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Modification of maize starch by dry heating treatment (DHT) and its use as gelling ingredients in fruit-based 3D-printed food for dysphagic people

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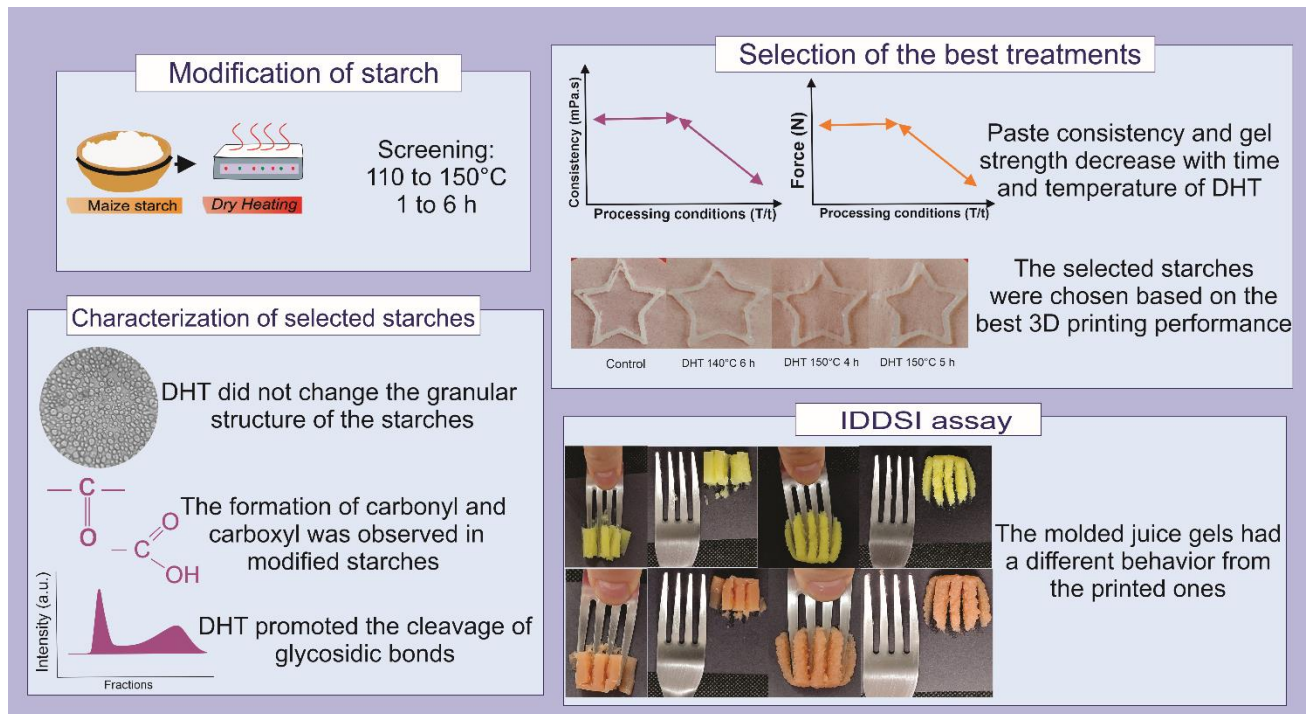
^c Université Paris-Saclay, CentraleSupélec, Laboratoire de Génie des Procédés et Matériaux, Centre Européen de Biotechnologie et de Bioéconomie (CEBB), 3 rue des Rouges Terres 51110 Pomacle, France, * corresponding author pedro.augusto@centralesupelec.fr

Abstract

This study explores the use of 3D printing technology to obtain food products for individuals with dysphagia. Maize starch was modified using dry heating treatment (DHT), under 30 different conditions (110-150°C, 1-6 h), to be used as gelling ingredients for fruit-based foods. The modified starches were assessed in relation to their 3D printing potential and the texture necessities of dysphagic diets (following the International Dysphagia Diet Standardization Initiative - IDDSI). The DHT conditions with better performance were then used for gelling two fruit juices with extreme pHs (orange and watermelon). The DHT treatment improved the printability of the modified maize starch, with the conditions at 140°C for 6 h, 150°C for 4 h and 5 h demonstrating the best performance. Furthermore, the gels produced using these modified starches and fruit juices were classified according to the IDDSI standards as level 5 (printed gels) and 6 (molded gels). Structure and properties of modified starches were also evaluated. In summary, this study highlights the potential of modified starches as gelling agents in 3D printing for creating food products tailored to individuals with dysphagia, thus expanding the application of starches in food production.

Keywords: Corn; Starch Modification; IDDSI assay; Fork test; Dysphagic diets; Tailor-made texture.

Graphical abstract



Highlights

- Dry Heating Treatment (DHT) was studied in a broad range of conditions.
- DHT reduced the pasting consistency and gel strength of starch.
- The starches could be used for gelling two fruit juices with different pHs.
- The printed gels differed from the molded ones in the IDDSI classification.
- Starch modification was characterized in relation to properties.

1 Introduction

3D printing has proved to be a valuable technology in food prototyping, due to the possibility of developing personalized foods in relation not only to shape, but also to composition and properties (Le-Bail et al., 2020). One of the most interesting applications for this technology is developing foods tailored to people who have difficulties in chewing and swallowing. This condition, known as dysphagia (Dick et al., 2020), is often associated with malnutrition, dehydration, chest infection, and potential risk of death (Cichero et al., 2013). Dysphagia affects a relevant percentage of elderly population, and recently reported to be a problem in patients who passed through intubation and extubation due to COVID-19 (Mohan and Mohapatra, 2020; Ortega et al., 2017).

One of the ways to reduce the impact of dysphagia is modifying the texture of solid foods and the consistency/viscosity of liquid foods. Some works have demonstrated the potential of 3D application in products for dysphagia, such as foods based on 3D printing using purees of fungi (Xing et al., 2022) and mushrooms (Liu et al., 2021), beef (Dick et al., 2021) and pork (Dick et al., 2020), fish (Kouzani et al., 2017) and vegetable (Pant et al., 2021). In all those cases, it is necessary to associate a functional ingredient to form gel for printing.

In fact, for an ingredient to be used as “printing ink” it must be able to flow through the print nozzle and then maintain its structure and stability after printing (Lille et al., 2018). Starches, for example, have been considered an interesting alternative due to its high availability and low cost. However, there are only few available sources of native starches, limiting their application. Modification processes can be an alternative to expand starch applications. In fact, the dry heating treatment (DHT) is a simple, safe and physical modification method of starch modification, that does not use any chemical reactive and does not produce effluents (Maniglia et al., 2020a), hence represent a useful method for food application.

DHT could generate starches with lower solubility, lower retrogradation, stronger gels, lower molecular size, and granule crystallinity (depending on the source and conditions). Some works have demonstrated the potential of DHT to modify starches for 3D printing

(Bitencourt et al., 2023; Maniglia et al., 2020b, 2020c; Sartori et al., 2023). Despite the growing number of works with 3D printing of foods, the evaluation of new ingredients, the impact on their properties, and application in a new product is still missing. Therefore, the objective of this study was to employ DHT to modify maize starch, subsequently utilizing it to create gels with fruit juices. Additionally, the study aimed to assess the suitability of these modified starch-based gels for both 3D printing applications and as components of dysphagic diets.

2 Material and methods

This work was divided in three steps as shown in fig. 1.

The first step promoted the DHT processing of maize starch, considering a broad range of processing conditions, and then conducting a screening to select the best ingredients for the desired purpose. The screening comprises the evaluations of starch pasting and gel properties, as well as the 3D printability of the obtained hydrogels. Some processing conditions were, then, selected for the next step in this work.

The second step focused on obtaining food analogues by using fruit juices and the selected modified starches, as ingredients for 3D printing. In this step, the obtained products were evaluated according to the International Food Standards for Dysphagia (IDDSI, 2019).

In the third step, the modified starches structure (molecular and granules) were evaluated in order to better describe their properties.

