



Structure, morphology and functionality of acetylated and oxidised barley starches



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ABSTRACT

Acetylation and oxidation are chemical modifications which alter the properties of starch. The degree of modification of acetylated and oxidized starches is dependent on the catalyst and active chlorine concentrations, respectively. The objective of this study was to evaluate the effect of acetylation and oxidation on the structural, morphological, physical–chemical, thermal and pasting properties of barley starch. Barley starches were acetylated at different catalyst levels (11%, 17%, and 23% of NaOH solution) and oxidized at different sodium hypochlorite concentrations (1.0%, 1.5%, and 2.0% of active chlorine). Fourier-transformed infrared spectroscopy (FTIR), X-ray diffractograms, thermal, morphological, and pasting properties, swelling power and solubility of starches were evaluated. The degree of substitution (DS) of the acetylated starches increased with the rise in catalyst concentration. The percentage of carbonyl (CO) and carboxyl (COOH) groups in oxidized starches also increased with the rise of active chlorine level. The presence of hydrophobic acetyl groups, carbonyl and carboxyl groups caused a partial disorganization and depolymerization of starch granules. The structural, morphological and functional changes in acetylated and oxidized starches varied according to reaction conditions. Acetylation makes barley starch more hydrophobic by the insertion of acetyl groups. Also the oxidation promotes low retrogradation and viscosity. All these characteristics are important for biodegradable film production.

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1. Introduction

Barley (*Hordeum vulgare*) is a cereal that ranks fourth in economic importance, after wheat, rice and maize (Arngren, Hansen, Eriksen, Larsen, & Larsen, 2011). Approximately three-quarters of the worldwide barley production is used for animal feed, while 20% is malted for use in alcoholic and non-alcoholic beverages, and 5% is employed as an ingredient in a range of food products (Blake, Blake, Bowman, & Abdel-Haleem, 2011). Barley can be an important starch source (between 65% and 68%) which is the main component of the grain. Starch in natural state has limited industrial applications due to its low shear stress resistance and thermal decomposition, coupled to high retrogradation and syneresis, although such shortcomings may be overcome by starch modification. In the literature, chemical, physical and enzymatic methods have been used to modify starches. Chemically modified starches have several industrial applications with specific properties;

however the modification degree of starch to be used in food is limited by legislation.

Starch acetylation is a chemical modification by which part of the hydroxyl groups of glucose monomers is converted into acetyl group, altering the molecular structure of the starch. Acetylated starches are produced with acetic anhydride with an alkaline agent, such as sodium hydroxide, as catalyst (Bello-Pérez, Agama-Acevedo, Zamudio-Flores, Mendez-Moltealvo and Rodrigues-Anbriz, 2010). Starch acetylation depends upon certain factors, such as starch source, reactant concentration, catalyst type, concentration, reaction time and suspension pH. Acetylated starches are used in fruit pies, gravies, salad dressings and filled cakes. Non-food applications of acetylated starches include wrap-sizing for textiles, biodegradable films and surface-sizing for papers and gummed tape adhesives.

Starch oxidation is mainly performed through the reaction of starch with an oxidizing agent under controlled pH and temperature and specific reaction time. In commercial conversions, usually sodium hypochlorite is used as the oxidizing agent. The degree of starch oxidation by hypochlorite is affected by many factors such

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as starch molecular structure, starch origin, packing of crystalline lamellae and the size of amorphous lamellae, suspension pH, reaction time, temperature, concentration of oxidants and catalyst (Wang & Wang, 2003). Oxidized starches may be used in batters and breading, as food coating, in confectionary as binders, as dairy texturizers, as well as in the paper, textile and laundry industries (Kuakpetoon and Wang, 2001; Vanier et al., 2012).

The characteristics of native barley starch have been investigated (Rojas, Wahlund, Bergenstahl, & Nilsson, 2008; You & Izydorczyk, 2007), and some studies on the acetylation and oxidation of barley starch have been reported (Bello-Pérez et al., 2010; Chávez-Murillo, Wang, & Bello-Pérez, 2008). Bello-Pérez et al. (2010) evaluated the effect of acetylation time on barley starch properties, but did not study the effect of catalyst concentration on these properties. Chavez-Murillo, Wang and Bello-Pérez (2008) oxidized barley starch with sodium hypochlorite; however these authors used higher concentrations of active chlorine as compared to our study. Therefore, this study aims to investigate the effect of different catalyst concentrations in the acetylation reaction and the oxidation at low levels of active chlorine on the properties of barley starch, since we did not find similar studies. Also the effects of acetylation and oxidation on the structural, morphological, physical–chemical, thermal and pasting properties of barley starch were evaluated.

