypochlorite [2,7]. In various chemical modification methods, oxidation treatment can effectively improve the function of starch. Oxidized starch has low viscosity, high thermal stability, low retrogradation and better binding, film-forming and clarity properties than native starch [8,9]. Many oxidants can be used to produce oxidized starch, and sodium hypochlorite is often applied to produce oxidized starch [10].

From a nutrition point of view, starch can be classified into three categories according to the digestion rate and digestion extent: rapidly digestible starch (RDS, the starch fractions digested within 20 min after ingestion), slowly digestible starch (SDS, the starch fractions digested between 20 and 120 min after ingestion), and resistant starch (RS, the starch fractions that cannot be digested in the small intestine after ingestion) [11,12]. RS can avoid hydrolysis to some extent in the small intestine of the human body and pass to the large bowel for fermentation; it is considered good for human health. RS has similar functional properties to fermented dietary fiber [13]. Chung et al. [6] reported that sodium hypochlorite oxidation treatment (0.48 g active chlorine/100 g starch) decreased the digestibility of corn starch because the substituted groups introduced to the starch molecules can cause hydrolytic enzymes to lose their activities, thus reducing the level of enzymatic hydrolysis of starches in the gelatinized starches. Therefore, chemical substitution can be used to increase the RS content and decrease the digestibility of starch. After the intake of RDS, the blood glucose level rapidly increases, while SDS is converted slowly into glucose and stabilizes the blood glucose level after ingestion [11]. Therefore, high SDS and RS contents in food can improve the health of obese and diabetic patients. As most starchy foods should be cooked before eating, the digestibility of gelatinized starch is an important property of starchy foods. Many researchers have studied the

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digestibility of chemically modified starch. However, the effects of chemical modification on starch digestibility in the gel phase are not completely understood.

Potato is an important starch crop, and considerable amounts of potato are used for starch production every year. Potato starch (PS) is unique compared to cereal starches due to its molecular structure and composition, granule morphology, and physicochemical properties [14]. Although the some functional and structural properties of many starches oxidized with sodium hypochlorite have been investigated by some researchers [2,8–10], there are few reports about sodium hypochlorite oxidation on PS. In addition, the nutritional fractions of oxidized starch (RDS, SDS, and RS) have not been discussed. The effects of sodium hypochlorite oxidation on the digestion behavior in native and gelatinized states of PS are also not understood. The objectives of this research were to modify PS using different concentrations of sodium hypochlorite (concentrations of 0.1–4.0 g active chlorine/100 g potato starch) and evaluate the physicochemical and functional properties of the modified PS. From the digestion profile, the digestibilities of the gelatinized starches were tested to compare the various starch fractions (SDS, RDS and RS) in the starch gel samples, and the causes of the changes were analyzed.

2. Materials and methods

2.1. Samples and materials

Native potatoes (*Solanum tuberosum* L., Huangmazi cultivar) were purchased from a local market (Suihua, Heilongjiang, China). Sodium hypochlorite (NaOCl) containing 10 g active chlorine/100 g was used in this experiment. All chemicals used were of analytical grade.

2.2. Preparation of potato starch

PS was prepared as described by Liu et al. [15] with some modifications. Potatoes were peeled, cubed (2 cm^3) and immersed in 0.1% sodium bisulphite at a 1:8 (kg:L) ratio for 20 min, and then crushed in a blender (JJ-2B, China) for 2 min. The suspension was passed through a 100-mesh standard sieve and stored at 4 °C for 24 h. Next, the sediment was collected, and the supernatant was removed. The potato starch was washed with distilled water three times and dried at 50 °C for approximately 24 h to reduce its moisture content to approximately 10%.

