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Air Oxidation of Corn Starch: Effect of Heating Temperature on Physicochemical Properties and In Vitro Digestibility

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Corn starch is heated (100, 120, 140, and 160 °C) under air convective conditions for 4 h. Scanning electron micrograph images show that the treatment produced pores and fractures on the granule surface. Hydroxyl groups of starch molecules are oxidized to carboxyl and carbonyl groups. Increasing heating temperature conditions lead to significant increases in the carboxyl and carbonyl groups contents. Solubility profiles increase while the apparent viscosity of the starch gels (5% w/v) decreases as heating temperature increases. X-ray diffraction shows that the modified starch heated at 160 °C has a crystallinity of 6.42% and a short-range ordering of 0.14 as revealed by Fourier-transform infrared ratio 1047/1022, which is significantly lower than the respective values of 24.42% and 0.2 exhibited by native starch. The onset, peak, conclusion gelatinization temperatures, and enthalpy of the modified starches tend to decrease slightly with increasing temperature. The air oxidation treatment affects the digestibility of corn starch, and as temperature increases, the rapidly digestible and slowly digestible starch fractions decrease, while the resistant starch fraction increases significantly. Overall, the results show that heating of corn starch at mild temperature conditions lead to important modifications of the molecular organization and to moderate oxidation of starch chains.

1. Introduction

Oxidation of starch chains takes place by conversion of hydroxyls first to carbonyls and then to carboxyls via oxidation reactions.[1] Oxidized starch offers several advantages over its native counterpart, including low viscosity of gels, improved thermal stability, and binding properties.[2] Importantly for food applications, oxidized starch exhibits reduced susceptibility to amylolytic enzymes, a property linked to reduced content of rapidly and slowly digestible starch (SDS) fractions.[3] Low retrogradation is a further important property induced by oxidation of starch molecules.[4] It has been postulated that the bulky carboxyl and carbonyl groups attached to the C3 and C4 carbons in conjunction to depolymerization of starch chains are responsible of the reduced retrogradation degree and amylolytic susceptibility of oxidized starches.[5]

Several approaches have been explored for the oxidation of starch from different botanical sources. Oxidized starch is obtained by exposing starch to an agent under certain pH and temperature conditions. Sodium hypochlorite is the most widely used agent for oxidation,[6] although sodium bromide, calcium hypochlorite, gaseous chlorine, and hydroperoxide have been also explored.[7] However, these chemical agents pose serious environmental problems, and their application in food products has been increasingly limited. Ozone has emerged as an alternative for oxidation of starch.[1,8–10] Ozone-based oxidized starches exhibit properties that are similar to those obtained by, for example, sodium hypochlorite.[1] Besides, ozone is a powerful oxidant with clean environmental impact.[1,8] It was reported that ozone oxidation induced a reduction in the apparent viscosity while raising the gel strength of different starch sources.[10] Air is also an oxidation agent able to lead to the formation of carbonyl and carboxyl groups. However, the oxidative capacity of air at relatively low temperatures leads to very low oxidation rates. In this way, air oxidation of starch chains can be carried by overcoming the thermodynamic barriers due to thermal and/or catalytic effects. Solid heterogeneous catalysis has been explored as a method for air starch oxidation. In the past decades, several works have been published on the effect of the catalyst agent on the oxidation extent of starches.

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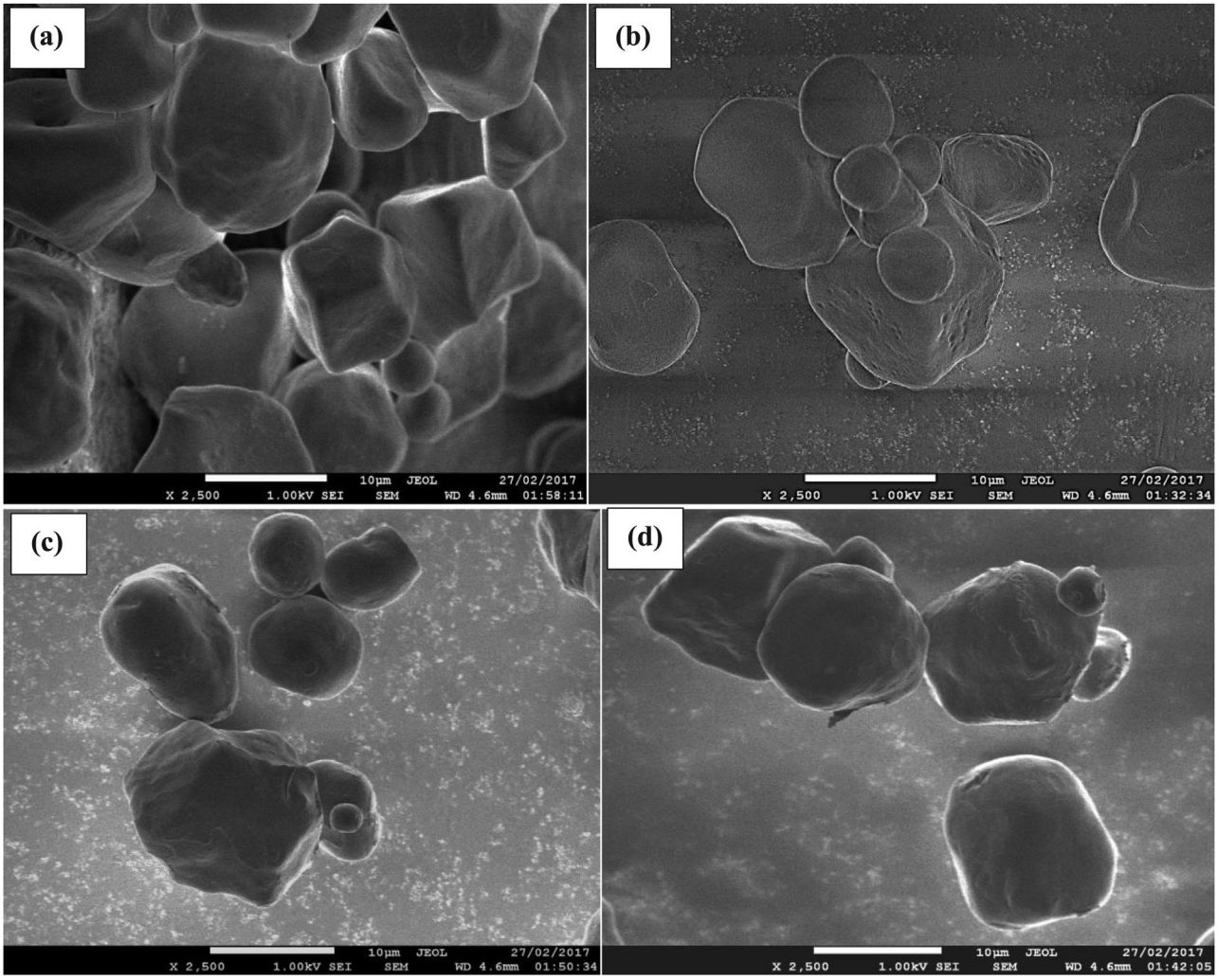

Figure 1. SEM images of modified corn starch granules: a) S_{100}, b) S_{120}, c) S_{140}, and d) S_{160}.

