

RESEARCH ARTICLE

Effect of damaged starch on wheat starch thermal behavior

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The influence of damaged starch (DS) on gelatinization and retrogradation wheat starch properties was investigated. Samples with different content of DS were obtained and evaluated. DSC was used for monitoring the changes in thermal behavior of the starch samples at different water amounts. Starch thermal transitions were affected simultaneously by DS content and water content. The Flory–Huggins parameters were modified by DS. A significant raise in the T_m , and x_{1-2} , and a decrease in ΔH_u was recorded. The AP retrogradation kinetics was evaluated by Avrami model. A significant increase of the AP crystallization rate was observed when DS increased. The results demonstrated the importance of the presence of physically damaged granules on wheat starch properties.

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1 Introduction

Starch is the primary component of wheat flour and plays a noteworthy role as a determinant of the quality of food product. Most of the functional attributes of starch are related to the temperature-dependent interactions of starch with water in the processes known as gelatinization, pasting, and retrogradation.

During gelatinization, starch granules take up water, swell, lose crystallinity, and leach AM [1]. Retrogradation is a complex reorganization process that consists of two separable events, a rapid and thermally irreversible gelation of AM and a slow and thermally reversible recrystallization of AP [2–4].

Granular integrity of starch can be affected by the mechanical action of the wheat milling process thus

producing what is called damaged starch (DS) [5]. Starch damage changes the structure of the granule which in turn affects rheological behavior and functional properties of the starch systems [6]. Several studies have shown that damage produces a range of fractions with different roles in the starch gelatinization process and swelling properties [7, 8].

Damage facilitates swelling of granules due to destruction of the forces which prevent granules from swelling in water [9]. Consequently, DS has the ability to absorb more water (between 200 and 430% its weight in water) than native granules (between 39 and 87%) [10]. It was suggested that, unlike of native starch, starch damaged mechanically gelatinizes spontaneously in cold water and this type of gelatinization has many similarities to gelatinization caused by heating [7].

A previous study reported evidence about the effect of DS on thermal properties of the dough and bread crumb [11]. The increment of the DS content of the wheat flour reduced the starch-gelatinization enthalpy and slightly changed the AP retrogradation rate at the beginning of storage time, although the differences were dependent on the flour type.

The aim of this study was to obtain a better understanding of the effect of DS on wheat starch gelatinization and retrogradation.

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Abbreviations: DS, damaged starch; Fv, water volume fractions; G-endoth, starch gelatinization endotherm; M1-endoth, starch melting endotherm; ΔT_g , gelatinization temperature range

2 Materials and methods

2.1 Samples

Unmodified (native) wheat starch (S5127 Sigma–Aldrich CAS Number 9005-25-8) was used for the sample's preparation. It had 10.7 g moisture/100 g, 0.18 g protein/100 g, 3.9% DS, and 31.1% AM/100 g. Unmodified wheat starch was milled in a Whisper Series Bench Top disk mill (Rocklabs, New Zealand) in order to cause a rupture of granules. Temperature was monitored during the milling; it was kept under 40°C. Four samples were obtained after milling and mixing: 3.8% DS (native starch from Sigma–Aldrich, unmilled in mill disk), 8.4, 12.9, and 23.8% DS. The values of DS were chosen to be in the range of damage equivalent to that induced by bread wheat dry roller milling.

Damaged starch content was evaluated according to AACC 76-30A method [12]. Analyses were performed in triplicate.

2.2 DSC

Thermal analyses were performed with a DSC823e Calorimeter and the thermograms were evaluated by STARe Default DB V9.00 software (Mettler Toledo, Switzerland).

2.3 Effects of water and damaged starch on starch gelatinization and retrogradation

Wheat starch samples (~20 mg) were weighed into DSC pans and distilled water was added with a Hamilton micro-syringe to achieve water volume fractions (Fv) of 0.82, 0.70, 0.60, 0.56, 0.51, 0.50, 0.48, 0.43, 0.37, and 0.35. Pans were hermetically sealed and allowed to rest for at least 12 h at room temperature before heating in the DSC to equilibrate the starch–water mixture. Samples were heated in the calorimeter from 30 to 120°C at 10°C/min. Gelatinized samples were stored at 4°C for 9 days. Samples were heated again from 30 to 120°C at 10°C/min. Onset temperatures (T_0), conclusion temperatures (T_c), and transition temperature ranges (ΔT), as well as, the enthalpy of starch gelatinization (ΔH_g) and retrogradation (ΔH_r) were determined.