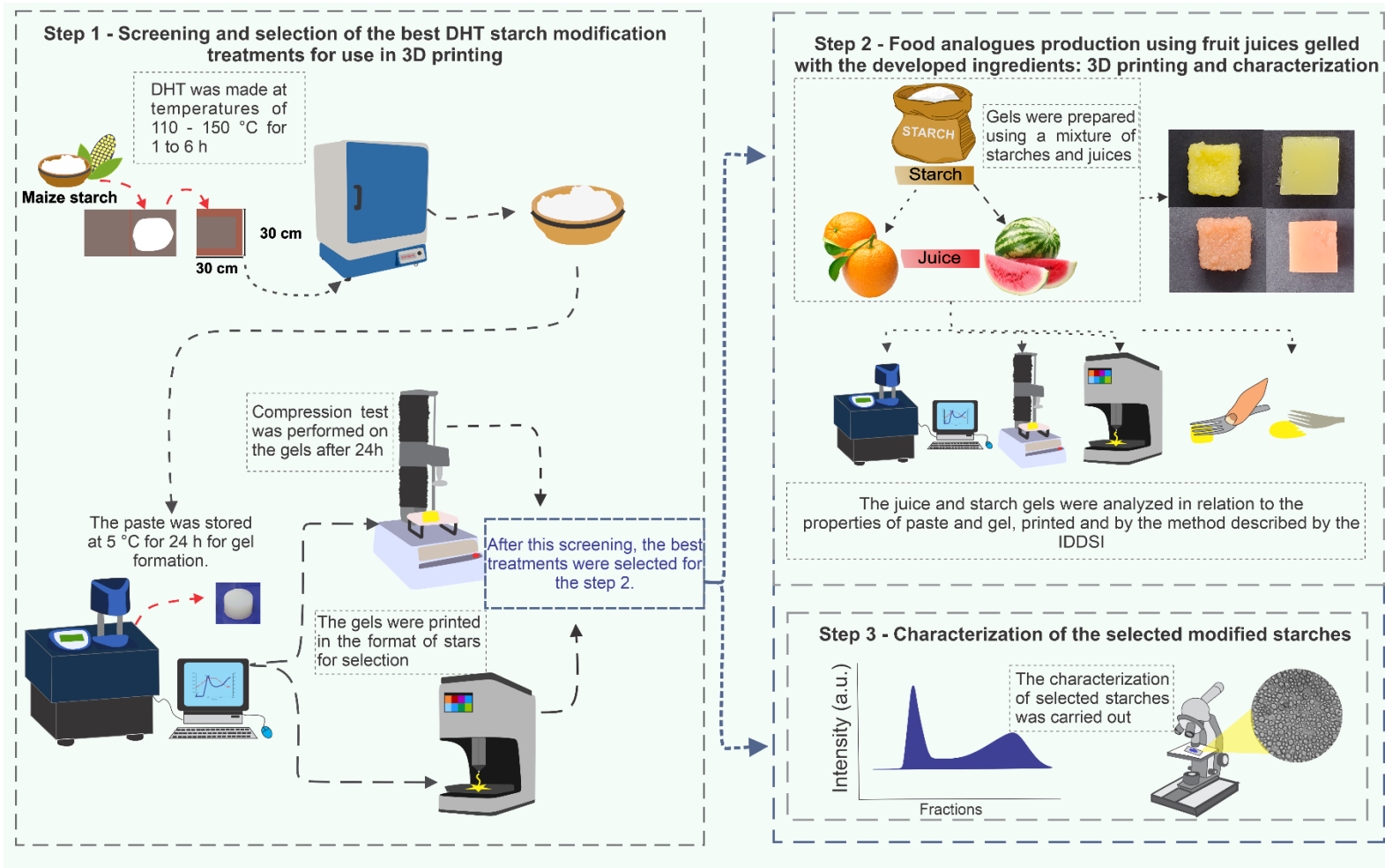


Fig. 1. Illustrative scheme of the steps of this work. Step 1 – modification of maize starch and selection of the best DHT conditions; Step 2 – Production of gels made by juices and starch-modified analyzing suitability for dysphagic diets; Step 3 – Characterization of the selected modified starches.

2.1 Step 01: Screening and selection of the best DHT starch modification treatments for use in 3D printing

2.1.1 Starch modification

Native maize (corn) starch was supplied by Ingredion Brasil Ingredients Ltd (~28% of amylose, Agri Cs 3400) with 12.3% of moisture and purity higher than 99%. The DHT treatment was carried out by varying temperatures from 110 to 150°C for 1 to 6 h. The purpose of this screening was to understand how DHT affected maize starch and which conditions would be most suitable for application in 3D printing.

The DHT treatment was conducted similarly to our previous studies (Maniglia et al., 2020b, 2020c): 30 g of starch were spread on aluminum foil (30x30 cm) in a ~1 cm layer. The package was closed and placed in a hot air stove (Marconi, MA 035/49, Brazil) under the conditions mentioned above. Subsequently, the starch package was cooled at room temperature. Then, they were sieved in 250 µm sieves and stored in closed glass flasks for the further analysis. Each process was conducted in three replicates.

2.1.2 Pasting properties

The Rapid Visco Analyzer (RVA-4, Newport Scientific Pvt. Ltd. Australia, with the Thermocline for Windows software, version 3.0) was used to evaluate the pasting properties of the modified and native starches. A suspension containing 3 g of starch (corrected for 14% wet basis) with 25 g water was subjected to temperature cycles of heating, holding, and cooling under constant shear. First, there was a heating to 50°C for 1 min, followed by a temperature increase to 95°C and maintained at this temperature for 5 min; after, cooling was started until reaching a temperature of 50°C at a rate of 6°C min⁻¹, where it remained for 2 min. The analysis was done in triplicate.

2.1.3 Hydrogel texture

The starch paste obtained after RVA were transferred to plastic cups (21 x 36 mm in height x diameter). The pastes were stored in a desiccator with water and kept at 5°C for 24 h for gelification. After this period, the compression test was performed using a plate probe (P/100) with a diameter of 10 mm, coupled to a texturometer (TA.XT Plus, Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kg-f (490.3 N). The probe was smeared with mineral oil. The hydrogels were demolded and compressed to 75% of their height. The force versus relative strain profile was observed. The analysis was performed in triplicate.

2.1.4 3D Printability

The starch paste was obtained using the RVA and stored in syringes (60 mL) at a temperature of 5°C for 24 h for the formation of hydrogels. Then, the syringes were coupled and immediately processed in a 3D printer (Food 3D Print, Wiiibox Sweetin, Wilking3D Technology Co. Ltd., Naajing, Jiangsu, China). The parameters such as diameter nozzle, speed and infill were previously tested through pre-tests. After pre-tests, a diameter nozzle of 0.84 mm and infill speed of 5 mm/s was selected to print the hydrogels at 25°C.

The hydrogels were printed in star shape in the dimensions 5 x 5 cm (width x length) and 6 layers as shown in Fig. 2. The geometry was created using Autodesk Tinkercad online and exported as an STL file. This figure was made by grouping two stars (one inside the other) so that it was possible to observe the formation of the corners and the connection of the lines. The model was opened in Ultimaker Cura 15.01.01, sliced and exported as an GCode file to be read by the printer.

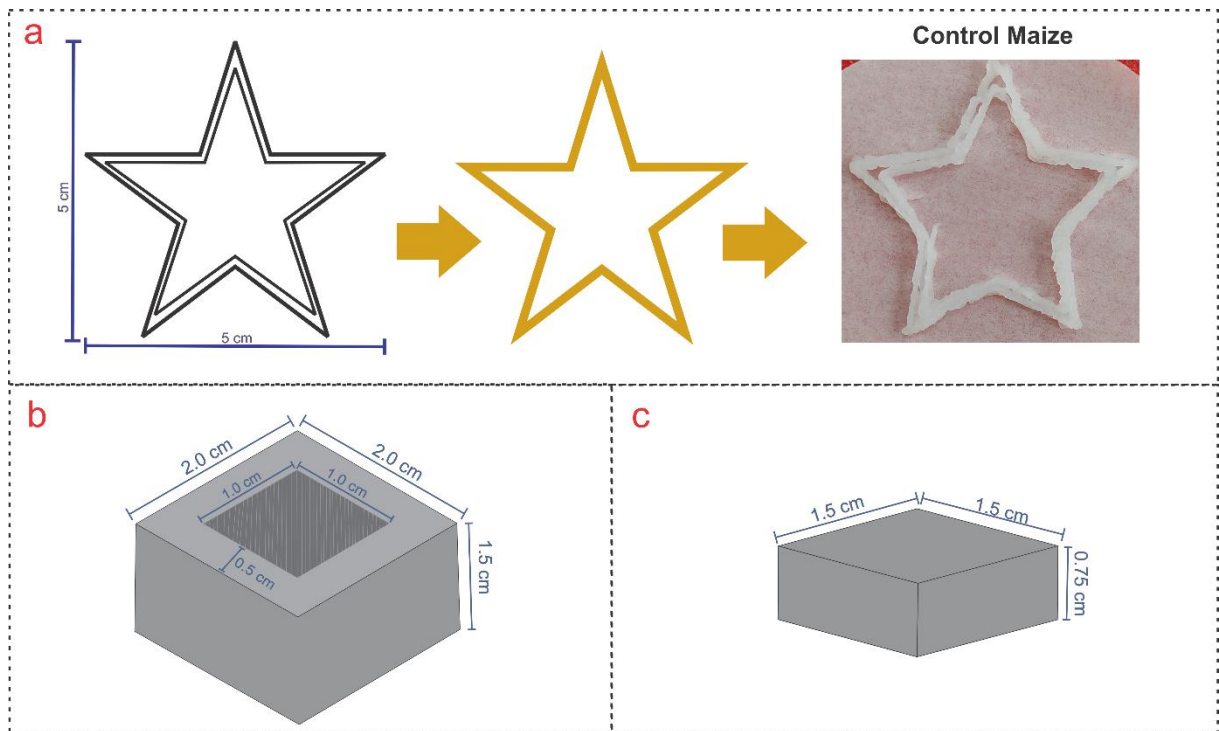


Fig. 2. Geometries selected for 3D printing evaluation. (a) Star format, based on 6 layers and two connected lines. (b) Cuboid model with an internal hole. (c) Cuboid model without internal hole (used for analysis described by IDDSI).

2.2 Step 2: Food analogues production using fruit juices gelled with the developed ingredients: 3D printing and characterization

2.2.1 Preparation of Juice gels

The selected starches were evaluated in relation to their capacity of forming gels with fruit juices (3 g of starch/25 g of juice) for 3D printing, with focus on dysphagic people. The fruits, without peel, were cut into pieces, which were introduced in a juice extractor with a 0.5 mm sieve (Juicer Centrifuge, Philips Walita, Taiwan, China). The gels were produced in the RVA equipment, as described in section 2.1.2, but replacing the water by the obtained orange and watermelon juices. These juices were selected to represent acid (orange, pH = 3.9) and low-acid (watermelon, pH = 5.1) fruit juices. The juice`s brix were 6.4 ± 0.1 (orange) and 7.87 ± 0.23 (watermelon).

The gels were made as described in item 2.1.3 and 2.1.4. The pastes were obtained by RVA and then they were transferred to plastic cups (21 x 36 mm in height x diameter) and syringes (60 mL), which were stored in a desiccator with water at 5°C for 24 h.

2.2.2 Printability of juice gels

To evaluate printability, 3D printing was performed in two different ways: as stars (as mentioned in item 2.1.4 and Fig. 2- a) and as cuboid model with an internal hole geometry. The cuboid (dimensions are indicated in Fig. 2- b) was analyzed using ImageJ 1.8 software (National Institutes of Health, U.S) to verify in which extent the printed food would correspond to the original model.

2.2.3 IDDSI assay and texture analyzer attachment

In order to analyze whether the gels had the appropriate texture for people with dysphagia, the standard test described by the IDDSI was performed (IDDSI, 2019).

Due to the characteristic of the gel, the fork pressure test was applied. This test is done by pressing down on the food sample by placing the thumb on the base of the fork, just below the prongs, and pressing down hard enough to cause blanching of the thumbnail. The pressure exerted by the thumb, in such case, is related with the one exerted by the tongue during swallowing (approximately 17 kPa) – and blanching occurs when the pressure overcomes mean arterial blood pressure, justifying the method (Cichero et al., 2017; IDDSI, 2019; Sungsinchai et al., 2019) . The tests were performed always by the same trained person. Both molded gels and printed gels in cuboid format were prepared. The gels were kept under refrigeration at 5°C for 24 h. The in-mold gels were unmolded and then the fork pressure test performed. The gels were printed as a cuboid (1.5x1.5x0.75 cm; with travel and infill speed of 10 mm/s, at 25°C) Fig. 2- c, for the dysphagia adequacy assay. The molded gels had the same dimensions as printed gels.