Harmon et al.[11] studied the air oxidation of corn starch catalyzed by ammonium meta vanadate at 35–40 °C and pH 9. The oxidized starch contained more carbonyl, but less carboxyl groups than commercially available oxidized starch. The air oxidation of potato starch over ammonium vanadate (V), led to a significant production of carbonyl and carboxyl groups.[12] Achremowicz et al.[13] showed that air oxidation of potato starch over Cu(II) catalyst favored the formation of carbonyl derivatives over the oxidation to starch carboxylates. Oxidation based on heterogeneous catalysts is commonly carried out at relatively low temperatures (about 35–45 °C). However, the use of heterogeneous catalysts might increase operational costs, as its separation from the product and recovery is difficult. An alternative is to dispense with the use of the heterogeneous catalyst, and to increase the temperature in order to raise the oxidative activity of the air flow. Besides, high thermal conditions disturb the starch structure, which eases the action of the oxidation reaction.[6] Air-based oxidation has been used, for instance, for pretreatment of husk for ethanol production where oxidation reactions take place at temperatures from 100 to 220 °C.[14] Kurdziel et al.[15] showed that air thermal treatment of barley and oat starches led to high oxidation levels comparable to that obtained with chemical agents (e.g., hypochlorite).

Reported results on air oxidation of starches are still scarce. Information on this line should provide valuable insights on the viability of the air oxidation approach as an alternative to starch oxidation based on chemical agents. In this way, the aim of the present work was to explore the effect of air heating at moderate temperatures (100–160 °C) on the oxidation of corn starch chains.

2. Results and Discussion

2.1. Morphology

Scanning electron micrographs of treated corn starch granules are shown in **Figure 1**. Granules showed a typical polyhedral geometry, with some face irregularities. In general, the thermal treatment induced only slight modifications on the granule geometry. Upon treatment, the surface of the granules presented visible erosion phenomena, possibly caused by disintegration of surface layer by thermal and oxidation effects. Similar patterns were observed in barley and oat starch granules modified with

Table 1. Characteristics of the modified corn starches.

Sample	Reducing sugars[g 100 g db^{-1}]	Amylose content[g 100 g db^{-1}]	Relative crystallinity[%]	Crystallinity content at 20°[%]	$R_{995/1022}$[-]	$R_{1047/1022}$[-]
S_C	1.86 ± 0.07^{g}	28.34 ± 0.61^{a}	24.42 ± 0.86^{g}	1.23 ± 0.11^{a}	0.54 ± 0.01^{a}	0.20 ± 0.01^{a}
S_{100}	3.76 ± 0.09^{f}	28.21 ± 0.45^{a}	16.23 ± 0.07^{f}	5.47 ± 0.87^{a}	0.51 ± 0.01^{b}	0.18 ± 0.01^{b}
S_{120}	6.52 ± 0.13^{e}	27.12 ± 0.54^{ab}	11.67 ± 0.11^{e}	11.84 ± 0.91^{b}	0.48 ± 0.01^{c}	0.17 ± 0.01^{c}
S_{140}	7.86 ± 0.16^{de}	26.53 ± 0.61^{c}	8.86 ± 0.12^{de}	21.26 ± 1.01^{bc}	0.40 ± 0.02^{d}	0.15 ± 0.02^{d}
S_{160}	9.73 ± 0.13^{d}	24.67 ± 0.55^{d}	6.42 ± 0.21^{a}	28.97 ± 1.02^{f}	0.38 ± 0.01^{de}	0.14 ± 0.01^{d}

Values are means ± standard error, of three replicates; Superscripts with different letters in same column indicate significant differences ($p \leq 0.05$); S_C: Control, S_X: Starch under heat treatment at "X" temperature.

Table 2. Carbonyl and carboxyl contents of modified starches.

Sample	Carbonyl(CO/100GU)	Carboxyl(COOH/100GU)
S_C	0.003 ± 0.001^{e}	0.021 ± 0.001^{e}
S_{100}	0.006 ± 0.001^{d}	0.043 ± 0.001^{d}
S_{120}	0.013 ± 0.002^{c}	0.076 ± 0.001^{c}
S_{140}	0.023 ± 0.001^{b}	0.142 ± 0.002^{b}
S_{160}	0.036 ± 0.002^{a}	0.193 ± 0.001^{a}

Values are means ± standard error, of three replicates; Superscripts with different letters in same column indicate significant differences ($p \leq 0.05$).

UV irradiation and thermal treatments,[15] in potato starch modified by sodium hypochlorite,[6] and arracacha starch modified with ozone.[10] The morphology of potato starch granules presented minor changes after ozonation as reflected by small fissures and pores on the granule surface.[8]

2.2. Reducing Sugars and Apparent Amylose Contents

The reducing sugars content in the starch granules increased significantly with the thermal treatment (**Table 1**), probably due to the depolymerization of starch chains by effect of thermal effects and oxidation. The higher the treatment temperature, the higher the reducing sugars content. Similar trend was observed for ozone modification of arracacha starch.[10] Recently, Li et al.[16] showed that thermal treatment of starch chains can lead to significant generation of reducing sugars (up to 33%) when temperatures are higher than 100 °C. Lima et al.[10] reported that the apparent amylose content decreased as the treatment temperature increased, an effect that has been ascribed to thermal depolymerization of short-size amylose chains to give reducing sugars. These authors postulated that oxidation of starch chains might result in molecules with a lower affinity to form iodine complexes, which in turn led to reduced levels of measured apparent amylose content.

2.3. Carbonyl and Carboxyl Contents

The carbonyl and carboxyl contents increased with the treatment temperature (**Table 2**). It has been pointed out that the presence of carbonyl and carboxyl groups are strong indicative of depolymerization of starch chains, which takes place by conversion of hydroxyls to carbonyls and carboxyls via oxidation reactions.[1] The increased values of the carbonyl and carboxyl contents suggested that the thermal treatment of starch granules under convective air flow involves oxidation of starch chains. The results in Table 2 are in line with recent report by Kurdziel et al.,[15] who showed that direct heating of barley and oat starches for 30 min at 210 °C led to a marked increase of carbonyl and carboxyl contents relative to the native untreated starches. In the present study, a positive Pearson correlation between the carbonyl content and treatment temperature ($r = 0.98$, $p < 0.01$) was obtained. Likewise, a positive relationship between carboxyl content and treatment temperature ($r = 0.94$, $p < 0.01$) was exhibited. Overall, the above results indicated that the thermal treatment under an air atmosphere resulted in the formation of carboxyl and carbonyl groups, accompanied by the hydrolysis of glycosidic linkages, promoting the reduction of the molecular size and the formation of reducing sugar groups.

