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## Structure, morphology and functionality of acetylated and oxidised barley starches



Shanise Lisie Mello El Halal<sup>a,\*</sup>, Rosana Colussi<sup>a</sup>, Vânia Zanella Pinto<sup>a,b</sup>, Josiane Bartz<sup>a</sup>, Marjana Radunz<sup>a</sup>, Neftali Lenin Villarreal Carreño<sup>c</sup>, Alvaro Renato Guerra Dias<sup>a</sup>, Elessandra da Rosa Zavareze<sup>a</sup>

<sup>a</sup> Department of Science and Agro-Industrial Technology, Universidade Federal de Pelotas, Pelotas, RS, Brazil

<sup>b</sup> Department of Food Science, University of Guelph, Ontario N1G 2W1, Canada

<sup>c</sup> Department of Electronic Microscopy, Course in the Engineering of Materials, Universidade Federal de Pelotas, Pelotas, RS, Brazil

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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 wrapping 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

\* Corresponding author. Tel./fax: +55 53 3275 7258.

E-mail address: [shanisemell@hotmail.com](mailto:shanisemell@hotmail.com) (S.L.M.E. Halal).

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 Mehlretter (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<sup>-1</sup> 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<sup>-1</sup> and 1200 cm<sup>-1</sup> 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).

Starch samples (approximately 2.5 mg, dry basis) were weighed directly in an aluminum pan and distilled water was added to obtain a starch–water ratio of 1:3 (w/w). The pan was hermetically sealed and allowed to equilibrate for one hour before analysis. Sample pans were then heated from 30 to 120 °C at a rate of 10 °C/min. An empty pan was used as control. The temperature at the onset of gelatinisation ( $T_o$ ), peak temperature ( $T_p$ ), temperature at the end of gelatinisation ( $T_c$ ) and enthalpy ( $\Delta H$ ) of gelatinisation were determined.

### 2.10. Scanning electron microscopy (SEM)

The morphology of starch granules was examined by scanning electron microscope (Shimadzu, SSX-550) according to the method described by Vanier et al. (2012). Starch samples were initially suspended in acetone to obtain a 1% (w/v) suspension, and samples were maintained in an ultrasound bath for 15 min, for individualization of the starch granules. A small quantity of each sample was spread directly on the surface of the stub and dried in an oven at 32 °C for 1 h. All the samples were subsequently coated with a thin gold layer and examined under scanning electron microscope at an acceleration voltage of 15 kV and 1000 $\times$  magnification.

### 2.11. Swelling power and solubility of starches

The swelling power and solubility of the starches were determined following Leach, McCowen, and Schoch (1959).

### 2.12. Pasting properties

The pasting properties of the starch samples were determined by Rapid Visco Analyser (RVA-4, Newport Scientific, Australia) with a Standard Analysis 1 profile (Newport Scientific., 1995). Viscosity was expressed in rapid visco units (RVUs). Starch (3.0 g of 14 g/100 g wet basis) was weighed directly on RVA canister and 25 mL of distilled water was then added. Parameters comprising pasting temperature, peak viscosity, breakdown, final viscosity and setback were recorded.

### 2.13. Statistical analysis

Analytical determinations for the samples were performed in triplicate and standard deviations were reported, except for X-ray peaks and relative crystallinity and thermal analysis. Means were compared by Tukey's test at 5% level of significance by analysis of variance (ANOVA).

## 3. Results and discussion

### 3.1. Percentage of acetyl groups and degree of substitution

Table 1 shows the effect of acetylation with different concentrations of catalyst on percentage of acetyl groups ( $Ac\%$ ) and degree of substitution ( $DS$ ) of barley starches.  $Ac\%$  and  $DS$  of starches increased significantly with increasing catalyst concentration. The acetylated barley starches showed  $DS$  ranging between 0.08 and 0.31, which is classified as low ( $<0.1$ ) and medium (0.1–1.0)  $DS$ , respectively (Table 1). Acetylated starches with low  $DS$  are used in food industry as agents of texture, consistency and stability in food and currently being studied in the development of biodegradable packaging and pharmaceutical applications. Starches with medium  $DS$  may be applied as substitutes for thermoplastic cellulose acetates (Biswas, Shogren, Selling, Salch, Willett and Buchanan, 2008).

**Table 1**

Acetyl percentage, degree of substitution and carbonyl and carboxyl contents of acetylation-treated and oxidization-treated starches.

Acetylation Starches <sup>a</sup>	Acetyl (%)	Degree of substitution
Native	0	0
11.0% NaOH <sup>b</sup>	2.14 $\pm$ 0.08 <sup>c</sup>	0.08 $\pm$ 0.00 <sup>c</sup>
17.0% NaOH	5.77 $\pm$ 0.29 <sup>b</sup>	0.22 $\pm$ 0.01 <sup>b</sup>
23.0% NaOH	7.54 $\pm$ 0.35 <sup>a</sup>	0.31 $\pm$ 0.01 <sup>a</sup>
Oxidation Starches <sup>a</sup>	Carbonyl content (CO/100 GU)	Carboxyl content (COOH/100 GU)
Native	0.01 $\pm$ 0.00 <sup>d</sup>	0.00 $\pm$ 0.00 <sup>c</sup>
1.0% active Cl <sup>c</sup>	0.09 $\pm$ 0.01 <sup>c</sup>	0.17 $\pm$ 0.01 <sup>b</sup>
1.5% active Cl	0.11 $\pm$ 0.00 <sup>b</sup>	0.21 $\pm$ 0.00 <sup>a</sup>
2.0% active Cl	0.15 $\pm$ 0.01 <sup>a</sup>	0.22 $\pm$ 0.01 <sup>a</sup>

<sup>a</sup> The results are the means of three determinations. Values with different letters in the same column are significantly different ( $p < 0.05$ ).

