Food Research International 128 (2020) 108803

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Preparation of cassava starch hydrogels for application in 3D printing using dry heating treatment (DHT): A prospective study on the effects of DHT and gelatinization conditions

Bianca C. Maniglia[a,b,c,d,*], Dâmaris C. Lima[d], Manoel D. Matta Junior[d], Patricia Le-Bail[b,c], Alain Le-Bail[a,c,*], Pedro E.D. Augusto[d,e]

[a] ONIRIS-GEPEA UMR CNRS 6144, Nantes, France
[b] BIA-INRA UR 1268, Nantes, France
[c] SFR IBSM INRA CNRS 4202, France
[d] Department of Agri-food Industry, Food and Nutrition (LAN), Luiz de Queiroz, College of Agriculture (ESALQ), University of São Paulo (USP), Piracicaba, SP, Brazil
[e] Food and Nutrition Research Center (NAPAN), University of São Paulo (USP), São Paulo, SP, Brazil

ARTICLE INFO

Keywords:
Starch modification
Novel ingredients
Starchy gels
Printability
3D food printing

ABSTRACT

3D printing is a technology capable of presenting creative, unique and intricate items in an attractive format, with specific compositions. However, novel ingredients must be developed to satisfy this new technological requirement. This work proposes dry heating treatment (DHT), a simple physical technique, as a method for modifying cassava starch, with particular focus on its use for 3D printing. DHT processing was conducted at 130 °C for 2 and 4 h (named DHT_2h and DHT_4h, respectively). Different gelatinization conditions (65, 75, 85, and 95 °C) were applied, and the hydrogels were evaluated considering different storage periods (1 and 7 days). Cassava starch properties were evaluated, focusing on the application of its hydrogels to 3D printing. The increase of DHT time produced a starch with higher carbonyl content and bigger granule size. It also reduced the water absorption index, increased the water solubility index, affected granule crystallinity and reduced molecular size. The longest storage period increased gel firmness. Increasing the temperature used in the gelatinization process reduced the gel strength of the native and DHT_2h. DHT_4h showed the lowest peak apparent viscosity and provided the strongest gels for all the evaluated conditions. Gels produced with DHT starches exhibited better printability than the native starch, mainly for the DHT_4h. This treatment was chosen to print 3D stars, and displayed better resolution than the native gels. Therefore, by using DHT, it was possible to obtain hydrogels with enhanced pasting properties, gel texture, and printability, thereby expanding the potential of applying cassava starch to 3D printing.

1. Introduction

Three-dimensional (3D) printing is an emerging technology in the food industry, with interesting possibilities. It consists in using computer-aided design (CAD) software to instruct a digital fabricating machine to shape 3D objects by the successive addition of material layers (Brunner, Delley, & Denkel, 2018). It is an interesting technique for overcoming certain common constraints and expanding possibilities in food processing. For example, Severini and Derossi (2016) stated that 3D printing can produce nutritional meals personalized for each person, based on individual age, physical condition, and nutrition and energy requirements. Indeed, specific compositions, shapes and properties can be obtained that can be useful for specific diets such as those for the elderly, children and persons with special needs. Consequently, numerous studies on 3D-food printing have recently demonstrated the value of this technology in the food industry (Azam & Zhang, 2018; Chen, 2016; Godoi, Prakash, & Bhandari, 2016; Liu, Bhandari, Prakash, & Zhang, 2018; Liu, Liang, Saeed, Lan, & Qin, 2019; Yang, Guo, Zhang, Bhandari, & Liu, 2019).

However, 3D-printing technology has generated new challenges for the food industry. In fact, it is necessary to better understand the relationships among the possible composition, structure (in different scales) and the obtained properties in order to develop 3D-printed products with the desired characteristics (sensorial, physic-chemical, nutritional, etc.). Therefore, most of the studies in the literature focused on factors influencing the rheology and printability of food material,

---

* Corresponding authors.
E-mail addresses: biancamaniglia@usp.br (B.C. Maniglia), alain.lebail@oniris-nantes.fr (A. Le-Bail).

https://doi.org/10.1016/j.foodres.2019.108803
Received 21 May 2019; Received in revised form 30 October 2019; Accepted 2 November 2019
Available online 21 November 2019
0963-9969/ © 2019 Elsevier Ltd. All rights reserved.

with greater demand for new ingredients and formulations. Novel ingredients are needed to achieve this goal, in particular hydrogels that provide good printability, and 3D products with well-defined geometries and good resolution.

Starches, in particular modified ones, can be used to produce hydrogels with possible applications for 3D printing (Maniglia et al., 2019). Starch is widely used as a thickening and gelling agent in many food formulations to improve the convenience and quality of final products due to its gelatinization properties (Zheng, 2018). Starch-based materials have specific characteristics such as biodegradability, biocompatibility and non-toxicity, which are attractive for applications ranging from the food industry to material engineering (Llanos & Tadini, 2018). However, although simple and cheap, native starches do not necessarily have the requisite properties to provide the application desired. As a result, starches are generally modified for industrial applications.

One interesting source of starch is cassava, a major ingredient used in the food industry. Brazil, one of the countries involved in this work, is the world's fifth largest producer of cassava, with 18.9 million tons produced in 2017 (FAO - Food and Agriculture Organization, 2019). Cassava presents positive characteristics because it is a starch-rich tuberous gluten-free root (interesting for people with celiac disease) (Liu et al., 2019), and highly tolerant to drought and harsh climatic conditions (Alves, 2002). It is available around-the-year, and it is considered as a reliable crop for food supply security (Liu et al., 2019; Zhu, 2015). Cassava starch shows high potential for application and it has been investigated by many researchers (Díaz, Dini, Viña, & García, 2018; Liu et al., 2019; Matta Junior, Castanha, dos Anjos, Augusto, & Sarmento, 2019). However, cassava starch is known for producing relatively "weak" gels that do not maintain their shape after being removed from the mold (Maniglia et al., 2019). Consequently, its modification is necessary for applications requiring strong gels.

Dry heating treatment (DHT) involves a simple physical technique to modify the structural and physicochemical properties of starch (Alcázar-alay, Angela, & Meireles, 2015). DHT consists of heating samples at temperatures between 110 and 150 °C for 1–4 h, keeping the starch moisture level low ($< 10\%$ w/w) (Oh, Bae, & Lee, 2018). The advantage of this treatment is that it is simple and safe (no chemical reagents are used). It does not generate effluents to be treated and the products obtained do not present traces of chemical components. Therefore, DHT is considered a "green technology" and bears a "clean label". For these reasons, different studies have recently been performed to evaluate the effect of DHT on starch and, more specifically, starch and polysaccharide mixtures (Chandanasree, Gul, & Riar, 2016; Ji, Yu, Xu, & Zhang, 2016; Liu, Hao, Chen, & Gao, 2019; Pramodrao & Riar, 2014; Sun, Gong, Li, & Xiong, 2014; Zou, Xu, Tian, & Li, 2019).

Chandanasree et al. (2016) evaluated the effect of hydrocolloids and dry heating on the characteristics of cassava starch. The authors showed that DHT is capable of modifying the physicochemical, thermal, pasting and morphological properties of cassava starch. However, the final properties of the hydrogels produced with cassava starch modified by DHT have not been studied. Indeed, very few works in the literature have focused in the final properties of the hydrogels obtained from pure starch processed by DHT (instead of flours and starch mixtures with other polysaccharides).

Our research team recently published a work involving cassava starch modification by ozone processing to obtain hydrogels with improved 3D printing properties (Maniglia et al., 2019). Investigations into the use of modified starches for this purpose are just beginning, and they augur the expansion of starch gel applications. Consequently, we believe DHT can be an interesting alternative to obtain starch hydrogels for the purpose of 3D printing.

In this context, the aim of this study was to investigate the effect of DHT and gelatinization conditions of cassava starch on its physical properties, focusing on its application for 3D printing. This work first dealt with the effect of dry heating treatment on starch structure (granule and molecular) and properties. Then, the hydrogels were evaluated for their paste and gel properties, including their printability, and the effects of gelatinization conditions and storage period were evaluated.

2. Material and methods

2.1. Material and dry heating treatment (DHT)

Regular native cassava starch (Amilogill 1500, moisture: 13.2 g/100 g, amylose content: 28.9 g/100 g and amylopectin content: 71.1 g/100 g) was provided by Cargill Agrícola - Brazil. All the chemicals were of analytical grade.

The DHT was based on the work of Chandanasree et al. (2016). A thin layer (~1 mm) of cassava starch (50 g) was distributed over a sheet of aluminum foil and covered with another sheet of aluminum foil. The lateral parts were closed with tape to form a closed envelope in order to avoid loss of material. The packed starch was then placed in a hot-air convective oven (MA 035, Marconi, São Paulo, Brazil), in which DHT was performed using air at 130 °C (air velocity 1 ± 0.1 m.s^{-1}) for 2 and 4 h (named DHT_2h and DHT_4h, respectively), following the conditions described by Chandanasree et al. (2016). After processing, the starch was cooled and stored in glass containers for further analysis.

2.2. Starch characterizations

2.2.1. Granule characterization: morphology, size distribution and crystallinity

The starch granules (native as control and modified) were observed using a light microscope (model L1000, Bioval, Brazil; with a 20 W halogen lamp, magnification of 40 x) and a digital camera of 5.1 megapixels (ECMOS C-Mount, Sony, Japão). The starch granules were dispersed in distilled water (1:1, v/v) and placed on a glass slide, which was covered by a glass cover slip and evaluated directly. A polarized light filter coupled to the system was used to observe the Maltese crosses.