In order to obtain quantitative information from the standard test of IDDSI an accessory compatible with the texture analyzer (TA.XT Plus, Stable Micro Systems Ltd., Surrey, United Kingdom) was also applied – as described by Pematilleke et al. (2022) and developed by

Lancha et al. (2022). Using the texturometer, controlled conditions of speed, rest time of the fork on the sample could be applied and recorded. Both the printed and moulded gel were analysed. For the test, the fork was attached to the texture analyzer and penetrated the gels until reaching a force of 4.8 N (the same force used during manual compression, measured by a scale). Upon reaching this force, the pressure was maintained for 5 s, then the pressure was removed, following the same standards of manual analysis. The test was conducted in triplicate.

2.2.5 Texture profile analysis

Finally, the texture profile analysis (TPA) was evaluated for both molded and printed gels, using the same 3D shape as that used for the fork pressure test (Fig. 2- c). The test was conducted at room temperature and three replications were measured. Both molded and printed gels followed the same conformations described above for the fork pressure test. A plate-plate probe of 35 mm of diameter (SMS P/35) was used. The parameters selected for this test were similar to those used by Xing et al. (2022), two compression cycles were carried out as follows: pre-test rate was 5 mm/s, test and post-test rate are 2 mm/s, holding time was 5 s and compression strain was 45%.

2.3 Step 3: Characterization of the selected modified starches

2.3.1 Granule characterization

The starch granular structure was analyzed by light microscope and under polarized light (model L1000, Bioval, Curitiba, Brazil; with a 20 W halogen lamp and a magnification of 40x). The starches were dispersed in aqueous solution, placed on glass slides, covered by a glass coverslip, and analyzed. A polarized light filter was attached to the microscope to observe the Maltese cross.

2.3.2 pH, carbonyl and carboxyl content

The pH of a 10.7% (w/w) starch suspension (25°C) was obtained using a potentiometer (model TEC-5, Tecnal, Piracicaba, Brazil).

The carbonyl and carboxyl content were obtained according to method described by Smith (Smith, 1967) and Chattopadhyay and Singhal (Chattopadhyay et al., 2002), with some modifications.

To obtain the carboxyl content, 2 g of starch (dry basis) was dispersed in 25 mL of HCl (0.1 M) solution and stirred for 30 min at 25°C. Then, the solution was vacuum filtered using filter paper (205 µm) and washed with 400 mL of distilled water. Subsequently, the starch was suspended in 300 mL of distilled water and brought to a boiling water bath, being stirred using a magnetic stirrer at 250 rpm for 15 min. After gelatinization, the paste was immediately titrated with NaOH solution (0.01 M) until pH 8.3. Native starch was used as a blank and the results were expressed as the amount of carboxyl groups per 100 glucose units (COOH/100GU), as described in equation 1.

$$\frac{COOH}{100GU} = \frac{((V_s - V_b) \cdot M \cdot 0.045 \cdot 100)}{SM} \quad \text{Equation 1}$$

Where:

V_s = Volume of NaOH (mL) required for the modified samples;

V_b = Volume of NaOH (mL) used in the blank;

M = Molarity of NaOH (mol/L);

SM = Sample mass (g) on dry basis.

For carbonyl content, 4 g of starch (dry basis) was dispersed in 100 mL of distilled water. The suspension was placed in a boiling bath with magnetic stirring (250 rpm) for 20 min for complete gelatinization. Then, the gelatinized sample was placed in a bath at 40°C until cooling. Afterwards, the pH of the solution was adjusted to 3.2 using HCl solution (0.1 M). Then, 15 mL of hydroxylamine solution (made with 5% of hydroxylamine hydrochloride, 20% of 0.5 M NaOH solution, and distilled water until the solution reach 200 mL) was added to the

sample, with remained in a 40°C water bath (Marconi, Piracicaba, Brazil) for 4 h. Finally, excess hydroxylamine was titrated with 0.1 M HCl until pH 3.2. The blank preparation followed all the steps described above, but without the addition of the sample. The carbonyl content result was obtained through equation 2 and expressed as the amount of carbonyl groups per 100 glucose units (CO/100GU).

$$\frac{CO}{100GU} = \frac{(V_b - V_s) \cdot M \cdot 0.028 \cdot 100}{SM} \quad \text{Equation 2}$$

Where:

V_b = Volume of HCl (mL) used in the blank;

V_s = Volume of HCl (mL) required for the modified samples;

M = Molarity of HCl (mol/L);

SM = Sample mass (g) on dry basis.

2.3.3 Molecular size distribution

The molecular size distribution was analyzed using gel permeation chromatography (GPC) as described by Song & Jane (Song and Jane, 2000) with some modifications. For this analysis the GE XK 26/70 column (Cytiva, United States), 2.6 cm in diameter and 70 cm in length, was packed with Sepharose CL-2B gel (Sigma, Sweden). After that, 0.1 g of sample was dissolved in 10 mL of dimethyl sulfoxide solution (90%) and placed in a boiling bath (~100°C) with constant stirring (250 rpm) for 1 h. After this period, the sample was removed from the boiling bath and placed in another bath, at 25°C, with constant agitation for 16 h. Subsequently, an aliquot of 3 mL of sample was mixed with 10 mL of absolute ethanol and placed in a centrifuge (Routine 420R, Hettich, USA), at 20°C, 3000 g for 30 min. Then, the supernatant was discarded, and the precipitate was suspended in 9 mL of water and heated until complete gelatinization. After reaching room temperature, an aliquot of 4 mL was injected into the chromatography column with an eluent solution (25 mmol·L⁻¹ of NaCl and 1 mmol·L⁻¹ of NaOH) at a rate of 25 mL·h⁻¹. Fractions were separated and collected 4 mL per tube using the fraction collector (Gilson, model FC203B, Middleton, England). After separating the

fractions, they were analyzed using the blue value method, as described by Juliano (1971) with modifications. For this, 1 mL of a stock solution of I_2/KI (1 g of potassium iodide (KI) and 0.1 g of iodine (I_2)) was added to the tubes containing the sample and read at 620 nm using a spectrophotometer (spectrometer Femto, Model 600S, São Paulo, Brazil). After that, a graph with absorbance values of each fraction was plotted and presented in absorbance at 630 nm vs fractions.

2.4 Experimental design and statical analysis

To carry out this work, all analyzes were performed in triplicate in a completely random design. The average values were calculated and, when appropriate, the Tukey multiple comparison was used through Minitab software (Minitab ® 19.1 2019, USA). A significance level of 5% was considered. Graphs were plotted using Excel (Microsoft 365 version 2307 build 16.0.16626.20198) and Origin software (9.9.5.171 Copyright © 1991-2022 OriginLab Corporation).

3 Results and Discussion

3.1 Step 1: Screening and selection of DHT conditions

The first column in Fig. 3 shows the pasting properties curves of all treatments and control, while the second column represents the deformation curves of the hydrogels, obtained by compression. It is possible to observe a reduction in the strength of the hydrogels and the consistency of the pastes as the time and temperature of DHT were increased. This behavior becomes more evident from the processing temperature of 120°C.

Different results are reported in the literature regarding starch modified by DHT and native starch. In high amylose rice starch, the pastes of DHT modified starch had higher apparent viscosities than the native one, when the starch was processed at 110°C; however, under conditions of 130°C 4 h, 150°C 2 and 4 h, the opposite behavior was obtained (Oh et al., 2018). Lei et al. (2020) observed an increase in apparent viscosity of maize paste when

the starch was processed at temperatures from 140 to 170°C, while the reduction was only observed from 190°C. A reduction in paste consistency was also reported for wheat (Maniglia et al., 2020b) and cassava (Maniglia et al., 2020c) starches. DHT can break the intra and/or inter molecular bonds between the hydrogen chains of starches, and excessive heat can cleave glycosidic bonds, resulting in a decrease in consistency (Li et al., 2013).

Although the behavior of cassava and wheat pastes were similar to that of maize starch, the hydrogel of cassava and wheat showed an increase in firmness when treated with DHT (Maniglia et al., 2020b, 2020c). Therefore, starch modification by DHT can generate both strong and weaker hydrogels, depending on process intensity and starch source, since each source reacts differently even with the same technological modification – due to the balance between molecular attractive and repulsive interactions (due to the formation of new functional groups) and molecular packing behavior (due to the new molecular size distribution), as discussed in section 3.3.

