

Dry heating treatment: A potential tool to improve the wheat starch properties for 3D food printing application

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1	Dry heating treatment: a potential tool to improve the wheat starch properties for 3D food
2	printing application
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13	
14	Abstract
15	The futuristic technology of three-dimensional (3D) printing is an additive manufacturing that
16	allows obtaining creative and personalized food products. In this context, the study of food
17	formulations (named as "inks") to be processed through 3D printing is necessary. This work
18	investigated the use of dry heating treatment (DHT), a simple and safe method, to improve the
19	wheat starch properties aiming to produce hydrogels to be used as "inks" for 3D printing.
20	Wheat starch was processed by dry heating for 2 (DHT_2h) and 4 h (DHT_4h) at 130 °C.
21	Modified wheat starches showed an increase in granule size, but processing did not alter the
22	granule's shape nor surface, neither alter the molecular functional groups. On the other hand,
23	DHT promoted slight molecular depolymerization, and reduction of starch crystallinity.
24	Hydrogels "inks" based on the modified starches showed lower peak apparent viscosity
25	during pasting, higher structural strength at rest, higher resistance to external stresses, higher
26	gel firmness, and lower syneresis than hydrogels based on native starch. The hydrogels based
27	on starch DHT_4h showed the best printability (greater ability to make a 3D-object by layer-
28	by-layer deposition and to support its structure once printed) and this "ink" showed better
29	reproducibility. Another point observed is that DHT extended the texture possibilities of
30	printed samples based on wheat starch hydrogels. These results suggested that DHT is a
31	relevant process to improve the properties of hydrogels based on wheat starch, making this
32	ink suitable for 3D printing application.
33	Keywords: modified starch, 3D food printing, additive manufacturing, personalized food,

34 food texture.

35 1. Introduction

The three-dimensional (3D) printing is an emerging technology to create personalized 36 objects from digital models through the successive layer-by-layer deposition of materials such 37 as plastic, metal, ceramics, or even living cells (Bhatia & Ramadurai, 2017). Currently, 3D 38 printing technology has been used for food printing, defining new borders for food processing 39 and being able to deliver a product that suits special consumer's criteria of taste, texture, cost, 40 convenience and nutrition. For instance, 3D food printing can create unique novel textured 41 foods, healthy foods, and smooth and easy-to-swallow foods for elderly people (Dankar, 42 43 Haddarah, Omar, Sepulcre, & Pujola, 2018).

Extrusion is the most common 3D printing method for food applications, being 44 relatively easy to develop and presenting different alternatives of "inks" (Guvendiren, Molde, 45 Soares, & Kohn, 2016; Tan, Toh, Wong, & Lin, 2018). This process depends heavily on the 46 47 physical properties of the material to be processed, which is one of the most important research topics about 3D printing (Liu, Liang, Saeed, Lan, & Qin, 2019). Therefore, it is 48 49 important to study physicochemical and rheological aspects of possible "inks" used to print in other words, their printability, i.e. their ability to make a 3D-object by layer-by-layer 50 51 deposition, to obtain a defined shape and to support its structure once printed (Godoi, Prakash, & Bhandari, 2016). 52

In this context, it is important to study the ability of starch sources to be used as "inks". As one of the most important carbohydrates in human diets and one of the most available in nature, starch is widely used as thickening and gelling agents in many food formulations (BeMiller, 2011). The gelatinized starch paste shows a shear-thinning behavior and instant responses to the applied shear strains, being easily extruded from the fine nozzle (Evans & Haisman, 1980; Le Tohic et al., 2018). Finally, the starch hydrogel can present good printability, depending on the sources and modification processes.