Particle size distribution was determined using a Laser Analyser (Partica LA-950 V2 Laser Particle Size Analyser HORIBA, Japan) and the LA-950 software for Windows (HORIBA, Japan). The samples were dispersed in ethanol (99.5%) and placed in an ultrasound bath for 5 min prior to analysis. The analysis was carried out eight times for each sample.

From the data obtained, the volume-based mean diameter (D[4,3], Eq. (1)), and the area-based mean diameter (D[3,2], Eq. (2); where n_i = the number of particles with diameter d_i), were calculated for each sample. Diameters d(0.1), d(0.5), and d(0.9) were also obtained, denoting the reduction in size, 10%, 50% and 90% respectively, of the particles.

$$D[4,3] = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3} \tag{1}$$

$$D[3,2] = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \tag{2}$$

An X-ray diffractometer (Shimadzu XRD 7000, Tokyo, Japan) with copper radiation was used to evaluate granule crystallinity, using the following working conditions: angle 2θ ranging from 3 to 40°, scan rate of 2°·min^{-1}, 40 kV and 30 mA. The starch samples were maintained in a desiccator containing saturated $BaCl_2$ solution (25 °C, aw = 0.900) for 10 days to ensure constant water activity. Three runs for each sample were analyzed. The curves obtained were smoothed using the Origin software, version 2018 (Microcal Inc., Northampton, MA, USA). The relative crystallinity was calculated as the ratio of upper diffraction peak area to the total diffraction area, following the method described by (Nara & Komiya, 1983) and considering 2θ ranging from 3 to 36°.

2.2.2. Molecular characterization: pH, molecular size distribution, carbonyl and carboxyl groups

All the analyses executed on this item were carried out in triplicate. The starch suspension (10.7 g starch/100 g suspension) pH was measured using a potentiometer (Tecnal, model TEC-5 mode, Piracicaba – Brazil). Carbonyl and carboxyl contents were determined according to the method described by Smith (1967) and Chattopadhyay, Singhal, and Kulkarni (1997), respectively, with small modifications.

The carbonyl content was determined as follows: the starch sample (2 g) was dispersed in distilled water (100 mL) and heated in a bath with boiling water under constant stirring for 30 min. The sample was cooled to 40 °C, the pH was adjusted to 3.2 using HCl solution (0.1 M), and 15 mL of hydroxylamine chloride solution (25 g of hydroxylamine hydrochloride diluted in 100 mL of NaOH 0.5 M) was added. The samples were incubated at 40 °C for 4 h, and then the excess hydroxylamine was titrated with 0.1 M HCl until pH 3.2 using an automatic titrator (Plus Titrino 848, Metrohm, Herisau, Switzerland). A blank was made without the sample but following the same procedures. The carbonyl content was calculated as the amount of carbonyl groups in relation to 100 units of glucose (CO/100 GU) according to Equation (3):

$$\frac{CO}{100GU} = \frac{(V_B - V_S).\ M,\ 0.028.\ 100}{W} \tag{3}$$

where:

Vs = the volume of NaOH required for the ozonated samples;
Vb = the volume of NaOH used in the blank;
M = the molarity of NaOH;
W = the sample mass in dry basis.

The carboxyl content was determined as follows: the starch sample (2 g) was dispersed in 25 mL of HCl solution (0.1 M) under stirring at 25 °C for 30 min. The residue was filtrated using a vacuum system with a qualitative filter paper (205 μm), and then washed with 400 mL of distilled water. Next, 300 mL of distilled water was added, and the dispersion was heated in a bath with boiling water under continuous stirring for 15 min. While it was still hot and under stirring, the sample was titrated with 0.01 M NaOH until pH 8.3 using an automatic titrator (Plus Titrino 848, Metrohm, Herisau, Switzerland). A blank was made with the unmodified starch but following the same procedures. Carboxyl content was expressed as the amount of carboxyl groups in relation to 100 units of glucose (COOH / 100 GU), according to Equation (4):

$$\frac{COOH}{100GU} = \frac{(V_S - V_b).\ M.\ 0.045.\ 100}{W} \tag{4}$$

where:

Vb = the volume of HCl used in the blank;
Vs = the volume of HCl required for the sample;
M = the molarity of HCl;
W = the sample mass in dry basis.

The starch molecular size distribution profile was determined using a gel permeation chromatography system, following the method of Song and Jane (2000), with some modifications. The system consisted of a glass column (GE Healthcare – 28988950 XK 27/70) packed with Sepharose CL-2B gel (Sigma, Sweden). Firstly, a solution with 0.1 g of starch with 10 mL of Dimethylsulfoxide (DMSO; 90%, Labsynth, Brazil) was prepared and heated in a bath with boiling water (1 h). Then, it was kept at 25 °C for 24 h under constant stirring. Next, 3 mL of this starch solution was mixed with 10 mL of absolute ethanol and centrifuged (30 min, 3000 g). The precipitated starch was dissolved in water (9 mL) and heated in a bath with boiling water (30 min). This starch solution (4 mL) was added in the chromatographic column with an eluent solution (25 mmol·L^{-1} of NaCl and 1 mmol·L^{-1} of NaOH), at a rate of 1 mL·min^{-1}. Aliquots of 4 mL were collected using a fraction collector (Gilson, model FC203B, Middleton, England) and then analyzed by the blue value method (Juliano, 1971), using a spectrophotometer at 620 nm of wavelength (Femto, model 600S, São Paulo - Brazil). Glucose was used as marker to indicate the end of the analysis.

2.2.3. Water absorption index (WAI) and water solubility index index (WSI)

The water absorption (WAI) and solubility (WSI) indexes were determined according to the methodology described by Anderson, Conway, and Peplinski (1970), with some modifications. To this end, 0.5 g (dry basis) of the material (MS, in Eqs. (5) and (6)) was weighed in a centrifuge tube, which was followed by the addition of 6 mL of distilled water. The suspension was heated at 65, 75, 85, and 95 °C in a water bath for 30 min. The suspension was then centrifuged at 3000 × g for 10 min. To quantify the soluble starch fraction (SS, in Eqs. (5) and (6)), the supernatant was removed and dried at 105 °C in an oven until constant weight. The tubes containing the precipitate (PT, in Eq. (5)) were weighed to determine the WAI, which is an indicator of starch swelling power and represents the amount of water that 1 g of insoluble starch (IS, in Eq. (5)) is able to absorb and retain. The WAI and the WSI were calculated according to Eqs. (5) and (6), respectively:

$$WAI\left(\frac{gwater}{gIS}\right) = \frac{PT - (MS - SS)}{(MS - SS)} \tag{5}$$

$$WSI\,(\%) = \frac{SS}{MS}X100 \tag{6}$$

2.2.4. Pasting properties

The starch pasting properties were determined using a Rapid Visco Analyzer - RVA-4 (Newport Scientific Pvt. Ltd., Australia, with Thermocline for Windows software, version 3.0). The standard conditions for starch characterization were employed, using a suspension of 10.7 g starch/100 g (correct to 14% moisture basis), following the procedure: keep at 50 °C for 1 min, then heat to 95 °C (6 °C·min^{-1}), maintain at 95 °C for 5 min), follow by cooling to 50 °C (6 °C·min^{-1}), and finally maintain at 50 °C for 2 min.

Furthermore, the effect of the gelatinization condition on the pasting properties was also evaluated by following the same procedure, but changing the highest temperature to 65, 75, and 85 °C, instead of 95 °C.

According to Castanha, da Matta Junior, and Augusto (2017), to eliminate any misinterpretation, the relative breakdown (RBD) and relative setback (RSB) were calculated. The Relative Breakdown (RBD) was calculated by the ratio between the values of Breakdown (BD) and the Peak Apparent Viscosity (PAV) to understand the facility of starch granule disruption. The relative setback (RSB) was calculated by the ratio between the Setback (SB) and the TAV (trough apparent viscosity) values, to understand the trend to retrogradation.

2.2.5. Gel firmness

Gel firmness was determined by a puncture assay using a texture analyzer TA TX Plus (Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kgf (490 N).

The samples used to measure gel firmness consisted of the hydrogels produced in the RVA analysis, which were placed in plastic cups (40 mm diameter × 20 mm height) and stored for 1 and 7 days at 5 ± 2 °C. The cups were kept in a desiccator with water at the bottom to avoid changes in moisture. The samples were then removed from the refrigerator and analyzed immediately to ensure a constant temperature.

The gels were penetrated to a distance of 4 mm using a cylindrical probe (P/0.5R) at 1 mm·s^{-1}. The equipment measured the force as a function of the penetration depth. Gel firmness was evaluated by the energy required to penetrate the material (calculated by the area below the curve force versus the distance of penetration).

Furthermore, the effect of the gelatinization condition was evaluated by using the different temperatures described on the “Pasting properties” section.

2.3. Hydrogel application: Evaluating 3D printing

Different hydrogels were produced with varying DHT processing times, gelatinization conditions and refrigerated storage times. They were evaluated through their potential to be used for 3D printing following two approaches.

Firstly, all the hydrogels were evaluated through a simple approach by extruding them with a syringe on a glass slide. In a previous study (Maniglia et al., 2019), we described this analysis as good indication of the material's printability, which had a good correlation with real 3D printing. The hydrogels obtained from the RVA were stored and then placed in a plastic syringe (die diameter: 1.5 mm). The gels were then extruded through the die over a glass slide (lines with ~6 cm), for a visual evaluation of the gel's consistency and moldability. The manual extrusion using the syringe was carried out ten times to ensure the reproducibility and veracity of this procedure. Pictures (Fig. 8) were obtained based on the visual aspect that most predominated in the extruded material. This approach was used to select conditions for actual 3D printing.