For gelatinization and retrogradation determinations the reference used was an empty DSC pan sealed with a lid.

2.4 Finding Flory–Huggins model parameter values

The Flory–Huggins model is given by Equation (1). T_m is the melting point of the polymer–diluent system, T_m° is the melting point of the pure polymer, R is the gas constant,

ΔH_u the heat of fusion per repeating unit of glucose, V_1 and V_2 are the molar volumes of the diluent and the repeating unit of the polymer and, x_{1-2} is the Flory–Huggins polymer–diluent interaction parameter and ϕ is the volume fraction.

Conclusion temperature from gelatinization thermograms was taken as the melting temperature (T_m), in case of the presence of a second peak, conclusion temperature of the second peak was used. The partial molar volumes were 18.1 cm³/mol for water and 97.5 cm³/mol [13, 14] for wheat starch, the ratio between these partial molar volumes was assumed to be constant and independent of temperature. In addition, it was assumed that the densities of the crystalline and the amorphous wheat starch are identical. T_m° , ΔH_u , and x_{1-2} were determined. Data was fitted with SIGMAPLOT 10 software (Systat Software, Inc., Germany).

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \left(\frac{R}{\Delta H_u} \frac{V_2}{V_1} \right) [\Phi_1 - X_{12}\Phi_1^2] \quad (1)$$

2.5 Effects of storage time and damaged starch on starch retrogradation

Wheat starch samples (~20 mg) were weighed into DSC pans and distilled water was added to achieve Fv of 0.56. Pans were hermetically sealed and allowed to rest for at least 12 h at room temperature before heating in the DSC to equilibrate the starch–water mixture. Samples were heated in the DSC from 30 to 120°C at 10°C/min. Gelatinized samples were stored at 4°C for 0, 2, 3, 6, 8, 10, and 15 days and heated again in the calorimeter from 30 to 120°C at 10°C/min. The enthalpy of starch retrogradation was determined. The reference used was an empty DSC pan sealed with a lid.

2.6 Crystallization kinetics

The kinetic of starch recrystallization was evaluated according to the Avrami model [15] at different storage times (0, 2, 3, 6, 8, 10, and 15 days). The DSC retrogradation results were analyzed using this model. The model can be expressed as:

$$\theta_t = \frac{\Delta H_\infty - \Delta H_t}{\Delta H_\infty} = e^{-kt^n} \quad (2)$$

Values for the Avrami model factors were estimated by fitting experimental points (SIGMAPLOT 10 software, Germany) for the enthalpy of AP retrogradation into the nonlinear regression equation where θ is the fraction of the recrystallization still to occur; ΔH_0 , ΔH_∞ , and ΔH_t are melting energy at zero time, ∞ , and t time, respectively; k is

a rate constant (usually used as $1/k =$ time constant to compare bread firming rate), and n is the Avrami exponent describing the type of crystal growth.

The values of the constants, k and n , were used to calculate the value of half-time for crystallization. Crystallization half-time, $t_{1/2}$, is another important crystallization kinetics parameter, is defined as the time taken from the start of the relative crystallinity until 50% completion. The $t_{1/2}$ is calculated according to the following equation:

$$t_{1/2} = \left(\frac{-\ln 0.5}{k} \right)^{1/n} \quad (3)$$

2.7 Statistical analysis

For each starch–water mixture, three independent DSC determinations were recorded. The data was statistically treated by variance analysis, the means were compared by the LSD Fisher test at significance level of 0.05 using the Infostat Statistical Software (Universidad Nacional de Córdoba, Argentina).