The values of carbonyl (0.003–0.036 CO/100 GU) and carboxyl (0.021–0.193 COOH/100 GU) contents of our corn starch indicate that the oxidation extent of the starch chains was moderate as compared to the values reported for corn starch and starches from other botanical origin oxidized by different methods. For instance, carbonyl (0.061 CO/100 GU) and carboxyl (0.27 COOH/100 GU) contents for corn starch oxidized with a 3% solution sodium hypochlorite were reported by Wang and Wang.[21] Maximum values of carbonyl and carboxyl contents of the order of 0.021% and 0.35%, respectively, were reported for potato starch oxidized by sodium hypochlorite.[3] Pigeon pea, lima bean, and jack bean starches subjected to ozonation at low temperatures (about 35 °C) had values of carboxyl and carbonyl contents of the order of 0.07% and 0.25%, respectively.[1] Carbonyl levels of up to 0.16% were reported for arracacha starch modified with ozone.[10]

2.4. Rheological Properties

Figure 2a,b show the storage and loss moduli behavior of the NS and the modified starch gels (5% w/v). The viscoelastic moduli exhibited constant values up to a shear strain of about 10%. G' storage modulus exhibited monotonous decreasing trend for larger shear-strain values, indicating the disruption of the gel structure by effect of the mechanical deformation. In contrast, G'' did not exhibit a monotonous decrease when exceeding a shear strain of ≈10%. As a matter of fact, G'' exhibited an overshoot, which can be ascribed to jamming effects of insoluble remnants in the starch gel.[22] The heating temperature at which starches were treated had an adverse effect in the viscoelasticity of the starch

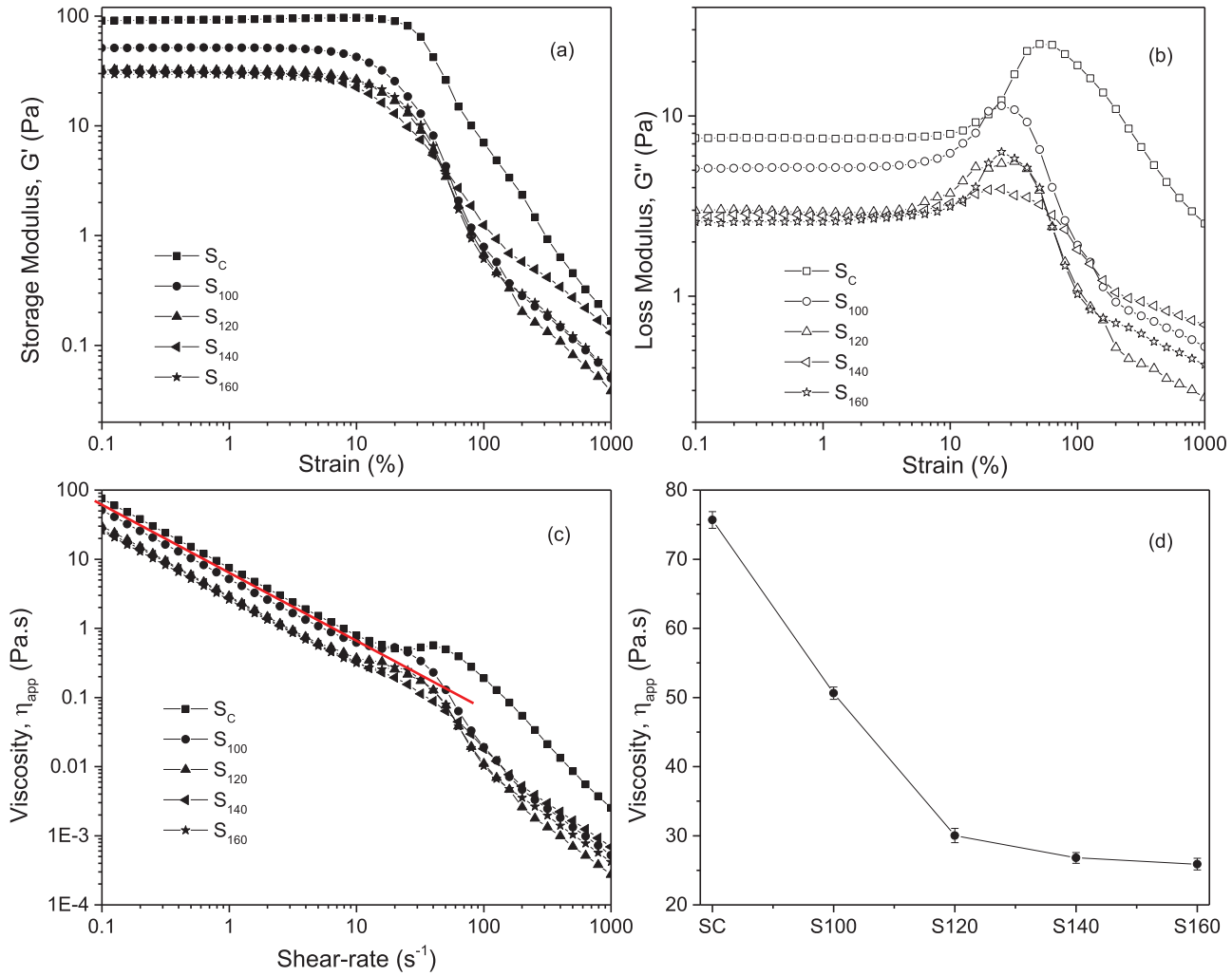

Figure 2. a) Storage, b) loss moduli as a function of strain%, and c) apparent viscosity as function of the shear rate for gels (5% w/v) of native and modified corn starches. d) Variation of the apparent viscosity at shear rate of 0.1 s^{-1}.

gels as the storage and loss moduli showed a marked decrease, which was larger the higher was the temperature. Similar trend was exhibited by the apparent viscosity (Figure 2c) where a typical shear-thinning behavior was observed for all samples. The apparent viscosity determined at a constant shear rate of 0.1 s^{-1}, which corresponds to the highest apparent viscosity value exhibited by all the starch gels, is plotted in Figure 2d. It can be observed that as air temperature was increased, and the extent of oxidation was increased, the apparent viscosity declined. This behavior has been documented previously.[2,10,23] Ozone treated corn starch gel showed a significant decrease in viscosity, which was attributed to partial amylose degradation by effect of oxidation reactions.[2] Starch (corn, sago, and tapioca) exposed to ozone for 10 min at different ozone generation times (OGT) exhibited non-Newtonian shear-thinning behavior.[2] Starch viscosity decreased drastically with increasing OGT. The effect was attributed to oxidation occurring primordially at the amorphous lamellae, leading to amylose depolymerization.[23] Ozone-based oxidation of arracacha starch produced large reductions of gel viscosity in pasting tests.[10]

2.5. Solubility

Figure 3 presents the degree of solubility as function of temperature of the native and treated starches. The solubility of the treated starches was significantly higher than the solubility of the native starch. It has been argued that the increase in solubility of starches treated by thermal processing is induced by improved interactions between amylose-amylose and amylose-amylopectin chains.[24] On the other hand, the formation of carboxyl groups promotes starch hydrophilicity while facilitating the access of water molecules to amorphous domains. The breakage of intramolecular hydrogen bonds as caused by oxidative degradation is also a solubility mechanism induced by oxidative processes.[25]

2.6. X-Ray Diffraction Analysis

The X-ray diffraction (XRD) spectrum of the native and modified corn starch samples is presented in **Figure 4**a. All samples exhibited a well-defined pattern for a typical A-type structure of