The selected gels were then processed in a 3D printer Stampante 3D (3DRAG V1.2, Futura Elettronica, Italy). The gels were produced following the same conditions. The suspension was stirred and heated until reaching the desired gelatinization condition, then maintained in this condition for 5 min. The gels obtained were transferred to the printer syringes (60 mL), which were closed using parafilm plastic and then stored in a refrigerator (5 ± 2 °C) for 7 days (chosen condition after evaluating the other results). The syringes were then removed from the refrigerator and immediately processed in the 3D printer. A 0.8 mm diameter nozzle was used. The nozzle height was set at 18 mm, with a speed of 20 mm/s and an extrusion rate of 30 mm/s at 20 °C. The physical model (star) was created using the Repetier Host V2.0.1 and Slic3r software (Hot-World GmbH & Co. KG, Willich, Germany). The dimensions of the star shape were 5 cm × 5 cm × 2 mm (Length × Width × Height). Pictures (Fig. 9) were obtained based on the visual aspect that most predominated in the printed material.

2.4. Experimental design and statistical analysis

A completely randomized design was applied with four replicates for each processing condition. To evaluate differences, analysis of variance (ANOVA) and Tukey's test at a 5% significance level were carried out with the software *Statistic 13* (StatSoft, USA).

3. Results and discussion

3.1. Starch characterizations

3.1.1. Granule characterization: Particle size distribution, morphology and crystallinity

Fig. 1 shows the particle size distribution (A) and specific particle diameters (B) of the control and modified cassava starches. The effect of DHT enlarged the particle sizes of the granules (Fig. 1A), which is consistent with the duration of the dry heating process: the D[4,3] varied from 17.8 μm for the control starch to 19.3 and 27.3 μm DHT_2h and DHT_4h, respectively (Fig. 1B). The dry heating process also increased the number of particles with bigger sizes considering the values d0.1, d0.5 and d0.9. Moreover, the differences on D[4,3] were more pronounced than on D[3,2] (although both presented statistical differences).

According to Lopez-Sanchez et al. (2011), the D[4,3] value is more influenced by large particles, whereas D[3,2] is more influenced by the smaller ones. Therefore, the results indicate that the dry heating process led to an increase in the diameter of the larger starch granules, but had less influence on the smaller ones (which is consistent with the distribution – Fig. 1A). Indeed, the moisture content of the cassava starch was reduced with the dry heating treatment (control: 13.2 g/100 g; DHT_2h: 6.8 g/100 g and DHT_4h: 6.7 g/100 g), which indicated that part of the water content in the samples was vaporized. Therefore, the increase in granule size can be associated to a possible expansion process in the starch granules due to water vaporization. Even so, the changes in starch properties observed were not linked to the low moisture level, but to the associated thermal effect of DHT. In order to confirm it, we also performed starch drying at 35 °C, a temperature generally accepted for drying without causing changes, until the same moisture level described previously was reached. No change was observed on the starch dried this way.

Fig. 2 shows the optical microscopy of the control and modified cassava starches using both nonpolarized and polarized light. The shapes of the cassava starch granules were polygonal, angular and truncated, as observed by Han et al. (2019). Polarized light microscopy shows all the granules with birefringent (Maltese cross is visible) and they seem to be intact. However, with higher magnification (1500 x) using scanning electron microscopy, Chandanasree et al. (2016) observed several fractures in the cassava starch modified in the same DHT conditions. Considering the fact that birefringence reflects the internal microstructure of starch granules, it shows that the dry heating treatment used did not significantly affect the internal microstructure of cassava starch granules. Indeed, heat treatment lasting 2 or 4 h did not alter the shape or promote degradation on the surface of the granules.

Another point is that particle aggregation was not observed (Fig. 2). Consequently, the increase in particle dimensions (Fig. 1) must be attributed to mechanisms other than aggregation, such as the expansion proposed. Further studies are needed to better understand this phenomenon.

The granule X-ray diffraction patterns are presented in Fig. 3(A), and their relative crystallinity in Fig. 3(B). All the samples showed peaks at 15°, 23°, 17°, and 18° (2θ), representing a typical type-A starch pattern (Liu et al., 2019). In addition, no significant difference ($p < 0.05$) was observed for the relative crystallinity between native starch and the DHT_2h sample. However, the DHT_4h sample showed significant reduction ($p < 0.05$) of this parameter compared with control and DHT_2h. Type-A starch polymorphs (with about six water molecules inside the helices) presented a more stable monoclinic structure (Chatpapamon, Wandee, Uttapap, Puttanlek, & Rungsardthong, 2019); consequently, this crystalline arrangement is less prone to change by dry heating treatment. This indicates that the crystalline structure of the starch was affected only after 4 h of dry heating treatment at 130 °C. Liu et al. (2019) indicated the decrease in crystallinity could be attributed to a reorientation of the double helices forming the crystalline array and/or crystallite disruption.

Sun, Xu, and Xiong (2014), Oh et al. (2018), and Liu et al. (2019) also observed the reduction of relative crystallinity when the DHT was applied in proso millet, high amylose rice and waxy potato starches. Therefore, DHT reduced the crystalline portion in different starch sources.

Therefore, the dry heating treatment changed the crystallinity (DHT_4h) of cassava starch, but without bigger changes in the granule morphology. Consequently, it was necessary to also evaluate the possible changes in starch molecules, as described in the following.

3.1.2. Molecular characterization: pH, molecular size distribution, carbonyl and carboxyl contents

Table 1 shows the pH, carbonyl and carboxyl contents of the native (control) and the modified cassava starches.

The dry heating treatment was capable of oxidizing the starch molecules, generating carbonyl groups that increased with processing time. However, this oxidation was not drastic enough to produce carboxyl groups, which indicates a difference in pH. Indeed, Kurdziel, Łabanowska, Pietrzyk, Sobolewska-Zielińska, and Michalec (2019) described that atmospheric oxygen, even though a weak oxidizing agent, can initiate oxidation to a smaller extent during thermal treatment, leading to the formation of carbonyl groups in heated starches. Chávez-

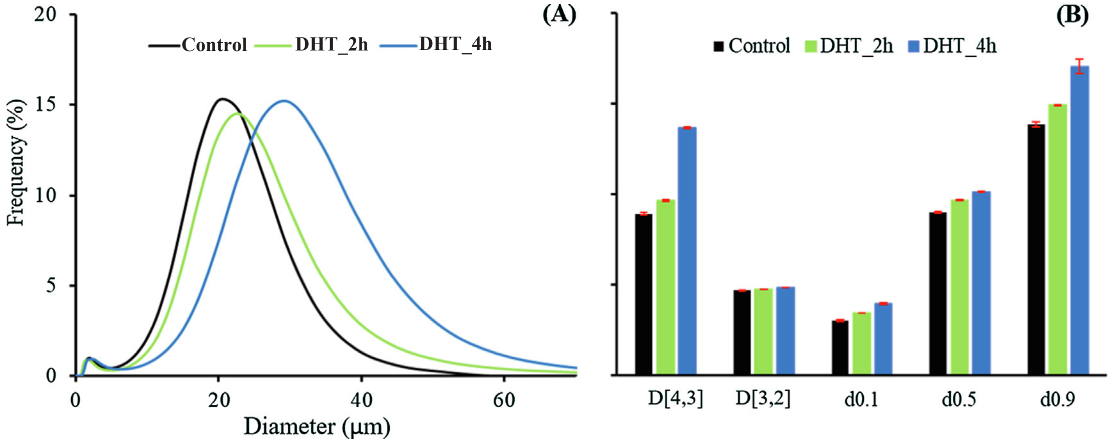


Fig. 1. Starch granule size of the control and modified cassava starches by dry heating: (A) Particle size distribution. (B) Specific diameters (D[4,3], D[3,2], d0.1, d0.5, d0.9) – vertical red bars are the standard deviations.

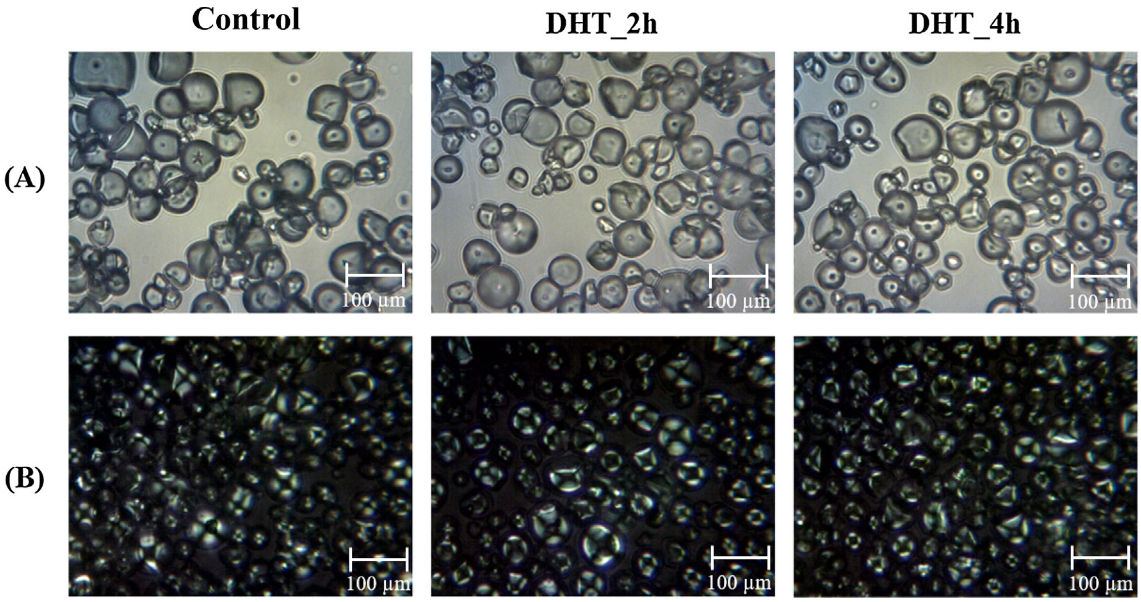


Fig. 2. Photographs from light microscopy (40×) using (A) nonpolarized and (B) polarized light of the control and modified cassava starches by dry heating treatment.