3 Results and discussion

3.1 Effects of water and damaged starch on starch gelatinization and retrogradation

Table 1 presents the DSC gelatinization parameters. All samples showed an endothermic peak, characteristic starch gelatinization (G-endotherm). This endotherm was followed by a shoulder (M1-endotherm) when the water amount was reduced.

DSC thermograms also showed an additional thermal transition peak at higher temperature than starch gelatinization peak, which has been attributed to the melting of the AM–lipid complex. The single endotherm caused by dissociation of AM–lipid complexes was disappearing as water content was reduced; which was in agreement with Biliaderis [16].

The gelatinization enthalpy was simultaneously affected by the DS content and water amount, the interaction between these factors was highly significant ($p < 0.0001$). Moisture content lower than 0.51 volume fraction of water (Fv) produced M1-endotherm development while successive decreases in moisture content caused a gradual reduction of gelatinization enthalpy (ΔH_g).

At the same time, ΔH_g decreased with the increase in DS content. This tendency was in agreement with the result published by Jovanovich et al. [17]. DS hydrates spontaneously in cold water, therefore, only the native

granules and a fragmented granules fraction contributed to enthalpy measured during DSC test [7, 11]. On the other hand, the diminution of the gelatinization enthalpy could also be associated to the decrease of the sample relative crystallinity [18]. In wheat starch samples with high levels of DS, a positive correlation between the enthalpy gelatinization and crystallinity was also found by Morrison et al. [7].

No clear trend was observed in the onset temperature (T_0) and gelatinization temperature range (ΔT_g) as a consequence of DS content. Nevertheless, an increase in T_0 and a decrease in ΔT_g were observed of the disappearance of the G-endotherm in the sample with 23.8% DS at 0.37 and 0.35 Fv, that is, only the M1-melting endotherm was registered due to the limited available water and spontaneous gelatinization of DS.

Several authors adapted the Flory–Huggins equation to provide a quantitative description of starch gelatinization or melting temperature in the water–starch system as a function of the starch concentration and the temperature [1, 19].

Table 2 shows the calculated Flory–Huggins parameters obtained from the application of the Flory–Huggins equation to the curves. As shown in Table 2, experimental data was well suited to this model since the r^2 values were close to 1.

The melting point of the pure polymer (T_m°) and the Flory–Huggins polymer–diluent interaction parameter (x_{1-2}) obtained for the native starch sample were 452 K and 0.34, respectively. These values were in the range of reported values [20–23]. A negative or small positive value of the polymer–diluent interaction parameter is related to a stable mixture [24] and indicates a strong enthalpic interaction. The heat of fusion per repeating unit of glucose (ΔH_u) for the unmodified starch sample was comparable to the other values [20, 22] and similar to the enthalpy of fusion of D-glucose, which has been reported to be around 30 kJ/mol [23]. The increment of DS content caused a significant raise in the T_m° and x_{1-2} , and a decrease in ΔH_u . The changes of x_{1-2} suggested a decrease in the enthalpic interaction between starch and water, and a decrease in the stability of the starch–water mixtures. In this sense, although the interactions established between water and polymer are more complex than pair interaction with the nearest neighbor assumed in the Flory–Huggins theory; probably the inter-polymer H-bonds were favored over polymer–water H-bonds, as a consequence, the melting point of the pure polymer values increased.

Table 1 shows the melting enthalpy of retrograded AP after 9 days of storing as a function of water and DS content. Storage temperature was kept constant in this analysis. Two endotherm peaks were observed in DSC profiles of the aged samples. The first endothermic transition (between 42.2 and 76.8°C) was associated with the