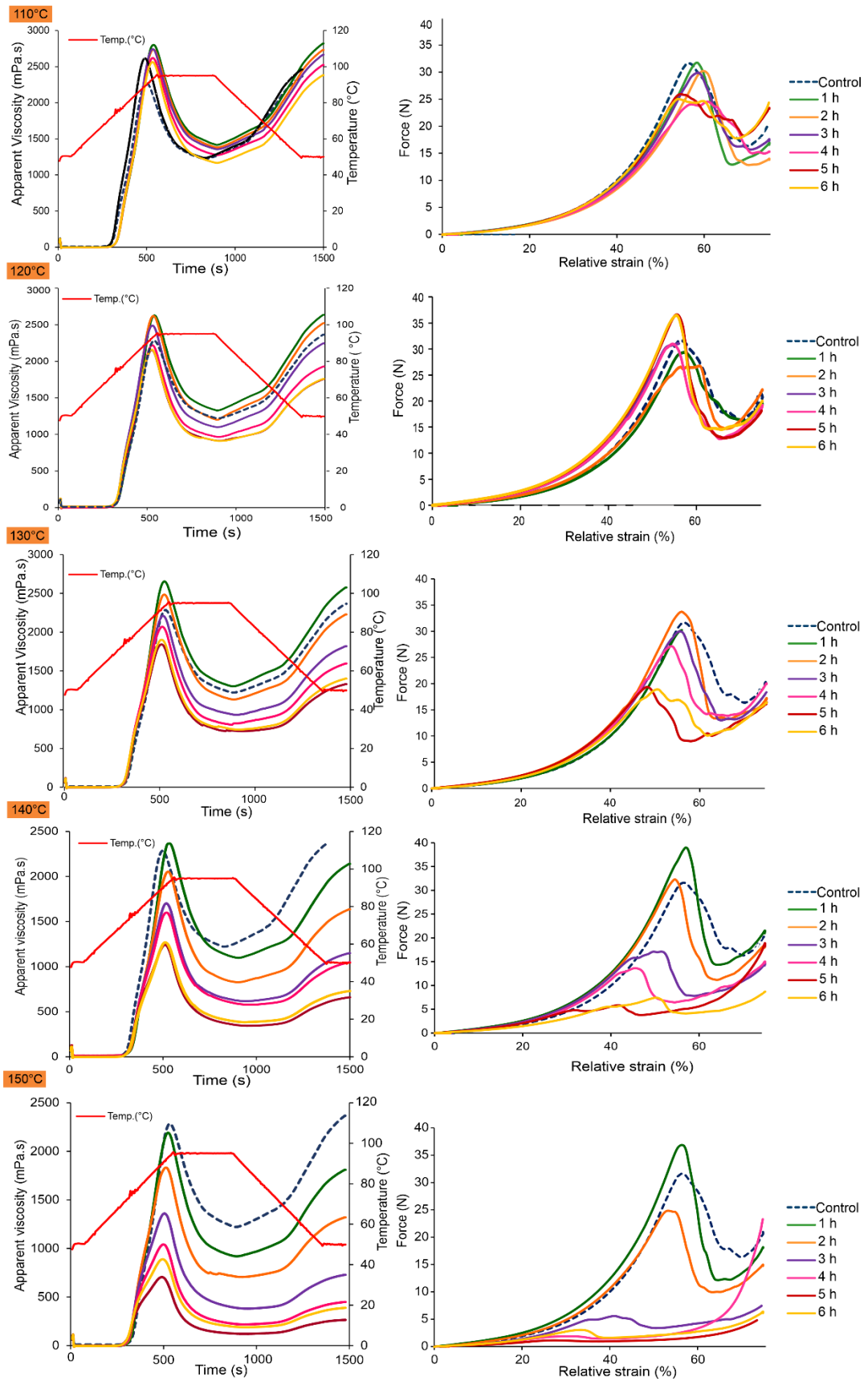


Fig. 3. The first column shows the curves of the starch pasting properties (native, without modification and the dry heating treatment modified starches for 1 to 6 h at 110 to 150°C). The

second column represents the force versus relative strain curves when evaluating the texture of the hydrogels obtained from each starch.

Table 1 shows the image of the 3D printed stars produced using the hydrogels from control and DHT-treated starches. At first, it is possible to observe that most of the hydrogels were able to be printed, although with different performances – evaluated as described in Table 1. However, the hydrogel obtained in the most drastic DHT condition (150°C for 6 h) could not be printed; being very weak, it was deposited in the form of drops instead of layers during extrusion.

Even though maize starch has a firm hydrogel in its native form (control maize), allowing its printability, it is possible to observe that the printed hydrogel presents irregularities on the lines, due to the plastic characteristic of this hydrogel. Three elements demonstrate this: (1) the star lines are not continuous and smooth, (2) the two side-by-side printed lines are separated, instead of being joined, and (3) the star points/edges are not well defined. Therefore, although the hydrogel from native maize starch can be used for 3D printing, the resolution of the obtained material is poor, highlighting the need for developing new ingredients, as modified starches.

Stars printed with hydrogels treated at 100-130°C for 1 to 6 h, 140°C for 1 to 5 h, and 150°C for 1 to 3 h were very similar to the control starch, showing irregularities within the lines and bad definition (mainly with line separation) (Table 2).

On the other hand, the hydrogels from the treatments DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h showed good definition, and they did not present irregularities on the lines. As described, the hydrogel obtained from the treatment at DHT 150°C 6 h was too weak that it was not possible to obtain a well-defined design.

Analyzing those results, it is interesting to note some important points. Very strong plastic hydrogels may have bad print quality, as their extrusion becomes difficult and discontinuous, generating designs with low definition and irregular surfaces. However, the

other extreme also does not present desirable characteristics for 3D printing: very weak hydrogels cannot sustain themselves and, in some cases, do not flow in the printer's nozzle, being dripped; they are not able to form a design with good definition. Finally, hydrogels printed from different sources modified by DHT show different behavior. For example, the DHT processing applied to cassava starch produced stronger hydrogels compared to the control; those hydrogels, when used in 3D printing, presented drawings with better definitions, well defined angles and conditions lines than the control (Maniglia et al., 2020c). It is important to highlight that the cassava starch is known to form a weak hydrogel, in comparison with other sources, being the maize starch hydrogel one of the strongest (Castanha et al., 2021). In wheat starch, DHT also promoted an increase in hydrogel strength, slightly improving their printability, with greater cohesiveness and more continuous lines in relation to the native starch gels (Maniglia et al., 2020b).

Therefore, each starch source responds differently to process conditions, affecting differently their properties and applicability. With those results, the following DHT conditions were selected for the next step, since their hydrogels demonstrated a smoothy and continuous performance when extruded from the nozzle, kept its structure after printing, there were no separation of the lines, presented high resolution, with well-defined angles, and showed no breakage of deposited lines, as shown in Table 1: DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h.

Another factor observed in the choice of treatments was the gel behavior during compression: the selected treatments present a breaking curve during compression that is more consistent with what is expected for a product when chewed by people with dysphagia. For example, the force during compression test increases for the control (native starch) up to ~40 N, where there is a break to ~25 N, from which the product continues to be compressed and the deformation resistance increases (Fig. 3). This behavior demonstrates a pattern of gel breaking (plastic behavior) instead of crumpling. Treatments with modified starches, show a much less pronounced drop (for example, in DHT 140°C for 6 h, the force increases until ~2 N

and then is reduced to ~1 N), indicating that there is no formation of large pieces with the breaking but only a continuous crumpling of the gel. This factor is important for individuals who have inefficient chewing ability, as large pieces of food can lead to a choking hazard (Cichero et al., 2013).

The selected starches were then evaluated in the second step.

Table 1. Parameters analyzed during and after 3D printing of the starch hydrogels, to define the best treatments to be used for printing the hydrogels. Symbols in each evaluation: ✓ = yes; ✗ = no.









Sample		Smoothy and continuously extruded from the nozzle	Keeps the structure after printing	Smoothy and continuously lines	Without separation of lines	Higher resolution (well-defined star points)	Broken deposited lines	Treatment selected for the next step
What is desired in each parameter →		✓	✓	✓	✓	✓	✗	✓
Control		✓	✓	✗	✗	✗	✓	✓
DHT 110°C 1 h		✓	✓	✗	✗	✗	✓	✗
DHT110°C 2 h		✗	✓	✗	✗	✗	✓	✗
DHT110°C 3 h		✗	✓	✗	✗	✗	✓	✗
DHT110°C 4 h		✗	✓	✗	✗	✗	✓	✗
DHT110°C 5 h		✗	✓	✗	✗	✗	✓	✗
DHT110°C 6 h		✗	✓	✗	✗	✗	✓	✗
DHT120°C 1 h		✗	✓	✗	✗	✗	✓	✗

Table 1. continues in the next page.















Sample		Smoothy and continuously extruded from the nozzle	Keeps the structure after printing	Smoothy and continuously lines	Without separation of lines	Higher resolution (well-defined star points)	Broken deposited lines	Treatment selected for the next step
What is desired in each parameter →		✓	✓	✓	✓	✓	✗	✓
DHT120°C 2 h		✗	✓	✗	✗	✗	✓	✗
DHT120°C 3 h		✗	✓	✗	✗	✗	✓	✗
DHT120°C 4 h		✗	✓	✗	✗	✗	✓	✗
DHT120°C 5 h		✗	✓	✗	✗	✗	✓	✗
DHT120°C 6 h		✗	✓	✗	✗	✗	✓	✗
DHT 130°C 1 h		✗	✓	✗	✗	✗	✓	✗
DHT 130°C 2 h		✗	✓	✗	✗	✗	✓	✗
DHT 130°C 3 h		✗	✓	✗	✗	✗	✓	✗
DHT 130°C 4 h		✗	✓	✗	✗	✗	✓	✗

Table 1. continues in the next page.

Sample		Smoothy and continuously extruded from the nozzle	Keeps the structure after printing	Smoothy and continuously lines	Without separation of lines	Higher resolution (well-defined star points)	Broken deposited lines	Treatment selected for the next step
What is desired in each parameter →		✓	✓	✓	✓	✓	✗	✓
DHT 130°C 5 h		✗	✓	✗	✗	✗	✓	✗
DHT 130°C 6 h		✗	✓	✗	✗	✗	✓	✗
DHT 140°C 1 h		✗	✓	✗	✗	✗	✓	✗
DHT 140°C 2 h		✗	✓	✗	✗	✗	✓	✗
DHT 140°C 3 h		✗	✓	✗	✗	✗	✓	✗
DHT 140°C 4 h		✗	✓	✗	✗	✗	✓	✗
DHT 140°C 5 h		✗	✓	✗	✗	✗	✗	✗
DHT 140°C 6 h		✓	✓	✓	✓	✓	✗	✓
DHT 150°C 1 h		✗	✓	✗	✗	✗	✓	✗

Table 1. continues in the next page.

Sample		Smoothy and continuously extruded from the nozzle	Keeps the structure after printing	Smoothy and continuously lines	Without separation of lines	Higher resolution (well-defined star points)	Broken deposited lines	Treatment selected for the next step
What is desired in each parameter →		✓	✓	✓	✓	✓	✗	✓
DHT 150°C 2 h		✗	✓	✗	✗	✗	✗	✗
DHT 150°C 3 h		✓	✓	✓	✗	✗	✗	✗
DHT 150°C 4 h		✓	✓	✓	✓	✓	✗	✓
DHT 150°C 5 h		✓	✓	✓	✓	✓	✗	✓
DHT 150°C 6 h		✗	✗	✗	✓	✗	✓	✗

3.2 Step 2: Food analogues production using fruit juices gelled with the developed ingredients: 3D printing and characterization

3.2.1 Printability, IDDSI and gel properties of gels made of starches with orange and watermelon juices

The selected starches and the control were used for gelling watermelon and orange juices, that were printed in two different 3D shapes (a star and a cuboid Fig. 4 column a). These juices were selected due to different pH's: orange juice is an acid food (pH= 3.9), while the watermelon juice is a low acid food (pH= 5.1). The printed stars from juice gels showed the same characteristics as their respective starches printed using only water, described in Table 1 and discussed in section 3.1. Regardless the type of juice, the control treatment presented discontinuous lines, which affects the resolution of the 3D design, although it managed to maintain the height of ~ 1.5 cm. On the other hand, DHT treatments at 150°C did not show self-sustaining characteristics during 3D printing, as they did not support the layers deposited above, as can be seen in the Fig. 4. For example, DHT 150°C 5 h with orange juice was 35% shorter than the model dimensions (Fig. 2 – b), although when printed in the star shape, this treatment was self-sustaining. Conversely, DHT 140°C 6 h demonstrated the best performance in 3D printing for smaller and larger prints, showing continuous line extrusion while supporting the layers deposited above, which is the desirable characteristics for 3D-printed inks.

