



Effects of continuous and cyclic dry heat treatment on the structure, thermal properties, and digestibility of buckwheat (*Fagopyrum esculentum*) starch

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Received: 4 September 2025 / Revised: 18 November 2025 / Accepted: 29 November 2025

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Abstract

Dry heat treatment (DHT) is a physical modification technique that offers environmental advantages and low operational costs. In this study, buckwheat starch was modified under continuous conditions for 3–15 h (DHT-C) and cyclic conditions with five cycles (DHT-R) at 130 °C. Native and modified starches were characterized for morphological, structural, pasting, and in vitro digestibility properties. Starches modified with four and five cycles exhibited reduced gelatinization enthalpy, and SEM (scanning electron microscopy) revealed more pronounced surface depressions. Thermal stability increased with treatment time, but excessive exposure reduced both stability (179 mPa.s for continuous sample over 15 h and 56 mPa.s for the modified sample with 5 cycles) and peak viscosity. X-ray diffraction revealed a Type A pattern, with higher relative crystallinity in DHT-C and DHT-R samples (15,75% for native sample and 20,57% for the modified sample with 5 cycles). The primary molecular structure remained unaffected. Modification increased rapidly digestible starch and decreased resistant starch in DHT C15 (67,77% and 20,54%, respectively) and DHT-R. These findings provide new insights into the technological functionality and digestibility of buckwheat starch following physical modification.

Research highlights

- Dry heat treatment (DHT) increased the relative crystallinity of buckwheat starch.
- Significant changes in granule surface morphology were observed after DHT.
- Longer treatment times and more cycles reduced the thermal stability of starch.
- DHT reduced the retrogradation tendency, improving functional stability.
- DHT increased rapidly digestible starch and decreased resistant starch content.

Keywords Technological properties · Dry heat treatment · Modified starch · Physical modification · Pseudo cereals

Abbreviations

XRD	X-ray diffraction	RVA	Rapid visco analyzer
DSC	Differential scanning calorimetry	RDS	Rapidly digestible starch
DHT	Dry heat treatment	RS	Resistant starch
FEG	SEM-field emission gun-scanning electron	SDS	Slowly digestible starch

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Introduction

According to the Food and Agriculture Organization (FAO), 2.2 million metric tons of buckwheat, a pseudocereal, were produced in 2023, with Russia being the largest producer, followed by China and Ukraine (FAO 2023). Approximately 60–80% of this pseudocereal is composed of starch,

which also includes resistant starch that provides health benefits (Gao et al. 2023). Buckwheat has broad applications in the food industry, including the production of pasta, such as noodles and bread, beer, and, in the case of hulls generated during grain processing, herbal teas. Due to its gluten-free nature, buckwheat flour and starch represents an alternative for producing products suitable for individuals with celiac disease. In addition, buckwheat starch has been used in instant soups, sauces, and beverages as a clean-label thickener, as well as in extruded snacks and breakfast cereals due to its good expansion properties.

Starch can be obtained from buckwheat using alkaline extraction that uses dilute alkali solutions, such as sodium hydroxide, to remove proteins and other associated components, resulting in starch with higher purity and improved functionality for industrial use. Starch in its native form may present certain limitations, depending on its botanical source, such as a tendency toward retrogradation and insolubility in cold water, requiring modifications for its application (Bet et al. 2018). Among the available techniques, physical modification stands out due to its eco-friendliness and regulatory acceptance in clean-label food applications. Physical modification has been widely used, as it has a low environmental impact and prevents the formation of chemical residues in the starch, ensuring a safe product for consumers (Zou et al. 2019).

Dry heat treatment (DHT) involves heating low-moisture starch (less than 10%) at high temperatures for periods ranging from minutes to days, either in cycles or continuously, which can degrade the crystalline region or increase the amorphous region, as well as alter its thermal properties (Oh et al. 2018). Application of DHT to corn starch (Lei et al. 2020), rice starch (Oh et al. 2018), and sweet potato starch (Gou et al. 2019) has resulted in changes in functional and technological properties. Zou et al. (2019) reported improved solubility and swelling power, reduced gelatinization temperatures, and increased granule surface cavities after DHT application.

In this context, modification on starch through DHT can affect pasting, gelatinization, retrogradation, and digestibility properties, improving its versatility for food applications. Despite the growing interest in pseudocereal starches, little is known about how dry heat treatment affects the molecular arrangement and functionality of buckwheat starch. A better understanding of these effects could expand the potential of this ingredient in developing nutritious and thermally processed foods. Therefore, this study investigates the effects of dry heat treatment, applied under both continuous and cyclic regimes, on the thermal behavior, structural organization, pasting characteristics, and enzymatic digestibility of buckwheat starch, aiming to expand its potential use in functional and thermally processed foods.

Materials and methods

Dehulled buckwheat grains were provided from the local market in Ponta Grossa, Paraná, Brazil. The enzymes α -amylase (EC 3.2.1.1, type VI-B, porcine pancreas, 19.6 U/mg) and AMG (EC 3.2.1.3, from *Rhizopus* sp., 21.1 U/mg) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All reagents used were of analytical grade.

Starch isolation

Buckwheat starch extraction followed the alkaline method described by Wang and Wang (2004), with modifications. Dehulled buckwheat grains were milled using an IKA M-20 knife mill (IKA-Werke, Staufen, Germany) to obtain flour. A starch/sodium hydroxide suspension (0.063 mol L^{-1} , 1:3 w/v) was prepared, shaken for 2 min, and left to stand for 18 h at 25 °C. The sedimented fraction was passed through 150 μm and 325 μm sieves then resuspended in deionized water with 0.1 mol L^{-1} HCl to adjust the pH.