<sup>b</sup> NaOH (solution of 50 g NaOH/100 g of water).

<sup>c</sup> Active Cl: concentration of active chlorine (g Cl/100 g barley starch, d.b.).

<sup>a,b,c,d</sup> Values with different letters in the same column are significantly different ( $p < 0.05$ ).

Bartz, Madruga, Klein, Pinto, and Dias (2012) studied acetylated rice starch with 23% amylose under similar conditions as current investigation and found higher  $DS$  (0.67) and higher  $Ac\%$  (14.13) when compared to the results found in this study (Table 1). Differences in  $DS$  and  $Ac\%$  of barley and rice acetylated starches under similar conditions may be assigned to different morphology of the granules, since the barley starch granules are bigger than rice starch granules (Bello-Pérez et al., 2010; Man et al., 2013). Other factors, such as amylose content, amylopectin structure and other starch components may affect the introduction of acetyl groups in the starch structure. Bello-Pérez et al. (2010) employed the same acetylation method to acetylate barley starch, although with different reaction times (0.5 h and 6 h), which showed higher  $DS$  (0.9 and 2.7, respectively) than the  $DS$  found in the current analysis (Table 1). Differences in the substitution degree of acetylated starches may be due to differences in reaction conditions such as time, temperature, catalyst and acetic anhydride concentrations.

### 3.2. Carbonyl and carboxyl group contents

The carbonyl and carboxyl contents of native and oxidized barley starches are listed in Table 1. Oxidation of barley starch with different concentrations of active chlorine promoted the formation of carbonyl and carboxyl groups. The carbonyl content of the starch increased progressively with the active chlorine concentration used as oxidizing agent. Although oxidation of barley starch formed carboxylic groups, ranging between 0.17 and 0.22 COOH/100 GU, no differences were extant between starches oxidized with 1.5% and 2.0% active chlorine (Table 1). Carboxyl content rates were similar to those found by Chávez-Murillo et al. (2008) who reported oxidized barley starch with concentrations of 1.5%, 3.0% and 5.0% active chlorine. Other studies (Chong, Uthumporn, Karim, & Cheng, 2013; Kuakpetoon & Wang, 2001) also reported an increase of carbonyl and carboxyl groups in starches from potato, maize and rice oxidized with sodium hypochlorite.

Oxidized barley starch showed a higher formation of carboxylic groups than carbonyl groups (Table 1). Sangseethong, Lertphanich, and Sriroth (2009) oxidized cassava starch with sodium hypochlorite in alkaline conditions and registered a formation of carboxylic groups higher than that of carbonyl groups. The type of functional groups formed on starch molecules during oxidation depends on

reaction conditions. The oxidation reaction in the above studies occurred at alkaline pH conditions which, according to Wurzburg (1986), favored the formation of carboxylic groups.

### 3.3. FTIR analysis

Fig. 1 shows FTIR spectra of the native, acetylated and oxidized starches. Barley native starch presented strong peaks in the 3000–3600  $\text{cm}^{-1}$  and 2950  $\text{cm}^{-1}$  regions, which correspond to OH and CH stretching, respectively; peaks at 1650  $\text{cm}^{-1}$  and 1420  $\text{cm}^{-1}$  correspond to OH and CH bending (Mano, Koniarova, & Reis, 2003).

Acetylated starches had strong absorption bands at 1735–1740  $\text{cm}^{-1}$  (C=O stretching of acetyl group), 1368  $\text{cm}^{-1}$  (C–H in acetyl group) and 1234  $\text{cm}^{-1}$  (C–O stretching of acetyl group) with evidence of acetylation. The 1735  $\text{cm}^{-1}$  peak increased as the catalyst increased from 11% to 23%. On the other hand, since the intensity of the hydroxyl group peak at 3000–3600  $\text{cm}^{-1}$  decreased (Fig. 1a), it has been suggested that the hydroxyl groups in the starch molecules were converted into acetyl groups.

When native and oxidized starches with 1.0%, 1.5% and 2.0% of active chlorine were compared, no difference among IR spectra was detected (Fig. 1b), even with oxidized starches showing higher carbonyl and carboxyl contents than native barley starch (Table 1). Above results explain why the carbonyl groups formed during oxidation are smaller than groups from the modification of acetylation. The hydroxyl groups in starch molecules are oxidized to carbonyl groups and then to carboxyl groups, which primarily takes place at C-2, C-3, and C-6. Oxidation may also cause depolymerization of starch molecules by cleaving  $\alpha$ -(1,4)-glucoside linkages (Kuakpetoon & Wang, 2008), whereas acetylation is obtained by the esterification of native starch with acetic anhydride, including acetyl groups in starch molecule (Bello-Pérez, Agama-Acevedo, Zamudio-Flores, Mendez-Moltealvo & Rodrigues-Anbriz, 2010).

