Properties of Oxidized Starch Prepared by Hydrogen Peroxide, Chlorine Dioxide and Sodium Hypochlorite

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Abstract. Chlorine peroxide, Sodium hypochlorite and hydrogen peroxide were chosen as oxidant to prepare potato oxidized starch, and the properties of oxidized starch were determined. The results showed that carbonyl content of oxidized starch prepared by H_2O_2 is 0.329%, much higher than other oxidized starch and potato starch. Gelatinized viscosity of oxidized starch prepared by ClO_2 is 15.69 Pa. s, significantly increased. All these starch were characterized by Fourier Thansform Infrared Spectroscopy (FT-IR). Different oxidized position and oxidized extent due to different oxidant were observed.

Introduction

Starch is a renewable and biodegradable macromolecule. It has attracted great interest and as an important raw material for low cost and abundant resource. However, the hydrophilic OH groups of the unmodified starch molecule tend to constitute intermolecular and intramolecular hydrogen bonds, limiting the application of the material for certain applications. Some oxidizing agents with different redox potentials have been tested to modify starch by introducing COOH and CHO groups [1]. At a suitable temperature and pH value, starch can be oxidized by periodate, chromic acid, permanganate, nitrogen dioxide, and sodium hypochlorite [2]. During oxidation, starch loses its original crystallization, and the hydroxyl groups in the glucose ring are partially oxidized to aldehyde or ketone groups, which weaken the hydrogen bonds between the starch chains [3].

Though the oxidized starch prepared by H_2O_2 has already been characterized [4], there is no report on properties of oxidized starch prepared by different oxidant. In previous studies, we found that when the hydroxyl groups in glucose ring of starch were oxidized to aldehyde groups, both the mechanical properties and hydrophobicity of thermoplastic starch were improved [5]. In this study, properties of oxidized starch with carboxyl of same content by Hydrogen Peroxide, Chlorine Dioxide and Sodium Hypochlorite were evaluated, and some properties of them were investigated.

Materials and Methods

Materials

Potato starch (10.8% moisture) was obtained from Jilin Qishen Food Company (technical grade, Changchun, Jilin, China). Hydroxyl peroxide (H_2O_2, 30%), Sodium hypochlorite, and Chlorine dioxide were purchased from Kelong Chemical Reagent.

All other chemicals and solvents used were of analytical grade (99.5%) and used without purification.

Preparation of Oxidized Starches

Oxidized starch prepared by hydroxyl peroxide, chlorine dioxide and sodium hypochlorite were produced according to the following procedures respectively [6-8]. 50g potato starch and 250mL distilled water were mixed and heated at 80℃ for 30 min with mild stirring. 1) 25mL H2O2 (30%) was added in the mixture after the temperature dropped to 40℃ for 4h. 2) Potato starch was oxidized with concentration of sodium hypochlorite at 6% and pH at 7.0 for 3h. 3) Starch slurry contain 0.15% chlorine dioxide and activator was stirred at 35℃ for 2.5h. The slurry was separated by slow-speed centrifugation and the precipitated product was washed with five 200mL portions of distilled water before drying for 24 h at 50℃ in a vacuum oven.

Determination of Carboxyl Content

The carboxyl content of oxidized starch was determined according to the modified procedure [9]. About 2g of oxidized starch sample was mixed with 25mL of 0.1mol/L HCl, and the slurry was stirred continually for 30 min with a magnetic stirrer. Subsequently, the slurry was vacuum-filtered through a medium porosity fritted glass funnel and washed with distilled water until without chlorine ion. The starch cake was then carefully transferred into a 150mL beaker. After mixed with 100mL water, the starch slurry was heated to 100℃ with continuous stirring for 3-5 min. The hot starch dispersion was then adjusted to 300mL with distilled water, and then standard NaOH solution was dripped into the sample solution slowly, and the titration end point was judgedby potentiometer (pH 8.3). A blank test was performed with unmodified starch. The carboxyl content was calculated as follows:

$$-COOH\ (\%) = (V_1/m_1 - V_0/m_0) \times c \times 0.045 \times 100 \quad (1)$$

V_1 and V_0 are the volumes of the consumed standard NaOH solution (mL) for the titration of samples and blank, m_1 and m_0 are the masses of the sample and unmodified starch, and c is the concentration of NaOH (mol/L), respectively.

Determination of Carbonyl Content

Carbonyl content was performed as described previously [10]. 5g of oxidized starch was dispersed in 100mL of distilled water, and the suspension was gelatinized by heating in a boiling water bath and then cooled to 40℃. 60mL of hydroxylamine reagent (25g hydroxylamine hydrochloride dissolved in 100mL of 0.5mol/L NaOH. Subsequently, the solution was made up to 500mL with distilled water) was added after adjusting pH to 3.2. The sample was covered with aluminum foil and placed in a water bath at 40℃ for 4 h. The excess hydroxylamine was determined by rapid titration of the reaction mixture to pH 3.2, with 0.1mol/L HCl. Blank test was performed with unmodified starch. Carbonyl content was calculated as follows:

$$-C{=}O\ (\%) = (V1 - V0) \times c \times 0.028 \times 100 \div m \quad (2)$$

V_1 and V_0 are the volumes of the consumed HCl standard aqueous solution (mL) for the titration of sample and blank, m is the mass of the sample, and c is the concentration of HCl (mol/L), respectively. The apparent viscosity of the cooked samples (6%) was measured by using coaxial rotary viscometer, with a rate of shear of 2000 or $350s^{-1}$ at 40℃. The residual copper was estimated by the atomic adsorption spectrometry.