In fact, some studies have already explored starchy products as "inks" for 3D printing, 60 like potato starch (Yang, Zhanga, & Bhandari, 2018), mashed potatoes (Liu et al., 2018), 61 62 potato puree (Dankar et al., 2018), wheat flour (Liu, Liang, Saeed, Lan, & Qin, 2019a), rice flour (Anukiruthika, Moses, & Anandharamakrishnan, 2020). Moreover, our group has 63 evaluated some alternatives to modify starches and improve the 3D printability, such as the 64 ozone and dry heating treatment of cassava starch (Maniglia et al. (2019) and Maniglia et al. 65 (2020)). However, the approach of starch modification for 3D printing application is still 66 under-explored in the literature, considering different sources and modification technologies. 67

Wheat starch is the third most-produced starch in the world, being a coproduct in the
vital gluten industry (Shevkani, Singh, Bajaj, & Kaur, 2017). It has an important role in many
food products (Agama-Acevedo, Flores-Silva, & Bello-Perez, 2019; Ubeyitogullari & Ciftci,
2016), being frequently used in gluten-free baked products (Houben, Höchstötter, & Becker,
2012). However, native wheat starch produces weak-bodied, cohesive, rubbery pastes when
heated and undesirable gels when the pastes are cooled (Punia, Sandhu, Dhull, & Kaur, 2019).

74 In this way, modification processes can be used to improve wheat starch properties and applicability. Among different possibilities, dry heat treatment (DHT) is a simple physical 75 76 method, considered a "green" technology (chemical-free, simple, safe and pollution-free) to 77 alter starch structure and functionality (Chandanasree, Gul, & Riar, 2016; Gou et al., 2019; K. 78 Liu, Hao, Chen, & Gao, 2019; Maniglia, Castanha, Le-Bail, Le-Bail, & Augusto, 2020; Oh, Bae, & Lee, 2018). Moreover, Maniglia et al. (2020) described that cassava starch DHT 79 80 resulted in stronger gels with better 3D printability than the native starch. It is worth mention each starch source reacts differently to each modification technology, justifying the present 81 82 work.

Wheat starch modification by DHT has scarcely been reported in the literature,
although some studies are available with wheat flour (Nakamura, Koshikawa, & Seguchi,
2008; Ozawa, Kato, & Seguchi, 2009; Seguchi, 2001) – where the observed changes are
mainly associated to the proteins.

Based on this context, this study aimed to use the DHT as a tool to improve the 3D printability of "inks" based on wheat starch hydrogels. To achieve it, firstly the effect of DHT was studied in relation to the wheat starch structure and properties. Then, the potential for 3D printing application was evaluated. The innovation of this study involves developing functional ingredients to be used as gelling and thickening agents to bring better printability for food products, also expanding the application and potential of wheat starch.

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94 2. Material and methods

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2.1 Material and dry heating treatment (DHT)

96 Native wheat starch (moisture content: 10.1 g/100 g) was purchased from Merck
97 KGaA (Germany). All the chemicals were of analytical grade.

The dry heating treatment (DHT) was based on the work of Chandanasree et al. (2016). Wheat starch (50 g) was distributed evenly in a thin layer (~ 1 mm) and packaged on aluminum foil, as an envelope (30 x 20 cm), which was closed with a high-temperature tape to avoid moisture loss. The envelope was then placed in a hot-air convective oven (XU032, Frances Etuves, Chelles, France) with air at 130 °C and 1 ± 0.1 m. s⁻¹ for 2 and 4 h (named DHT_2h and DHT_4h, respectively).

104 The temperature was recorded using a datalogger with six K-type thermocouples 105 (AOIP Datalog, Ris-Orangis, France) of 0.5 mm diameter for measuring the temperature in 106 different locations within the sample (Supplementary Fig. S1A). The treatment time was 107 counted from the moment where all parts of the envelope reached the processing temperature 108 (130 °C) - the heat-up time was 20 min (Supplementary Fig. S1B). After processing, the 109 starch was cooled, sieved (250 μ m), and stored in glass containers for further analysis.

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111 2.2 Granule characterization: morphology and size distribution

The starch granules morphology (control and modified) was observed using a light microscope (model L1000, Bioval, Curitiba, Brazil; with a 20 W halogen lamp, the magnification of 40 x) and a digital camera of 5.1 megapixels (MT9P001, Aptina, Colorado, USA). The starch granules were dispersed in distilled water (1:1, v/v). Then, they were placed on a glass slide, covered by a glass coverslip, and directly evaluated. A polarized light filter coupled to the system was used to observe the Maltese crosses.