Further, starch crystallinity may be determined by FTIR spectroscopy (Van Soest, Jeroin, Tournois, Wit, & Vliegthart, 1995) by monitoring the changes which occur from semi-crystalline to amorphous domains within the starch granule. IR absorbance bands at 1035–1048  $\text{cm}^{-1}$  and 1015–1022  $\text{cm}^{-1}$  are generally employed to determine crystallinity and amorphous regions, respectively, where the amount of short-range ordering of the starch samples may be expressed by the ratio of intensity of these characteristic bands in starch (Van Soest et al., 1995). Native, acetylated and oxidized barley starches were deconvoluted for better resolution of overlapping peaks. Fig. 1c shows deconvoluted barley starch spectrums. The ratio 1047/1018  $\text{cm}^{-1}$  was calculated to represent the amount of crystalline to amorphous phase in native and modified starches (Table 2). The decreasing in bands ratio resulted from the loss of crystallinity during the starch modification process. Ratio for native starch was 0.51 and decreased in proportion to an increase of catalyst concentration during the acetylation process (Table 2). The results were consistent with X-ray diffraction results that showed lower crystallinity when compared to that of native barley starch (Table 2). The oxidation of barley starch also decreased the crystallinity by reducing the ratio for oxidized starch with 2% active chlorine when compared to native starch (Table 2).

### 3.4. X-ray diffraction

The X-ray diffraction patterns of the native, acetylated and oxidized barley starches presented strong peaks at 15°, 17°, 18°, 19 and 23° ( $2\theta$ ), characteristic of type A cereal starches (Fig. 2 and Table 2), as reported in corn, barley and rice starches (Chávez-Murillo et al., 2008; Zavareze, Storck, Castro, Schirmer, & Dias, 2010).

Esterification reduced the relative crystallinity of acetylated starches with different catalyst concentrations when compared

to native starch. Ac% increase of acetylated barley starches reduced the relative crystallinity from 26.67% (native) to 23.49% (23% NaOH solution) (Table 2). According to Diop, Li, Xie, and Shi (2011), the crystallinity of cereal starches is attributed to the formation of double helices by intermolecular hydrogen bonds in the amylopectin segments. As shown in Fig. 1a, the acetyl groups replaced some hydroxyl groups of starch, which reduced the formation of inter- and intra-molecular hydrogen bonds and resulted in a partial destruction of the original ordered crystal structure (Zhang, Xie, Zhao, Liu, & Gao, 2009).

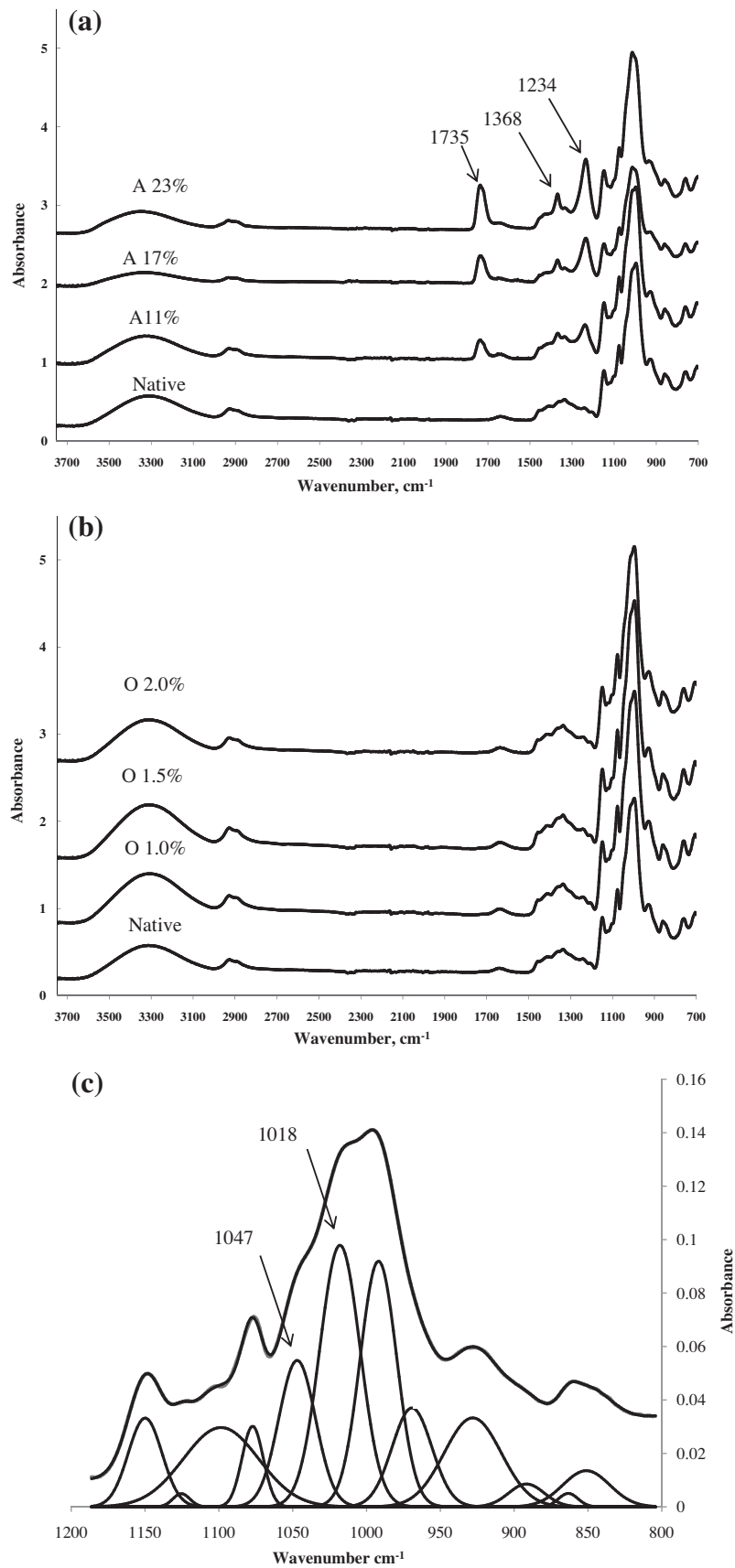
Oxidation with different active chlorine concentrations affects peak intensities and relative crystallinity of barley starches (Table 2). In their study on corn starch modified with sodium hypochlorite, Kuakpetoon and Wang (2006) reported low concentrations of oxidant. Oxidation occurred mainly in the amorphous region of granules with the degradation of the starch molecules, which may increase the relative crystallinity of starch. These authors also reported that high concentrations of oxidant reduced crystallinity due to a likely degradation of the crystalline region. Since the oxidation of barley starch decreased relative crystallinity in all oxidation degrees, it is suggested that there had been a degradation of the crystalline region even at low oxidant concentration (1.0% active chlorine) (Table 2).