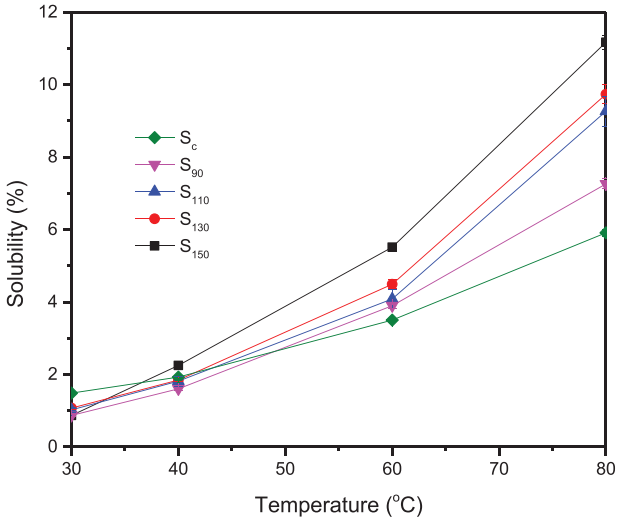

Figure 3. Solubility of native and modified corn starches.

cereal starch. The well-resolved peaks at 15°, 17.5°, 20°, and 23° were noticeable in all diffractograms. The relative crystallinity was computed as indicated by removing first the baseline and second the estimated amorphous region (Figure 4b).[26] The results are shown in Table 1. The heating process had a negative effect in the crystallinity content of the corn starch, and the effect was more pronounced as the heating temperature was increased. In fact, the relative crystallinity was about 24.42% for the native starch (S_c), about 16.23% for S_{100} and decreased to 6.42% for S_{160}. Similar trend was reported for barley and oat starches heated for 30 min at 210 °C.[15] The diminishing of the relative crystallinity was linked to the reduction of the intensity of the peaks at 17.5° and 23°, which in turn was ascribed to disassociation of amylopectin chains. It has been reported that annealing led to reduced intensities of X-ray diffraction patterns of potato and cassava starches, an effect that was attributed to disruption and orientation of crystalline structures in starch granules.[26] In the native corn starch, the well-resolved peak at 20° was almost invisible. However, the importance of this peak relative to the other prominent peaks increased with the heating process. To quantify this effect, the contribution of the peak at 20° with respect to the crystallinity content (Figure 4c) was estimated and reported in Table 1. The relative contribution of the peak at 20° was about 1.23% for the native starch, and showed a progressive increase with the heating temperature to achieve values of about 28.97% for S_{160}. It has been postulated that the XRD peak at 20° reflects the strong crystallinity structure of amylose–lipid complexes, which are formed upon heating.[27] Kurdziel et al.[15] reported the preservation of the peak at 20° for oat starch subjected heating treatment. More detailed information on the effect of the treatment temperature in the XRD pattern was obtained by a multivariate analysis via PCA of the diffractograms exhibited in **Figure 5**a.[28] The PCA revealed that the first principal component (PC1) accounted for 94.01% of the variability of the XRD diffractograms. Figure 5a shows the variation (i.e., loadings) of the PC1 with respect to the diffraction angle. It is noted that PC1 was negative over the whole diffraction angle range, meaning that the treatment temperature had an adverse effect in the relative intensity

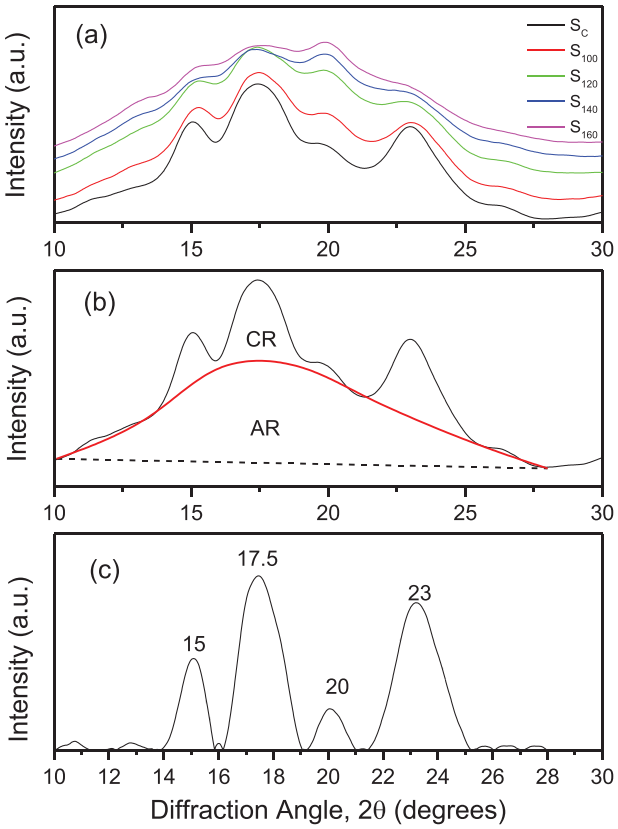

Figure 4. a) XRD spectrum of the native and modified corn starch samples. b) Illustration of the computation of the relative crystallinity. CR and AR refer respectively to crystalline and amorphous region. The dotted line corresponds to the baseline. c) Crystallinity peaks resulted from removing the amorphous region.

of the diffractograms. Interestingly, the largest value was located at about 17.5°, indicating that this peak exhibited the largest variability with the heating temperature. Smaller contributions were displayed by the peaks at about 15° and 20°. In this way, these peaks can be taken as distinctive indicators to discriminate the effect of the heating temperature within a 94.01% accuracy. Figure 5b presents the PCA score plots, from where the distance from the native starch sample (S_c) provides a measure of the effect of the heating temperature in the XRD pattern. It is noted that the distance of the score points of the native starch to the score point of the modified starches increased continuously with the increasing temperature. The highest increase of distance was between S_{100} and S_{120}, which means that temperatures higher than 100 °C had a marked effect in the internal organization of the starch granule. It has been pointed out that water mobility has an important role in the internal granule structure as water molecules promote the disruption of intra- and intermolecular hydrogen bonding in granules resulting in this way in decreased regularity of the starch chain packing.[27]

2.7. Fourier-Transform Infrared Analysis

More detailed information on the order of starch chains was obtained by conducting a quantitative analysis of the

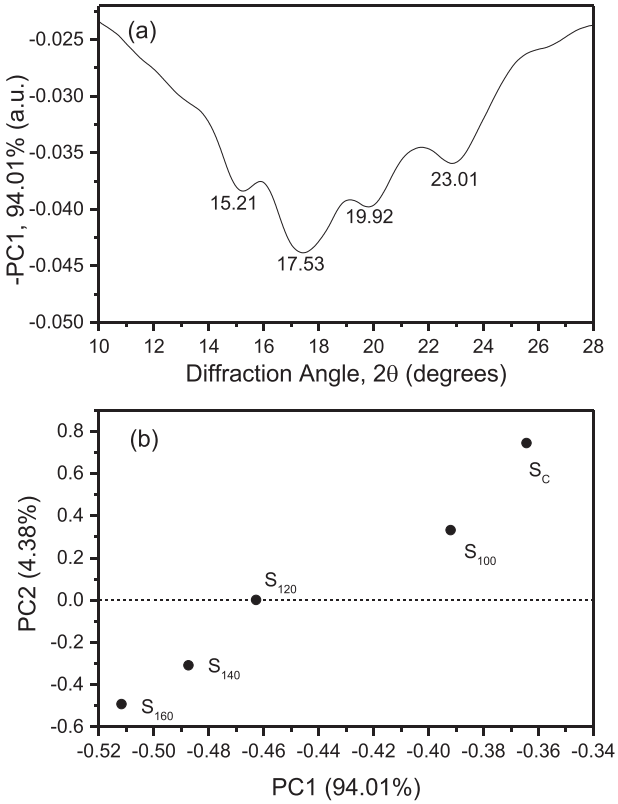

Figure 5. a) First principal component as function of the diffraction angle for the XRD spectra shown in Figure 2a. b) Score plot of the first and second components.