The neutralized starch was centrifuged ($9,300 \times g$, 5 min, 20 °C) in a refrigerated centrifuge (Himac CR-21 GII / Hitachi, rotor R14A). The surface protein layer was removed. The extracted starch was dried (24 h, 40 °C) and stored in airtight containers in a desiccator until analysis.

Dry heat treatment modification

The dry heat treatment modification was carried out as described by De Oliveira Maior et al. (2024). The extracted buckwheat starch underwent a pre-drying step to reduce its moisture content below 10%. Thus, it was dried in an oven with air circulation oven 45 °C for 24 h. 20 g of starch was subjected to continuous heating at 130 °C for 3, 6, 9, 12, and 15 h, and coded as DHT C3, DHT C6, DHT C9, DHT C12, and DHT C15, respectively. For repeated DHT treatments, heating cycles (130 °C / 3 h) followed by cooling cycles (25 °C / 1 h) were applied and coded as DHT R-2, DHT R-3, DHT R-4, and DHT R-5 for 2, 3, 4, and 5 cycles, respectively. Since the 3 h continuous treatment (DHT C3) is equivalent to one repeated cycle (DHT R-2), only DHT C3 was included in the comparison. All modified samples were stored in a desiccator until analysis.

X-ray diffraction (XRD) analysis

X-ray diffraction data were obtained using an Ultima 4 X-ray diffractometer (Rigaku, Japan) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$), voltage of 40 kV and current of 20 mA. The diffraction patterns were recorded over a 2θ range of 5°–40°, with a scanning speed of 2° min^{-1} and a step size of 0.02° (Bet et al. 2018). The relative crystallinity

(RC%) was calculated based on the ratio of the crystalline to the total area using untreated sample patterns, according to Eq. (1), where RC represents the relative crystallinity, A_c represents the crystalline area, and A_a represents the amorphous area (Nara and Komiya 1983).

$$RC (\%) = \left(\frac{A_c}{A_c + A_a} \right) \times 100 \quad (1)$$

Field emission gun—scanning electron microscopy (FEG-SEM)

A field emission scanning electron microscope (FEG-SEM) MIRA 3 (Tescan, Czech Republic) was used to evaluate the morphology of the samples. The electron beam voltage was set to 15 kV in the field emission gun, generated by a tungsten filament lamp. The samples needed to be coated with gold and palladium, as the biopolymer is non-conductive. To determine the granule diameter, 20 granules were measured, considering two opposite points across the longest axis of each granule (Ito et al. 2018).

Pasting properties

An RVA-4 (Newport Scientific, Australia) was used to evaluate the pasting properties of native and modified starch. A suspension of 8% (w/w, dry basis) starch in water (28 g total mass) was prepared and subjected to a heating and cooling cycle under agitation at a constant temperature rate. The samples were heated from 50 °C to 95 °C, maintained at that temperature for 6 min, and then cooled down for a total analysis time of 23 min (Cheng et al. 2024).

Thermal properties analysis

For the Differential Scanning Calorimetry analysis, a DSC-Q200 (TA Instruments, USA) previously calibrated with indium (99.99% purity; and fusion standards of 156.6 °C; $\Delta H_{\text{fusion}} = 28.56 \text{ J g}^{-1}$) was used. The applied air flow rate was 50 mL min⁻¹, with a heating range from 30 to 100 °C at a rate of 5 °C min⁻¹. Approximately 2 mg of each sample was weighed and mixed with 8.0 µL of deionized water in hermetically sealable aluminum pans (Bet et al. 2018).

In vitro digestibility

The in vitro digestibility of starches was determined based on Demiate et al. (2016), with modifications. A sample of starch (0.90 g) was suspended in 20 mL of sodium acetate buffer (0.1 M; pH 5.2). The tubes were placed in a water bath at 37 °C for 5 min to stabilize the temperature.

Subsequently, 5 mL of an enzyme solution containing pancreatic α -amylase and amyloglucosidase from *Aspergillus niger* (Sigma- Aldrich Co., St. Louis, MO) was added with continuous agitation in a water bath (100 beats per min). Two aliquots (0.250 mL) of the reaction were withdrawn after 20 min and 120 min of incubation, designated as rapidly digestible starch (RDS) and slowly digestible starch (SDS) contents, respectively, and transferred to tubes containing 10 mL of 66% (w/w) ethanol. The portion remaining unhydrolyzed after 120 min is defined as resistant starch (RS). The tubes were centrifuged for 5 min (1000 × g), and the supernatant fraction was used for glucose determination using the GOPOD (Glucose Oxidase–Peroxidase) method. For the determination of total glucose (TG), the total starch assay kit was applied following the Association of Official Analytical Communities (AOAC) Method 996.11. The values obtained for G20, G120, and TG were used to calculate RDS, SDS, and RS according to Eqs. (2), (3), and 4, with 0.9 as the conversion factor from glucose to starch.

$$RDS\% = (G20 \times 0,9) \times 100 \quad (2)$$

$$SDS\% = [(G120 - G20) \times 0,9] \times 100 \quad (3)$$

$$RS\% = [(TG - G120) \times 0,9] \times 100 \quad (4)$$

Statistical analysis

Analysis of variance (ANOVA) was used to evaluate the behavior of the samples. Tukey's tests were conducted to determine differences between means at a confidence level of 95% ($p < 0.05$) (Ito et al. 2018). The Statistica v.14 software was used in this work (TIBCO, Palo Alto, USA).