### 3.5. Thermal properties

Table 3 shows the thermal properties of native, acetylated and oxidized starches, such as onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), final temperature ( $T_c$ ) and gelatinisation enthalpy ( $\Delta H$ ). The acetylated starches had lower  $T_o$ ,  $T_p$ ,  $T_c$  and  $\Delta H$  when compared to that of native starch (Table 3). Mirmoghtadaie, Kadivar, and Shahedi (2009) have similarly obtained a reduction in the thermal properties of acetylated oat starches and Bello-Pérez, Agama-Acevedo, Zamudio-Flores, Mendez-Moltealvo and Rodrigues-Anbriz (2010) in their studies on acetylated barley starch at different reaction times to produce starches with low  $DS$  (0.9) and high  $DS$  (2.7) also reported a reduction in thermal properties due to acetylation. According to these authors the extent of the reduction in the thermal properties of starches modified by acetylation were dependent on other extrinsic factors to the reaction, such as granule shape and size, amylose and amylopectin ratio, organization of crystals and the structural organization of the amylopectin clusters.

The  $\Delta H$  shows a general measure of crystallinity and indicates loss of the molecular order (Singh, Kaur, & McCathy, 2007). Reduction in  $\Delta H$  suggests that the acetyl groups alter the amylopectin double helices. Furthermore, the introduction of voluminous groups along the starch chain enhances structural flexibility and also contributes towards the reduction of gelatinisation temperature of modified starch. Reduction of thermal parameters of barley starch is consistent with the decrease in crystallinity after acetylation (Tables 2 and 3).

The gelatinisation temperatures of barley starches oxidized at different concentrations of active chlorine were similar to those of native starch. The oxidized starches showed a lower gelatinisation enthalpy when compared to that of native starch (Table 3). According to Sangseethong, Termvejsayanon, and Siroth (2010), sodium hypochlorite caused weakening of starch granules due to partial degradation of starch molecules in the crystalline lamellae. Consequently, less energy was required to gelatinize the starch. These authors noted the need for less energy for gelatinisation of oxidized cassava starch when compared to that required by native starch. Other authors (Sandhu, Kaur, Singh, & Lim, 2008; Sangseethong et al., 2009) also reported a decrease in gelatinisation enthalpy of oxidized cassava and corn starches when compared to native starch.



**Fig. 1.** FTIR spectrum of acetylated (a) and oxidized (b) starches compared to native barley starch. FTIR spectrum representing an example of the deconvoluted patterns (c) of barley starch. A11%: 11% NaOH acetylated starch, A17%: 17% NaOH acetylated starch, A23%: 23% NaOH acetylated starch, O1.0%: 1.0% active Cl oxidized starch, O1.5%: 1.5% active Cl oxidized starch and O2.0%: 2.0% active Cl oxidized starch.

**Table 2**  
Spectral ratios of 1047/1018 ( $\text{cm}^{-1}$ ) representing the amorphous to crystalline phase, peak intensities from X-ray diffractograms and relative crystallinity of native, acetylated and oxidized barley starches.

