

Crystallinity, thermal and gel properties of oat starch oxidized using hydrogen peroxide

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Abstract

The effects of oat starch oxidation at different hydrogen peroxide concentrations (0.5%, 1.0%, and 1.5%) on the physicochemical, crystallinity, thermal and textural properties of starch were investigated. The carbonyl content, carboxyl content, crystallinity, gelatinization characteristics, swelling power, solubility, gel hardness and gelation property of the starches were evaluated. The extraction yield of oat starch was 31.51% with 99% purity. The oxidation promoted the insertion of carbonyl and carboxyl groups and reduced the relative crystallinity, gelatinization enthalpy, swelling power, and solubility of starch. The gels of oxidized starches had a higher hardness, adhesiveness, gumminess, and a lower cohesiveness when compared to native starch gels. The oxidized oat starch with 0.5% and 1.0% hydrogen peroxide form gels at lower concentrations when compared to native starch. portrayed the most antioxidant compounds (37.41 ± 0.01 mg GAE/g DW and 4.54 ± 0.02 mg CE/g DW) and capacities (2.00 ± 0.01 μ mol TEAC/g DW and 0.84 ± 0.01 μ mol TEAC/g DW) amongst four species of seaweed.

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Introduction

Native and modified starches have a wide application in various industries, such as textiles, paper, pharmaceuticals, steel, plastic, and food (Kuakpetoon and Wang, 2006). The production of modified starches has been expanded in order to increase their usefulness in industrial applications. Oxidation is a chemical modification using different oxidants, and sodium hypochlorite is the most widely used in the commercial production of oxidized starch (Zhang *et al.*, 2009; Dias *et al.*, 2011).

The hydrogen peroxide is oxidizing agent considered of low environmental impact since not generate prejudicial byproducts, and is preferred when you want chlorine-free processes (Sangseethong *et al.*, 2010). In addition, the Joint Expert Committee on Food Additives (JECFA) of Hong Kong (Aplevicz and Demiate, 2007) evaluated the safety of hydrogen peroxide and found that the intake of small amounts of hydrogen peroxide (up 3%) produced no toxicological effect due to the rapid chemical decomposition by a catalase enzyme from the intestinal cells.

In the starch oxidation process the oxidizing agent reacts with the free hydroxyl groups in the glucose monomers, resulting in the formation of

carbonyl and/or carboxyl groups. Thus, it is possible to estimate the oxidation level of the starch by the number of carbonyl and carboxyl groups present in the material (Singh and Sandhu 2007). The extent of the change in the structure and physicochemical properties of oxidized starch will depend on factors such as the botanical origin of native starch, the type of oxidizing agent, and the reaction conditions. Thus, the starch subjected to oxidation acquires desirable properties industrially, such as the ability to generate slurries with a high solid content, high transparency, and a resistance to retrogradation (Vanier *et al.*, 2012).

The main commercial sources of starch are corn, potato, rice, wheat, and cassava; however, among other promising sources for obtaining starch are oat grains (*Avena sativa*). According to Hoover *et al.* (2003), there are considerable differences between the physicochemical properties of oat starch and other cereal starches. These differences have been attributed to the higher bound lipid content, co-leaching of amylose and amylopectin, higher relative crystallinity, smaller amylose chain length, and the smaller granule size of oat starches. A study about the oxidation of oat starch with sodium hypochlorite was performed by Berski *et al.* (2011) who reported increased amylose content and a reduction in the

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starch paste viscosity. However, there are no studies on oat starch oxidation using hydrogen peroxide as the oxidizing agent. Some studies involving oxidation with hydrogen peroxide with different concentrations and reaction times for potato starch (Parovuori *et al.*, 1995, Tolvanen *et al.*, 2009; Łabanowska *et al.*, 2011; Pietrzyk *et al.*, 2012), barley starch (Forsell *et al.*, 1995), cassava starch (Sangseethong *et al.*, 2010; Dias *et al.*, 2011), pea and sweet potato starches (Zhang *et al.*, 2012), rice starch (El-Sheikh *et al.*, 2010) and maize starch (Zhang *et al.*, 2009) have been reported. The objective of this study was to evaluate the effect of oxidation with hydrogen peroxide in thermal, crystallinity and the gel properties of oat starch.