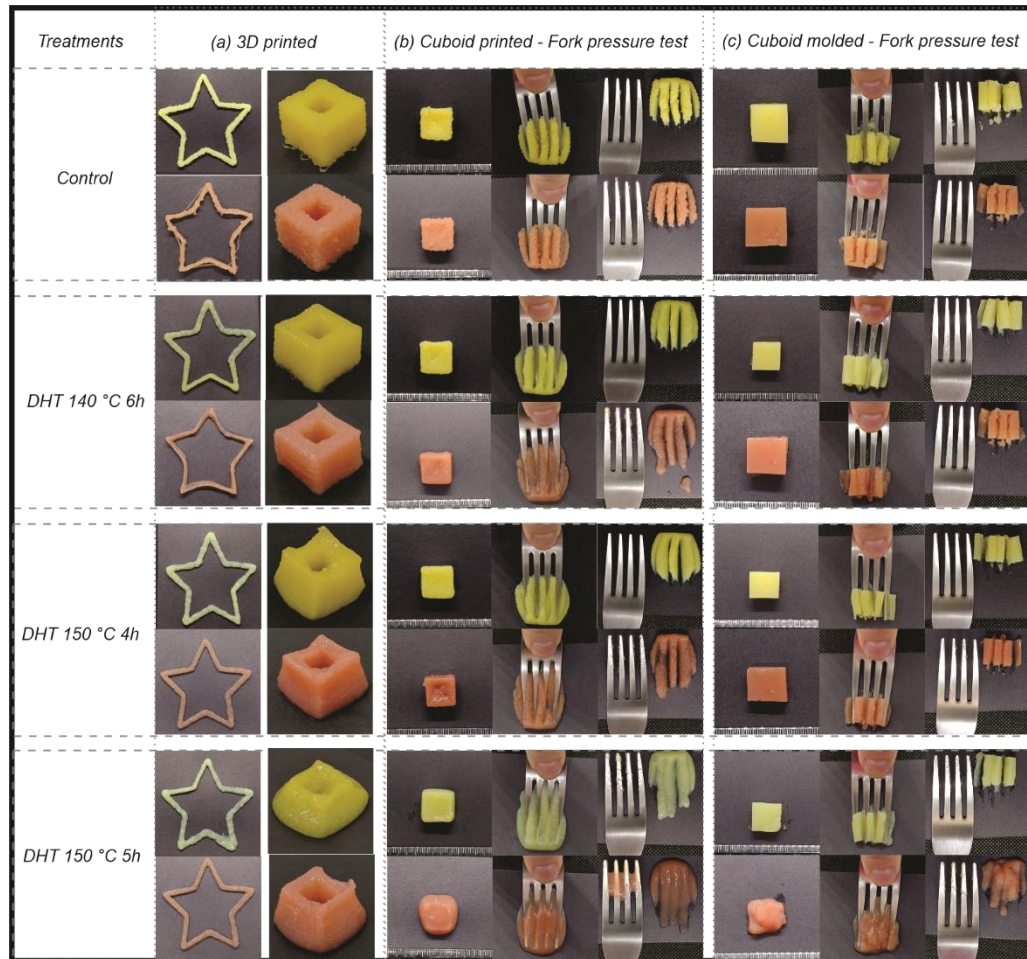


Fig. 4. Images of gels based on control and modified starches by dry heating (DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h) and juice fruits: orange and watermelon (a) shapes printed in 3D; (b) IDDSI assay - fork pressure test using printed gel; (c) IDDSI assay – fork pressure test using molded gel.

Fig. 4 b and c show the molded and printed gels made with DHT-modified maize starch and orange and watermelon juices, before, during and after penetration with the fork, as described by IDDSI standard. Table 2 present the classification of the gels according to the fork pression test described by IDDSI.

During the fork pression test, the gels behave differently. All gels deform and do not return to their original shape. Except for DHT 150°C for 5 h, it is observed that the gels assume the shape of the fork after compression, as can be seen in Fig. 4. The printed gels are penetrated without noticing the thumbnail turned white, being characterized by the IDDSI as

level 5 – “minced and moist” (IDDSI, 2019). The molded gels were characterized as level 6 – “soft and bite-sized” (IDDSI, 2019). The difference between printed and molded gels can be related with the processes that occur after gelling. While the molded gel is only demolded after gelling, the one used for 3D printing is extruded through the nozzle, when it undergoes a sequential process of high and low shear conditions (Chen et al., 2019) – therefore being submitted to a higher extent of mechanical disintegration. This can explain why the molded gels presented a firmer structure than the printed gels.

Level 5 foods are recommended for people who have very weak masticatory muscles; asymmetric chewing capacity; poor language lateralization skills; significant fatigue in chewing over time; low rotational chewing capacity; poor perception of appropriate bite sizes; impulsiveness during eating (Cichero and Correspondence, 2020). Level 6 foods are suitable for people whose masticatory muscles are weak; there is fatigue when chewing over time; asymmetric chewing ability; reduced rotation chewing ability; potentially poor perception of appropriate bite sizes (Cichero and Correspondence, 2020). Therefore, the obtained gels can be intended for individuals with different needs, which can be interesting depending on the purposes.

Table 2. Classification of modified starch and orange and watermelon juice gels using the IDDSI test. Symbols in each evaluation: ✓ = yes; ✗ = no.



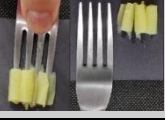





	Sample	Easy to mash with a fork	Blanched white is noted	Shape recovery after fork removed	Can be easily broken with the fork	Separate thin liquid	Level	
	What is desired in each parameter for level 5 →	✓	✗	✗	✓	✗	Level 5	
	What is desired in each parameter for level 6 →	✓	✓	✗	✓	✗	Level 6	
Gel molded	Control		✓	✓	✗	✓	✗	Level 6
			✓	✓	✗	✓	✗	Level 6
	DHT 140°C 6 h		✓	✓	✗	✓	✗	Level 6
			✓	✓	✗	✓	✗	Level 6
	DHT 150°C 4 h		✓	✓	✗	✓	✗	Level 6
			✓	✓	✗	✓	✗	Level 6
	DHT 150°C 5 h		✓	✗	✗	✓	✗	Level 5
			✓	✗	✗	✓	✗	Level 5

Table 2. continues in the next page.









Gel printed	Sample		Easy to mash with a fork	Blanched white is noted	Shape recovery after fork removed	Can be easily broken with the fork	Separate thin liquid	Level
	What is desired in each parameter for level 5 →		✓	✗	✗	✓	✗	Level 5
	What is desired in each parameter for level 6 →		✓	✓	✗	✓	✗	Level 6
Control		✓	✗	✗	✓	✗	Level 5	
		✓	✗	✗	✓	✗	Level 5	
DHT 140°C 6 h		✓	✗	✗	✓	✗	Level 5	
		✓	✗	✗	✓	✗	Level 5	
DHT 150°C 4 h		✓	✗	✗	✓	✗	Level 5	
		✓	✗	✗	✓	✗	Level 5	
DHT 150°C 5 h		✓	✗	✗	✓	✗	Level 5	
		✓	✗	✗	✓	✗	Level 5	

Fig. 5 presents the results obtained from the fork test using an attachment coupled to the texture analyzer. For molded gels made with orange juice, it is possible to observe that the control required greater energy to be penetrated, followed by DHT 140°C for 6 h, while DHT 150°C for 4 and 5 h showed no difference between them. On the other hand, in the gels molded with watermelon juice, there was no difference between the gels made with modified starch, only the control differed. For the printed gels, there was no difference between the modified starches, only between them and the control, which showed higher values regardless of the used juice. The results obtained in this analysis agree with those observed in the hardness parameter in the TPA analysis (Fig. 6) described below.

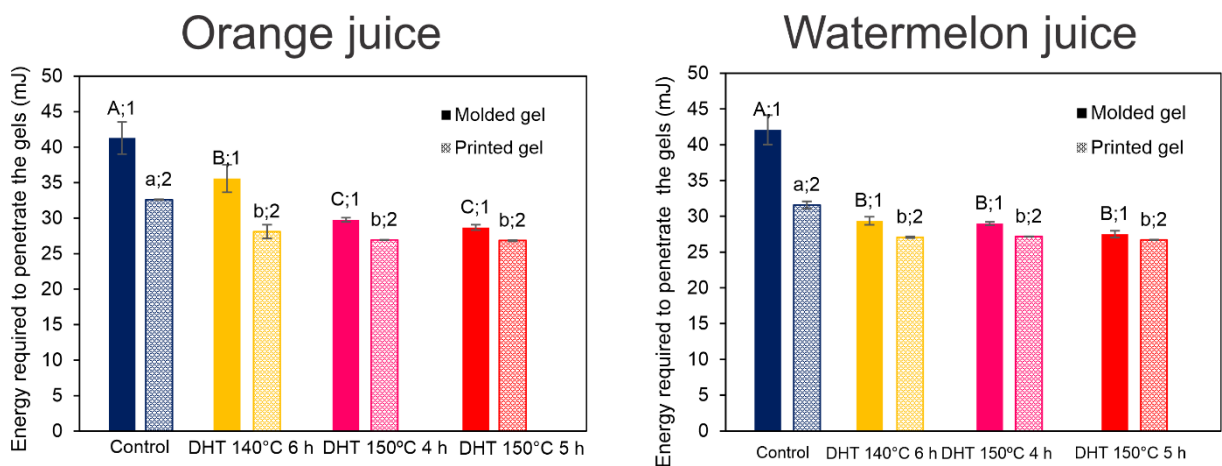


Fig. 5. Energy required to penetrate the gel (mJ) obtained from the fork test using a texture analyzer attachment on 3D printed and molded cuboids for previously selected gels based on control starch and starch modified with orange and watermelon juice. The gels are based on control and modified starches by dry heating (DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h) (average \pm standard deviation). Statistical analysis by Tukey's test ($p < 0.05$): Different uppercase letters indicate a significant difference between the molded gels for the different treatments; different lowercase letter indicates a significant difference between printed gels for the different treatments; different numbers indicate significant difference between molded and printed gels for the same treatment.