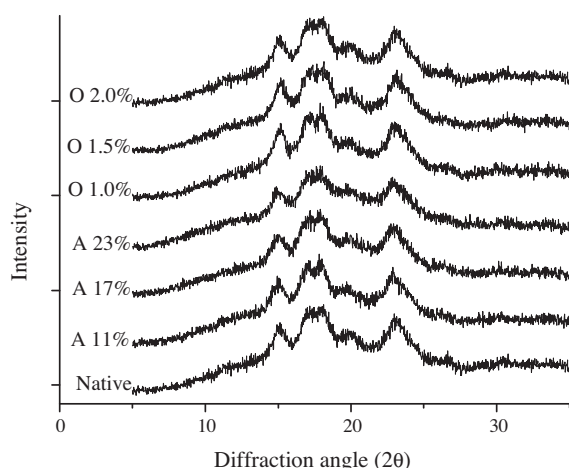
Modifications	Treatments	Ratio 1047/1018 $\text{cm}^{-1a}$	Peak intensities					RC(%) <sup>d</sup>
			15.0°	17.0°	18.0°	19.0°	23.0°	
Acetylation	Native	0.51 <sup>a</sup>	426	532	380	402	492	26.67
	11% NaOH <sup>b</sup>	0.49 <sup>b</sup>	446	562	390	368	492	26.06
	17% NaOH	0.48 <sup>b</sup>	410	544	382	416	468	25.39
	23% NaOH	0.45 <sup>c</sup>	416	524	420	396	466	23.49
Oxidation	Native	0.51 <sup>a</sup>	426	532	380	402	492	26.67
	1.0% active Cl <sup>c</sup>	0.50 <sup>b</sup>	478	584	410	386	484	25.95
	1.5% active Cl	0.51 <sup>a</sup>	462	548	376	370	504	25.01
	2.0% active Cl	0.49 <sup>c</sup>	406	494	342	342	454	25.02

<sup>a</sup> The results are the means of three determinations, with less than 0.004 of SD. Values with different letters in the same column for each modification (acetylation and oxidation) are significantly different ( $p < 0.05$ ).

<sup>b</sup> NaOH (solution of 50 g NaOH/100 g of water).

<sup>c</sup> Active Cl: concentration of active chlorine (g Cl/100 g barley starch, d.b.).

<sup>d</sup> RC = relative crystallinity.



**Fig. 2.** X-ray diffractograms of native, acetylated and oxidized barley starches. A11%: 11% NaOH acetylated starch, A17%: 17% NaOH acetylated starch, A23%: 23% NaOH acetylated starch, O1.0%: 1.0% active Cl oxidized starch, O1.5%: 1.5% active Cl oxidized starch and O2.0%: 2.0% active Cl oxidized starch.

**Table 3**  
Thermal properties of native, acetylated and oxidized barley starches.

Modifications	Treatments	Gelatinisation temperatures <sup>b</sup>			Enthalpy (J/g)
		$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	
Acetylation	Native	59.49	63.28	67.43	8.92
	11% NaOH <sup>a</sup>	53.26	60.24	64.19	3.00
	17% NaOH	59.00	61.90	64.70	3.11
	23% NaOH	49.68	56.27	60.54	1.28
Oxidation	Native	59.49	63.28	67.43	8.92
	1.0% active Cl <sup>b</sup>	60.76	63.45	67.82	4.61
	1.5% active Cl	61.85	64.74	68.02	6.72
	2.0% active Cl	61.77	65.15	69.76	6.82

<sup>a</sup> NaOH (solution of 50 g NaOH/100 g of water).

<sup>b</sup> Active Cl: concentration of active chlorine (g Cl/100 g barley starch, d.b.).

### 3.6. Morphology of starch granules

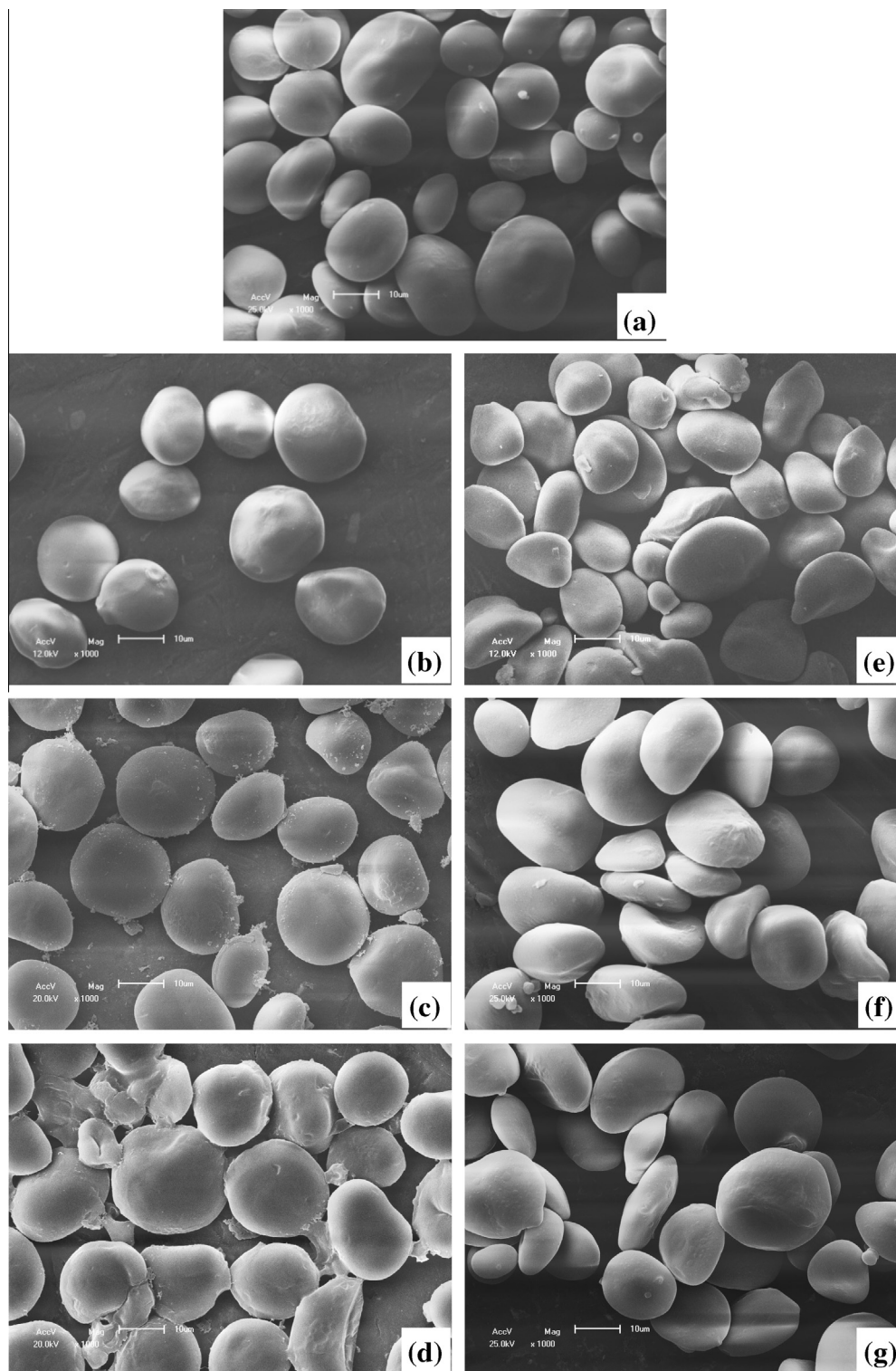
The scanning electron micrographs (SEM) of native, acetylated and oxidized barley starches granules are shown in Fig. 3. Barley starch has small and large-sized granules with lenticular and irregular shapes (Fig. 3). Acetylation with catalyst concentrations above