Materials and Methods

Material

Oat grains from the IAC-7 cultivar were donated by the Cerealle Indústria e Comércio de Cereais Ltda, Pelotas, Brazil. The hulled oat grains, which were not stabilized, were kept in the freezer ($-18^{\circ}\text{C} \pm 2$), conditioned to 11% moisture, and then ground in a hammer mill, Perten LM 3100 (30 mesh sieve). The flour was packed in polyethylene bags and stored at $4^{\circ}\text{C} \pm 2$ in the fridge until the starch was extracted.

Extraction of starch

Oat starch was isolated by the sodium hydroxide solution, as described by Wang and Wang (2004), with some modifications. The oat flour was shaken vigorously in 0.18% sodium hydroxide (NaOH) in a 1:4 (w/v) ratio and soaked for 18 hours. Then it was blended and passed through a 63 μm screen and centrifuged at 1200xg for 5 minutes. The soft top layer was carefully removed, and the underlying starch layer was re-slurried. The starch layer was then washed twice with 0.18% NaOH and centrifuged. The starch layer was washed with distilled water and centrifuged. The starch was re-slurried and treated with 1.0 mol.L⁻¹ hydrochloric acid (HCl) to a pH 6.5 and centrifuged. The neutralized starch was washed with distilled water three times and dried at 40°C until the moisture content of the samples reached about 11%. The starch isolated from the oats showed approximately 99% purity (0.36% protein, 0.41% fat and 0.12% ash) on a dry basis.

Starch oxidation

Starch oxidation was performed according to the method described by Dias *et al.* (2011), with some modifications. The starch (200 g (d.b.)) was suspended in 300 mL of distilled water at 40°C, and hydrogen peroxide (H₂O₂) was added in three concentrations

(0.5, 1.0, and 1.5% of H₂O₂). The pH was adjusted for 5.0 with 0.1 mol.L⁻¹ HCl and NaOH solutions. The reaction was conducted in a glass reactor, maintained at 40°C with constant stirring for a period of 4 hours and 0.01 g ferrous sulfate (FeSO₄)/100 g starch was used as a catalyst. The slurry was then filtered by suction with a Buchner filter funnel, washed with 1200 mL of distilled water, resuspended in 600 mL of distilled water and re-filtered; then it was dried in a forced air oven at 40°C until the moisture content of the samples reached about 11%.

Amylose, carbonyl and carboxyl contents

The amylose content was determined using the method proposed by Martinez and Cuevas (1989). The carbonyl content was determined according to the titrimetric method as described by Smith (1967). The carboxyl content of the starches was determined according to Parovuori *et al.* (1995), with some modifications, a blank test was performed with native starch.

X-ray diffraction

X-ray diffractograms of the starches were obtained with an X-ray diffractometer (XRD-6000, Shimadzu, Brazil). The scanning region of the diffraction ranged from 5° to 30° with a target voltage of 30 kV, a current of 30 mA, and a scan speed of 1°/min. The relative crystallinity (RC) of the starch granules was calculated as described by Rabek (1980), using the following equation $\text{RC} \% = (\text{Ac} / (\text{Ac} + \text{Aa})) * 100$; where Ac is the crystalline area; and Aa is the amorphous area on the X-ray diffractograms.

Thermal properties

The gelatinization characteristics of the oat starches were determined using differential scanning calorimetry (TA-60WS, Shimadzu, Kyoto, Japan). Starch samples (approximately 3.5 mg on a dry basis) were weighed directly in an aluminum crucible (Mettler, ME-27331); and distilled water was added to obtain an aqueous suspension containing 70% water. The pan was hermetically sealed and allowed to equilibrate for 1 h before analysis. An empty pan was used as a reference. The sample pans were then heated from 10°C to 95°C at a rate of 5°C /min.

Swelling power and solubility

The swelling power and solubility of the starches were determined as described by Leach *et al.* (1959). The swelling power was represented as the ratio of wet sediment weight to initial dry sample weight (deducting the amount of soluble starch). Solubility

was expressed as the percentage of the dried solid weight based on the dry sample weight.

Gelation properties

The minimum amount of oat starch concentrate required to form a strong gel was determined by the method described by Sathe and Salunke (1981), with modifications. Oat starch concentrate dispersions at different levels (3%, 6%, 9%, and 12%) were added to 10 mL of 20 mM phosphate buffer (pH 7.0) in test tubes. The tubes with the dispersions were heated at 90°C for 1 h, then rapidly cooled, and kept in a refrigerator at 4°C for 2 h. The tubes were then inverted to determine which oat starch concentrate amounts formed a firm gel that did not fall out of or slip down the walls of the tube when it was inverted.