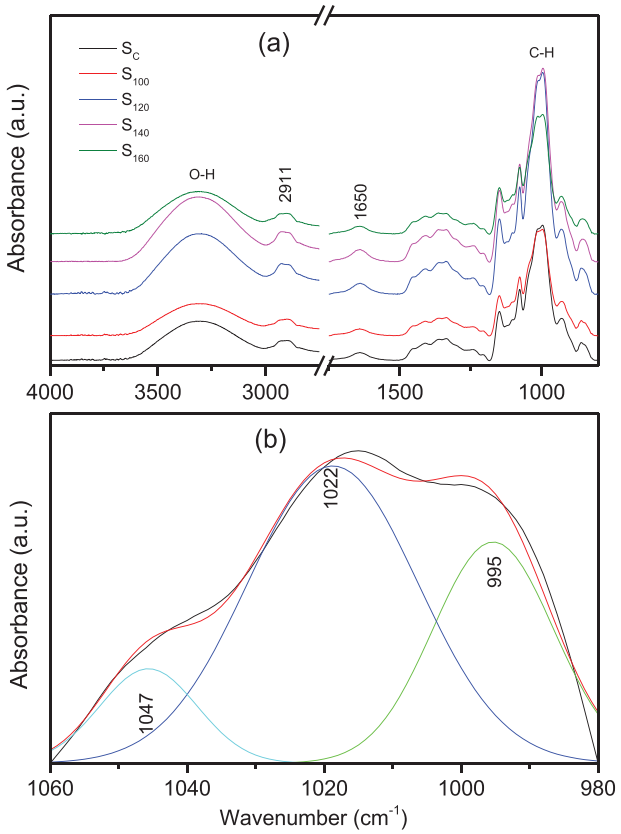

Figure 6. a) FTIR spectra of the native and modified corn starch samples. b) Illustrative deconvolution of the polysaccharides region.

Fourier-transform infrared (FTIR) spectrum. The spectra of native and modified corn starches showed a typical pattern of polysaccharides (**Figure 6**a). A wide band centered at about 3400 cm^{-1} is ascribed to O–H bond stretching. A smaller band located at 2800–3000 cm^{-1} is linked to C–H bond stretching and lipids attached to the granule surface.[29] On the other hand, the band at about 1650 cm^{-1} is ascribed to H_2O bending vibrations and reflects water molecules physically absorbed in the amorphous region of starch granules.[30] The large band centered at about 1020–980 cm^{-1} is distinctive of polysaccharides and reflects the skeletal mode vibrations of C–H functional groups. It has been reported that the band at 1047 cm^{-1} reflects the amount of short-range ordered structures (e.g., double-helix), while the band at 1022 cm^{-1} is characteristic of amorphous domains.[31] Also, the band at 995 cm^{-1} is water sensitive, reflecting intramolecular hydrogen bonding of hydroxyl group at the carbon C6 of the glycolic ring. In this way, the ratio 1047/1022 is an index of the intermolecular short-range order in starch granules, while the ratio 995/1022 quantifies the amount of hydrated structures relative to amorphous domains. These ratios are obtained by the numerical deconvolution of the FTIR spectrum via three Gaussian functions (Figure 6b), and the results are presented in Table 1. Both FTIR ratios decreased with the heating treatment, which confirms the reducing of the crystallinity and short-range order of starch granules upon direct heating treatment. In particular, the progressive reduction of the ratio 995/1022 is linked to the loss of water molecules by effect of evaporation. Marked reduction of the FTIR ratio 1047/1022 by effect of different oxidation methods have been reported, and these methods include direct heating and UV irradiation of oat and barley starches.[15] Heat treatment led to the disruption of the lamellae structure of corn starch granules, an effect that is probably linked to the reduction of the short-ranger crystallinity detected by the 1047/1022 ratio.[32] As it was done for the XRD spectra, a PCA of the FTIR spectra was carried out to quantify the dominant variability component. **Figure 7**a shows that the PC1 accounted for 88.87% of the total variability, and besides the PC1 contribution was negative for all wavenumber values. This means that the heating temperature had a negative effect in the molecular organization of corn starch. The largest effect was exhibited for the polysaccharide region linked to the C–H vibrations. The score plot in Figure 7b indicates that the heating temperature had a progressive effect in the modification of the starch structure. A sharp distancing can be observed between S_{100} and S_{120}, which may be reflecting important losses of water molecules as the heating temperature was increased beyond 100 °C.

2.8. Thermal Properties

The gelatinization properties of the native and modified starches are presented in **Table 3**. It was found that the thermal treatment led to significant reduction of the gelatinization temperatures and enthalpy, an effect that is more noticeable for higher

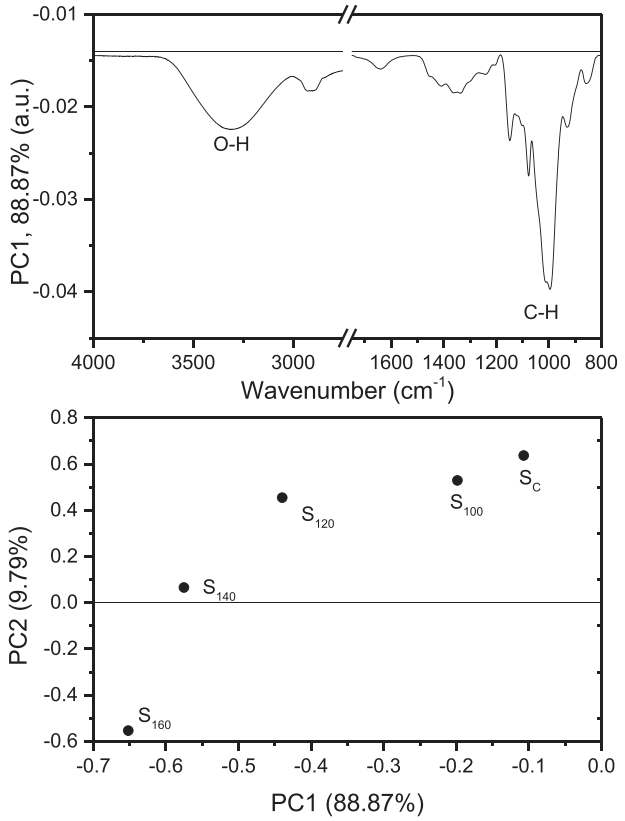

Figure 7. a) First principal component as function of the wavenumber for the FTIR spectra shown in Figure 4a. b) Score plot of the first and second components.