17% NaOH solution (Fig. 3c and d) affected the morphology of the barley starch granules showing less smooth surface than in native as well as agglomerates formation. A high concentration of catalyst (23% NaOH solution) revealed a partial disintegration of granules with slight gelatinisation (Fig. 3d). These results agree with Sha et al. (2012) who verified that the granule surface of acetylated starch was less smooth than in native one, but the starch granules still kept a relatively complete particle structure. As the acetyl groups increased, the intermolecular hydrogen bonds were damaged and more starch granules were disrupted. These authors also suggested that the crystalline regions were also involved in the reaction; the difference was that crystalline granules did not collapse.

Oxidation at different levels of active chlorine did not affect the size and shape of starch granules (Fig. 3a, e–g). Kuakpetoon and Wang (2001) reported no differences in the morphology of potato, corn and rice starches granules when oxidized with sodium hypochlorite at concentrations between 0.8% and 2.0% active chlorine. Differences were registered in morphology when oxidized at 5.0% level of active chlorine. Vanier et al. (2012) reported no changes in the morphology of starch granules of oxidized common beans with 0.5% and 1.0% of active chlorine. However, when these authors performed oxidization at 1.5% level of active chlorine, the granules presented imperfections on their external structures, featuring a surface rougher than that of native starch granules.

### 3.7. Swelling power and solubility

The swelling power and solubility of native, acetylated and oxidized starches are shown in Table 4. Acetylation reduced swelling power of barley starches as catalyst concentration increased (Table 4). Sanchez-Rivera, Flores-Ramírez, Zamudio-Flores, González-Soto, & Rodríguez-Ambríz (2010) also found this behavior in the case of acetylated maize and banana starches and related the fact to lower swelling capacity in the starches due to the introduction of voluminous acetyl groups which, in higher amounts, confer hydrophobicity and may decrease the starch water absorption and retention capacity. However, Ayucitra (2012), who studied the acetylation of corn starch at different acetylation degrees ( $DS$ : 0.08–0.21), found an increase in swelling power for acetylated starches when compared to that in native starch. The above author reported that there was repulsion among starch molecules which facilitated an increase in water percolation within the amorphous regions of the granules and a consequent increase in swelling capacity.



**Fig. 3.** Scanning electron micrographs of barley starches: native starch (a), 11% NaOH acetylated starch (b), 17% NaOH acetylated starch (c), 23% NaOH acetylated starch (d), 1.0% active Cl oxidized starch (e), 1.5% active Cl oxidized starch (f) 2.0% active Cl oxidized starch (g).

The acetylated starches with low catalyst concentration (11% and 17% of NaOH solution) showed a reduction in solubility when compared to that in native starch. However when barley starch was acetylated with high catalyst concentration (23% of NaOH solution), there was an increase in solubility when compared to that in native starch (Table 4). Ayucitra (2012) also found higher solubility for acetylated starches taking native starch as a basis. The solubility increase of acetylated starch may be due to the

structural reorganization that weakens the granules and enhances the amylose leaching.