Results and discussion

X-ray diffraction (XRD) analysis

Crystallinity is considered an important parameter for starch classification and can be categorized into types A, B, and C according to the intensity of the crystalline and amorphous peak areas, as shown in Fig. 1. These patterns reflect the crystalline organizations of amylopectin double helices and vary according to botanical origin and processing conditions (Nara and Komiya 1983).

A type A diffraction pattern was observed for both native and DHT-modified buckwheat starches, with peaks at 15°, 17°, 18°, and 23°, which are characteristic of cereal starches (Fig. 1). Dry heat treatment promoted an increase in peak intensity; however, no changes in the diffraction pattern were observed. The preservation of the A-type pattern after

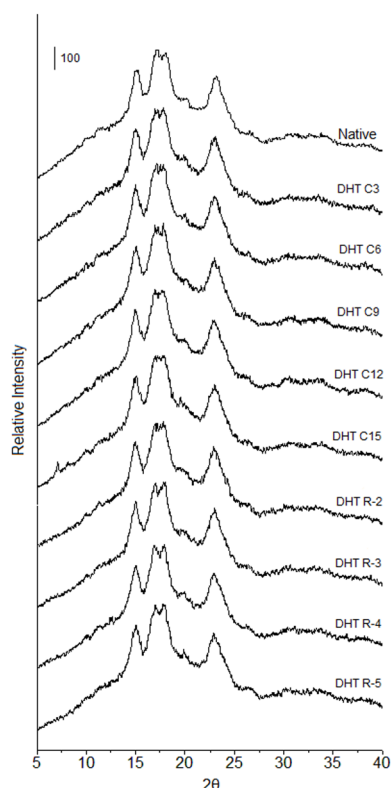


Fig. 1 X-ray diffraction patterns of native starch, DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively, and DHT R: repeated dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/1 h), respectively

DHT indicates that the crystalline regions were not fully disrupted, suggesting thermal resistance of the granular structure under the applied conditions. Similar results for the same botanical source have been previously reported (De Borsato et al. 2022). In this study, a single peak was observed at 20°, which may be associated with the

formation of amylose–lipid complexes, consistent with Lei et al. (2020).

Potato starch subjected to DHT in continuous and repeated cycles exhibited a change in the diffraction pattern from B to C due to the disappearance of peaks at 5.6°, 20°, and 22° 2θ (De Oliveira Maior et al. 2024). Zou et al. (2019) observed that the application of DHT to waxy maize starch was unable to alter the diffraction pattern, which remained type A. This suggests that the botanical source of the starch and the initial diffraction pattern play an important role in the modifiability of this parameter. Starches with a type A diffraction pattern are less susceptible to disruption due to smaller branching with monoclinic double helices and lower molecular mobility (Velázquez et al., 2025).

Native buckwheat starch exhibited the lowest relative crystallinity (RC) (Table 1) among all starches analyzed, with a value of 15.75%. DHT modification at 130 °C increased RC, showing a significant difference from native starch, except for the DHT C9 sample. Between continuously modified samples, showed a reduction in crystallinity with increasing exposure time. In contrast, starches modified by repeated cycles showed an increase in RC compared to the native sample, with RC also increasing with the number of cycles. The samples from cycles 4 and 5 exhibited the highest crystallinity values, 21.14% and 20.57%, respectively.

A reduction in relative crystallinity has previously been reported for starches subjected to dry heat treatment, including maize (Lei et al. 2020), potato (De Oliveira Maior et al. 2024), and rice (Oh et al. 2018). However, in the present study, the observed increase in RC may indicate an expansion of the crystalline region, as crystallinity can be attributed to crystal size, crystalline content, double helix orientation, and the extent of interaction between double helices (Jin and Wang 2020; He et al. 2025).

Table 1 Thermal properties and relative crystallinity of native and modified buckwheat starch^{1,2}

Samples	$T_o/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_c/^\circ\text{C}$	$\Delta H_{\text{gel}} / \text{J.g}^{-1}$	RC (%)
Native	59,60±0,02 ^{ab}	65,76±0,01 ^c	72,03±0,04 ^{abc}	9,42±0,06 ^{de}	15,75±0,65 ^f
DHT C3	59,12±0,07 ^{de}	65,33±0,03 ^c	70,85±0,16 ^c	8,81±0,07 ^{ef}	20,51±0,55 ^{ab}
DHT C6	59,53±0,15 ^{abc}	66,54±0,02 ^a	72,58±1,21 ^a	15,22±0,54 ^a	17,32±0,20 ^e
DHT C9	59,28±0,07 ^{cd}	65,36±0,02 ^c	71,10±0,19 ^{bc}	7,62±0,09 ^g	17,05±0,43 ^{ef}
DHT C12	59,75±0,01 ^a	65,35±0,01 ^c	70,90±0,23 ^c	9,53±0,02 ^{cde}	17,78±0,78 ^{de}
DHT C15	58,95±0,06 ^f	64,92±0,02 ^f	70,96±0,18 ^c	10,44±0,31 ^b	18,13±0,60 ^{de}
DHT R-2	59,35±0,05 ^{bcd}	65,35±0,01 ^c	70,96±0,40 ^c	9,68±0,41 ^{bcd}	18,70±0,33 ^{cd}
DHT R-3	59,30±0,17 ^{cd}	65,55±0,01 ^d	71,06±0,10 ^{bc}	10,33±0,27 ^{bc}	19,75±0,18 ^{bc}
DHT R-4	59,76±0,12 ^a	65,77±0,01 ^{bc}	72,21±0,13 ^{ab}	8,48±0,36 ^f	21,14±0,16 ^{ab}
DHT R-5	59,67±0,02 ^a	65,82±0,02 ^b	71,79±0,03 ^{abc}	8,42±0,15 ^f	20,57±0,29 ^{ab}