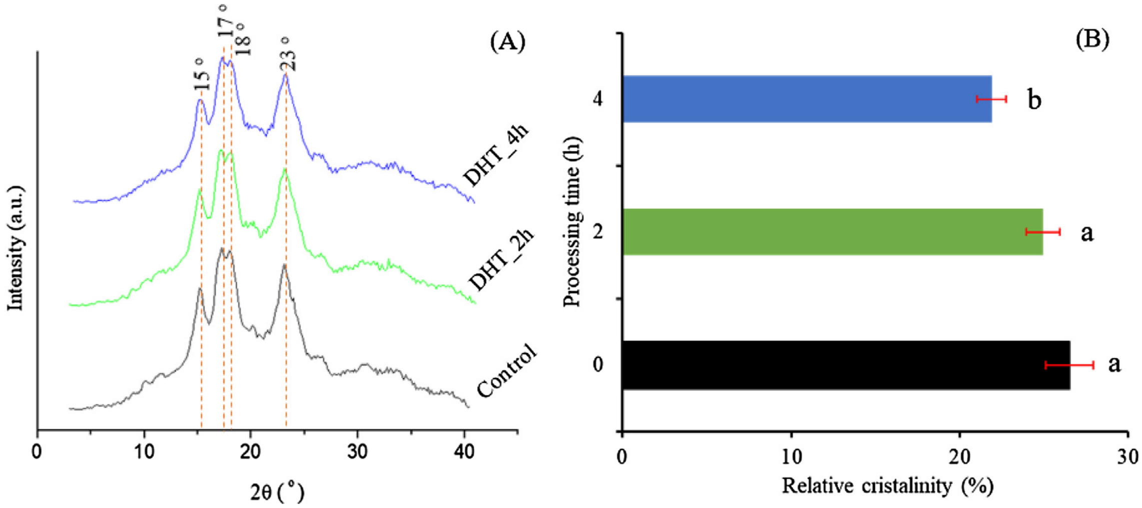


Fig. 3. (A) Diffractogram and (B) relative crystallinity of the starch samples (control, DHT_2h, and DHT_4h) – horizontal red bars are the standard deviations; different small caps indicate significant difference among treatments, as revealed by Tukey's test, $p < 0.05$.

Table 1
pH, carbonyl and carboxyl contents of the control and modified cassava starches by dry heating treatment (average ± standard deviation).

Samples	pH	Carbonyl content (CO/100 GU)	Carboxyl content (COOH/100 GU)
Control	5.45 ± 0.19^a	0.00 ± 0.00^c	0.00 ± 0.00^a
DHT_2h	5.23 ± 0.11^a	0.06 ± 0.01^b	0.00 ± 0.00^a
DHT_4h	5.32 ± 0.17^a	0.22 ± 0.03^a	0.00 ± 0.00^a

a, b, c: different letters in the same column indicates significant difference among treatments, as revealed by Tukey's test, $p < 0.05$.

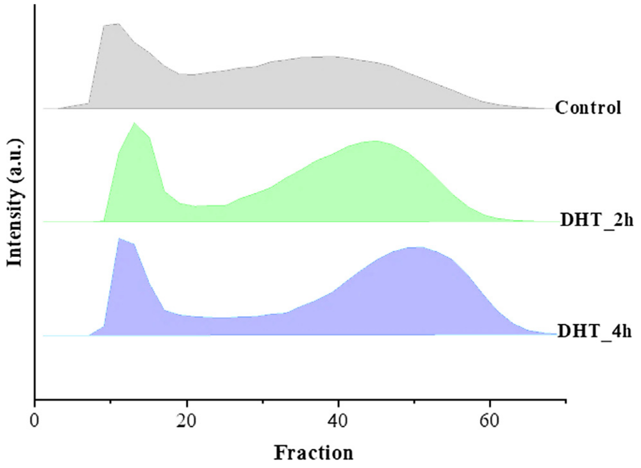


Fig. 4. Molecular size distribution of the starch samples (control, DHT_2h, and DHT_4h).

Murillo, Wang, and Bello-Pérez (2008) mentioned that starch heating can lead to new functional carbonyl and carboxyl groups formed mainly at the C-6 and C-2 or C-3 carbon atoms of glucose units in the starch structure.

Fig. 4 shows the molecular size distribution of the control and modified cassava starches. The dry heating treatment reduced the size of the molecules to intermediate size (Fig. 4): the second peak increased and scrolled to the right, indicating that the molecules modified by dry heating were retained longer in the chromatographic column due to their lower size. DHT was thus responsible for cleaving the links present between the glucopyranose units (Haq et al., 2019). In addition, the DHT samples showed a narrow peak for the large molecules (first peak), reflecting that the treatment also affected the bigger molecules.

As observed, the DHT promoted different molecular changes in the cassava starch: the hydroxyl groups were oxidized to carbonyl groups (Table 1), and molecular depolymerization was also observed (Fig. 4). Li et al. (2013) also observed that the dry heating method can break the intra- and inter-molecular hydrogen bonds of waxy rice starch. In addition, based in the results shown in Fig. 4, this depolymerization occurred mainly for the intermediate size molecules, resulting in two groups of molecules that are more defined (large and small molecules size) than those of native starch (high fraction of molecules of intermediate size).

The dry heating treatment was capable of changing the molecular structure of cassava starch and displayed that it is an effective treatment for starch modification. Consequently, it can also change the properties of starch, which we evaluate in the following.

3.1.3. Water absorption index (WAI) and water solubility index index (WSI)

Table 2 shows the water solubility index (WSI) and the water absorption index (WAI) of the control and modified cassava starches.

The WSI and WAI increased gradually from 65 °C for all the treatments. This temperature is related to the onset of gelatinization, which promotes hydrogen bond cleavage and irreversible and progressive water absorption (Pelissari, Andrade-Mahecha, Sobral, & Menegalli, 2012). Hydrogen bond cleavage and water fixation at higher temperatures gave rise to free hydroxyl groups and allow starch granules to continue swelling, thereby increasing starch solubility (Limberger, Da Silva, Emanuelli, Comarela, & Patias, 2008).

Starches treated by DHT showed lower WAI than the control at all the temperatures evaluated, and this became more pronounced as the processing time increased. This result can be associated with the starch depolymerization promoted by DHT (Fig. 4). DHT reduced the capacity of the starch to maintain its integrity due to the weakening of the links between starch chains, whose glycosidic bonds were cleaved, leading to the reduction of starch granule swelling during gelatinization (Liu et al., 2019). The WSI was higher for the starches treated by DHT than the control, and it also became more pronounced as processing time increased. The molecular cleavage promoted by DTH easily disrupted the starch granules, especially at higher temperatures. Therefore, the longer the DHT time, the greater the molecular breakdown and, therefore, the higher the solubility of the granules.

3.1.4. Pasting properties

Fig. 5 shows the RVA curves and Table 3 shows the associated pasting parameters in different gelatinization conditions (65, 75, 85, and 95 °C). The peak apparent viscosity was higher for the native starch than those treated by dry heating, whatever the gelatinization conditions. In addition, a more significant reduction in the peak apparent viscosity was observed as processing time increased.

When the aqueous slurry of starch is heated, the granules can absorb water and swell; the swollen granules rub against each other under stirring in RVA, increasing the apparent viscosity (Hu et al., 2018). The peak viscosity represents the maximum resistance during gelatinization, demonstrating the swelling of the starch granules before disintegration (Gou et al., 2019). In Fig. 5, the behavior observed indicates that the starch granules treated by DHT showed a reduction in their capacity to maintain their integrity. This was due to the weakening of the associations between starch chains, whose glycosidic bonds were cleaved (molecular depolymerization, Fig. 4), thereby reducing the swelling power (WAI in the Table 2).

Similar behavior can be found in the literature. A reduction of the peak and final viscosities of millet, pea and corn starches was observed by Sun et al. (2014) and Sun, Sun, and Xiong (2013) after DHT at 130 °C for 2–4 h. Gou et al. (2019) also observed the reduction of the peak and final viscosities for sweet potato heat treated at 130 °C for 18 h.

The trough and final apparent viscosities showed similar tendencies to the peak viscosity, decreasing significantly ($p < 0.05$) as exposure time increased. The same behavior was observed by (Sun et al., 2013) working with DHT on pea starch.

The relative breakdown (RB) increased according to the time of exposure to heat. This indicates that the new intermolecular association produced by DHT becomes easier when compared with the native starches.