The swelling power of barley starch oxidized by low level of active chlorine (1.0%) showed no significant difference when compared to native starch. However, barley starch oxidized with 1.5% and 2.0% active chlorine had a lower swelling power when compared to native starch (Table 4). The reduction in the binding capacity of starch to water after oxidation is due to carbonyl and

**Table 4**  
Pasting properties and swelling power and solubility of native, acetylated and oxidized barley starches.

Parameters <sup>a</sup>	Native	Acetylation			Native	Oxidation		
		NaOH (%) <sup>b</sup>				Active Cl (%) <sup>c</sup>		
		11.0	17.0	23.0		1.0	1.5	2.0
Pasting temperature (°C)	85.6 ± 1.2 <sup>a</sup>	60.3 ± 0.9 <sup>b</sup>	57.4 ± 0.1 <sup>c</sup>	55.5 ± 0.1 <sup>d</sup>	85.6 ± 1.2 <sup>a</sup>	67.5 ± 0.4 <sup>b</sup>	67.5 ± 0.6 <sup>b</sup>	66.8 ± 0.5 <sup>b</sup>
Peak viscosity (RVU)	267.8 ± 3.4 <sup>a</sup>	120.4 ± 3.3 <sup>d</sup>	156.0 ± 1.9 <sup>c</sup>	176.8 ± 3.1 <sup>b</sup>	267.8 ± 3.4 <sup>a</sup>	186.9 ± 5.7 <sup>b</sup>	135.0 ± 1.5 <sup>c</sup>	108.5 ± 0.8 <sup>d</sup>
Breakdown (RVU)	52.7 ± 5.1 <sup>a</sup>	41.6 ± 2.8 <sup>b</sup>	14.3 ± 0.3 <sup>c</sup>	8.3 ± 1.0 <sup>d</sup>	52.7 ± 5.1 <sup>d</sup>	126.0 ± 3.4 <sup>a</sup>	108.9 ± 1.6 <sup>b</sup>	88.3 ± 0.9 <sup>c</sup>
Final viscosity (RVU)	295.8 ± 10.3 <sup>a</sup>	111.1 ± 2.1 <sup>d</sup>	222.1 ± 2.9 <sup>c</sup>	265.9 ± 3.6 <sup>b</sup>	295.8 ± 10.3 <sup>a</sup>	107.3 ± 2.7 <sup>b</sup>	56.3 ± 0.1 <sup>c</sup>	45.0 ± 0.4 <sup>d</sup>
Setback (RVU)	57.6 ± 3.1 <sup>c</sup>	32.4 ± 1.6 <sup>d</sup>	80.3 ± 1.1 <sup>b</sup>	97.4 ± 1.4 <sup>a</sup>	57.6 ± 3.1 <sup>a</sup>	46.3 ± 0.4 <sup>b</sup>	30.2 ± 0.0 <sup>c</sup>	24.7 ± 0.1 <sup>d</sup>
Swelling power (g/g)	14.0 ± 0.2 <sup>a</sup>	12.2 ± 0.4 <sup>b</sup>	10.9 ± 0.9 <sup>b,c</sup>	9.7 ± 0.3 <sup>c</sup>	14.0 ± 0.2 <sup>a</sup>	13.3 ± 0.1 <sup>a</sup>	6.5 ± 0.2 <sup>b</sup>	6.6 ± 0.8 <sup>b</sup>
Solubility (%)	8.9 ± 0.7 <sup>b</sup>	6.7 ± 0.4 <sup>c</sup>	4.7 ± 0.3 <sup>c</sup>	11.7 ± 0.4 <sup>a</sup>	8.9 ± 0.7 <sup>c</sup>	31.8 ± 0.4 <sup>b</sup>	57.5 ± 1.0 <sup>a</sup>	59.0 ± 0.5 <sup>a</sup>

<sup>a</sup> The results are the means of three determinations. Values with different letters in the same row for each modification (acetylation and oxidation) are significantly different ( $p < 0.05$ ).

<sup>b</sup> NaOH (solution of 50 g NaOH/100 g of water).

<sup>c</sup> Active Cl: concentration of active chlorine (g Cl/100 g barley starch, d.b.).

<sup>a,b,c,d</sup> Values with different letters in the same row for each modification (acetylation and oxidation) are significantly different ( $p < 0.05$ ).

carboxyl groups and to the structural depolymerization of the starch. Although oxidation at low levels occurs primarily in the amorphous region of starch granules, a partial hydrolysis of the amylopectin chains occurs at high oxidant levels.

According to Tester and Morrison (1990), amylopectin is primarily responsible for the binding capacity of starch with water. Wang and Wang (2003) reported that the reduction of the starch swelling power by oxidation was due to the hydrolysis of amylopectin chains at high temperatures. These authors reported that the presence of a sponge in the granule structure is able to imbibe water during heating, but cannot retain the absorbed water under centrifugation. It has therefore been suggested that oxidized barley starches had a depolymerization of amylopectin since they revealed a lower swelling power when compared to that of native starch. Sanchez-Rivera, Flores-Ramírez, Zamudio-Flores, González-Soto and Rodríguez-Ambríz (2010) and Vanier et al. (2012) also found similar behavior in corn and common beans oxidized starches, respectively.

The solubility of native and oxidized starches ranged between 8.9% and 59.0%. The modified starches showed high solubility in water when compared to the native one (Table 4). The increase in solubility of oxidized starches is attributed to the weakening of the internal structure of the starch granules and to amylose depolymerization (Sandhu et al., 2008). Thus, it is believed that since part of amylose of oxidized barley starches was cleaved, it contributed towards high solubility. Wang and Wang (2003) oxidized corn starch by varying the concentration of active chlorine between 0 and 3.0% and showed a substantial increase in solubility with an increase in the sodium hypochlorite concentration, with values ranging between 7.9% and 66.3% in solubility, respectively, at 95 °C.