Table 3. Thermal properties of modified starches.

Sample	T_o[°C]	T_p[°C]	T_c[°C]	ΔH[J g^{-1}]
S_C	58.28 ± 0.29^a	72.76 ± 0.69^a	89.43 ± 0.73^a	13.48 ± 0.29^a
S_{100}	57.25 ± 0.12^b	71.27 ± 0.55^a	88.62 ± 0.43^a	7.76 ± 0.16^b
S_{120}	56.42 ± 0.12^b	70.36 ± 0.56^{ab}	88.38 ± 0.34^{ab}	6.67 ± 0.19^{bc}
S_{140}	56.73 ± 0.13^b	69.78 ± 0.57c	87.72 ± 0.42^c	6.03 ± 0.17^c
S_{160}	56.76 ± 0.09^b	68.69 ± 0.53^d	86.96 ± 0.39^d	5.67 ± 0.25^d

Values are means ± standard error, of three replicates; Superscripts with different letters in same column indicate significant differences ($p \leq 0.05$); T_o: Onset temperature; T_p: Peak temperature; T_c: Conclusion temperature; ΔH: Enthalpy.

temperatures. These results suggest that the disruption of the native granule integrity by thermal shocks was the main factor affecting the gelatinization parameters. Oladebeye et al.[1] found slight variations in the gelatinization parameters for pigeon pea, lima bean, and jack bean starches upon gaseous ozone treatment. Kurdziel et al.[15] reported similar results for oat and barley starches heated at 210 °C for 30 min. It was postulated that thermal treatment led to defragmentation of starch chains. Besides, dehydration of glucose rings at relatively high temperature might induce destruction of crystalline structures as revealed by XRD and FTIR analyzes. Thermal effects might be also behind the reduction of the gelatinization parameters. For instance, Lim et al.[33] reported reductions of the gelatinization enthalpy with

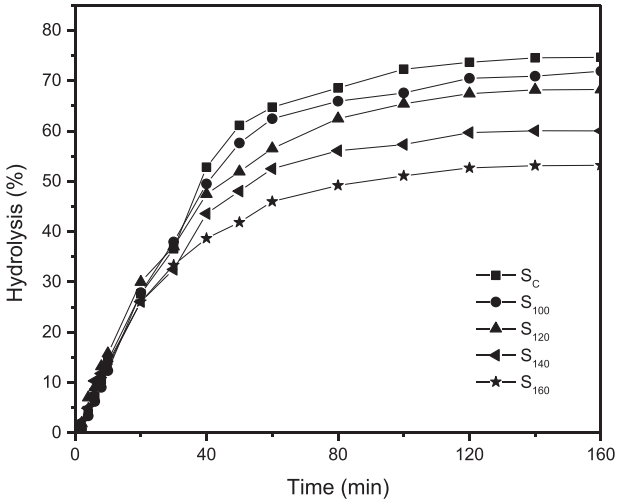

Figure 8. Kinetics of the enzymatic hydrolysis of native and modified corn starch samples.

the severity (e.g., temperature level) of the thermal treatment, an effect that was linked to partial destruction of crystalline domains into the starch granule. Similar result was found by Liu et al.,[34] who reported that the higher thermal treatment temperature always decreased all the endotherms below that temperature.

2.9. In Vitro Digestibility

The kinetics of the enzymatic degradation of the native and modified corn starches is presented in **Figure 8**. The heat treatment had a negative effect in the enzymatic hydrolysis of the starch chains, and this effect was accentuated for high treatment temperatures. Equation (3) was used to fit the experimental data and the resulting parameters were reported in **Table 4**. The kinetics constant k_H exhibited a slight increase with the treatment temperature, although the limiting hydrolysis showed the opposite trend. In fact, the parameter $C\infty$ decreased from 77.42 g per 100 db for native starch to about 53.20 g per 100 g db for starch treated at 160 °C. The contents of the starch fractions readily digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) are given in Table 4. In line with the kinetics pattern, the RDS decreased from 29.62 g per 100 db for native starch to 24.14 g per 100 g db for modified starch at 160 °C. A more important variation was exhibited by the SDS fraction as the value decreased from 44.02 g per 100 g db for native starch to 28.52 g per 100 g db for S_{160}. On the other hand, the RS fraction of the modified starches was significantly higher (29.55–47.34 g per 100 g db) than in native starch (26.36 g per 100 g db). These results showed that the heating modification led to important reductions in the susceptibility of corn starch to amylolytic reactions. Bean starch subjected to ozone treatment exhibited an increase in RS fraction.[35] The oxidation of potato starch by sodium hypochlorite at 35 °C led to an important reduction of the digestible starch fractions.[3] The reduction of the amylolytic susceptibility was attributed to the oxidation of starch chains. Oxidation of the hydroxyl groups of the C1 and C2 carbons in glucose leads to the formation of carbonyl and carboxyl groups, which in

Table 4. Hydrolysis kinetics parameters and in vitro digestible fractions of the modified starches.

Sample	$k_H \times 10^2$[min^{-1}]	C_∞[g 100 g db^{-1}]	RDS[g 100 g db^{-1}]	SDS[g 100 g db^{-1}]	RS[g 100 g db^{-1}]
S_C	2.73 ± 0.11^{c}	77.42 ± 0.61^{a}	29.62 ± 0.63^{a}	44.02 ± 0.17^{g}	26.36 ± 0.75
S_{100}	2.78 ± 0.09^{c}	73.60 ± 0.71^{b}	27.85 ± 0.43^{f}	44.60 ± 0.23^{g}	29.55 ± 0.93^{b}
S_{120}	2.69 ± 0.11^{c}	69.71 ± 0.72^{c}	26.96 ± 0.34^{c}	37.45 ± 0.24^{a}	32.59 ± 0.83^{c}
S_{140}	2.89 ± 0.12^{b}	61.43 ± 0.69^{d}	25.76 ± 0.42^{e}	33.91 ± 0.28^{c}	40.33 ± 0.86^{cd}
S_{160}	3.16 ± 0.09^{a}	53.50 ± 0.74^{e}	24.14 ± 0.39^{cd}	28.52 ± 0.25^{d}	47.34 ± 0.76^{cd}

Values are means ± standard error, of three replicates; Superscripts with different letters in same column indicate significant differences ($p \leq 0.05$); RDS: Rapidly digestible starch; SDS: Slowly digestible starch; RS: Resistant starch.

turn offer stearic opposition to the active site of the amylolytic enzymes.[36] Although physicochemical modifications (e.g., solubility and crystallinity) had some impact, the carbonyl and carboxyl groups produced by oxidation reactions are the main responsible of the modification of the corn starch digestibility.