The relative setback viscosity (RSB) is related to the potential for retrogradation in starches, and a higher RSB represents a greater chance for retrogradation (Gou et al., 2019). The RSB values of the DHT_4h starch were higher than the control and the DHT_2h starches (Table 3). Moreover, for the control and the DHT_2h starches, increasing gelatinization temperature (up to 75 °C) reduced the RSB values; however, the variation of the temperature did not affect this parameter of the DHT_4h starch. Therefore, the dry heating treatment and the gelatinization conditions cooperated differently regarding the retrogradation phenomenon. This can be explained by molecular depolymerization. As discussed before, the dry heating treatment led to a reduction of molecular size, in particular that of molecules of intermediate size, forming two well-defined groups with larger and smaller molecules. Similar molecule sizes are more suitable for re-association due to better pairing; also, smaller molecules have higher mobility to re-associate (Castanha

Table 2
Water absorption index (WAI) and water solubility index (WSI) of the control and modified cassava starches by dry heating treatment (average ± standard deviation).

WAI

Samples	65 °C	75 °C	85 °C	95 °C
Control	8.74 ± 0.37^{Ca}	9.47 ± 0.25^{Ca}	10.59 ± 0.47^{Ba}	11.83 ± 0.33^{Aa}
DHT_2h	4.39 ± 0.34^{Db}	5.90 ± 0.13^{Cb}	6.96 ± 0.21^{Bb}	8.01 ± 0.14^{Ab}
DHT_4h	3.83 ± 0.24^{Db}	4.55 ± 0.26^{Cc}	5.90 ± 0.59^{Bc}	6.92 ± 0.22^{Ac}

WSI

Samples	65 °C	75 °C	85 °C	95 °C
Control	1.02 ± 0.20^{Bb}	2.44 ± 0.34^{Ac}	2.52 ± 0.16^{Ac}	2.75 ± 0.17^{Ac}
DHT_2h	2.36 ± 0.37^{Da}	8.86 ± 0.64^{Cb}	12.16 ± 0.84^{Bb}	21.83 ± 1.68^{Ab}
DHT_4h	2.39 ± 0.35^{Da}	13.72 ± 1.13^{Ca}	19.41 ± 1.72^{Ba}	26.93 ± 1.72^{Aa}

A, B, C, D: different big caps in the same line indicates significant difference in each treatment among different temperatures (Tukey's test, $p < 0.05$). a, b, c: different small caps in the same column indicates significant difference among treatment in the same temperature (Tukey's test, $p < 0.05$).

et al., 2017), explaining the behavior observed.

However, in addition to the changes in molecular size distribution (Fig. 4), the starches processed using DHT showed new intermolecular associations due to the replacement of hydroxyl groups by carbonyl groups (Table 1). Consequently, other parameters also varied.

DHT for 2 h did not change the pasting temperature. However, the DHT_4h samples showed slightly higher pasting temperatures (when the gelatinization conditions were 65, 75, or 85 °C) than the other samples. This might result in the presence of smaller molecules that need a higher energy level to gelatinize than large size molecules (Castanha et al., 2017).

It is interesting to note that the behaviors of pasting properties of the DHT starches were similar to that observed for cassava starch modified by ozone in our last work (Maniglia et al., 2019). By comparison, the DHT modified starch method has the advantage of being simpler than the ozone method. However, the use of heating in the DHT implies an energy cost that must be evaluated in each case.

The results indicate that this method can produce starches with good properties for forming a strong gel and good printability. However, to confirm this, it is necessary to also evaluate the changes occurring in the hydrogels obtained. This was carried out as follows.

3.1.5. *Gel firmness*

Fig. 6 shows the gel firmness produced by the different DHT conditions, gelatinization conditions and storage periods at 5 °C. Fig. 7 shows a photograph of each gel.

Dry heating treatment resulted in stronger hydrogels: for all the gelatinization and storage conditions, the starch processed through DHT for 4 h resulted in stronger gels when compared with the control and that processed for 2 h. The gels produced by DHT_2h starch did not result in a behavior as pronounced as the DHT_4h, but the gels were stronger than those produced by control starch. This is also highlighted in Fig. 7. This result is important as stronger gels are in general preferable in industrial applications – in particular considering 3D printing applications.

When gelatinized starch paste is subjected to cooling, the extent of the viscosity increase is mainly governed by the rapid re-association of linear amylose chains via the formation of a molecular matrix (Gunaratne & Corke, 2007). Starch retrogradation is not favored by chains that are too short or too long; there is an optimum size at which this process becomes favorable (Wang, Li, Copeland, Niu, & Wang, 2015). Therefore, even considering the molecular cleavage, the balance between molecular size and interactions (through the changes of

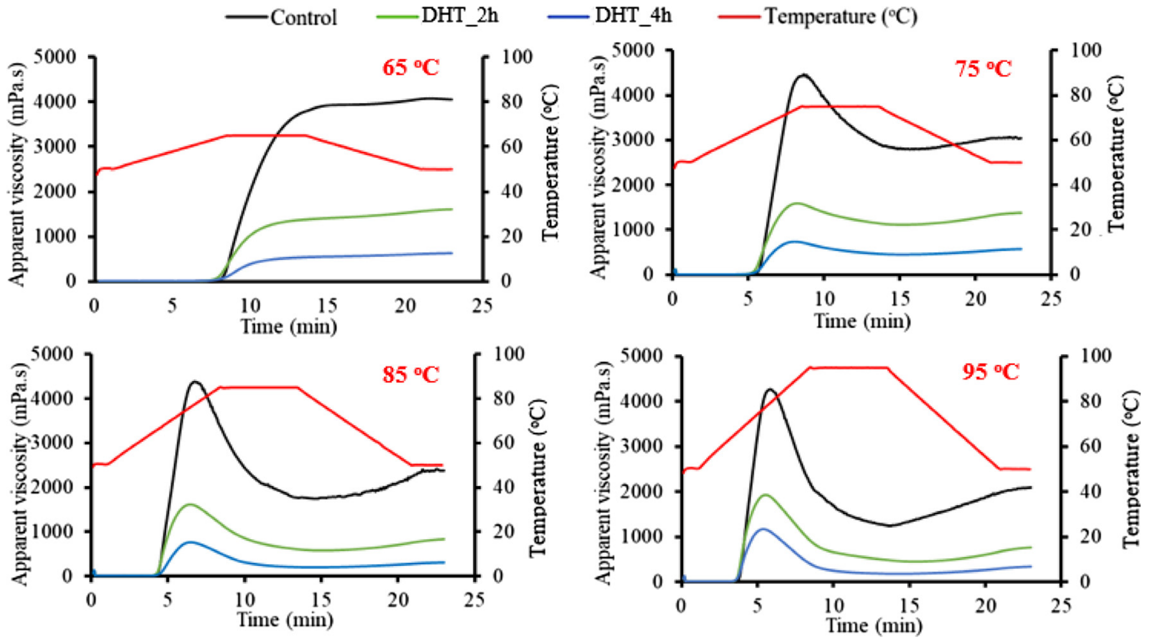


Fig. 5. RVA curves of the control and cassava starches treated by dry heating in different gelatinization conditions (65, 75, 85 and 95 °C).

Table 3

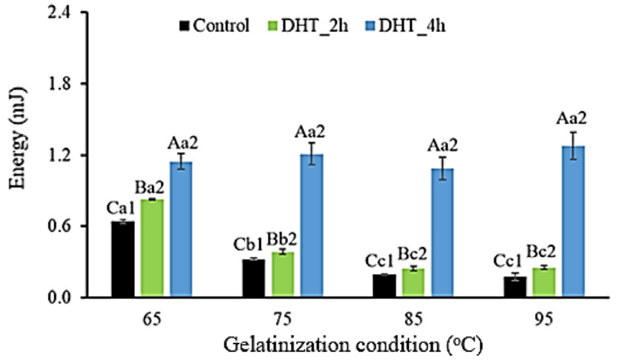
Pasting parameters of the control and modified cassava starches by dry heating treatment in different gelatinization conditions (average ± standard deviation).

Sample	GC (°C)	PAV (mPa·s)	TAV (mPa·s)	RBD (mPa·s)	FAV (mPa·s)	RSB (mPa·s)	PT (°C)
Control	65	3699.00 ± 31.08^{bA}	2670.75 ± 28.37^{aA}	0.00 ± 0.00^{A}	4061.25 ± 11.38^{aA}	52.08 ± 3.56^{aB}	64.09 ± 0.13 ^{dB}
	75	4418.25 ± 44.70^{aA}	2110.50 ± 77.57^{bA}	33.41 ± 0.54^{cC}	3031.00 ± 42.79^{bA}	46.74 ± 2.98^{aB}	64.55 ± 0.05^{cB}
	85	4451.75 ± 84.24^{aA}	1750.50 ± 31.13^{cA}	60.68 ± 0.37^{bC}	2471.00 ± 86.02^{cA}	41.15 ± 2.63^{bB}	65.51 ± 0.02^{bB}
	95	4412.00 ± 73.54^{aA}	1261.00 ± 26.87^{dA}	70.76 ± 0.12^{aC}	1850.00 ± 70.71^{dA}	44.80 ± 1.74^{bB}	66.33 ± 0.04^{aA}
DHT_2h	65	1398.50 ± 44.01^{bB}	1086.50 ± 68.63^{aB}	0.00 ± 0.00^{dA}	1646.75 ± 54.06^{aB}	52.82 ± 1.86^{aB}	63.91 ± 0.08 ^{dB}
	75	1622.50 ± 38.04^{aB}	930.00 ± 17.09^{bB}	35.34 ± 1.08^{cB}	1384.75 ± 36.43^{bB}	46.91 ± 1.40^{aB}	64.75 ± 0.04^{cB}
	85	1668.50 ± 39.03^{aB}	593.00 ± 27.14^{cB}	63.68 ± 0.26^{bB}	871.50 ± 24.03^{cB}	42.14 ± 2.56^{bB}	65.54 ± 0.05^{bB}
	95	1677.00 ± 14.14^{aB}	270.00 ± 14.14 ^{dB}	82.20 ± 0.03^{aB}	384.50 ± 6.36 ^{dB}	42.54 ± 1.11^{bB}	66.35 ± 0.06^{aA}
DHT_4h	65	570.25 ± 29.41^{bC}	406.00 ± 11.89^{aC}	0.00 ± 0.00^{dA}	780.75 ± 8.38^{aC}	89.87 ± 3.79^{bA}	64.91 ± 0.02^{cA}
	75	752.50 ± 12.04^{aC}	347.75 ± 10.81^{bC}	38.44 ± 0.37^{cA}	655.50 ± 23.30^{bC}	90.93 ± 3.84^{aA}	65.85 ± 0.20^{aA}
	85	787.00 ± 25.13^{aC}	198.00 ± 6.06^{cC}	74.83 ± 0.75^{bA}	353.50 ± 32.60^{cC}	90.47 ± 2.98^{aA}	66.08 ± 0.32^{aA}
	95	754.00 ± 27.50^{aC}	103.67 ± 1.53^{dC}	85.67 ± 0.35^{aA}	200.33 ± 4.16^{dC}	93.26 ± 3.80^{aA}	66.47 ± 0.25^{aA}