The granule size distribution was determined using the dynamic light scattering (DLS) of Malvern Master Size (3000, Malvern Instruments Ltd, Worcestershire, UK). The samples were dispersed in the air. The analyse was carried out 4 times for each sample. From the obtained data, the volume-based mean (D[4,3]) and the area-based mean (D[3,2]) diameters were calculated. The diameters d(0.1), d(0.5), and d(0.9) were also obtained, describing the dimension that 10 %, 50 %, and 90 % of the granules were smaller, respectively.

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125 2.3 Molecular characterization: pH, functional groups, molecular size distribution

pH values were measured in the starch suspension of 10.7% (w/w) in distilled water,
under constant stirring at room temperature (25 °C), using a potentiometer (model TEC-5
mode, Tecnal, Piracicaba, Brazil).

The carboxyl and carbonyl contents were determined by the method of Smith (1967) and Chattopadhyay, Singhal, & Kulkarni (1997), respectively, with some modifications, as described by Maniglia et al. (2020). Their content was expressed as the number of carboxyl (COOH / 100 GU) or carbonyl (CO/100 GU) groups in relation to 100 units of glucose. The analyses were done in triplicate. The changes in the functional groups were also evaluated using the infrared spectroscopy technique. Fourier transform infrared (FTIR) spectroscopy was conducted using a Spectrum 100^{TM} FTIR instrument (Perkin-Elmer, Shelton, USA) equipped with an attenuated total reflection (ATR) accessory. All the spectra were the average of 16 scans from 4000 cm^{-1} to 650 cm⁻¹ and were acquired at a resolution of 4 cm⁻¹.

- The molecular size distribution profile (control, DHT_2h, and DHT_4h) was
 determined using a gel permeation chromatography (GPC) system, according to Song & Jane
 (2000), with some modifications described by Maniglia, Lima, Junior, et al. (2019).
- 142

143 2.4 Thermal and crystalline properties of starch

The thermal properties during starch gelatinization were determined using a Multi-Cell 144 Differential Scanning Calorimeter (MC-DSC) – (TA Instruments, Lindon, USA). The starch 145 samples were weighed and hydrated directly into the ampoules (10 g dry starch / 100 g 146 147 suspension). An ampoule with deionized water was used as a reference and three runs for each sample were analysed. The MC-DSC heating program consisted of going from 20 to 120 148 149 °C at a rate of 2 °C/min. The onset temperature (To), the peak temperature (Tp), the conclusion temperature (Tc), and the enthalpy (ΔH) associated with the starch gelatinization 150 151 interval were calculated with the aid of the Universal Analyzer software (TA Instruments, 152 New Castle, USA).

The crystallinity of starch samples was determined by X-ray diffraction (XRD). 153 Before the XRD analysis, the starch samples were maintained in a desiccator containing a 154 saturated BaCl₂ solution (25 °C, $a_w = 0.900$) for 7 days to ensure constant water activity. The 155 sample was examined by X-ray diffraction equipment Inel X-ray equipment (Inel, Centre-Val 156 de Loire, France) operated at 40 kV and 30 mA. The CuKa radiation (0.15405 nm) was 157 selected using a quartz monochromator. Diffracted intensities were monitored (2 θ) by a 158 sensitive detector (CPS 120, Inel, Centre-Val de Loire, France). The resulting diffraction 159 diagrams were normalized between 3 and 30 $^{\circ}$ (2 θ). The curves obtained were smoothed using 160 the Origin software, version 2018 (Microcal Inc., Northampton, USA). The relative 161 crystallinity was calculated as the ratio of upper diffraction peak area to the total diffraction 162 area, following the method described by Nara & Komiya (1983) and considering 20 ranging 163 from 3 to 30 $^{\circ}$. 164

165 2.5 Starch pasting behaviour and hydrogel properties (rheology and firmness)