3. Conclusions

The present work provided information on the effect of air temperature on the functional and digestibility properties of corn starch. It was shown that the direct heating of corn starch by means of a convection air flow led to the formation of carbonyl and carboxyl groups, an effect that was accentuated for high temperatures (up to 160 °C). While reported oxidation processes use oxidation agents (e.g., sodium hypochlorite, ozone, and UV irradiation), this work showed that heated air was able to lead to moderate starch oxidation. Corn starch modified by air oxidation showed physicochemical and digestibility properties similar to starches oxidized by other oxidation agents. In particular, the contents of rapidly and SDS fractions showed significant decrease, while the resistant starch fraction increased significantly as treatment temperature increased, and these changes are linked with the oxidation extent as quantified by carboxyl and carbonyl groups.

4. Experimental Section

Materials: Native corn starch (NS; CAS number 9005-25-8, amylose content 25.3%, moisture content 10.5%, pH 4.8; ash 0.5%, protein 0.1%), D-(+)-glucose (CAS 50-99-7, purity N 99.5%), α-amylase from porcine pancreas (CAS A3176, pH 5.5–8.0, 51–54 kDa, 5 IU mg^{-1}), and amyloglucosidase (CAS A3306, > 300 u/mL) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other reagents used were analytical grade and purchased from Metroquim (Mexico City, Mexico). All water used in the experiments was deionized.

Starch Treatment: NS (50 g) was placed in a stainless-steel tray and thermally treated in a forced-air oven (SW-17TA, Blue-M, New Columbia, PA, USA) at different temperatures (20 °C taken as control, and 100, 120, 140, and 160 °C taken as treatment temperatures) for 4 h. Each treatment was carried out in triplicate. The treated sample was washed five times with distilled water to remove products of the treatment (e.g., reducing sugars). The resulting pasta was dispersed in water and centrifuged (Model Z 513 K, Hermle Labortechnik, Wehnigen, Germany) at 6000 × *g* for 10 min. The supernatant was discarded, and the precipitate was dried in the forced air oven at 35 °C for 5 h, and finally ground. The modified starch samples were coded as S_x, respectively, where "*x*" stands for the treatment temperature.

Scanning Electron Microscopy: Starch particles were mounted on carbon sample holders using double-side sticky tape and were observed using a JEOL JMS 7600F scanning electron microscope (Akishima, Japan) with the GB-H mode at 1 kV accelerating voltage. Micrographs at 2500 × magnification were presented. Samples were not metalized since the microscopy equipment operated under ultra-vacuum conditions.

Determination of Reducing Sugars and Amylose Content: The reducing sugars contained in the native and modified starch samples after treatment (i.e., before washing) were estimated by the 3,4-dinitrosalicylic acid method using a solution of 10 mM glucose as standard.[16] On the other hand, the amylose content was determined as follows: The starch sample (500 mg) was mixed with 1 mL of ethanol and then dispersed in 10 mL of KOH (1 N) for 1 h at 35 °C to achieve complete dissolution. The volume was adjusted to 100 mL with distilled water in a volumetric flask. Subsequently, 2 mL of the resulting suspension were taken and 50 mL of distilled water and 100 µL of alcoholic phenolphthalein solution (1% w/v) were added. HCl (0.1 N) was added dropwise until a slight pink color was expressed. Then, 2 mL of iodine solution (2.0 g of potassium iodide and 0.2 g of iodine in 100 mL of distilled water) were added to the neutralized solution and adjusted to 100 mL in a volumetric flask. The dispersion was allowed to rest for 30 min for fully color development. The amylose content was calculated from the ratio of absorbance measurements at 620/510 nm. Scans were performed by 201 UV–vis Spectrophotometer (Spectronic Genesys 2, Thermo Electron Corporation, Madison, WI, USA).

Determination of the Contents of Carbonyl and Carboxyl Groups: The carbonyl content of the modified starch was obtained by the titrimetric method.[17] The content of carbonyl group was given as the number of carbonyl groups per 100 glucose units (CO per 100 GU):

$$\frac{\text{CO}}{100\ \text{GU}} = \frac{(Vb - Vs) \times M \times\ 0.028\ \times\ 100}{W} \tag{1}$$

Here, 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 dry basis weight, and *M* is the molarity of HCl. The content of carboxyl was estimated by the method described by Chattopadhyay et al.[18] The content of carboxyl was expressed as the carboxyl groups per 100 glucose units (COOH per 100 GU):

$$\frac{\text{COOH}}{100\ \text{GU}} = \frac{(Vb - Vs) \times M \times 0.045 \times 100}{W} \tag{2}$$

In this case, 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 dry basis weight, and *M* is the molarity of the NaOH.

Rheological Properties: Starch dispersions (5 g per 100 mL) were heated at 95 °C for 20 min in a water bath, followed by cooling down at room conditions. The gel formed was allowed to equilibrate for 1 h prior to undergo measurements in a Physica MCR 300 rheometer (Physica Messtechnik GmbH, Stuttgart, Germany). Strain sweep (0.1–1000%), at 1 Hz was applied and the storage (G') and loss (G'') moduli were obtained. Also the apparent viscosity-shear rate behavior was determined by applying a shear rate ramp from 0.1–1000 s^{-1}. All the experiments were carried out at 25 °C, and the experimental data were obtained by means of the (US200/32 V2.50) equipment's software.

Solubility: The starch sample was dispersed in distilled water (1 g per 100 mL), placed in centrifuge tubes and heated to temperatures 30, 40, 60

and 80 °C for 30 min, in a water bath under intermittent shaking. Afterward, the tubes were cooled down to room temperature and centrifuged at 3500 × *g* for 15 min. The supernatant was dried at 95 °C for 8 h. The solubility was estimated as

$$\text{Solubility}\ (\%) = \frac{W_{ds}}{W_s} \times 100 \quad (3)$$

Here, W_{ds} is the weight of the dried supernatant and W_s is the weight of the sample.

X-Ray Diffraction: Measurements were conducted in an X-ray diffractometer (D8 Advance, Bruker, Germany) operated at 40 kV and 40 mA. Samples were scanned over an angular range of 4° to 40° (2θ) at a scanning speed of 0.05° min^{-1}. Relative crystallinity of the samples was calculated as follows:

$$\text{RC}\ (\%) = \frac{A_c}{A_c + A_a} \times 100 \quad (4)$$

Here, A_c is the crystalline area and A_a is the amorphous area on the X-ray diffractogram.

Fourier-Transform Infrared: Measurements were obtained from a Perkin Elmer spectrophotometer (Spectrum 100, Perkin Elmer, Waltham, MA, USA) endowed with a crystal diamond universal ATR sampling accessory. The FTIR spectrum was reported as the mean value of five measurements for each sample. A numerical deconvolution procedure with Gaussian functions (half-width of 15 cm^{-1}, resolution enhancement 1.5) was carried out to obtain individual contributions for distinctive bands.

Thermal Properties: The thermal properties of starch samples were estimated by a differential scanning calorimeter equipment (DSC-1 Mettler-Toledo, Switzerland). The starch sample and distilled water with ratio 1:3 were weighed and placed in a 40 µL DSC aluminum pan. After sealing, the starch-water mixture was allowed to equilibrate at room temperature for 1 h. The pan was heated from 25 to 100 °C at 10 °C min^{-1} to scan the thermal changes. An empty pan was used as reference. The gelatinization parameters (onset temperature T_o, peak temperature T_p, conclusion temperature T_c, and enthalpy ΔH) were estimated by means of the software of the equipment.