Table 1. Gelatinization and retrogradation parameters as measured by DSC

Samples	Fv	Gelatinization			Retrogradation		
		ΔH_g	T_0	ΔT_g	ΔH_r	T_0	T_r
3.8 DS	0.82	6.8 ^c	60.3 ^{ab}	11.3 ^a	1.5 ^{ab}	44.2 ^a	16.7 ^a
8.4 DS		6.1 ^b	61.4 ^b	12.8 ^b	1.9 ^b	44.0 ^a	19.3 ^a
12.9 DS		5.0 ^a	61.1 ^b	12.2 ^{ab}	1.1 ^{ab}	43.2 ^a	19.8 ^a
23.8 DS		4.6 ^a	59.8 ^a	12.7 ^b	1.0 ^a	43.3 ^a	19.7 ^a
3.8 DS	0.70	7.9 ^c	61.0 ^b	10.2 ^a	1.8 ^a	44.3 ^{bc}	19.2 ^a
8.4 DS		6.7 ^b	62.0 ^c	11.8 ^b	2.6 ^b	44.8 ^c	18.9 ^a
12.9 DS		6.7 ^b	61.0 ^b	11.4 ^b	2.7 ^b	42.9 ^{ab}	19.5 ^a
23.8 DS		5.6 ^a	58.7 ^a	14.9 ^c	2.1 ^{ab}	42.2 ^a	20.0 ^a
3.8 DS	0.60	8.0 ^c	60.4 ^b	25.5 ^c	2.5 ^a	43.8 ^a	20.8 ^a
8.4 DS		6.6 ^b	61.3 ^c	14.2 ^a	3.3 ^b	42.8 ^a	23.4 ^a
12.9 DS		6.7 ^b	60.6 ^b	15.6 ^a	3.5 ^b	44.0 ^a	21.8 ^a
23.8 DS		5.8 ^a	57.8 ^a	21.9 ^b	2.5 ^a	43.6 ^a	21.7 ^a
3.8 DS	0.56	7.8 ^c	59.9 ^b	29.5 ^a	3.0 ^a	44.2 ^a	21.8 ^a
8.4 DS		7.4 ^{bc}	60.7 ^b	29.5 ^a	3.2 ^a	43.3 ^a	23.7 ^a
12.9 DS		6.7 ^b	60.2 ^b	29.1 ^a	3.6 ^a	44.0 ^a	22.5 ^a
23.8 DS		5.2	58.0 ^a	28.5 ^a	3.1 ^a	43.4 ^a	23.3 ^a
3.8 DS	0.51	7.8 ^c	60.3 ^b	34.2 ^a	3.1 ^a	42.4 ^a	28.0 ^a
8.4 DS		6.3 ^b	61.0 ^c	33.2 ^a	3.4 ^a	45.6 ^a	24.5 ^a
12.9 DS		6.2 ^b	60.0 ^b	34.4 ^a	3.5 ^a	44.7 ^a	24.6 ^a
23.8 DS		4.4 ^a	57.9 ^a	31.3 ^a	3.3 ^a	43.9 ^a	24.9 ^a
3.8 DS	0.50	7.4 ^b	60.4 ^b	36.8 ^a	2.3 ^a	42.6 ^a	26.0 ^a
8.4 DS		5.5 ^a	61.0 ^b	33.5 ^a	3.5 ^b	43.8 ^a	26.6 ^{ab}
12.9 DS		5.3 ^a	60.4 ^{ab}	35.6 ^a	3.9 ^b	45.3 ^a	24.7 ^a
23.8 DS		4.3 ^a	59.2 ^a	38.8 ^a	2.3 ^a	42.9 ^a	28.6 ^b
3.8 DS	0.48	6.5 ^b	60.7 ^a	39.2 ^b	2.2 ^a	43.9 ^b	25.5 ^a
8.4 DS		6.1 ^b	61.0 ^a	38.6 ^{ab}	3.6 ^c	44.8 ^{bc}	25.8 ^a
12.9 DS		4.3 ^a	60.7 ^a	37.1 ^a	4.1 ^d	45.4 ^c	24.6 ^a
23.8 DS		3.5 ^a	60.2 ^a	40.2 ^b	3.1 ^b	42.4 ^a	29.7 ^b
3.8 DS	0.43	4.2 ^{ab}	61.0 ^a	42.6 ^a	2.3 ^a	45.1 ^b	19.4 ^a
8.4 DS		4.3 ^b	61.2 ^a	42.6 ^a	3.6 ^{ab}	45.8 ^b	26.6 ^b
12.9 DS		3.3 ^a	60.6 ^a	42.3 ^a	4.1 ^b	46.1 ^b	25.7 ^b
23.8 DS		3.3 ^a	59.2 ^a	44.3 ^a	3.2 ^{ab}	43.3 ^a	28.1 ^b
3.8 DS	0.37	2.1 ^a	60.8 ^a	48.9 ^b	2.7 ^a	45.8 ^{ab}	28.7 ^{ab}
8.4 DS		2.5 ^c	59.7 ^a	52.9 ^b	2.5 ^a	43.8 ^a	31.0 ^b
12.9 DS		3.4 ^c	59.7 ^a	51.0 ^b	3.9 ^b	47.2 ^b	26.6 ^a
23.8 DS		1.7 ^b	81.0 ^b	29.0 ^a	3.0 ^a	45.0 ^{ab}	29.3 ^{ab}
3.8 DS	0.35	2.2 ^a	60.2 ^{ab}	51.7 ^b	2.8 ^a	47.5 ^a	28.4 ^a
8.4 DS		2.1 ^b	59.9 ^a	53.9 ^b	2.5 ^a	45.1 ^a	30.9 ^a
12.9 DS		2.8 ^c	63.1 ^b	51.1 ^b	3.8 ^b	48.1 ^a	27.5 ^a
23.8 DS		1.9 ^b	85.7 ^c	29.3 ^a	2.8 ^a	46.5 ^a	29.4 ^a