Starch pasting properties were determined using a Rapid Visco Analyzer (RVA4, 166 Newport Scientific Pvt. Ltd., Warriewood, Australia) with Thermocline for Windows 167 software, version 3.0. The RVA analysis consisted of heating, retention, and cooling cycle 168 under constant shear (160 rpm). Following the standard conditions for starch characterization, 169 170 starch suspensions of 10.7 g starch / 100 g (correct to 14 % moisture basis) were prepared for the RVA analyses. The procedure used was: keep at 50 °C for 1 min, then heat up to 95 °C (6 171 °C.min⁻¹ and maintained 5 min), followed by cooling to 50 °C (6 °C.min⁻¹), and finally, 172 maintained at 50 °C for 2 min. 173

174 Different parameters are obtained to describe the pasting behaviour: peak apparent viscosity - PAV (the maximum paste apparent viscosity achieved in the heating stage), 175 through apparent viscosity – TAV (minimum paste apparent viscosity achieved after holding 176 at the maximum temperature), final apparent viscosity – FAV (the apparent viscosity at end of 177 178 run), breakdown - BD (difference between PAV and TAV), setback - SB (the difference between FAV and PAV), and pasting temperature – PT (the temperature at which starch 179 180 granules begin to swell and gelatinize due to water uptake). For a better interpretation of these parameters, the relative breakdown (RBD) and relative setback (RSB) were also calculated, 181 182 following the study of Castanha, Matta Junior, & Augusto (2017). The RBD (calculated as the ratio between the BD and PAV values) can be associated with the facility of starch granules to 183 disrupt, while the RSB (calculated as the ratio between the SB and TAV values) can be 184 185 associated to the retrogradation tendency.

Hydrogels were prepared by dispersing starch in distilled water (10.7 g dry starch/ 100 g, being the starch mass corrected to 14 % moisture basis), and then heating it at 85 ± 2 °C in glass containers in a water bath for 20 min. Then, the pastes were placed in plastic cups (40 mm diameter × 20 mm height) and stored for 24 h in the refrigerator (5 ± 2 °C) to gelling. The cups were kept in a desiccator with water at the bottom to ensure uniform moisture. The obtained hydrogels were evaluated in relation to their viscoelasticity and firmness behaviours.

The viscoelastic properties were analysed by oscillatory stress sweep using a HAAKE MARS rheometer (Vane FL40, ThermoFisher, Karlsruhe, Germany). The hydrogels were loaded between the stainless steel parallel plates geometry (with a diameter of 25 mm and a gap of 1 mm), trimmed, and their edge was covered with silicon oil to prevent water vaporization. The stress sweep measurements were carried out at 22 °C with a logarithmically increasing shear stress at a frequency of 0.1 Hz (initial stress 0.001 Pa). This analysis was conducted in triplicate.

The hydrogel firmness was determined by a puncture assay using a texture analyzer 199 TA TX Plus (Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kgf (490.3 N). 200 The samples were removed from the refrigerator and analysed immediately to ensure a 201 constant temperature. The samples were penetrated until a distance of 4 mm using a 202 cylindrical probe (P/0.5R, 0.5 in of diameter) at $1 \text{ mm} \cdot \text{s}^{-1}$. The equipment measured the force 203 as a function of penetration depth. Gel firmness was evaluated by the energy required to 204 penetrate the material (calculated by the area below the curve force versus distance of 205 penetration). This analysis was conducted in triplicate. 206

207

208 2.6 Syneresis measurement

Syneresis was determined according to the method of Yeh & Yeh (1992). Briefly, starch suspensions (5 % w/w) were gelatinized at 85 °C for 20 min in a temperaturecontrolled water bath followed by cooling to room temperature. The pastes were then stored for 24 h at 4 °C. Syneresis was measured gravimetrically as the amount of water (g water/ 100 g gel) released after centrifugation at 1500 g for 15 min. Triplicate of the results were read and the mean reported.

- 215
- 216 2.7 3D printing process

The "inks" (starch hydrogels

The "inks" (starch hydrogels) were prepared identically as described on the last section. After heating, the hydrogels were transferred for the printer syringes (60 mL), cooled to room temperature to form a weak gel-like structure, and stored in the refrigerator (5 ± 2 °C) for 24 h before the printing.