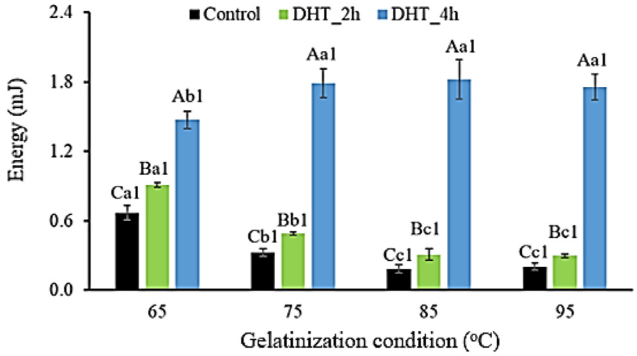
GC: gelatinization condition, Peak Apparent Viscosity (PAV), Through Apparent Viscosity (TAV), Relative Breakdown (RBD), Final Apparent Viscosity (FAV), Relative Setback (RSB) and Pasting Temperature (PT).

a - d: different small caps in the same column indicate significant difference among different gelatinization temperatures for each DHT treatment, as revealed by Tukey's test, $p < 0.05$.

A - C: different big caps in the same column indicate significant difference among DHT treatments (0, 2, and 4 h of dry heating) and considering the same temperature of gelatinization, as revealed by Tukey's test, $p < 0.05$.



1 day of storage



7 days of storage

Fig. 6. Firmness (measured as the energy necessary for a punctual assay) of the gels produced with starch samples (control, DHT_2h, and DHT_4h) in different gelatinization condition and storage period. Statistical evaluation by Tukey's test ($p < 0.05$): A – C: different big caps indicate significant difference among DHT treatments in the same gelatinization condition; a - c: different small caps indicate significant difference among different gelatinization condition, by the same starch DHT sample; 1–2: different numbers indicate significant difference among the same starch DHT sample, in the same gelatinization condition, but with different storage period.

hydroxyl to carbonyl groups) of DHT_4h starch gave more favorable results with the formation of stronger gels. In another experiment conducted by our research group (Maniglia et al., 2019), we observed similar behavior for cassava starch processed by ozone technology: by changing the ozonation process conditions, both weaker and stronger gels could be obtained. In that case, the molecular interaction changes as a result of depolymerization and the presence of both carbonyl and carboxyl groups.

The gels processed by DHT were stronger after 7 days of refrigerated storage (Figs. 6 and 7), which did not occur with the native starch. According to Wang et al. (2015), retrogradation is an ongoing process, which initially involves the rapid recrystallization of amylose molecules (short-term retrogradation) followed by the slow recrystallization of amylopectin molecules (long-term retrogradation). This behavior is expected to be more complex in modified starches, since both amylose and amylopectin change their size and interaction due to the newly formed carbonyl groups. The starches processed by DHT showed greater uniformity in the size of the smaller and larger molecules, although separated into two groups (Fig. 4). Therefore, the association of the smaller (amylose) and larger (amylopectin) molecules was more effective for the modified starch, favoring short and long-term retrogradation.

The increase in hydrogel firmness is an important result, possibly reflecting the better formation of defined shapes during 3D printing – which is particularly important for cassava starch. Therefore, the 3D printing potential was evaluated.

3.2. *Hydrogel application: Evaluating 3D printing potential*

Gel printability directly determines whether food can be produced from 3D printing and handled with dimensional stability capable of not spreading on surfaces, and of supporting its own weight during layer-by-layer deposition (Godoi et al., 2016; Liu et al., 2019).

Fig. 8 shows images of the simulated printing, considering different dry heating treatment times, gelatinization conditions and storage periods. In general, all the gels produced could be extruded by a syringe and produce a straight line. However, different trends were observed when attempting to obtain a defined shape, which is important to ensure a good resolution of the printed object.

In all the gelatinization conditions, the DHT_4h starch showed more defined lines with a thinner aspect, indicating that these gels presented stronger consistency (agreeing with the results obtained for the gel firmness), spreading less on the surface. On the other hand, the native starch appeared less adapted for 3D printing application when the gel was produced at temperatures up to 65 °C. Indeed, the "lines" produced by such gels were larger and spread more on the surface than the other gels. Indeed, cassava starch is known to produce relatively "weak" gels that do not maintain their shape after being removed from the mold.

The higher storage period (7 days) led to more defined lines that spread less. These results are in accordance with the gel strengths

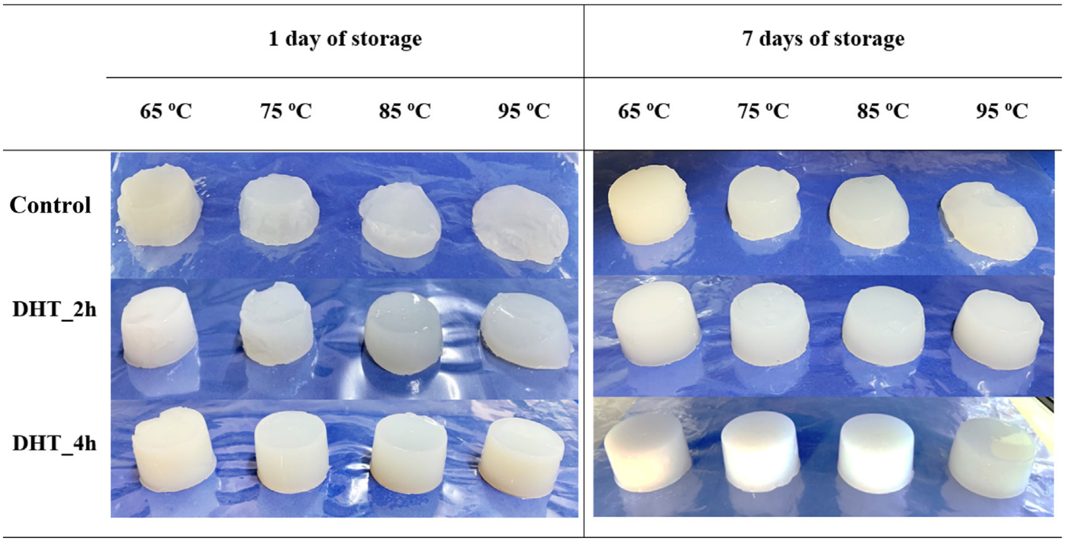


Fig. 7. The visual aspect of the gels produced with starch samples (control, DHT_2h, and DHT_4h) in different gelatinization conditions and storage periods.

obtained, which indicates that this property is adequate for evaluating hydrogel printability.

In the conditions evaluated, DHT_4h starch appeared as the best candidate for 3D printing application, as it could be used as a gelling agent. To evaluate if the dry heating treatment really improved the printability of this gel, star-shaped products were printed by a 3D printer using DHT_4h gels produced at 65 and 95 °C. Fig. 9 shows the result obtained, in comparison with the control (native starch) gel produced at the same temperatures.

In Fig. 9, we can conclude that when the gels were produced using the lowest gelatinization temperature condition (65 °C), it was possible to print stars with both gels. However, it can be seen that the star produced with DHT_4h gels gives higher resolution (well-defined star tips). Comparing the moldability of the gels produced in the highest gelatinization temperature condition (95 °C), the control starch did not provide good printability, and spread over the surface. On the other hand, the DHT_4h gels produced at this temperature showed good printability, resulting in a star with the best resolution.

Therefore, our results are very interesting since gels with lower apparent viscosity and the ability to form stronger gels can be obtained by altering the DHT process conditions. These characteristics imply that the use of cassava starch can be expanded to industrial applications, such as 3D food printing.