¹Values are means±SD. Values with the same letters within the same column are not significantly different ($p < 0.05$). T_o : onset gelatinization temperature; T_p : peak gelatinization temperature; T_c : conclusion gelatinization temperature; ΔH_{gel} : enthalpy change of gelatinization

²Native: native buckwheat starch; DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively; DHT R: repeated dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/1 h), respectively

The observed increase in relative crystallinity may be associated with an expansion of the crystalline region and a reduction in the amorphous region, which is related to starch paste formation (Jin and Wang 2020).

Thermal properties analysis

The gelatinization process occurs within the starch granule when exposed to heat and excess water. The temperature data are presented in Table 1. The onset temperature (T_o) ranged from 58.95 to 59.76 °C, with the starch modified continuously for 15 h (DHT C15) showing the lowest value, while the starches modified by repeated cycles 4 and 5 exhibited higher values, similar to DHT C15, but not significantly different from native starch.

The peak temperature (T_p) reflects the thermal stability of starch crystallites; higher T_p values indicate a more stable and ordered crystalline arrangement (Sun et al. 2021). Regarding T_p , the starch modified continuously for 6 h presented the highest value. Although DHT C6 showed the highest T_p , starches treated with repeated cycles (DHT R-4 and DHT R-5) also exhibited elevated values for T_o , T_p and T_c , indicating cumulative structural reorganization. DHT promotes the reorganization of amylose and amylopectin chains, resulting in a more crystalline structure. The crystalline regions of starch require more energy to be disrupted, which increases the temperature needed to initiate gelatinization (Gou et al. 2019).

The conclusion temperature (T_c) of native starch did not differ significantly from that of modified starches, with differences observed only among the modifications. Comparing starches modified by repeated cycles, cycle 2 exhibited the lowest temperature, which increased with the number of cycles.

The enthalpy of gelatinization (ΔH_{gel}) was highest for DHT C6 starch, differing significantly from the other starches. This result aligns with its elevated gelatinization temperatures. For starches treated with repeated cycles, enthalpy was higher for cycles 2 and 3 compared to native starch, although cycle 2 did not differ significantly from the native starch. However, enthalpy decreased with an increasing number of cycles and differed from native starch, which may be explained by partial disintegration and gelatinization of the granular structures (Gou et al. 2019). These findings are consistent with those reported by De Oliveira Maior et al. (2024), who observed similar enthalpy reductions in potato starch subjected to DHT at 120 °C.

Changes in enthalpy reflect the content of double-helix structures; therefore, a decrease indicates a reduction in double-helix content, suggesting partial granule damage in DHT R-4 and R-5 starches (Gou et al. 2019). High gelatinization temperatures combined with low energy requirements

confer greater thermal stability to starch, enhancing its applicability in foods exposed to high temperatures (Fonseca et al. 2021).

Altogether, the thermal behavior of DHT-modified buckwheat starch highlights its potential for use in thermally processed food systems, where controlled gelatinization and enhanced stability are crucial for product quality and functionality.

Field emission gun—scanning electron microscopy (FEG-SEM)

Figure 2 shows the scanning electron microscopy (SEM) images of native and dry heat treatment buckwheat starch granules under different conditions. The morphology of starch granules, granule size, and surface characteristics is an important parameter.