The printing process was carried out in a 3D printer (Stampante 3DRAG V1.2, Futura Electronica, Gallarate, Italy) presented in Fig. 1. The syringes with the hydrogels were removed from the refrigerator and immediately positioned in the 3D printer. A nozzle with diameter of 0.8 mm and height of 18 mm was coupled in the syringes. The 3D printing conditions were: nozzle movement of 5 mm/s and an extrusion rate of 4.5 mg/s at 20 °C.

Three physical models (heart, star, and cylinder shapes) were created using the Repetier Host V2.0.1 and Slic3r software (Hot-World GmbH & Co. KG, Willich, Germany). The dimensions of the cylinder shape were 2 cm x 4 cm (diameter × height), for the star shape were $2.5 \text{ cm} \times 2.5 \text{ cm} \times 2 \text{ mm}$ (Length × Width × Height), and for the heart shape were $5 \text{ cm} \times 6 \text{ cm} \times 2 \text{ mm}$ (Length × Width × Height). 5 samples were printed for each hydrogel and

shape. All the printing experiments were carried out at room temperature. After printing, the 231 232 samples were photographed.

The reproducibility of the 3D printed samples was evaluated considering the weigh 233 and the dimensions of the sample printed. Each printed cylinder was weighed in analytical 234 balance (AZ214, Sartorius, Göttingen, Germany) and their dimensions (height and diameter) 235 were measured in five different positions using a digital paquimeter (CD-6 CSX-B model, 236 Mitutoyo, Roissy-en-France, France). 237

Printed samples in cylinder shape were conditioned in a refrigerator (at 5 ± 2 °C) for 238 239 24 h, inside of a desiccator with water to avoid dehydration. Then, these printed samples were used for texture analysis. 240

241

242 2.8

Texture profile of the printed hydrogels

A texture analyser TA-XT+ (Stable Microsystems, Surrey, UK) was used to assess the 243 printed cylinders. These analyses were conducted immediately in the samples removed from 244 the refrigerator in triplicates for each sample. 245

The texture profile analysis (TPA) measurement consisted of two compression-246 decompression cycles separated by a time interval of 10 s, at a rate of 1 mm/s, using a 247 cylindric probe (25 mm diameter, Code P/25, Stable Micro System Ltd., Surrey, UK). The 248 probe compressed the sample to 25 % (6.25 mm) of the initial height (25 mm) before 249 250 decompression using a 50 kgf (490.3 N) load cell.

All the textural parameters were measured and calculated by the instrument software 251 from the resulting force-deformation curves, including hardness, adhesiveness, cohesiveness, 252 springiness, gumminess, and chewiness. 253

254

2.9 255 Experimental design and Statistical analysis

A completely randomized design was conducted. All processes and analyses were 256 carried out at least in triplicate. To evaluate differences, analysis of variance (ANOVA) and 257 Tukey's test at a 5 % significance level were accomplished by using the software Statistic 13 258 259 (StatSoft, USA).

260

Results and Discussion 261 3.

262 3.1 Starch granule: size distribution and morphology

Fig. 2 shows the granule size distribution (A) and specific diameters (B) for the 263 control and modified wheat starch. The samples displayed a unimodal size distribution and 264 265 DHT resulted in larger granules sizes (Fig. 2A), being this effect consistent with the duration of the dry heating process: the D[4,3] varied from 21.7 µm for the control starch to 22.6 and 266 24.1 µm for DHT_2h and DHT_4h, respectively (Fig. 2B). The same was observed for the 267 D[3,2], varied from 13.3 µm for the control starch to 13.7 and 14.1 µm for DHT_2h and 268 DHT_4h, respectively (Fig. 2B). Since the parameter D[4,3] is more sensitive to larger 269 granules, while D[3,2] is more sensitive to the fraction of smaller granules (Lopez-Sanchez et 270 al., 2011), it is noted that the greatest effect of the DHT occurred for the larger granules. This 271 behavior is similar to that observed for cassava starch treated with DHT (Maniglia et al., 272 273 2020). It can be associated with a possible expansion in the starch granule due to water vaporization, such as during flash vaporization. In fact, part of the water content in the 274 samples was vaporized during DHT, as reflected by the moisture of modified wheat starches 275 (control: 10.1 g/100 g; DHT 2h: 4.7 g/100 g and DHT 4h: 4.5 g/100 g). The dry heating 276 277 process also increased the number of granules with bigger sizes considering the d0.1, d0.5, and d0.9 values. 278