Fv, water volume fraction; T_0 , onset temperature; T_c , conclusion temperature; ΔT , temperature range; ΔH , enthalpy of starch. ΔH values are expressed in J/g of starch (10.7 g/100 g moisture). Temperatures and ΔT are expressed in °C. Statistical comparisons were made as a function of the DS level to each Fv. Values followed by different letters in the same column at each Fv are significantly different ($p < 0.05$).

AP retrogradation, and the second transition (between 98.0 and 118.9°C) was attributed to the melting of AM–lipid complexes. The later was disappearing from the thermograms when the water was reduced.

The enthalpy retrogradation of AP after 9-days aging was simultaneously affected by the DS content and water

amount, the interaction between these factors was highly significant ($p < 0.0001$).

Damaged starch content generally increased the enthalpy of AP retrogradation up to 12.9% DS and a subsequent decrease with 23.8% DS, reaching similar values to native starch.

Table 2. Flory–Huggins parameters

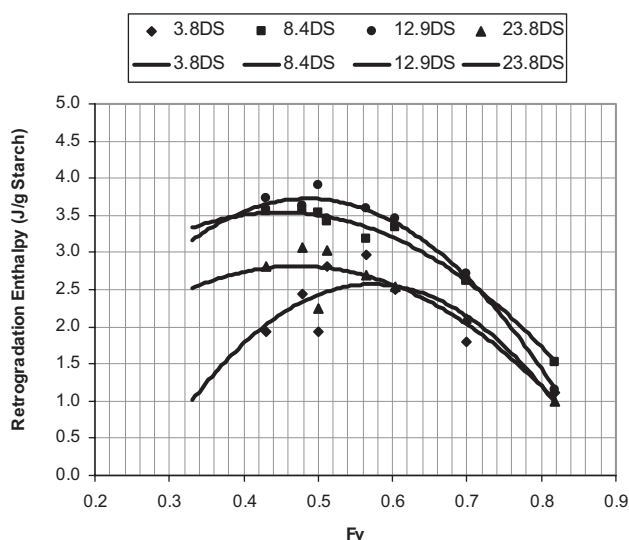
Sample (% DS)	ΔH_u	x_{1-2}	T_m°	r^2
3.8	37.93 ^c	0.34 ^a	452 ^a	0.962
8.4	20.27 ^{ab}	0.59 ^{bc}	518 ^{bc}	0.928
12.9	22.94 ^b	0.55 ^b	498 ^b	0.946
23.8	18.95 ^a	0.59 ^c	529 ^c	0.952

T_m° , is the melting point of the pure polymer (K); ΔH_u , the heat of fusion per repeating unit of glucose (kJ/mol); x_{1-2} : is the Flory–Huggins polymer–diluent interaction parameter. Statistical comparisons were made as a function of the DS level. Values followed by different letters in the same column are significantly different ($p < 0.05$).