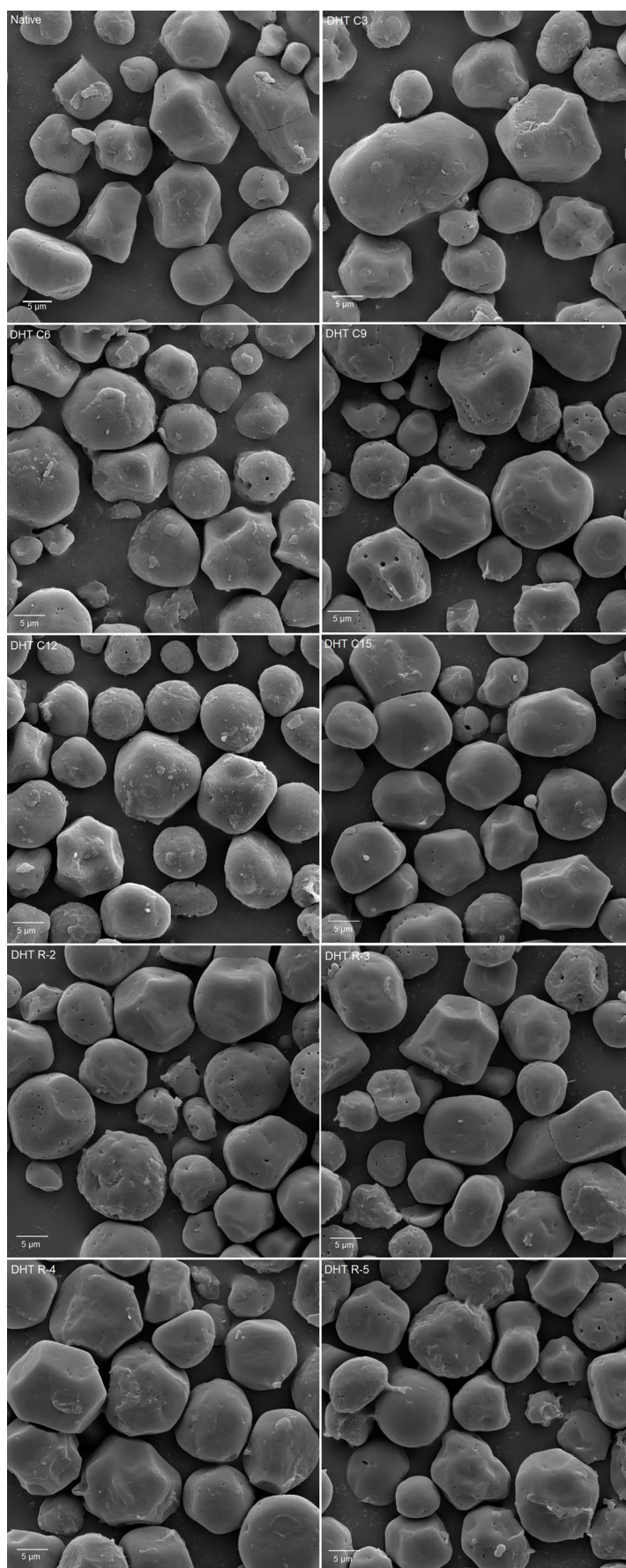
Native buckwheat starch granules exhibited polygonal and oval shapes, with an average diameter ranging from 6.03 to 7.48 μm , showing no significant size variation among them. In addition, granules displayed smooth surfaces, without cracks or fissures. De Borsato et al. (2022), when analyzing buckwheat starch, observed polygonal and spherical granules with an average diameter of 1–7.5 μm .

After dry heat treatment, significant alterations in the surface structure of the granules were observed. In the DHT C3 and DHT C6 samples, fissures, roughness, and small depressions on the granules were noted. These changes may be associated with partial rearrangement of the starch amorphous regions without complete disruption of the granular structure. This suggests that the granule core remained intact despite superficial damage. This behavior is consistent with Siwatch Yadav and Yadav (2022) who reported that moderate thermal treatments cause surface alterations without leading to full gelatinization.

Under DHT C6 and DHT C9 conditions, morphological changes became more pronounced, with increased porosity, deep depressions, and structural deformations. These modifications indicate that higher intensity heat treatment promotes greater internal redistribution of starch structure, possibly due to the volatilization of residual moisture and polymer chain reorganization. The elevated temperature applied during the modification enhances molecular mobility, which can be an important role in promoting starch granule rupture or pore formation throughout the DHT treatment (Zhou et al. 2021).

From a functional perspective, these morphological changes may positively affect technological properties such as water absorption capacity, solubility, and enzymatic digestibility, as well as favor applications in food formulations that require higher surface reactivity of starch granules. Such features may be particularly advantageous in

Fig. 2 Micrographs of native starch, DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively, and DHT R: repeated dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/ 1 h), respectively