In Vitro Starch Digestibility: The amylolytic hydrolysis of native and modified starch samples was done following the method of Englyst et al.[19] The RDS was the starch hydrolyzed within the first 20 min of incubation, and the SDS the starch digested between 20 and 120 min. Undigested starch after 120 min was considered as the resistant starch (RS) fraction. The kinetics of in vitro digestion was numerically fitted (i.e., least-squares) by the following first-order exponential model of Goñi et al.[20]

$$C\ (t) = C_\infty\ \ (1 - \exp(-k_H t)) \quad (5)$$

Here, $C(t)$ is the total hydrolyzed starch, $C\infty$ is the equilibrium concentration, and k_H is the hydrolysis rate constant.

Statistical Analysis: All the experiments were conducted in triplicate. Experimental data were analyzed by means of analysis of variance and reported as mean value ± standard deviation. Significant differences were estimated via Tukey's HSD test ($p < 0.05$) with the SPSS 22.0 statistical software for Windows (SPSS, Inc., Chicago, IL, USA).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

air oxidation, corn starch, crystallinity, digestibility

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[1] A. O. Oladebeye, A. A. Oshodi, I. A. Amoo, A. A. Karim, *Starch* **2018**, *70*, 1700367.
[2] H. T. Chan, R. Bhat, A. A. Karim, *J. Agric. Food Chem.* **2009**, *57*, 5965.
[3] F. Zhou, Q. Liu, H. Zhang, Q. Chen, B. Kong, *Int. J. Biol. Macromol.* **2016**, *84*, 410.
[4] M. M. Sánchez-Rivera, F. J. L. García-Suárez, M. V. Del Valle, F. Gutierrez-Meraz, L. A. Bello-Pérez, *Carbohydr. Polym.* **2005**, *62*, 50.
[5] O. B. Wurzburg, in *Modified Starches: Properties and Uses* (Ed: O. B. Wurzburg), CRC Press, Boca Raton, FL **1986**, pp. 17–41.
[6] S. Pietrzyk, T. Fortuna, L. Juszczak, D. Gałkowska, M. Bączkowicz, M. Łabanowska, M. Kurdziel, *Int. J. Biol. Macromol.* **2018**, *106*, 57.
[7] R. E. Wing, *Starch* **1994**, *46*, 414.
[8] N. Castanha, M. D. da Matta Jr., P. E. D. Augusto, *Food Hydrocolloids* **2017**, *66*, 343.
[9] A. O. Oladebeye, A. A. Oshodi, I. A. Amoo, A. A. Karim, *Food Chem.* **2013**, *141*, 1416.
[10] D. C. Lima, J. Villar, N. Castanha, B. C. Maniglia, M. D. Matta Jr., P. E. D. Augusto, *Food Hydrocolloids* **2020**, *108*, 106066.
[11] R. E. Harmon, S. K. Gupta, J. Johnson, *Starch* **1971**, *23*, 125.
[12] A. Bala-Piasek, P. Tomasik, *Carbohydr. Polym.* **1999**, *38*, 41.
[13] B. Achremowicz, D. Gumul, A. Bala-Piasek, P. Tomasik, K. Haberko, *Carbohydr. Polym.* **2000**, *42*, 45.
[14] S. Banerjee, R. Sen, R. A. Pandey, T. Chakrabarti, D. Satpute, B. S. Giri, S. Mudliar, *Biomass Bioenergy* **2009**, *33*, 1680.
[15] M. Kurdziel, M. Łabanowska, S. Pietrzyk, J. Sobolewska-Zielińska, M. Michalec, *Carbohydr. Polym.* **2019**, *210*, 339.
[16] F. Li, L. Liu, Y. An, W. He, N. J. Themelis, G. Li, *J. Cleaner. Prod.* **2016**, *112*, 1049.
[17] N. L. Vanier, E. R. Zavareze, V. Z. Pinto, B. Klein, F. T. Botelho, A. R. G. Dias, M. C. Elias, *Food Chem.* **2012**, *131*, 1255.
[18] S. Chattopadhyay, R. S. Singhal, P. R. Kulkarni, *Carbohydr. Polym.* **1997**, *34*, 203.
[19] H. N. Englyst, S. M. Kingman, J. H. Cummings, *Eur. J. Clin. Nutr.* **1992**, *46*, S33.
[20] I. Goñi, A. G. Alonso, F. S. Calixto, *Nutr. Res.* **1997**, *17*, 427.
[21] Y. J. Wang, L. Wang, *Carbohydr. Polym.* **2003**, *52*, 207.
[22] H. Carrillo-Navas, G. A.-D. L. Rosa, D. Gómez-Luría, M. Meraz, J. Alvarez-Ramirez, E. J. Vernon-Carter, *Carbohydr. Polym.* **2014**, *110*, 156.
[23] H. T. Chan, C. P. Leh, R. Bhat, C. Senan, P. A. Williams, A. A. Karim, *Food Chem.* **2011**, *126*, 1019.
[24] E. d. R. Zavareze, A. R. G. Dias, *Carbohydr. Polym.* **2011**, *83*, 317.
[25] S. L. M. El Halal, R. Colussi, V. Z. Pinto, J. Bartz, M. Radunz, N. L. Carreño, A. R. G. Dias, E. d. R. Zavareze, *Food Chem.* **2015**, *168*, 247.
[26] S. Brückner, *J. Appl. Crystallogr.* **2000**, *33*, 977.
[27] R. Hoover, C. Smith, Y. Zhou, R. M. W. S. Ratnayake, *Carbohydr. Polym.* **2003**, *52*, 253.
[28] C. Pozo, S. Rodríguez-Llamazares, R. Bouza, L. Barral, J. Castaño, N. Müller, I. Restrepo, *J. Polym. Res.* **2018**, *25*, 266.
[29] L. Chen, Y. Tian, B. Sun, C. Cai, R. Ma, Z. Jin, *Food Chem.* **2018**, *242*, 131.
[30] R. Kizil, J. Irudayaraj, K. Seetharaman, *J. Agric. Food Chem.* **2002**, *50*, 3912.
[31] J. J. van Soest, H. Tournois, D. de Wit, J. F. Vliegenthart, *Carbohydr. Res.* **1995**, *279*, 201.
[32] Z. Liu, C. Wang, X. Liao, Q. Shen, *Food Hydrocolloids* **2020**, *108*, 106081.
[33] S. T. Lim, E. H. Chang, H. J. Chung, *Carbohydr. Polym.* **2001**, *46*, 107.
[34] H. Liu, L. Yu, L. Chen, L. Li, *Carbohydr. Polym.* **2007**, *69*, 756.
[35] S. Simsek, M. Ovando-Martínez, K. Whitney, L. A. Bello-Pérez, *Food Chem.* **2012**, *134*, 1796.
[36] R. Hoover, Y. Zhou, *Carbohydr. Polym.* **2003**, *54*, 401.