Fig. 3 shows the optical microscopy of the control and treated wheat starches using 279 both nonpolarized and polarized light. The microscopies show wheat starch granules with 280 lenticular morphology with a large variety of granules size, which is consistent with previous 281 observation (Hruska, Arevao, Muñoz, & Avila, 2019). While the birefringence effect (Maltese 282 cross is visible) can be seen in all the images, the processed samples showed a shine 283 reduction. Chung, Liu, & Hoover (2010) attributed this behavior to the temperature elevation 284 at the center of the starch granule, which supposedly damage the amylopectin double helices 285 structure. The same behavior was observed by Liu et al. (2019) in the case of dry heating 286 treatment for waxy potato starch. Once the Maltese crosses still can be seen, it indicates the 287 288 thermal energy provided was not sufficient to destroy amylopectin double helices structure.

These results indicated that DHT did not alter the shape nor altered the granules surface; however, it slightly affected the internal microstructure of wheat starch granules and promoted an expansion of the granule size – which can affect starch properties.

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DHT processing did not change the pH of the wheat starches suspensions (control: 5.90 \pm 0.10, DHT_2h: 6.06 \pm 0.15, and DHT_4h: 5.98 \pm 0.18), and no carbonyl and carboxyl formation was found. It indicates that DHT did not promote starch oxidation. It is interesting to observe that cassava starch, at the same processing conditions, presented carbonyl groups formation (Maniglia et al., 2020), highlighting each starch source are differently affect by processing.

Fig. 4(A) shows the vibrational spectra of the control and modified starches. All 300 samples showed the same characteristic bands at 3323 cm⁻¹, 2934 cm⁻¹, 1648 cm⁻¹, 1339 301 cm⁻¹, 1150 cm⁻¹, 1020 cm⁻¹, and 996 cm⁻¹. The bands at 3500 and 2900 cm⁻¹ are associated 302 with OH bonds and CH₂ deformation, respectively (Kačuráková & Mathlouthi, 1996). Bands 303 at 1650 cm⁻¹ are associated with water molecules absorbed in the amorphous region (Kizil, 304 Irudayaraj, & Seetharaman, 2002) and the stretching vibration of the CO band (amide I). The 305 peak at 1339 cm⁻¹ can be associated to OH bending due to the primary or secondary alcohols 306 (Muscat, Adhikari, Adhikari, & Chaudhary, 2012). The fingerprint region of starch is the 307 bands at 1200-900 cm⁻¹ (showed in Fig. 4(B)) and this region provided information about 308 changes in the polymeric structure and conformation of starch (Dankar et al., 2018). The 309 intense IR band at 996 cm⁻¹ can be mainly attributed to skeletal mode vibrations of $\alpha \ 1 \rightarrow 4$ 310 skeletal glycoside bonds (Jao & Ko, 2002). In addition, the middle strong peaks at 1150 cm⁻¹ 311 and 1060 cm⁻¹ are mainly attributed to the stretching vibration of CO and bending vibration 312 of C-O-H (Hou et al., 2019). The band at 1060 cm⁻¹ has been linked to amorphous structures 313 (Xiong, Li, Shi, & Ye, 2017). On the other hand, the band at 996 cm⁻¹ can be associated with 314 the single helix crystalline related to hydrogen bonds of anhydroglucose unit (Xiong et al., 315 2017). 316

It was not observed a significant difference between the presence and intensity of the bands in control and modified starches. These results indicate and confirm that the dry heating treatment did not modify the functional groups.