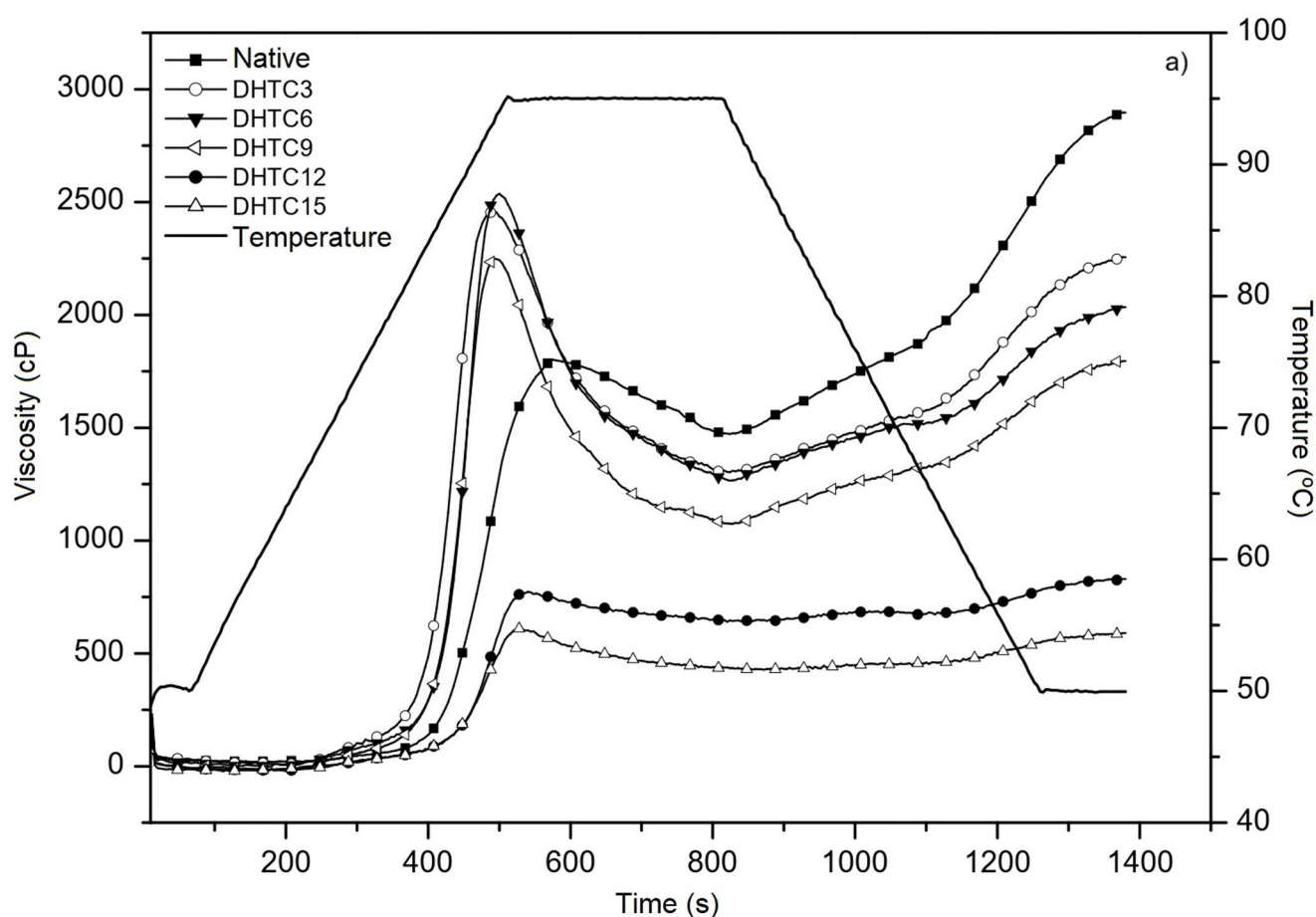


Fig. 3 a RVA curves of native buckwheat starch and starch modified, DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively, **b** RVA curves of starch modified, DHT R: repeated

dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/1 h), respectively

systems where surface-enzyme interactions are critical for functionality.

These results are in agreement with Zhang et al. (2021) analyzing normal and waxy wheat starch, who highlighted that the surface morphology of starch granules can be significantly altered by physical treatments.

Pasting properties

To evaluate the pasting properties of starch, it was suspended in water and subjected to heating and cooling, with the data presented in Fig. 3; Table 2. A temperature of 130 °C was selected for starch modification because several studies have shown that this temperature produces a more resistant gel, higher hydration, and disruption of hydrogen bonds, which lowers the onset temperature of paste formation (Oh et al. 2018).

The RVA profile indicates how starch viscosity is affected by time and temperature, providing information on the gelatinization and retrogradation processes, which

can influence its application in foods. The formation of crosslinks strengthens the interactions between amylose and amylopectin, requiring higher thermal energy for gelatinization to occur at higher temperatures, which explains the differences in pasting temperatures between native and modified starches (Oliveira et al. 2018).

Breakdown reflects the degree of starch granule disintegration, affecting thermal stability, as it is obtained from the difference between peak viscosity and minimum viscosity (Teobaldi et al. 2025). Starch thermal stability increased with modification time; however, longer exposure led to reduced stability, as observed for DHT C12, DHT C15, DHT R-4, and DHT R-5, which exhibited lower breakdown compared to native starch. This suggests that, after a certain modification time, the starch displays lower thermal stability. Similar results were reported by Zhang et al. (2021) for normal wheat starch.

The decrease in enthalpy observed in DSC analysis for DHT R-4 and DHT R-5 samples corroborates the lower breakdown values shown in Table 2 for these samples,