Gel texture profile

Gel textures were determined with a Texture Analyzer (TA.XTplus, Stable Micro Systems, Goldaming, UK) and were prepared according to Chaud and Sgarbieri (2006), with modifications. Dispersions at 12% concentration in 20 mM phosphate buffer (pH 7.0) were prepared in the tubes with a 36 mm diameter and 65 mm height. The samples was pre-heated at 40°C for 3 min, then transferred to a 90°C bath for 30 min and further cooled rapidly, and maintained for 30 min at 8°C. The gels were punctured at 1.0 mm.s⁻¹ to a distance of 10.0 mm using a stainless steel cylindrical probe with a 20 mm diameter (P/20). The hardness, adhesiveness, cohesiveness and gumminess were evaluated.

Statistical analysis

Analytical determinations for the samples were performed in triplicate, and standard deviations were calculated. A comparison of the means was ascertained by Tukey's test to a 5% level of significance using an analysis of the variance (ANOVA).

Results and Discussion

Starch extraction yield

The starch extraction yield obtained from the IAC-7 oat flour was 31.51%. This result was similar to that reported by Hoover *et al.* (2003), who evaluated the starch extraction yield of six Canadian oat cultivars and reported extraction efficiency between 30.9% and 32.3%. Hoover and Senanayake (1996) also found values for the starch extraction yield of 35.2% and 34.0% for the two oat cultivars. The extraction yield of cereal starches varied according to the source, cultivar, chemical composition and extraction method.

Table 1. Chemical characteristics of native and oxidized oat starches

Treatment ¹	Amylose (%)	Carbonyl content	Carboxyl content
		(CO/100 GU)	(COOH/100 GU)
Native	34.24 ± 0.09 ^a	0.007 ± 0.000 ^a	-
0.5% H ₂ O ₂ ²	35.24 ± 0.05 ^a	0.026 ± 0.011 ^a	0.037 ± 0.010 ^a
1.0% H ₂ O ₂	35.41 ± 0.17 ^a	0.029 ± 0.007 ^a	0.053 ± 0.008 ^a
1.5% H ₂ O ₂	35.54 ± 0.26 ^a	0.036 ± 0.001 ^a	0.055 ± 0.012 ^a

¹ Different letters in the same column statistically differ (p < 0.05)

² H₂O₂: hydrogen peroxide

Studies with other cereal starches showed the influence of the amylose/amylopectin ratio on the starch extraction yield. According to Zavareze *et al.* (2009) who isolated the starch from rice starches with low, medium and high amylose, and also using alkaline method, they obtained a low extraction yield for the low amylose rice starch (28.9%) as compared to medium and high amylose starches (46.7% and 56.3%, respectively).

The low extraction yield of the oat starch, when compared to other botanical sources, might be due to the small granule size (3 to 10 µm) and strong adherence to lipids and proteins (Mua and Jackson, 1995). It is likely that, during the extraction of starch, at the time of withdrawal of the deposited protein slurry from the precipitate starch after centrifugation, a part of the starch fraction was removed that had not completely been detached from the proteins and lipids.

Amylose, carbonyl and carboxyl contents

The amylose content, carbonyl and carboxyl groups of the oat starches are shown in Table 1. The oat starch had amylose content between 34.14% and 35.54%. According to some studies, the amylose content of the oat starch is variable between 14% and 33% (Hoover and Senanayake, 1996; Hoover *et al.*, 2003; Berski *et al.*, 2011). The variation of amylose content of oat starch might be due to a varietal differences and the method used for determination.

Oxidation did not affect the amylose content of the oat starches. The oxidation level of oat starch was low and so there was not probably a strong depolymerization of the chains of amylose and amylopectin. Berski *et al.* (2011) oxidized oat starch with sodium hypochlorite and found a small increase in this polymer chain. An increase in amylose content

Table 2. Relative crystallinity and thermal properties of native and oxidized oat starches

Treatment	RC ² (%)	Ti (°C)	Tp (°C)	Tf (°C)	ΔT (Tf-Ti)	ΔH (J/g)
Native	44.4	57.42	62.85	67.71	10.29	7.15
0.5% H ₂ O ₂ ¹	31.0	59.72	63.16	67.70	7.98	7.90
1.0% H ₂ O ₂	28.8	58.51	62.76	67.88	9.37	7.39
1.5% H ₂ O ₂	28.6	58.78	62.86	68.09	9.31	6.33

¹H₂O₂: Hydrogen peroxide

²RC: Relative crystallinity

in oxidized starch was also reported by other authors (Fortuna *et al.*, 2002).