For 3D food printing, a material of sufficient viscosity is desirable for easy extrusion through a small nozzle and high enough to be cohesive without deformation as layers are deposited above (Chen, Xie,

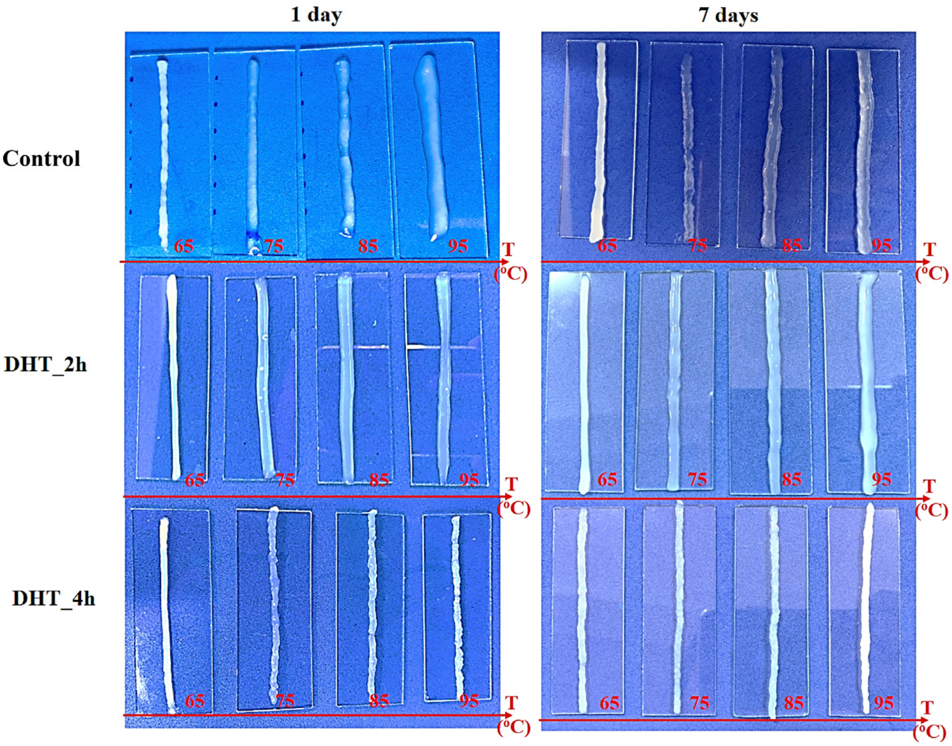


Fig. 8. Images of simulated printing with the cassava starch gels produced with the different starch samples (control, DHT_2h, and DHT_4h) in different gelatinization conditions and storage period.

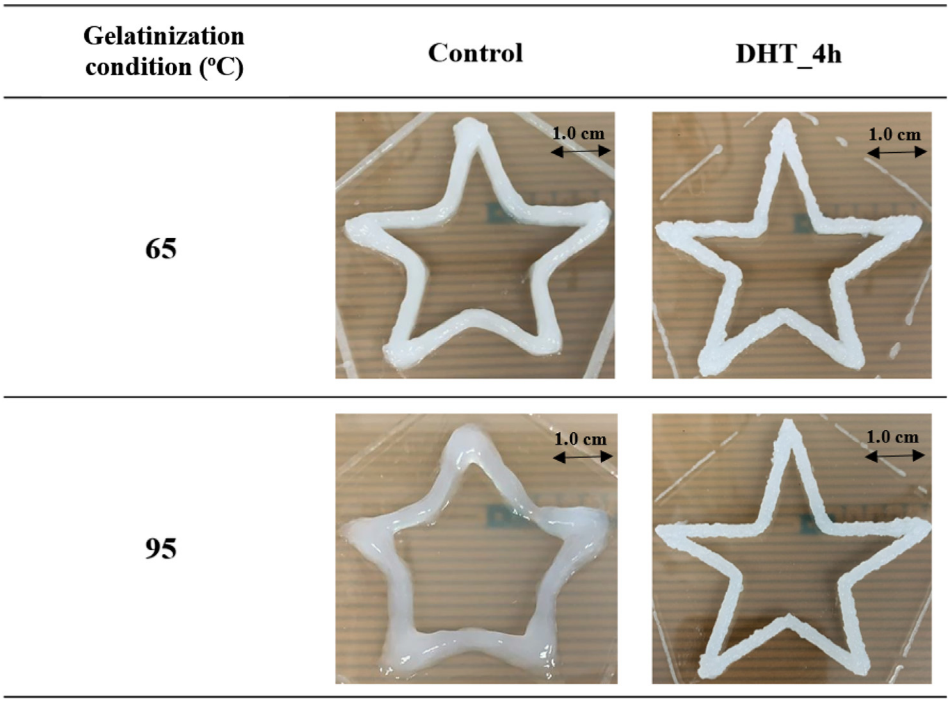


Fig. 9. Images of the stars printed by 3D printing based on control and DHT_4h gels produced using gelatinization condition of 65 and 95 °C.

Chen, & Zheng, 2019).

Indeed, this work produced modified cassava starch with enhanced properties, bearing a "clean label", using simple and safe physical treatment (DHT), that can be used as an ingredient for 3D printing.

4. Conclusion

This work demonstrated that the simple and efficient technique of DHT can expand the application of cassava starch, in particular for 3D printing.

Using DHT to modify the molecular and granular characteristics of cassava, resulted in the reduction of the peak apparent viscosity and increased gel firmness. The temperature used to promote gelatinization and the storage period were parameters that affected each starch treatment and their hydrogels differently. Gels produced with starch treated by DHT for 4 h resulted in stronger hydrogels for all the gelatinization conditions (65, 75, 85, and 95 °C), notably in the case of storage for 7 days. Gel firmness was consistent with the profile of gel printability. Indeed, DHT_4h treatment produced hydrogels with good printability, resulting in 3D products with well-defined geometries and good resolution.

Therefore, using DHT, we could obtain cassava starch with new and potentially interesting properties, thereby expanding the potential of using cassava starch in 3D printing.

Declaration of Competing 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 paper.

Acknowledgements

The authors are grateful to:

- the Région Pays de la Loire (France) / RFI "FOOD 4 TOMORROW" for funding the post-doctoral fellowship "STARCH-3D" of B. Maniglia;
- the São Paulo Research Foundation (FAPESP, Brazil) for funding project n° 2016/18052-5 and 2019/05043-6;
- the National Council for Scientific and Technological Development (CNPq, Brazil) for funding the productivity grant of P.E.D. Augusto (306557/2017-7);
- the Technology Center of Cereal and Chocolate from the Food Technology Institute (ITAL, Brazil), in the name of Dr. Izabela Dutra Alvim, for the particle size distribution analysis;
- the "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES)" - Finance Code 001, through the D.C. Lima Ph.D. scholarship for providing partial funding;
- Anthony OGE from ONIRIS-GEPEA for technical support in 3D printing applications.

References

Alcázar-alay, S. C., Angela, M., & Meireles, A. (2015). Physicochemical properties, modifications and applications of starches from different botanical sources. *Food Science and Technology, 35*(2), 215–236. https://doi.org/10.1590/1678-457X.6749.

Alves, A. A. C. (2002). Cassava botany and physiology. *Cassava: Biology. Production and Utilization, 1*, 67–89.

Anderson, R. A., Conway, Hf, & Peplinski, A. J. (1970). Gelatinization of corn grits by roll cooking, extrusion cooking and steaming. *Starch-Stärke, 22*(4), 130–135.

Azam, S. M. R., & Zhang, M. (2018). Study on 3D printing of orange concentrate and material characteristics. *Journal of Food Process Engineering, 41*(5), 1–10. https://doi.org/10.1111/jfpe.12689.

Brunner, T. A., Delley, M., & Denkel, C. (2018). Consumers' attitudes and change of attitude toward 3D-printed food. *Food Quality and Preference, 68*, 389–396. https://doi.org/10.1016/j.foodqual.2017.12.010.

Castanha, N., da Matta Junior, M. D., & Augusto, P. E. D. (2017). Potato starch modification using the ozone technology. *Food Hydrocolloids, 66*, 343–356. https://doi.org/10.1016/j.foodhyd.2016.12.001.

Chandanasree, D., Gul, K., & Riar, C. S. (2016). Effect of hydrocolloids and dry heat modification on physicochemical, thermal, pasting and morphological characteristics of cassava (Manihot esculenta) starch. *Food Hydrocolloids, 52*, 175–182.

Chatpapamon, C., Wandee, Y., Uttapap, D., Puttanlek, C., & Rungsardthong, V. (2019). Pasting properties of cassava starch modified by heat-moisture treatment under acidic and alkaline pH environments. *Carbohydrate Polymers, 215*, 338–347. https://doi.org/10.1016/j.carbpol.2019.03.089.

Chattopadhyay, S., Singhal, R. S., & Kulkarni, P. R. (1997). Optimisation of conditions of synthesis of oxidised starch from corn and amaranth for use in film-forming applications. *Carbohydrate Polymers, 34*(4), 203–212. https://doi.org/10.1016/S0144-8617(97)87306-7.

Chávez-Murillo, C. E., Wang, Y., & Bello-Pérez, L. A. (2008). Morphological, physicochemical and structural characteristics of oxidized barley and corn starches. *Starch - Stärke, 60*(11), 634–645. https://doi.org/10.1002/star.200800016.

Chen, Z. (2016). Research on the impact of 3D printing on the international supply chain. *Advances in Materials Science and Engineering, 1–16*. https://doi.org/10.1155/2016/4173873.

Chen, H., Xie, F., Chen, L., & Zheng, B. (2019). Effect of rheological properties of potato, rice and corn starches on their hot-extrusion 3D printing behaviors. *Journal of Food Engineering, 244*, 150–158. https://doi.org/10.1016/j.jfoodeng.2018.09.011.

Díaz, A., Dini, C., Viña, S. Z., & García, M. A. (2018). Technological properties of sour cassava starches: Effect of fermentation and drying processes. *LWT - Food Science and Technology, 93*, 116–123. https://doi.org/10.1016/j.lwt.2018.03.029.