Since water is plasticizer of amorphous regions, the recrystallization process of the starch gels is sensitive to the water content. DSC studies have indicated that maximum crystallinity in gels occurs at water contents between 35 and 45%, which shows that retrogradation process is controlled by the water available during aging [16, 25, 26].

Figure 1 shows the retrogradation enthalpy versus water amount showing the bell shaped plots. The maximum of retrogradation ranged between ~ 0.45 and ~ 0.58 Fv (water content 0.35 and 0.48 w/w). The samples with high DS (8.4, 12.9, and 23.8%) had lower values of Fv (0.45–0.48 Fv) than the sample with low (3.8%) DS (0.56 Fv) associated to the maximum of retrogradation.

The onset temperature and temperature range of melting of the retrograded AP did not change with the content of DS, although a decrease on T_0 was observed with

**Figure 1.** Effects of DS and water contents on retrogradation enthalpy.

23.8% DS when the volume fractions of water were 0.37 and 0.35.

It has been generally accepted that DSC melting endotherms of retrograded starch pastes or gels at a temperature below 100°C are attributed to AP crystallization. Different authors have confirmed that AM content, AP fragmentation, and water content have a crucial role on the transition enthalpy. It was reported that AM may enhance the crystallization of AP during retrogradation, and this effect depends on the residual water content [27, 28]. Klucinec and Thompson [29] suggested that the retrogradation behavior of high-AM starches could be due to the differences in AM–AP ratio, the chain length distribution, and the molecular size of branched molecules.

3.2 Effects of damaged starch on starch retrogradation

Table 3 shows the melting enthalpy of retrograded AP as a function of DS content up to 15 days of storing. Water content and storage temperature were kept constant in this analysis.

As was expected, retrogradation enthalpy increased gradually with the storage time. Results indicated that the melting enthalpy increased dramatically during the first 2 days of storage, increased more slowly between 2nd and the 10th day, and remained relatively constant thereafter (Table 3).

Damaged starch content significantly increased the retrogradation enthalpy up to the 3rd day of storage (Table 3). Similar results were found in a previous study [11] working with different flours, two wheat cultivars and a triticale cultivar. In this previous article, AP retrogradation was evaluated up to 7 day storage time, DS influenced at

Table 3. Melting enthalpy (ΔH_r) of retrograded AP as function of DS content at 2, 3, 6, 8, 10, and 15 days of storing

Time (days)	3.8%DS	8.4%DS	12.9%DS	23.8%DS
2	1.43 ^a	2.29 ^b	2.88 ^d	2.57 ^c
3	1.70 ^a	2.03 ^b	2.90 ^c	2.67 ^c
6	2.24 ^a	2.56 ^{ab}	3.02 ^b	2.80 ^b
8	2.93 ^a	2.82 ^a	2.90 ^a	2.90 ^a
10	2.95 ^a	2.90 ^a	3.62 ^c	3.33 ^b
15	3.09 ^a	3.39 ^b	3.48 ^b	3.29 ^{ab}

ΔH_r values are expressed in J/g of starch (10.7 g/100 g moisture). Statistical comparisons were made as a function of the DS level to each retrogradation day. Values followed by different letters in the same row are significantly different ($p < 0.05$).

1 and 3 days of storage time, although differences were dependent on the flour type.

A higher extent of crystallization but also higher perfection and the size of crystals formed during recrystallization could explain the higher melting enthalpies found at short storage times when DS increased.

Crystallization kinetics at 4°C of gelatinized starch were affected by DS content, especially at short storage times. As shown in Table 4, recrystallization kinetics data was well suited to the Avrami equation since the r^2 values were close to 1. The value of the Avrami exponent (n) and the rate constant (k) varied from 0.43 to 0.98 and from 0.29 to 1.27, respectively. The Avrami exponent (n) of native starch was close to 1; similar results were obtained by Yaoqi et al. [30] for rice starch and by Mua and Jackson [31] for corn AP fraction. Also, Russell [32] working with starches with different AP contents informed that n lower to the unity fitted best Avrami model. Reported values of the Avrami exponent for wheat starch ranged between 0.33 and 1.26 depending on storage period and temperature [25, 33, 34]. Despite the wide variation in reported n values, it was not found reference to the DS content of the samples.