2.3. Potato starch oxidation

PS oxidation was performed as described by Chong et al. [16] with some modifications. PS (50 g) was dissolved in 450 g of deionized water in a 1-L container to obtain the starch slurry. The starch slurry was stirred continuously at 35 °C in a water bath and the pH level of the starch slurry was adjusted to 9.5 with 1 M NaOH, and then treated with sodium hypochlorite to obtain the oxidized starch. Sodium hypochlorite was added slowly under stirring for 30 min, until reaching different final concentrations (0, 0.1, 0.2, 1.0, 2.0, 3.0 and 4.0 g of active chlorine for 100 g of starch). An additional 30 min reaction period was continued at pH 9.5, which was maintained using a 1.0 M H_2SO_4 solution during the reaction. The slurries were adjusted to pH 7.0 by adding 1.0 M H_2SO_4 after the reaction. The samples were then suction filtered using a Buchner filter funnel, washed with a two-fold volume of distilled water and dried in a blast dryer (101-3AB, China) at 50 °C for approximately 24 h to reduce the moisture content of the oxidized starch to approximately 10%.

2.4. Carbonyl and carboxyl contents

The carbonyl content of the oxidized PS was measured by the titrimetric method [17]. The carbonyl content was expressed as the number of carbonyl groups per 100 glucose units (CO/100 GU), as calculated using the following equation:

$$\frac{\text{CO}}{\text{100GU}} = \frac{(V\text{b} - V\text{s}) \times M \times 0.028 \times 100}{W}$$

where *V*s is the volume of HCl required for the sample (mL), *V*b is the volume of HCl used for the blank (mL), *W* is the sample weight (dry basis) and *M* is the molarity of HCl.

The carboxyl content was determined as described by Chattopadhyay et al. [18]. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU), as calculated by the following equation:

$$\frac{\text{COOH}}{\text{100 GU}} = \frac{(V\text{s} - V\text{b}) \times M \times 0.045 \times 100}{W}$$

where *V*b is the volume of NaOH used to test the blank (mL), *V*s is the volume of NaOH required for the sample (mL), *W* is the sample weight (dry basis), and *M* is the molarity of the NaOH.

2.5. Polarized light microscopy (PLM)

The crystal structures of the samples were observed using polarized microscope (BS203IP, Chongqing Photoelectric Instrument Co., Ltd., Chongqing, China). The PS samples were regulated in a certain proportion to form an emulsion (10%, w/v). A drop of the liquid was placed on a glass slide, covered with a coverslip, and placed on the objective table. Then, the sample was viewed using objective and eyepiece magnifications of 40× and 10×, respectively.

2.6. Scanning electron microscopy (SEM)

The morphologies of the PS granules were observed by SEM (S-3400N, Hitachi, Tokyo, Japan). The native and oxidized PS samples were suspended in acetone at 1% (w/v). Each sample was spread directly onto the surface of the stub and dried in an oven at 32 °C for 1 h. Then, all of the samples were coated with gold and examined in the SEM under an acceleration voltage of 5 kV and at a magnification of 400×.

2.7. X-ray diffraction

X-ray diffractograms of the native and oxidized PS were determined using an X-ray diffractometer (D/MAX 2200, Rigaku, Tokyo, Japan). The scanning region of the diffraction ranged from 5° to 30° with a target voltage of 40 kV, current of 30 mA and scan speed of 2°/min. The relative crystallinity (RC) of the starch granules was calculated as following the equation:

$$\text{RC\%} = \left[\frac{Ac}{Ac + Aa}\right] \times 100$$

where *Ac* is the crystalline area, *Aa* is the amorphous area on the X-ray diffractograms.

2.8. Swelling power and solubility determination

The swelling power and solubility of the native and oxidized PS were measured according to Leach et al. [19] with some modifications. The PS (1.0 g) was mixed with 50 mL of distilled water. The suspensions were heated at 60, 65, or 70 °C for 30 min with water shock. Then, the gelatinized PS samples were cooled to room temperature and centrifuged at 1000 × *g* for 20 min. The supernatants were dried at 110 °C until a constant weight was obtained so that