2. Materials and methods

2.1. Materials

Barley grains (*Hordeum sativum*) from cultivar BRS 195 were provided by the Universidade de Passo Fundo (–28.258254, –52.403421, in State of Rio Grande do Sul, Brazil). The barley starch contained 27.7% of amylose content. All the chemicals and reagents used in this work were of analytical grade.

2.2. Starch isolation

Barley starch was isolated by method described by Bello-Pérez et al. (2010), dried at 40 °C for 16 h until approximately 9% moisture content and stored at 17 ± 2 °C in a sealed container. The starch isolated from barley showed approximately 99% purity (0.2% protein, 0.6% fat and 0.1% ash).

2.3. Acetylation of starch

Starch acetylation was performed according to method described by Mark and Mehltretter (1972), with some modifications. One hundred grams of starch were weighed (dry basis), dispersed in 200 mL of acetic anhydride in a reaction flask and stirred at 500 rpm with a mechanical stirrer (Fisatom, 712, São Paulo, Brazil) for 5 min. Sodium hydroxide solution was used as the catalyst. The 11%, 17% or 23% NaOH solutions (50 g NaOH/100 g water) were added slowly to the starch suspensions with acetic anhydride. The NaOH concentrations (11%, 17% and 23%) were calculated based on the amount of starch. Each reaction was conducted at 100 °C and stirred for 1 h. The flask was then taken out of the container till the reaction medium reached 50 °C. Starch was further precipitated with 100 mL of ethyl alcohol solution (96%). It was immediately filtered by suction with a Buchner filter funnel (Whatman filter No. 4). The residue was washed with ethyl alcohol and then with distilled water till most of the acetic anhydride was removed. The resulting paste produced by these washes was dried at 40 °C for 16 h up to approximately 9% moisture content.

2.4. Determination of acetyl percentage (Ac%) and degree of substitution (DS)

Acetyl percentage (Ac%) and degree of substitution (DS) were determined titrimetrically, following method by Wurzburg (1986). DS is defined as the average number of sites per glucose unit that possesses a substituent group (Whistler & Daniel, 1995).

2.5. Starch oxidation

Starch oxidation was performed according to method described by Wang and Wang (2003), with some modifications. About 35% starch slurry was prepared by adding distilled water to 100 g of starch (dry basis) in a 1L-glass reactor. The starch slurry was maintained at 35 °C by occasionally turning off the heating mantle, whilst pH level was adjusted to 9.5 with 0.5 N NaOH. Twenty grams of sodium hypochlorite (1 g of active chlorine and 100 g of starch resulting in 1.0% active chlorine, w/w) was slowly added to the starch slurry over a period of 30 min while maintaining the pH level at 9.5 with 1 N HCl. After the addition of sodium hypochlorite, the slurry pH value was maintained at 9.5 with 1 N NaOH for an additional 50 min. It was then adjusted to pH 7.0 with 1 N HCl, filtered by suction with a Buchner filter funnel (Whatman filter No. 4), washed with a twofold volume of distilled water and dried in a convection oven at 40 °C for 16 h up to approximately 9% moisture content. The same procedure was applied for 1.5% and 2.0% (w/w) active chlorine concentrations.

2.6. Carbonyl and carboxyl contents

The carbonyl content was determined according to the titrimetric method described by Smith (1967). The carboxyl content of the oxidized starch was determined according to procedure by Chattopadhyay, Singhal, and Kulkarni (1997).

2.7. FTIR analysis

Starch samples were characterised by using a FTIR spectrometer (IRPrestige21, Shimadzu Corp. Japan) equipped with an attenuated total reflection (ATR) accessory (Pike Tech, Madison, WI.) according to the method described by Vanier et al. (2012). Tests were set at 4 cm^{–1} resolution and an average of 100 scans were taken for each sample. Starch samples were placed on the ATR crystal for analysis, at room temperature (22 ± 2 °C). The FTIR spectrum in the region between 800 cm^{–1} and 1200 cm^{–1} was a fitted curve by using the Gaussian function with the Grams/32 spectral analysis software (Galactic Industries Corp., Salem, NH).

2.8. X-ray diffraction

X-ray diffractograms of the native, acetylated and oxidized barley starches were obtained with an X-ray diffractometer (XRD-6000, Shimadzu, Brazil). The scanning region of the diffraction ranged between 3° and 45°, with a target voltage of 30 kV, current of 30 mA and scan speed of 1°/min. The relative crystallinity (RC) of the starch granules was calculated as described by Rabek (1980) by the equation: $RC(\%) = (Ac/(Ac + Aa)) * 100$; where Ac is the crystalline area; Aa is the amorphous area on the X-ray diffractograms.

2.9. Thermal analysis

The gelatinisation characteristics of starches were determined by differential scanning calorimetry (TA-60WS, Shimadzu, Kyoto, Japan) according to the method described by Vanier et al. (2012).

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