### 3.8. Pasting properties

Table 4 shows the pasting properties of native, acetylated and oxidized barley starches analyzed with Rapid Visco Analyser (RVA). Acetylated barley starches showed lower pasting temperature when compared to native starch (Table 4), which decreased with increasing catalyst concentration in acetylation reaction. The reduction in the pasting temperature of acetylated starch was due to the incorporation of functional groups to the structure of the starch, which decreased the attractive forces in the amorphous region and weakened the intramolecular hydrogen bonds in the granule. Consequently, paste formation required lower temperatures (Gonzalez & Perez, 2002).

Regardless of *DS*, the acetylated starches showed significant reduction in peak viscosity and final viscosity when compared to native starch (Table 4). Bello-Pérez et al. (2010) also acetylated

barley starch but employed different reaction times to obtain starches with low *DS* (0.9) and high *DS* (2.7). In fact, they reported a significant reduction in paste viscosity, especially for starch with high *DS*. The reduction in viscosity of the acetylated starch is related to the decreased ability of swelling of the granules due to a possible partial disruption which occurred by the introduction of acetyl groups. These groups conferred hydrophobicity and decreased the water absorption and retention capacity of the starch. Reduction in paste viscosity may also be attributed to the depolymerization of the starch chains during acetylation.

When acetylated barley starches were compared between each other, it was noted that viscosity increased progressively with increasing *DS* (Tables 1 and 4). High starch viscosity with higher *DS* (176.8 RVU) when compared to starch with lower *DS* (120.4 RVU) may be related to a greater inclusion of acetyl groups which may form cross-links between them, featuring higher molecular weight attributed to increased water absorption and viscosity.

Since acetylation reduced breakdown with increasing *DS*, this phenomenon indicated that acetylation increased the stability of barley starches during heating and shearing. Acetylated starch with low *DS* (0.08) showed a reduction in the setback when compared to native starch. However acetylated starches with *DS* 0.22 and 0.31 showed a higher setback when compared to that of native starch (Table 4).

Although oxidation reduced the pasting temperature of barley starches, different levels of active chlorine used in the modification failed to affect the pasting temperature (Table 4). Kuakpetoon and Wang (2001) also reported a reduction in the pasting temperature with increasing sodium hypochlorite concentration used to oxidize potato, corn, and rice starches. According to these authors, the reduction of pasting temperature suggested that the oxidized starch granules swelled more easily because the strength of the association among starch molecules was weakened by repulsion with carboxyl groups due to the introduction of water in starch granules.

Peak and final viscosity rates of oxidized barley starches were lower than native starch. They were reduced according to increasing concentrations of active chlorine (Table 4). Starch viscosity depends on oxidation degree. Partial cleavage of the glycosidic linkages occurs in higher oxidant concentrations with a reduction of viscosity. Vanier et al. (2012) also reported a viscosity reduction in oxidized common beans starches with higher concentrations of active chlorine (1.0% and 1.5%).

Although oxidized starches showed a higher breakdown than native starch, oxidized barley starch with higher active chlorine concentration provided lower breakdown (Table 4). Among the oxidized starches, the starch with a higher degree of oxidation has a greater tendency to resist shear forces during heating.



The oxidation of barley starches reduced the retrogradation trend with increased active chloride level (Table 4). According to Muñoz, Weber and Chang (2004), starch retrogradation is a phenomenon that should be minimized because it is the reconstruction of a more rigid structure due to ease the rearrangement of amylose chains during storage of the food product, resulting in increased water loss from the system and hardening of the final product. The reduction of retrogradation of oxidized starches compared to that of native starch may be attributed to the degradation of starch molecules and an increase in oxidation degree that favors the leaching of amylose, and consequently a reduction in retrogradation speed. Furthermore, the introduction of voluminous groups such as carbonyl and carboxyl groups inhibits the re-association of the chains and reduces the retrogradation tendency (Liu et al. 2014).

#### 4. Conclusion

The introduction of acetyl groups was confirmed by FTIR spectroscopy and the oxidation of barley starches was confirmed by the presence of carbonyl and carboxyl groups. Different concentrations of catalyst in the acetylation reaction and different concentrations of active chlorine in the oxidation promoted structural and functional changes in barley starch. The acetylated starch with the highest concentration of catalyst (23% NaOH solution) showed the highest degree of substitution (0.31) and the oxidized starch with the highest concentration of active chlorine (2.0%) showed the highest degree of oxidation presenting 0.15 CO/100 GU and 0.22 COOH/100 GU.

Acetylated starches with DS above 0.22 showed morphological changes in the granules. However, oxidation did not affect the barley starch morphology. Acetylation and oxidation reduced relative crystallinity, enthalpy, swelling power, pasting temperature and viscosity of barley starches. Acetylated starches were more stable to heating and shearing than native starch. While oxidized starches were less stable to these parameters than native starch. Oxidized starches had a significant increase in solubility when compared to native starch.

Further research should evaluate the production of biodegradable films by employing acetylated and oxidized barley starches. Acetylation makes barley starch more hydrophobic by the insertion of acetyl groups and partial depolymerization of amylose and amylopectin molecules can occur. In oxidation, the presence of carbonyl and carboxyl groups in the starch increases the spaces between the chains and makes more difficult the re-approximation of the amylose molecules. Consequently, retrogradation is reduced. The reduced retrogradation and the low viscosity of the oxidized starches are important properties for their application in biodegradable films.

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