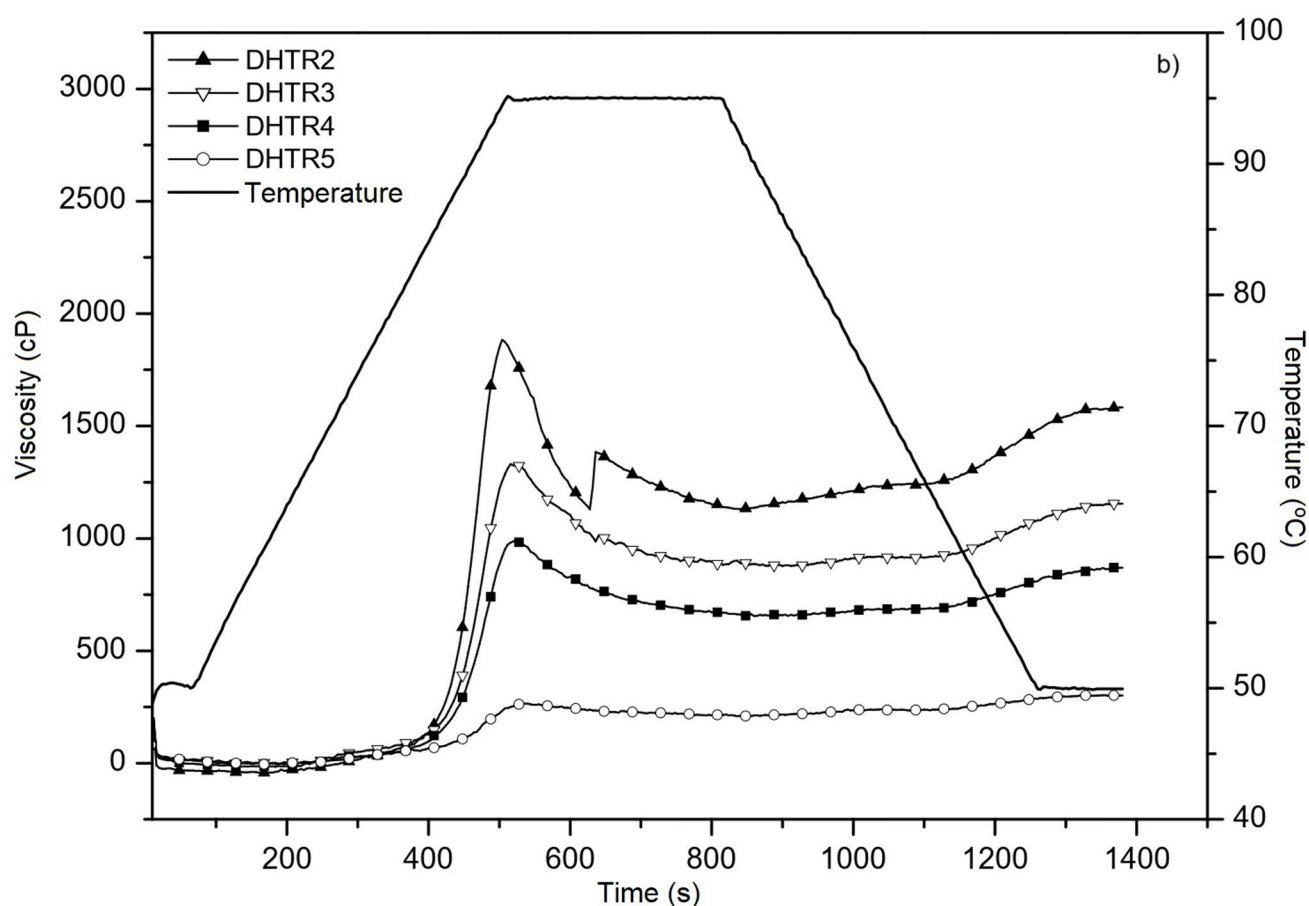


Fig. 3 (continued)

Table 2 Rapid visco analyzer (RVA) pasting profile data of native starch and its modifications^{1,2}

Samples	Peak viscosity / mPa.s	Breakdown / mPa.s	Final viscosity / mPa.s	Setback / mPa.s	Pasting temperature / °C
Native	1798 ^e ±2,52	326 ^f ±2,89	2895 ^a ±1,53	1422 ^a ±1,73	84,20 ^{cd} ±0,23
DTH C3	2455 ^b ±0,58	1151 ^c ±2,31	2254 ^b ±2,08	950 ^b ±3,79	74,23 ^f ±0,62
DTH C6	2535 ^a ±2,52	1268 ^a ±3,06	2033 ^c ±2,31	766 ^c ±3,21	82,00 ^e ±0,40
DTH C9	2248 ^c ±1,15	1174 ^b ±2,31	1794 ^d ±1,73	719 ^d ±2,89	81,20 ^e ±0,38
DTH C12	771 ^h ±1,53	130 ^h ±3,06	830 ^h ±0,58	189 ^h ±1,53	87,60 ^b ±0,38
DTH C15	608 ⁱ ±2,08	179 ^g ±3,06	589 ⁱ ±1,15	160 ⁱ ±2,08	88,02 ^b ±0,43
DHT R-2	1882 ^d ±1,73	750 ^d ±2,52	1580 ^e ±1,53	449 ^e ±1,53	83,73 ^d ±0,56
DHT R-3	1329 ^f ±1,15	452 ^e ±1,53	1154 ^f ±1,73	276 ^f ±2,08	85,25 ^c ±0,41
DHT R-4	987 ^g ±1,53	331 ^f ±1,53	870 ^g ±0,58	214 ^g ±1,15	84,43 ^{cd} ±0,35
DHT R-5	266 ^j ±2,08	56 ⁱ ±2,52	300 ^j ±0,58	90 ^j ±1,53	91,25 ^a ±0,40

¹Values are means±SD. Values with the same letters within the same column are not significantly different ($p < 0.05$)

² Samples: native buckwheat starch; DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively; DHT R: repeated dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/1 h), respectively

indicating that the starch exhibited lower stability during gelatinization, requiring less energy for paste formation (Hui et al. 2024).

Following a similar trend, peak viscosity increased at the beginning of modification compared to native starch,

both for continuous and repeated treatments; however, after 12 h and cycle 3, a decrease in this parameter was observed. Peak viscosity is related to the water-holding capacity of starch, so the reduction in peak viscosity with increasing modification time and cycles can be explained by enhanced

Table 3 Content of RDS (rapidly digestible starch), SDS (slowly digestible starch) and RS (resistant starch) in native buckwheat starch and its modifications^{1,2}

Samples	RDS (%)	SDS (%)	RS (%)
Native	27,90±1,32 ^c	11,37±1,23 ^a	60,73±0,09 ^a
DHT C3	32,60±1,53 ^c	9,43±3,87 ^a	57,96±5,40 ^a
DHT C6	27,39±1,06 ^c	16,10±2,81 ^a	56,52±3,87 ^a
DHT C9	22,45±5,19 ^c	13,48±0,52 ^a	64,08±4,67 ^a
DHT C12	22,45±0,29 ^c	14,88±2,94 ^a	62,67±3,23 ^a
DHT C15	67,77±6,79 ^{ab}	11,70±5,79 ^a	20,54±1,00 ^{bc}
DHT R-2	58,57±4,52 ^b	18,26±3,45 ^a	23,17±1,07 ^{bc}
DHT R-3	64,92±1,22 ^{ab}	10,65±1,58 ^a	24,43±0,36 ^b
DHT R-4	72,48±2,65 ^a	14,90±4,94 ^a	12,62±2,29 ^c
DHT R-5	65,40±2,02 ^{ab}	10,47±0,07 ^a	24,12±1,94 ^{bc}

¹Values are means±SD. Values with the same letters within the same column are not significantly different ($p < 0.05$)

² Samples: native buckwheat starch; DHT C: continuous dry heat treatment at 130 °C for 3, 6, 9, 12 and 15 h, respectively; DHT R: repeated dry heat treatment with 2, 3, 4 and 5 cycles (1 cycle: 130 °C/3 h; 25 °C/1 h), respectively

intramolecular interactions among starch molecules due to DHT modification (Zhang et al. 2021).