Fig. 6 shows the results of TPA analysis for the orange and watermelon juice gels made with the control and DHT-modified starches (DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h). The hardness parameter represents the peak force in the first compression cycle, being bigger for the molded gels than the printed gels, for both juices. Moreover, it was possible to observe that the control treatment was stronger than the modified treatments. This result is in accordance with those obtained for pure starch-water gels, presented in section 3.1.

The gumminess of the gels represents the product of hardness and adhesiveness (Liu et al., 2019) and is defined as the energy expected to break down a semisolid food to a state ready for swallowing (Nishinari and Fang, 2018). The results indicated that the modified starches needed less energy to prepare them for swallowing when compared to the control (i.e., smaller gumminess). This characteristic could make the gels more suitable for dysphagic diets, because they need to be soft, moist and require minimal chewing effort (Suebsaen et al., 2019). This result, therefore, is of high importance for the evaluated purpose.

The adhesiveness must also be evaluated, since it is an important characteristic in foods for this public (the food must be as less “adhesive” as possible to avoid the risk of choking) (Suebsaen et al., 2019). In this work, printed gels were more adhesive than molded gels, regardless of the type of juice. In addition, the modified starches showed higher adhesiveness values than the control. However, it is important to highlight this adhesiveness was measured between the samples and the probe and texturometer surfaces, both made of metal, and the comparison with the interaction between the samples and the human body is hard to be done. Tribological studies, considering appropriate surfaces, therefore, are necessary in further studies – although it is still a challenge to mimic the oral surfaces (Rudge et al., 2019).

The cohesiveness parameter represents the ratio between the force area of the second compression curve and the force area of the first area compression curve (Liu et al., 2019), providing information about crumbliness and the energy needed to chew the food (Fizman et al., 2013). Molded gels obtained higher values than the printed ones. There was no difference

between the treatments in relation to the printed gels, while the molded gels made from modified starches presented higher values than the control. This factor may indicate that the molded gel made from the control starch had stronger internal bonds, that holds it together in a bolus and prevents it from disintegrating into fragments during swallowing (Kurotobi et al., 2018). This characteristic is undesired for foods in dysphagic diet, being the DHT modification here proposed a good approach when the focus is this special food application.

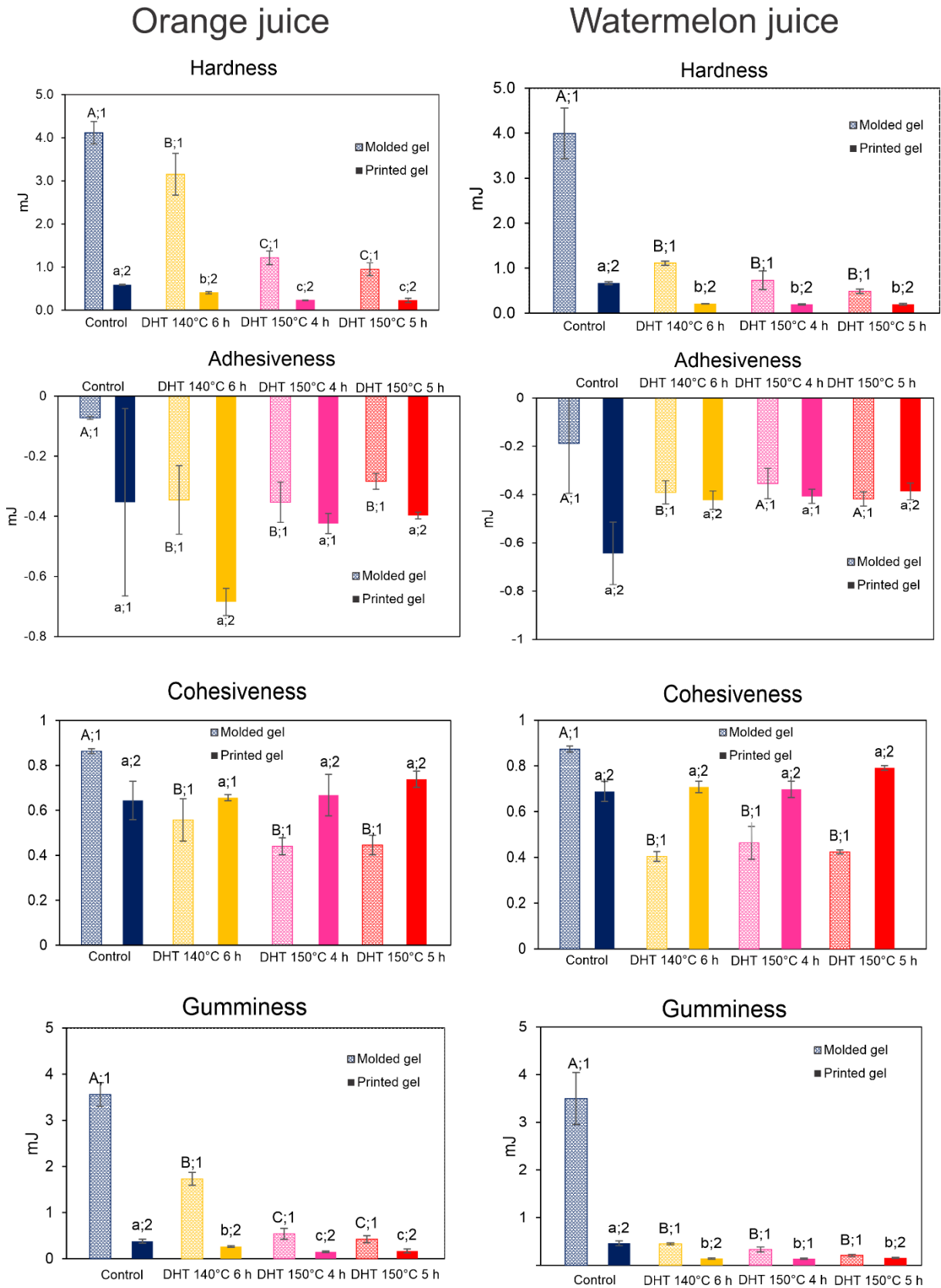


Fig. 6. Texture parameters of the molded and printed gels in square shape, the first column were gels made with orange juice and the second column were gels made with watermelon juice. The gels are based on control and modified starches by dry heating (DHT

140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h) (average \pm standard deviation). Different uppercase letters indicate a significant difference between the molded gels for the different treatments; different lowercase letter indicate a significant difference between printed gels for the different treatments; different numbers indicate significant difference between molded and printed gels for the same treatment, as showed by Tukey's test, $p < 0.05$.

3.3 Step 3: Characterization of the selected starches

3.3.1 Granular and molecular structure

Fig. 7 shows the results of light microscopy and the Maltese crosses observed from polarized light of the starch granules. The maize starch granules presented small, heterogeneous, irregular format, with roughness, and depressions, both for the control and for the starches treated with DHT. No changes on visual or crystalline appearance were observed with DHT, indicating that even at high temperatures and for relatively long times, DHT did not cause changes in the granular structure of maize starch. Similarly, no changes or agglomerations were observed in the structure of DHT-treated granules of other starches sources, such as cassava (Lima et al., 2021; Maniglia et al., 2020c). Lei et al. (2020) observed agglomerations of starch granules with increasing temperature of DHT in maize starch, forming large lumps. However, this was not observed in the present work.

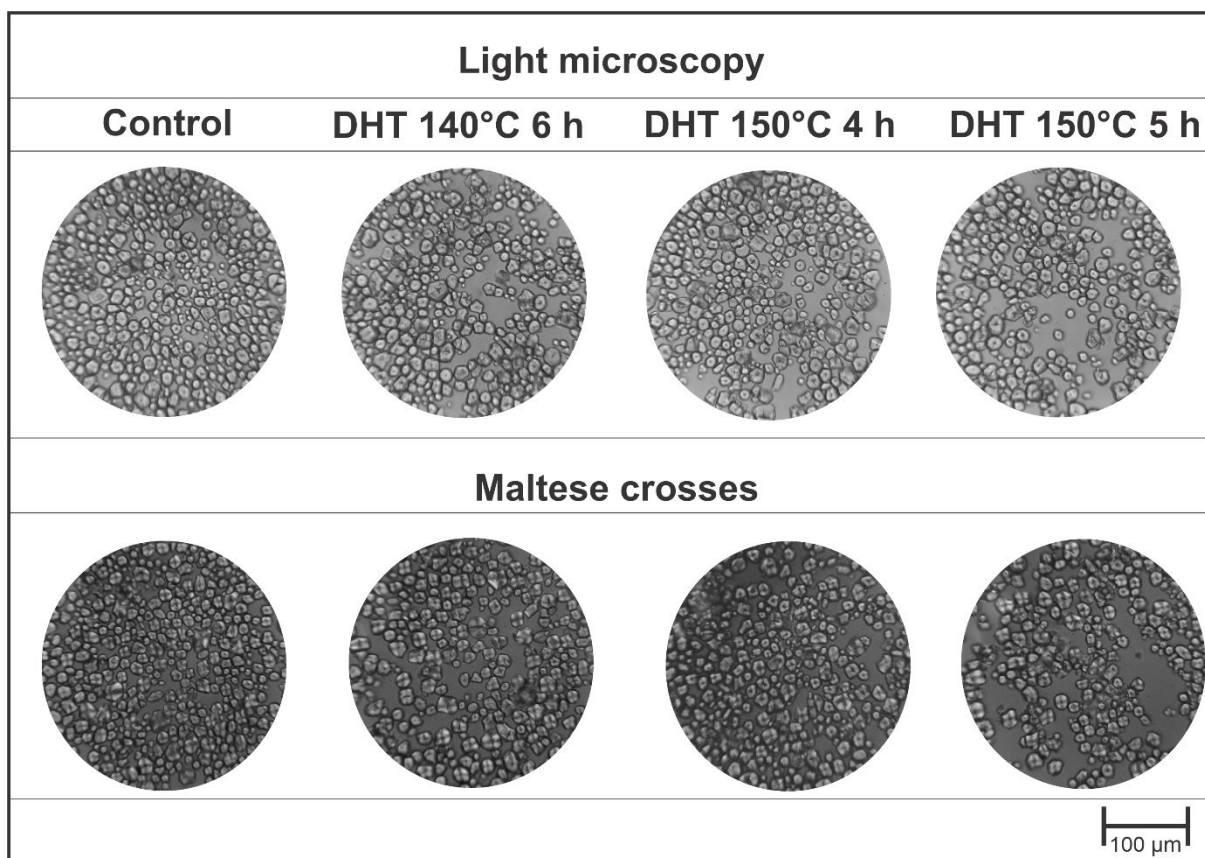


Fig. 7. Morphology of control and dry heating modified starches obtained by light microscope, with and without polarized light.