Oxidized starches with hydrogen peroxide showed a higher content of carbonyl groups when compared to native starch (Table 1). Among the starches treated with hydrogen peroxide, regardless of the level of oxidation, there was no significant difference in the carbonyl and carboxyl contents, this may be probably due to the high amylose content and high resistance of oat starch to oxidation with hydrogen peroxide.

The starch oxidized with 1.5% hydrogen peroxide had a carbonyl content of about 5 times higher than the native starch. The carboxyl content in all treatments was higher than those of carbonyls. A similar result was described by Shirai *et al.* (2007) which oxidized waxy and normal maize, sweet potato and Peruvian carrot starches, using hydrogen peroxide as the oxidant. According to Halal *et al.* (2015) oxidized barley starch with sodium hypochlorite also found a higher value of carboxyl than carbonyl for all levels of oxidation.

Metal ions are often used in the starch oxidation by hydrogen peroxide to increase the content of functional groups in the modified starch and the catalysts efficiency follow the order: Cu > Fe > WO₄ (Parovuori *et al.*, 1995). According to Pietrzyk *et al.* (2012) that studied the influence of Cu(II) ions on physicochemical properties of potato starch oxidised by hydrogen peroxide, reported that during starch oxidation by hydrogen peroxide part of catalyst (metal ions) may be incorporated into starch structure. However in this study was used FeSO₄ as catalyst.

X-ray diffraction and thermal properties

Patterns of X-ray diffraction of the native and oxidized oat starches were characteristic of type A cereal starch as defined by peaks at 2θ of 15°, 17°, 17.8°, 19° and 23° (data not shown), and were also reported by Kuakpetoon and Wang (2001) and Halal

et al. (2015), in corn and barley starches, respectively. Oxidation with different hydrogen peroxide concentrations reduced the relative crystallinity of the oat starch (Table 2). The crystallinity of the starch was considered a major determinant of the extent of oxidation. There was a decrease of 13.4%, 15.6% and 15.8% in the relative of crystallinity in the hydrogen peroxide levels of 0.5%, 1.0% and 1.5%, respectively. The reduction of the relative crystallinity of oxidized starches with a higher hydrogen peroxide concentration indicated a greater partial depolymerisation of the amylopectin chains.

According to Kuakpetoon and Wang (2001), the starch oxidation level in terms of the carboxyl content was strongly related to the degree of relative crystallinity. As shown in Table 1, the formation of carbonyl and carboxyl groups had a significant increase as compared to the native starch, thus promoting changes in the relative crystallinity of oxidized oats starches. Halal *et al.* (2015) oxidized barley starch with 1%, 2% and 3% of active chlorine using sodium hypochlorite as the oxidant, and reported a slight reduction in the relative crystallinity. Kuakpetoon and Wang (2006) oxidized corn starch with 0.8%, 2.0% and 5.0% of active chlorine and also observed a reduction in the relative crystallinity of oxidized starches with 2% and 5% of active chlorine. These authors attributed this reduction in relative crystallinity to the degradation of the crystalline region.

The thermal properties of native and oxidized oat starches, such as the onset temperature (To), peak temperature (Tp), final temperature (Tf), the temperature difference Tf-To (ΔT), and the gelatinization enthalpy (ΔH), are shown in Table 2. The oxidized oat starch had a small increase in the onset gelatinization temperature in comparison with native starch. The increase in the gelatinization temperature could be attributed to the depolymerization of the amorphous region of the granules which destabilized the crystalline lamellae. According to Sangseethong *et al.* (2010), first, the amorphous region was degraded with a destabilizing that affected the crystalline region. Berski *et al.* (2011) oxidized the oat starch with sodium hypochlorite and observed a reduction in the onset and peak gelatinization temperatures, with no differences in the values of gelatinization enthalpy. The differences in Tf-Ti (Table 2) suggest that the degree of heterogeneity of crystallites within the granules of the starches was different. The oxidation of oat starches, using hydrogen peroxide, decreased the ΔT; therefore the introduction of carbonyl and carboxyl groups increased the homogeneity of the crystallites.