Setback, calculated as the difference between final viscosity and minimum viscosity, reflects the tendency of starch retrogradation. Setback was higher for native starch and decreased with longer modification times and repeated cycles, suggesting that the applied treatment reduces retrogradation tendency, which may be beneficial for applications such as bread. The reduction in final viscosity and setback indicates improved crystalline structure and a decrease in the amount of short-chain amylopectin (Gou et al. 2019).

Thermally treated samples with 4 and 5 cycles, DHT R-4 and DHT R-5, respectively, exhibited effective morphological modifications, as observed in granule SEM images, which is consistent with the reductions in breakdown and peak viscosity and the increase in setback, corroborating findings reported by De Oliveira Maior et al. (2024) for potato starch.

In vitro digestibility

Table 3 presents the digestibility data of native and modified buckwheat starch, which can be classified into three categories: RDS (rapidly digestible starch), SDS (slowly digestible starch), and RS (resistant starch).

It is evident that the application of DHT modification influenced the digestibility of buckwheat starch. After 15 h of continuous modification and with repeated cycles, significant differences were observed compared to native starch, showing an increase in rapidly digestible starch. The highest RDS values were observed for DHT C15 (67.77%), DHT R-3 (64.92%), DHT R-4 (72.48%), and DHT R-5 (65.40%). This increase indicates that overall starch digestibility

rose with longer modification times and a higher number of cycles. Zhang et al. (2021) reported similar behavior for normal wheat starch modified by DHT, whereas waxy wheat starch exhibited a decrease.

Starches with type A X-ray diffraction patterns are more susceptible to enzymatic digestion due to shorter amylopectin chains and a higher density of branching (Gaenssle et al. 2021). Additionally, starches with porous surfaces are more prone to enzymatic attack (Dong et al. 2021). As observed in the FEG-SEM images of starch granules, longer modification times and cycles resulted in starches with greater cavity presence, leading to an increase in rapidly digestible starch content.

The amount of SDS is influenced by the amorphous structure of the starch granule, while RS is affected by the presence of a well-organized crystalline structure (Zou et al. 2019). The SDS content did not show significant differences among the samples, whereas the resistant starch fraction exhibited significant changes, indicating that the amorphous structure of the granule was not substantially affected.

Resistant starch content was higher in continuously modified starches up to 12 h, with no significant differences among them. After 15 h of modification and repeated cycles, RS content decreased, with DHT R-4 exhibiting the lowest value (12.62%). For sweet potato starch, RS content increased with longer modification times and a higher number of cycles (Gou et al. 2019).

The increase in RDS and the reduction in RS following DHT treatment indicate higher enzymatic accessibility of the starch, similar to observations in chickpea starch reported by Zhang et al. (2024). According to Oh et al. (2018), the physical sensitivity and accessibility are weakened by gel strength rather than changes in starch structure induced by dry heat. Sensitivity may be correlated with microstructure, which is altered during DHT treatment (Zou et al. 2019).

Conclusions

Modification of buckwheat starch through dry heat treatment (DHT) at 130 °C, under continuous and cyclic conditions, induced significant changes in its technological properties. Samples subjected to 4 and 5 cycles of modification exhibited increases in the onset, peak, and conclusion temperatures of gelatinization, accompanied by a reduction in enthalpy, as evidenced by DSC and RVA analyses. These changes are relevant for applications in products requiring specific viscosity profiles. Despite the modifications, certain structural characteristics, such as infrared spectra and X-ray diffraction patterns, remained unchanged, as did granule size, with only superficial morphological alterations observed. Cyclic modification influenced crystallinity and pasting properties,

likely due to the effects of cooling between cycles. The reduction in gelatinization enthalpy suggests potential for industrial use due to lower energy requirements. Furthermore, starches with high resistant starch (RS) content and low rapidly digestible starch (RDS) content, particularly those modified continuously, opens possibilities for applications in products such as low-moisture baked goods, cookies, dry mixes, and capsules. Starches with high RS content are suitable for functional foods, while those with higher RDS, obtained through cyclic modifications, may be used in formulations aimed at glycemic response control.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13197-026-06578-y>.

Acknowledgements The authors sincerely thank the C-LABMU-UEPG for making their facilities available. LGL and IMD are research fellows supported by CNPq.

Author contributions TDLD: Writing—original draft, Methodology, Formal analysis. LOM: Writing—original draft, Validation, Formal analysis. DB: Formal analysis. MASCF: Writing—review & editing, Investigation. IMD: Writing—review & editing, Methodology, Investigation. LGL: Writing—review & editing, Writing—original draft, Supervision, Methodology. All authors have read and agreed to the published version of the manuscript.

Funding The Article Processing Charge (APC) for the publication of this research was funded by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) (ROR identifier: 00x0ma614). This research received financial support from CNPq.

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this study.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

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