Table 3 presents the pH of the starches in aqueous solution, with a slight decrease for the starches treated by DHT 150°C 4 h and DHT150°C 5 h. This decrease may be related to the emergence of new functional groups, as demonstrated in Fig. 8 by the increase in both carbonyl and carboxyl contents. Carbonyl and carboxyl are functional groups that replace the hydroxyl radicals due to oxidation of starches. In this work, both carbonyl and carboxyl groups were formed during DHT, resulting in new interactions among the starch molecules and, consequently, new properties (such as gel texture). Although most of the works in the literature demonstrate the formation of carbonyl groups in starches processed by DHT, this process is in general conducted at levels where carboxyl groups are not formed (Kurdziel et al., 2019; Lima et al., 2021; Maniglia et al., 2020c). In this work, however, more severe DHT conditions

were applied, resulting in the formation of both functional groups, in different concentrations in each condition, thus expanding the possibilities of molecular interaction.

Table 3. pH of control and modified maize starches (DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h).

Treatments	pH
Control	5.25 ± 0.007 ^a
DHT 140°C 6 h	5.23 ± 0.014 ^a
DHT 150°C 4 h	4.96 ± 0.035 ^b
DHT 150°C 5 h	4.84 ± 0.007 ^c

Average ± standard deviations; variations followed by the same letter do not differ significantly (p < 0.05).

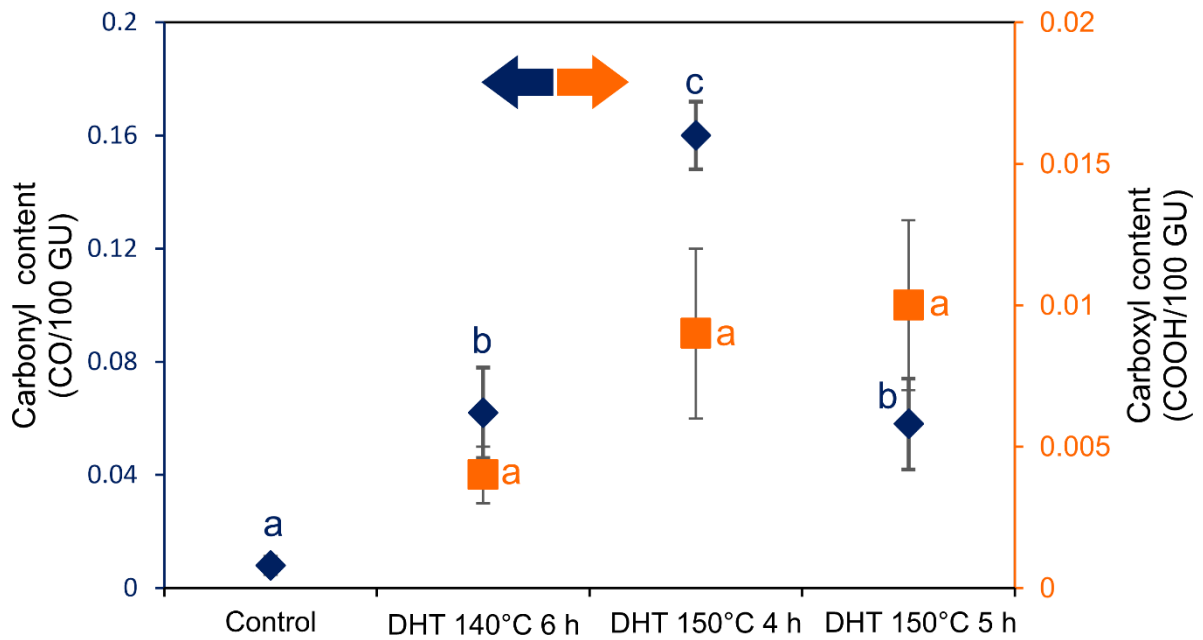


Fig. 8. Carboxyl (COOH) and carbonyl (CO) content of control and dry heating modified maize starches (DHT 140°C 6 h, DHT 150°C 4 h and DHT 150°C 5 h). Average ± standard deviations; variations followed by the same letter do not differ significantly (p < 0.05).

Simultaneously with the appearance of new functional groups, it was possible to observe a partial molecular depolymerization - Fig. 9 presents the molecular size distribution profiles by gel permeation chromatography. According to this technique, the first peak that elutes through the column is composed of large molecules, which are retained for a short time in the pores of the column. In the case of starch molecules, it is mainly attributed to amylopectin - larger and highly branched molecules. The second group, on the other hand, is the one composed of smaller molecules and that would be retained in the column longer - in this case, amyloses and smaller chains obtained after cleavage. The control treatment (native starch) presents two well-defined peaks and smaller amount of intermediate fraction. However, as the time and temperature of DHT increases, it is possible to observe a reduction in the first peak, an increase in the intermediate fraction and second peak, indicating the partial molecular depolymerization. Similar results were described for cassava (Lima et al., 2021; Maniglia et al., 2020c), wheat (Maniglia et al., 2020b), and maize starches (Lei et al., 2020). The new molecular size distribution result in new molecular packing profile, which together with the new functional groups result in new interactions and network properties – reflecting the observed changes in pasting properties, printing, and texture properties of the gels.

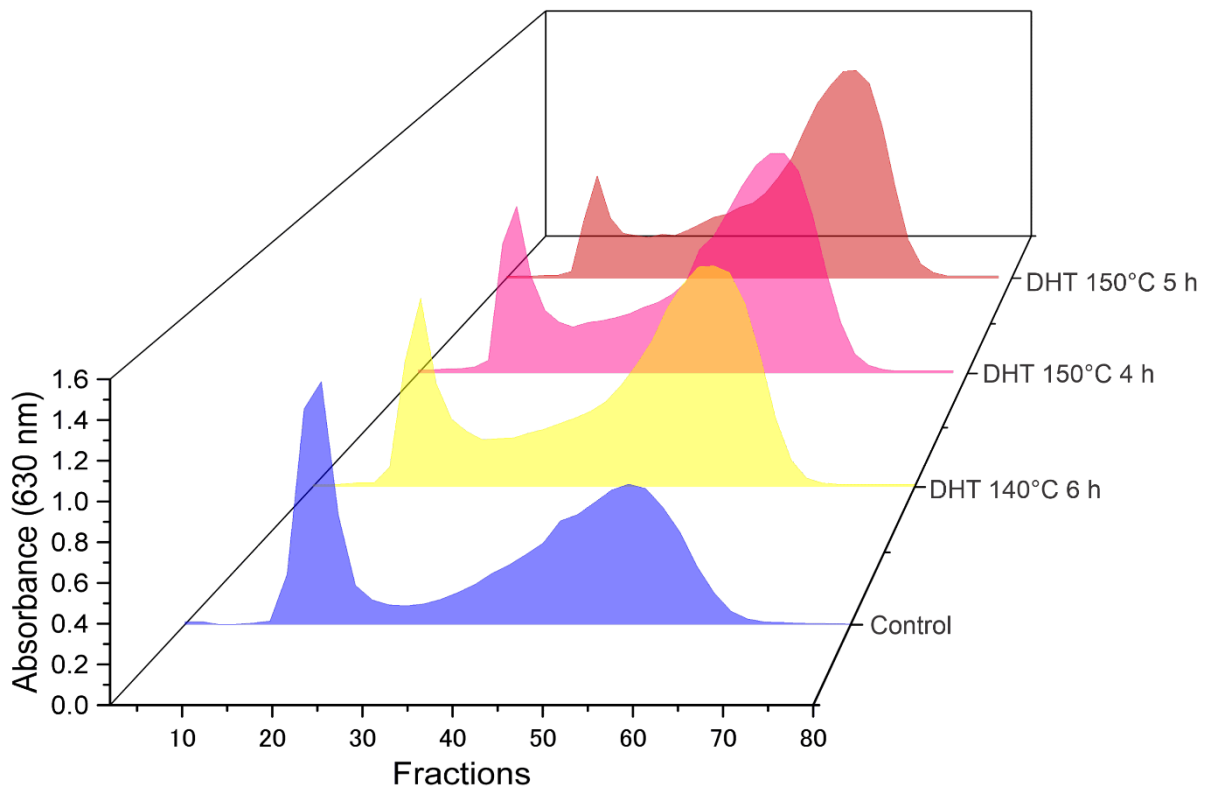


Fig. 9. Molecular size distribution profiles of dry heating modified and control maize starches – gel permeation chromatography analyzed by the blue value method.

3.3.2 Pasting Properties

Fig 10. and Table 4 present the pasting properties of the selected starches gelling orange and watermelon juices (i.e., the paste was produced using the juices and the starches, as described on section 2.2.1). Similarly, to the results obtained with water (section 3.1), DHT processing reduced the consistency of pastes made with juices.

When the starch solution is heated in the RVA, the granules absorb a large amount of water and start to swell; increasing shearing when these swollen granules squeeze past each other (Liu, 2005). Table 4 shows DHT reduced the pasting temperature (PT), the temperature recorded when the increase in apparent viscosity occurs, indicating the treatment decreases the strength of the granules.