FAO - Food and Agriculture Organization. (2019). Production crop data. Retrieved September 23, 2019, from http://www.fao.org/faostat/en/#data/QC/visualize.

Godoi, F. C., Prakash, S., & Bhandari, B. R. (2016). 3d printing technologies applied for food design: Status and prospects. *Journal of Food Engineering, 179*, 44–54. https://doi.org/10.1016/j.jfoodeng.2016.01.025.

Gou, M., Wu, H., Saleh, A. S. M., Jing, L., Liu, Y., Zhao, K., ... Li, W. (2019). Effects of repeated and continuous dry heat treatments on properties of sweet potato starch. *International Journal of Biological Macromolecules, 129*, 869–877. https://doi.org/10.1016/j.ijbiomac.2019.01.225.

Gunaratne, A., & Corke, H. (2007). Effect of hydroxypropylation and alkaline treatment in hydroxypropylation on some structural and physicochemical properties of heat-moisture treated wheat, potato and waxy maize starches. *Carbohydrate Polymers, 68*(2), 305–313. https://doi.org/10.1016/j.carbpol.2006.12.004.

Han, H., Hou, J., Yang, N., Zhang, Y., Chen, H., Zhang, Z., ... Guo, S. (2019). Insight on the changes of cassava and potato starch granules during gelatinization. *International Journal of Biological Macromolecules, 126*, 37–43. https://doi.org/10.1016/j.ijbiomac.2018.12.201.

Haq, F., Yu, H., Wang, L., Teng, L., Haroon, M., Khan, R. U., ... Nazir, A. (2019). Advances in chemical modifications of starches and their applications. *Carbohydrate Research, 476*, 12–35. https://doi.org/10.1016/j.carres.2019.02.007.

Hu, X., Guo, B., Liu, C., Yan, X., Chen, J., Luo, S., ... Wu, J. (2018). Modification of potato starch by using superheated steam. *Carbohydrate Polymers, 198*, 375–384. https://doi.org/10.1016/j.carbpol.2018.06.110.

Ji, Y., Yu, J., Xu, Y., & Zhang, Y. (2016). Impact of dry heating on physicochemical properties of corn starch and lysine mixture. *International Journal of Biological Macromolecules, 91*, 872–876. https://doi.org/10.1016/j.ijbiomac.2016.06.040.

Juliano, B. O. (1971). A simplified assay for milled-rice amylose. *Cereal Science Today, 16*, 334–340.

Kurdziel, M., Łabanowska, M., Pietrzyk, S., Sobolewska-Zielińska, J., & Michalec, M. (2019). Changes in the physicochemical properties of barley and oat starches upon the use of environmentally friendly oxidation methods. *Carbohydrate Polymers, 210*, 339–349. https://doi.org/10.1016/j.carbpol.2019.01.088.

Li, Y., Zhang, H., Shoemaker, C. F., Xu, Z., Zhu, S., & Zhong, F. (2013). Effect of dry heat treatment with xanthan on waxy rice starch. *Carbohydrate Polymers, 92*(2), 1647–1652. https://doi.org/10.1016/j.carbpol.2012.11.002.

Limberger, V. M., Da Silva, L. P., Emanuelli, T., Comarela, C. G., & Patias, L. D. (2008). Modificação química e física do amido de quirera de arroz para aproveitamento na indústria de alimentos. *Quimica Nova, 31*(1), 84–88. https://doi.org/10.1590/S0100-40422008000100018.

Liu, Z., Bhandari, B., Prakash, S., & Zhang, M. (2018). Creation of internal structure of mashed potato construct by 3D printing and its textural properties. *Food Research International, 111*(March), 534–543. https://doi.org/10.1016/j.foodres.2018.05.075.

Liu, K., Hao, Y., Chen, Y., & Gao, Q. (2019). Effects of dry heat treatment on the structure and physicochemical properties of waxy potato starch. *International Journal of Biological Macromolecules, 132*, 1044–1050. https://doi.org/10.1016/j.ijbiomac.2019.03.146.

Liu, Y., Liang, X., Saeed, A., Lan, W., & Qin, W. (2019). Properties of 3D printed dough and optimization of printing parameters. *Innovative Food Science & Emerging Technologies, 54*, 9–18. https://doi.org/10.1016/j.ifset.2019.03.008.

Liu, R., Sun, W., Zhang, Y., Huang, Z., Hu, H., & Zhao, M. (2019). Preparation of starch dough using damaged cassava starch induced by mechanical activation to develop staple foods: Application in crackers. *Food Chemistry, 271*, 284–290. https://doi.org/10.1016/j.foodchem.2018.07.202.

Llanos, J. H. R., & Tadini, C. C. (2018). Preparation and characterization of bio-nano-composite films based on cassava starch or chitosan, reinforced with montmorillonite or bamboo nanofibers. *International Journal of Biological Macromolecules, 107*, 371–382. https://doi.org/10.1016/j.ijbiomac.2017.09.001.

Lopez-Sanchez, P., Nijsse, J., Blonk, H. C. G., Bialek, L., Schumm, S., & Langton, M. (2011). Effect of mechanical and thermal treatments on the microstructure and rheological properties of carrot, broccoli and tomato dispersions. *Journal of the Science of Food and Agriculture, 91*(2), 207–217. https://doi.org/10.1002/jsfa.4168.

Maniglia, B. C., Lima, D. C., Junior, M. D. M., Le-Bail, P., Le-Bail, A., & Augusto, P. E. D. (2019). Hydrogels based on ozonated cassava starch: Effect of ozone processing and gelatinization conditions on enhancing printability for 3D-printing applications. *International Journal of Biological Macromolecules, 138*, 1087–1097.

Matta Junior, M. D., Castanha, N., dos Anjos, C. B. P., Augusto, P. E. D., & Sarmento, S. B. S. (2019). Ozone technology as an alternative to fermentative processes to improve the oven-expansion properties of cassava starch. *Food Research International*. https://doi.org/10.1016/j.foodress.2019.04.050.

Nara, S., & Komiya, T. (1983). Studies on the relationship between water-satured state and crystallinity by the diffraction method for moistened potato starch. *Starch - Stärke, 35*(12), 407–410. https://doi.org/10.1002/star.19830351202.

Oh, I. K., Bae, I. Y., & Lee, H. G. (2018). Effect of dry heat treatment on physical property and in vitro starch digestibility of high amylose rice starch. *International Journal of Biological Macromolecules, 108*, 568–575. https://doi.org/10.1016/j.ijbiomac.2017.11.180.

Pelissari, F. M., Andrade-Mahecha, M. M., Sobral, P. J.do A., & Menegalli, F. C. (2012). Isolation and characterization of the flour and starch of plantain bananas (Musa paradisiaca). *Starch - Stärke, 64*(5), 382–391. https://doi.org/10.1002/star.201100133.

Pramodrao, K. S., & Riar, C. S. (2014). Comparative study of effect of modification with ionic gums and dry heating on the physicochemical characteristic of potato, sweet potato and taro starches. *Food Hydrocolloids, 35*, 613–619. https://doi.org/10.1016/j.foodhyd.2013.08.006.

Severini, C., & Derossi, A. (2016). Could the 3D printing technology be a useful strategy to obtain customized nutrition? *Journal of Clinical Gastroenterology, 50*(2), 175–178.

Smith, R. J. (1967). *Production and use of hypochlorite oxidized starches. Starch chemistry and technology*. New York: Academic Press.

Song, Y., & Jane, J.-L. (2000). Characterization of barley starches of waxy, normal, and high amylose varieties. *Carbohydrate Polymers, 41*(4), 365–377. https://doi.org/10.1016/S0144-8617(99)00098-3.

Sun, Q., Gong, M., Li, Y., & Xiong, L. (2014). Effect of dry heat treatment on the physicochemical properties and structure of proso millet flour and starch. *Carbohydrate Polymers, 110*, 128–134. https://doi.org/10.1016/j.carbpol.2014.03.090.

Sun, Q., Sun, C., & Xiong, L. (2013). Mechanical, barrier and morphological properties of pea starch and peanut protein isolate blend films. *Carbohydrate Polymers, 98*(1), 630–637. https://doi.org/10.1016/j.carbpol.2013.06.040.

Sun, Q., Xu, Y., & Xiong, L. (2014). Effect of microwave-assisted dry heating with xanthan on normal and waxy corn starches. *International Journal of Biological Macromolecules, 68*, 86–91. https://doi.org/10.1016/j.ijbiomac.2014.04.032.

Wang, S., Li, C., Copeland, L., Niu, Q., & Wang, S. (2015). Starch retrogradation: A comprehensive review. *Comprehensive Reviews in Food Science and Food Safety, 14*(5), 568–585. https://doi.org/10.1111/1541-4337.12143.

Yang, F., Guo, C., Zhang, M., Bhandari, B., & Liu, Y. (2019). Improving 3D printing process of lemon juice gel based on fl uid fl ow numerical simulation. *LWT - Food Science and Technology, 102*, 89–99. https://doi.org/10.1016/j.lwt.2018.12.031.

Zheng, H. (2018). Polymers for structure design of dairy foods. *Polymers for food applications* (pp. 509–528). Springer.

Zhu, F. (2015). Composition, structure, physicochemical properties, and modifications of cassava starch. *Carbohydrate Polymers, 122*, 456–480. https://doi.org/10.1016/j.carbpol.2014.10.063.

Zou, J., Xu, M., Tian, J., & Li, B. (2019). Impact of continuous and repeated dry heating treatments on the physicochemical and structural properties of waxy corn starch. *International Journal of Biological Macromolecules, 135*, 379–385.