Fig. 5 shows the molecular size distribution of the control and treated wheat starches. The first peak consists of molecules of larger size and more ramifications, which can be associated with amylopectins, while the second peak represents molecules of smaller size and a linear structure, which can be associated with amyloses. DHT reduced the molecular size (Fig. 5): the first peak was slightly reduced, the fraction of molecules with intermediary size was also reduced, and the second peak was increased; moreover, the first and second peaks

scrolled to the right. It indicates the DHT promoted the formation of molecules with lower 326 size (which are retained longer in the chromatographic column) due to depolymerization 327 promoted by cleavage of glycosidic linkages. The depolymerization affected mainly the 328 intermediate size molecules. Maniglia et al. (2020) also observed this behaviour for cassava 329 starch, although with a much more accentuated effect. These results are also consistent with 330 the study of Lei et al. (2020) involving maize starch. The authors observed the temperature 331 increasing of DHT reduced drastically the long-amylose chains, while more short-amylose 332 chains were formed. 333

The molecular results reinforce each starch source are differently affect by processing.Consequently, further structure and properties evaluations are needed.

336

337 3.3 Thermal and crystalline properties of starch

The differential scanning calorimetry (DSC) thermograms (A) and the X-ray diffractograms (B) of the control and modified wheat starches are shown in Fig. 6. The gelatinization properties were obtained (Table 1) from Fig. 6(A). There was no difference in the onset (To) and the final (Tf) temperatures among treatments. The peak temperature (Tp) increased significantly (p < 0.05) as the treatment period increased, and the gelatinization enthalpy (Δ H) was reduced (p < 0.05) only for the DHT_4h starch. Lei et al. (2020) also observed a reduction of the gelatinization enthalpy (Δ H) for maize starch treated by DHT.

The enthalpy of gelatinization is an indirect measure of the amount of starch 345 crystalline region (or double helices structure) which are broken during heating (Liu, Yu, Xie, 346 & Chen, 2006). Therefore, ΔH reduction can indicates the formation of weaker structures, 347 which were less crystalline. In fact, Fig. 6(B) show the typical A-type diffraction pattern of 348 349 wheat starch, with two singlet peaks (2 θ) at 15° and 22.8°, a doublet peak (2 θ) at 16.8° and 17.8°, and two weak peaks (2 θ) at 5.6° and 20°. In addition, Fig. 6(B) shows the relative 350 crystallinity of DHT_4h was lower than control and DHT_2h starches. Therefore, the XRD 351 results are consistent with the DSC results, indicating that DHT reduced the double-helical 352 crystals and decreased the order of starch crystalline structure - as also observed by (Lei et 353 al., 2020). 354

The thermal and crystalline results are consistent with the behavior observed by optical microscopy about the reduction of Maltese crosses brightness in modified starches. All these results pointed out that the DHT reduced the crystalline zones of wheat starch. Even so, the starch properties must be evaluated. 359

360 3.4 Starch pasting properties

Fig. 7 (A) shows the RVA curves for control and wheat starch treated by DHT. Table2 shows the pasting parameters obtained from RVA and the parameters.

The dry heating treatment significantly (p < 0.05) decreased the peak apparent viscosity (PAV), and there was a greater effect on this parameter as treatment time increased. This effect can be associated with cleavage of glycosidic linkages which resulted in weakening of starch granules resulting in minor capacity to maintain the granule integrity (Chung, Min, Kim, & Lim, 2007).

The pasting temperature (PT) is the temperature at which starch granules begin to swell due to water uptake (Gałkowska & Juszczak, 2019). DHT applied for 4 h slightly increased PT, which can be related with the presence of a greater fraction of small-sized molecules, that require more energy to gelatinize than large-size molecules similar to that observed by Lima et al., (2020).

Moreover, as the dry heating treatment period increased, a significant reduction (p < 0.05) of the through apparent viscosity (TAV) and final apparent viscosity (FAV) occurred. It can be associated with the thermal degradation of crystalline structures (observed in DSC and XRD analysis) and depolymerization (cleavage of glycosidic linkages) promoted by DHT (Zou, Xu, Tian, & Li, 2019).

The increase of the DHT period also increased the RBD and reduced the RSB parameters, when compared to control starch (data shown in Table 2), indicating that the granules are more fragile, more susceptible to rupture, and less prone to re-associate. According to Castanha et al. (2017), this behavior can be attributed to the change in the molecular size distribution.