Determination of Viscosity

The viscosity [pa. s] of the oxidized starch was determined with an viscometer at 25.0 ±0.1℃ in water at a gelatinized sample concentration of about 50mg/mL.

Measurement of Clarity and Retrogradation

The 0.01g/mL water solution of oxidized starch was gelatinized by heating in boiling water and cooled to room temperature. The light transmittance was measured in a spectrophotometer at 650 nm, a control tube contain distilled water was prepared in parallel to each test sample. After deposited for 24h, light transmittance was measured again. Retrogradation obtained by the difference.

FT-IR Spectroscopy

The IR spectra were obtained from samples in KBr pellets using a 170SX FT-IR spectrophotometer (Nicolet, Madison, WI, USA).

Results and Discussions

Characteristics of Oxidezed Starch

The carboxyl content of oxidized starches prepared from potato starch was all qualified to about 0.2%. After dehydrated to powder, essential characteristics such as carbonyl content, viscosity, clarity and retrogradation were investigated. Table 1 shows the Carbonyl content of gelatinized starch oxidized with different oxidant. Bidzinska et al found that the reation of oxidant with gelatinized starch did not go to completeness [11]. When hydrogen peroxide chosen as oxidant, significant increase in the carbonyl content of oxidized starch to 0.329%. In contrast, when oxidant shifted to sodium hypochlorite, viscosity of oxidized starch maximized to 15.69 Pa. s. At the same time, no matter what kinds of oxidant was chosen, only an insignificant increase in the clarity and retrogradation were found. This indicated that oxidized starch prepared by different oxidant shown different characteristics.

Table 1. Carbonyl content, viscosity, clarity and retrogradation of oxidized starch

	Potato starch	Oxidized starch prepared by H_2O_2	Oxidized starch prepared by ClO_2	Oxidized starch prepared by NaClO
Carboxyl content (%)	0	0.20	0.20	0.20
Carbonyl content (%)	0	0.329	0.009	0.045
Viscosity (Pa.s)	5.255	0.11	0.074	15.69
Clarity	0.4041	0.704	0.534	0.692
Retrogradation	0.2582	0.252	0.431	0.316

FT-IR Analysis

The FT-IR spectra of oxidized starch prepared by different oxidant are shown in Fig. 1. The spectra show an intense band at 1637 cm-1, which was assigned to deformation vibrations of water molecules absorbed by starch [12]. The broad band at 1735 cm-1 is characteristic of C=O groups (stretching vibration), produced by oxidation of

hydroxyl groups to aldehyde and carboxyl groups [13]. FT-IR spectra of oxidized starch prepared with H2O2 (Figure 1, Curve (a)) exhibited a higher intensity of this absorption peak than other starches (curve (b, c, d)) correlating with its higher carbonyl content as measured by titration (see Table. 1). The band at 2927 cm-1 was attributed to CH2- asymmetric stretching vibration. The absorptions at 1460 cm-1 and 1300 cm-1 may be attributed to the C-H bending vibration [14, 15].

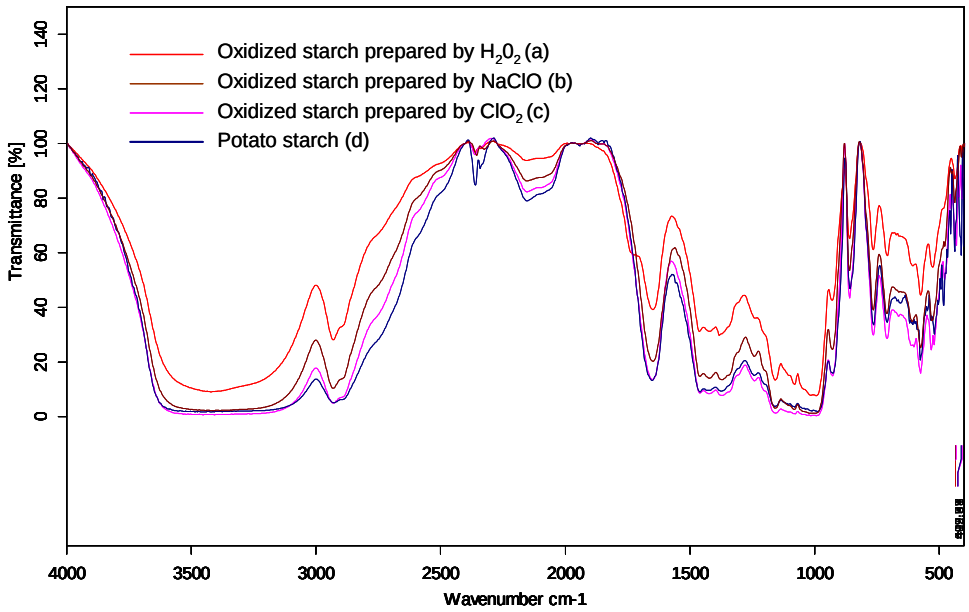

Figure 1 The FT-IR spectra of oxidized starch prepared by different oxidant

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