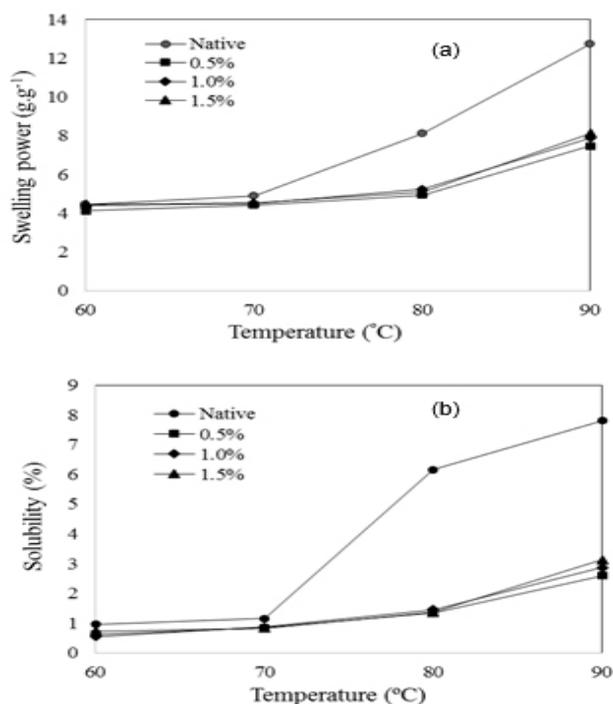


Figure 1. Swelling power (a) and solubility (b) of native and oxidized oat starches

The gelatinization enthalpy is considered as an indication of a loss of molecular organization and disruption of hydrogen bonds within the granule. There was a reduction in the gelatinization enthalpy of the oxidized starch in a higher level of oxidation (1.5% H₂O₂) when compared to the native starch. From the suggestion that, with a higher concentration of oxidant agent, there was a weakening of the starch granules from the partial degradation of the molecules of the crystalline lamella, less energy was therefore required to cause the gelatinization. The reduction in gelatinization enthalpy was also related to reduction in the relative crystallinity of the starch promoted by oxidation (Table 2).

Swelling power and solubility

The swelling power and solubility curves of the native and oxidized oat starch are shown in Figure 1. Oxidation of the oat starch reduced the swelling power and solubility of starches. This behavior was also reported by Sandhu *et al.* (2008) and Olayinka *et al.* (2013), who oxidized white sorghum starch (6% active chlorine by 10 min of reaction) and corn starch (1% of active chlorine for 50 min of reaction), respectively. The reduction in the swelling power of the starch granules may be due to lower enthalpy of gelatinization which was explained by partial degradation of the molecules of the crystalline lamella and this reduced the ability of granules to retain water after centrifugation. According to Wang and Wang (2003), the oxidized starch granules were able to absorb water during heating, but were not able

Table 3. Gelation property of native and oxidized oat starches

Starch concentration (%)	Treatment			
	Native	0.5% H ₂ O ₂ ²	1.0% H ₂ O ₂	1.5% H ₂ O ₂
3	Fluid	Fluid	Fluid	Fluid
6	Fluid	Fluid	Fluid	Fluid
9	Fluid	Gel	Gel	Fluid
12	Gel	Gel	Gel	Gel
MCG ¹	12	9	9	12

¹ MCG: Minimum concentration of gelling

² H₂O₂: Hydrogen peroxide

to retain water under centrifugation in the same way as native starch, thereby reducing the swelling power.

The oxidation reduced the solubility of the oat starch in all hydrogen peroxide concentrations (Figure 1b). However, according to Halal *et al.* (2015), who studied the oxidation of barley starch using sodium hypochlorite, they reported an increase in the solubility of oxidized starches as compared to native starch; and this was attributed to the weakening of the internal structure of the starch granules and to amylose depolymerization. Then, they related that, when part of the amylose of oxidized barley starches was cleaved, it contributed towards a high solubility. However, the reduction of the solubility of the oxidized oat starch could be explained by the presence of the carbonyl and carboxyl groups in the amylose molecules; for the presence of these groups increased the number of hydrogen bonds, thus reducing the leaching of amylose. The reduction of the solubility of the starch can indicate that there was a strengthening of the links, with the increase in the interactions between the molecules of amylose and amylopectin; this was from the amylopectin molecules as the source, forming a structure more stable and reducing the leaching of amylose molecules. The increased of gelatinization temperature measured by DSC also can be responsible by strengthening of the interactions between the amylose and amylopectin molecules of oxidized starches.