Peak viscosity occurs at the equilibrium between swelling and leaching of the polymers, being recorded as PAV (Liu, 2005). The PAV parameter represent the highest apparent viscosity reached by the slurry during heating (Balet et al., 2019). The starches treated with DHT had lower PAV values compared to the control (Table 4), which can be associated with cleavage of glycosidic bonds resulting in granules with less ability to maintain their integrity (Chung et al., 2007).

After the granules rupture, the leached polymers align, decreasing the apparent viscosity by breakdown (BD), which is obtained by the difference between PAV and PAV - TAV being the minimum viscosity reached before cooling (Liu, 2005). The parameter relative breakdown (RBD) was defined to better understand the variation of the samples consistency, being obtained by the difference between the values BD and PAV (Castanha et al., 2017). As seen in Table 4, there was an increase in RBD values for modified starches, indicating the molecules association is facilitated when compared to the native one (Maniglia et al., 2020b).

After the rupture and alignment of the molecules, a reassociation of the starch molecules occurs, increasing the apparent viscosity of the paste until reaching the final apparent viscosity (FAV). This reassociation is described by setback (SB) parameter, which is calculated by the difference between TAV and FAV (Liu, 2005) - and since these values change simultaneously, this parameter was described as relative setback (RSB), calculated by the ratio between SB and TAV (Castanha et al., 2017). The modification caused a slight increase in the RSB values compared to control starches. This same behavior was observed in cassava and wheat starches (Maniglia et al., 2020c, 2020b).

FAV is related to the stability of the cooked and cooled pasting under low shear (Liu, 2005). As indicated in Table 4, there was a reduction in FAV values for DHT-modified starches. The decrease in apparent viscosity indicates a lower level of retrogradation (Balet et al., 2019).

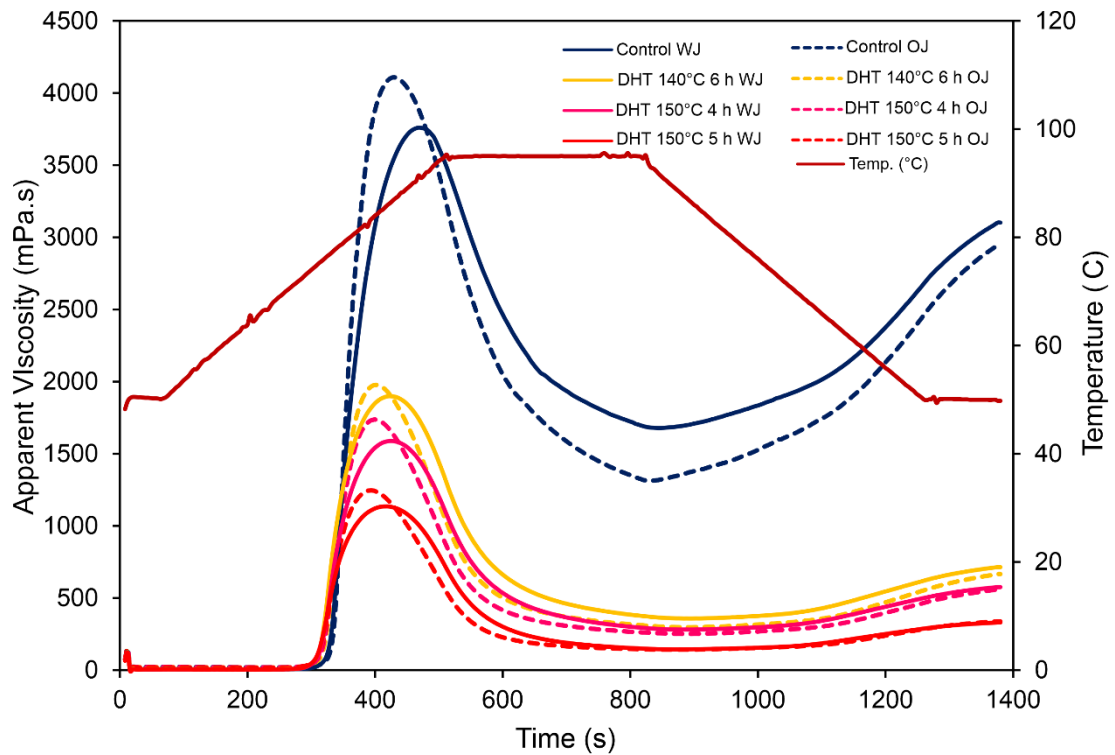


Fig. 10. Pasting properties of selected starches (control and modified) blended with watermelon (WJ) and orange (OJ) juices.

Table 4. Pasting parameters from RVA of selected starches (control and modified) blended with orange (OJ) and watermelon (WJ) juices (average \pm standard deviation)

Samples	PAV (mPa·s)	TAV (mPa·s)	RBD (%)	FAV (mPa·s)	RSB (%)	PT (°C)
Control OJ	4111.0 \pm 12.8 ^a	1313.3 \pm 24.9 ^a	68.05 \pm 0.005 ^a	2946.7 \pm 20.4 ^a	124.4 \pm 0.06 ^a	76.4 \pm 0.03 ^a
Control WJ	3759.7 \pm 53.4 ^b	1679.0 \pm 31.1 ^b	55.34 \pm 0.003 ^b	3102.0 \pm 45.3 ^b	84.76 \pm 0.01 ^b	76.0 \pm 0.05 ^a
DHT 140°C 6 h OJ	1977.7 \pm 66.9 ^c	298.7 \pm 17.4 ^c	84.90 \pm 0.003 ^c	667.3 \pm 34.8 ^c	123.5 \pm 0.01 ^a	75.4 \pm 0.48 ^b
DHT140°C 6 h WJ	1899.0 \pm 53.0 ^{cd}	359.0 \pm 23.5 ^{cd}	81.11 \pm 0.007 ^d	714.7 \pm 37.7 ^{cd}	99.2 \pm 0.03 ^c	74.8 \pm 0.05 ^{bc}
DHT 150°C 4 h OJ	1733.7 \pm 86.2 ^{de}	252.0 \pm 13.0 ^d	85.46 \pm 0.003 ^c	559.0 \pm 22.7 ^{de}	121.9 \pm 0.03 ^a	75.2 \pm 0.02 ^c
DHT150°C 4 h WJ	1588.7 \pm 82.9 ^e	281.3 \pm 20.0 ^d	82.29 \pm 0.005 ^d	576.0 \pm 34.8 ^e	104.8 \pm 0.03 ^c	74.8 \pm 0.14 ^c
DHT 150°C 5 h OJ	1247.0 \pm 119.5 ^f	143.0 \pm 18.3 ^e	88.57 \pm 0.004 ^f	339.0 \pm 39.3 ^f	137.3 \pm 0.03 ^d	74.8 \pm 0.06 ^c
DHT150°C 5 h WJ	1134.3 \pm 141.9 ^f	144.7 \pm 25.4 ^e	87.30 \pm 0.007 ^f	330.7 \pm 51.3 ^f	129.2 \pm 0.05 ^{ad}	74.8 \pm 0.03 ^c

Peak Apparent Viscosity (PAV), Through Apparent Viscosity (TAV), Relative Breakdown (RBD), Final Apparent Viscosity (FAV), Relative Setback (RSB) and Pasting Temperature (PT). Different letters in the same column indicates significant difference among samples, as showed by Tukey's test, $p < 0.05$.

4 Final consideration

This work developed ingredients based on starch submitted to the dry heating treatment (DHT) for 3D printing of food products for dysphagia. 30 conditions of DHT were evaluated in maize starch, through analysis of pasting properties, texture (compression analysis) and 3D printing. Three DHT conditions that resulted in better were used to gel two juices of different pHs. These gels were analyzed according to their ability to be printed in three different geometries, fork pressure test of the IDDSI, pressure test with the fork but using the texturometer and TPA test. With these analyses, it was possible to conclude that the pH did not have a great impact on the formation of gels. Factors such as time and temperature of DHT had greater impacts, and only DHT 140°C 6 h gel was able to sustain itself (considering both juices). This was, thus, considered the best treatment for 3D printing, under the analyzed conditions. Regarding the characterization as food for dysphagic diets, it was possible to select two levels described by the IDDSI standards: level 5 for printed gels and level 6 for molded gels. Finally, a characterization of the selected starches was performed, in relation to their granular and molecular properties.

It should be mentioned that despite the objective of this study was fulfilled, this work does not intend to be a reference from the medical nor nutritional points of view. Consequently, future clinical studies are needed before recommendation into different dysphagic diets and different food products must be evaluated to form a complete diet. Different levels of dysphagia, associated with an overall clinical evaluation, demand specific approaches in relation to food and nutrition. Aspects such as possible allergens, sensitivity, and intolerance must also be considered before any prescription.

Even so, we highlight the importance of this work, and future ones, focused on developing the necessary ingredients to produce tailored food products for special needs.

5 Conclusions

This work demonstrated the use of DHT treatment to modify maize starch for application in 3D printing, elaborating juice gels, and evaluating the applicability as food for dysphagia. 30 conditions of DHT were evaluated, from 110 to 150°C during 1 to 6 h. DHT reduced the consistency of the starch paste, producing both carbonyl and carboxyl groups, and promoting partial depolymerization. Consequently, the starch properties were changed: DHT processing produced weaker maize starch gels, with better printability when compared to the control. Food analogues were produced using two fruit juices (orange, as a high-acid juice, and watermelon, as a low-acid juice) and the modified starches, as gelling ingredients. Those gels were produced both by molding and 3D printing, resulting in foods characterized at levels 5 and 6 by the IDSSI. Of all treatment conditions, DHT 140°C 6 h showed the best printability, forming gels with both juices prone to dysphagic diets at levels 5 and 6. Therefore, this study developed and characterized ingredients to be used as “food inks” in 3D printing focusing on food for special needs.

As future studies, we highlight the importance of developing further ingredients for 3D printing of foods with different demands/necessities, as well as developing new correlations to describe starch modification better and quicker at molecular level – for example using FTIR (Fourier-Transform Infrared Spectroscopy), FT-NIR (Fourier-Transform Near-Infrared Spectroscopy) or NMR (Nuclear Magnetic Resonance).

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