Avrami exponent of one represented rod-like growth from instantaneous nuclei, two rod-like growth from sporadic nuclei, three disc-like growths from instantaneous or sporadic nuclei, and four spherulitic growths from instantaneous or sporadic nuclei [15]. According to this article, the recrystallization of wheat starch gels at 4°C has instantaneous nucleation, followed by rod-like growth of crystals. Even though DSC results from high DS samples best fitted a model with lower n than low DS sample, the increment of DS up to 23% seemed not change this behavior.

The rate constant (K) is related to crystal nucleation rate and growth processes [35]. The constant values significantly ($p < 0.05$) increased when DS increased (Table 4), which indicated that DS improved the nucleation process and the crystal growth rate.

Table 4. Kinetics of crystallization parameters and half-time for AP crystallization

Samples (% DS)	n	k (days ⁻¹)	$t_{1/2}$ (days)	r^2
3.8	0.98 ^c	0.29 ^a	2.48 ^c	0.984
8.4	0.50 ^b	0.64 ^b	1.17 ^b	0.969
12.9	0.37 ^a	1.27 ^c	0.20 ^a	0.970
23.8	0.43 ^{ab}	1.07 ^c	0.37 ^a	0.985

n , Avrami exponent; k , rate constant; and $t_{1/2}$, crystallization half-time. Statistical comparisons were made as a function of the DS levels. Values followed by different letters in the same column are significantly different ($p < 0.05$).

As shown in Table 4, the $t_{1/2}$ values decreased with increasing DS content. The smaller the value of $t_{1/2}$ is, the higher the crystallization rate is, which means that the increment of DS content significantly increased the AP crystallization rate.

The nucleation rate depends both on a thermodynamic factor and on a transport factor. The former represents the driving force for transformation and increases when the difference between crystal melting temperature and crystallization temperature increases. The transport term depends on the rate of molecular movements in the amorphous phase [36, 37].

Crystal growth follows the nucleation step and requires the diffusion of the molecules to the nuclei surface [37]. It is known that the diffusion coefficient decreased significantly with increasing molecular size of the diffusant.

AP retrogradation involves a crystallization process of the outer branches and is a slow process which can take several days [38]. The slow crystallization process of polymers is due to the limit of molecular motions that are required for molecular arrangements to form the crystalline structure [37].

Morrison and Tester [8] working with ball milled wheat starches detected that AM was slightly depolymerised only after severe milling, but AP was converted to low MW fragments at all levels of damage, and molecular size tended to decrease with increasing milling time, indicating further breakdown of fragments. Later, Tester et al. [39], using analytical ultracentrifugation and pea and maize starches, determined that the attrition process produced granule damage but also incremented the fragmentation of AP molecules generating AM-like material and some fragmented AP. However, the AM appeared to resist degradation by the milling process.

As was described, molecular motion is fundamental to crystallization in amorphous material. This consideration together with the evidence of fragmentation of AP molecules, as a consequence of starch damage, suggested that the increase of recrystallization kinetics due to the increment of DS was related to the decrease of MW of AP molecules.

4 Conclusions

This study confirmed that the gelatinization enthalpy was simultaneously affected by the DS content and water amount. The Flory–Huggins models suggested a decrease in the enthalpic interaction between starch and water, and a decrease in the stability of the starch–water mixtures.

This study also showed that retrogradation in wheat starch gels was controlled by the amount of water present during aging, but also DS affected this process. High DS

decreased the water content associated to the maximum of the extent of AP retrogradation.

The increment of DS content significantly increased the extent of AP retrogradation and the AP crystallization rate.

It was suggested that AP fragmentation explained the changes in the recrystallization kinetics. More studies are needed to confirm the described behavior, since others factors, as water availability, swelling, leaching, granular integrity during gelatinization, associated to DS could influence the retrogradation kinetics.

To summarize DS content significantly affected the thermal behavior of wheat starch and should be considered when evaluating these properties.

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