Gelation property

The gelation behaviors of native and oxidized oat starches are shown in Table 3. The concentration of native oat starch required for gel formation was 12%, while the oxidized starches with 0.5% and 1.0% hydrogen peroxide showed a gel formation at a concentration of 9%. The reduction in concentration required for the gel formation in the oxidized starches in low levels of oxidant (0.5% and 1.0% H₂O₂) could

Table 4. Texture profile analysis of native and oxidized oat starches

Treatment ¹	Hardness (g)	Adhesiveness (g.s ⁻¹)	Springiness (mm)	Cohesiveness	Gumminess (g)
Native	19.29 ± 1.23 ^b	-34.51 ± 4.78 ^c	0.94 ± 0.01 ^a	0.86 ± 0.11 ^a	16.58 ± 1.79 ^b
0.5% H ₂ O ₂ ²	26.30 ± 2.09 ^b	-72.53 ± 15.34 ^b	0.91 ± 0.01 ^a	0.77 ± 0.02 ^{ab}	20.28 ± 1.08 ^{ab}
1.0% H ₂ O ₂	35.11 ± 4.74 ^a	-106.19 ± 11.53 ^a	0.92 ± 0.03 ^a	0.65 ± 0.03 ^b	22.78 ± 3.07 ^a
1.5% H ₂ O ₂	35.07 ± 4.25 ^a	-86.52 ± 3.59 ^b	0.93 ± 0.01 ^a	0.69 ± 0.03 ^b	23.22 ± 1.60 ^a

¹ Different letters in the same column statistically differ (p < 0.05).

² H₂O₂: Hydrogen peroxide.

be explained by the strength of hydrogen bonds due to the presence of the carbonyl and carboxyl groups. However, at higher concentration of the oxidant (1.5% H₂O₂) a higher concentration of starch was required for the gel formation as compared to the oxidized starches with lower oxidant levels (0.5% and 1.0% H₂O₂). This result suggested that, in addition to the insertion of carbonyl and carboxyl groups in starch molecules oxidized with 1.5% hydrogen peroxide, which are responsible for the strengthening of bonds, there was a slight depolymerisation of the amylopectin molecules that may have weakened the interactions of the starch molecules in the water.

Similar results were reported by Adebowale *et al.* (2006), who oxidized bean starch with sodium hypochlorite and reported that the minimum concentration of starch for gel formation was 8%, while for native starch 10% was necessary. However, Lawal (2004) who oxidized new cocoyam starch with sodium hypochlorite, and reported that the minimal concentration of the oxidized starch for gel formation was 10%, while native starch gelled with 8%.

Gel texture profile

The hardness, adhesiveness, springiness, gumminess and cohesiveness of the gels of native and oxidized oat starches are shown in Table 4. The oxidation of oat starch, at higher concentrations of the oxidizing agent (1.0% and 1.5% H₂O₂) promoted an increase in hardness, adhesiveness and gumminess of the gel when compared to native starch. The gel hardness was mainly caused by the retrogradation of the starch which was associated with water loss (syneresis) and crystallization of amylopectin, making it a harder gel (Sandhu and Singh, 2007). The increase observed in the gel hardness of oxidised oat starch might be from increased hydrogen bonding due to the formation of carbonyl and carboxyl groups. Dias *et al.* (2011) oxidized fermented cassava starch using hydrogen peroxide and also reported an increase in gel hardness. These

authors reported that the differences in gelation of oxidized starches might be explained not only by the oxidation intensity by introducing carbonyl groups and carboxyl and depolymerization, but also by the different effect of hydrogen peroxide on the change of reaction conditions, acting in different locations of the components of the basic units of starch; and this could generate a range of products that could interact with each other.

Cohesiveness was the measure of the degree of difficulty in breaking down a gel's internal structure. The starch gels oxidized with 1.0% and 1.5% hydrogen peroxide had a lower cohesiveness as compared to native starch gel (Table 4), which indicated that the oxidized starch gel was more sensitive to disruption. Hou *et al.* (2007) evaluated the effect of the oxidation of potato starch with hydrogen peroxide at different scales (laboratory and pilot) on the gel texture profile and reported that oxidized starch gels had a lower hardness, adhesiveness and cohesiveness than native starch.

Conclusion

The oxidation of oat starch with hydrogen peroxide was confirmed by the presence of carbonyl and carboxyl groups. Oxidation reduced the relative crystallinity, gelatinization enthalpy, the swelling power, and the solubility of the oat starch, plus increased the onset gelatinization temperature. The texture profile of oat starch gels was also affected by oxidation. The oxidation increased the hardness, adhesiveness, and gumminess of the oat starch gels. The oat starch oxidized with lower oxidation levels formed gel at lower concentrations when compared to native starch.

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