Therefore, pasting properties confirm the structural modifications due to DHT processing, as well as they indicate hydrogels can present unique properties.

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386 3.5 Hydrogel properties: rheology, firmness, and syneresis

Fig. 7 shows the results of (B) oscillatory stress sweep analysis, (C) gel firmness, and (D) the energy required in a puncture assay, considering the control and the wheat starch modified by DHT (2 and 4 h). Table 2 shows the parameters obtained from oscillatory stress sweep analysis.

Fig. 7(B) shows the representative storage (G') and loss (G'') modulus curves: the G' 391 in this plateau region is a measure of the elasticity of material at very small deformation and 392 it can be taken as a measure of the structural strength of mechanical rigidity of material at rest 393 394 (Lille, Nurmela, Nordlund, Metsä-Kortelainen, & Sozer, 2018; Mezger, 2006). Moreover, for both control and modified starches, G' > G'' which indicates that all samples show a 395 solid/elasticity dominating gel-like structure. G' increased with the DHT period, as well as the 396 ration G'/G'', which indicates this treatment promoted the formation of a gel with greater 397 rigidity and capacity to recover the shape after suffering stress. Therefore, this hydrogel 398 399 probably shows good properties to be printed, because it can recover better the shape when it 400 is deposited on the surface – being this evaluated in the next section.

401 The yield stress ($\mathbf{\sigma}_{0,G'}$) is the stress where G' starts to decrease after the plateau region (Table 2), which indicates the stress at which the network/structure of the material starts to 402 break down. The $\sigma_{0,G'}$ can be related to the ability of the material to keep its shape under 403 gravity and the stresses generated by material layers deposited on top of it (Lille et al. 2018). 404 The $\sigma_{0,G'}$ value was greater as the DHT period increases. According to Lille et al. (2018), a 405 406 material with high structural strength at rest (G') and a certain degree of resistance to external stresses ($\mathbf{O}_{0,\mathbf{G}}$) is required to ensure good printability of a material. In this way, we can 407 observe that the DHT improved these rheological parameters of the wheat starch hydrogel, 408 indicating that it can be a better material to be used in 3D printing. 409

Fig. 7(C) and 7(D) show the gels produced with modified starches showed higher firmness than the control, and this behavior was more accentuated as the treatment period increased. The molecular depolymerization promoted by DHT (Fig. 5) probably resulted in size distribution that better re-associate and packing, forming a stronger three-dimensional network structure. In this way, DHT promoted the formation of stronger gels, expanding the industrial applications of wheat starch.

During starch gels cooling, molecular retrogradation and amylose tendency to crystallize releases water from the gels – which is called synereis. The syneresis prejudices the printability of the hydrogels, as well as the consumer perception. DHT reduced syneresis, which is an interesting result: control: 7.38 ± 0.71 g water/ 100 g gel, DHT_2h: 5.19 ± 0.19 g water/ 100 g gel, DHT_4h: 3.62 ± 0.13 g water/ 100 g gel). As a result, these "inks" appeared well adapted to 3D printing use - in fact, this behavior can be seen in Fig. 8. Pictures of the syneresis in the hydrogels are shown in the Supplementary Fig. S2. 423

424 3.6 3D printing performance and characterization

425 Fig. 8 shows the star, heart, and cylinder shaped structures, printed using the hydrogels based on control and modified starches as "inks". Overall, the printed samples in our work 426 427 were very similar to the pre-designed virtual model, indicating that the 3D printing could achieve precise printing with a personalized design using wheat hydrogels. All hydrogels 428 429 could be smoothly extruded from the nozzle. However, the hydrogel based on control starch showed a scattering on the surface and a syneresis effect (visible in the star shape, which is 430 consistent with the results presented in Section 3.4). The modified starches showed higher gel 431 consistency, without spreading on the surface. The hydrogel based on DHT_4h starch showed 432 433 the best resolution with the lines having higher cohesiveness and being more continuous. The behavior of the hydrogels after 3D printing can be associated with the rheological parameters: 434 the hydrogels with higher G' and $\sigma_{0,G'}$ showed the best printability. 435

Texture is an important sensory attribute of food acceptability (Yu, Ren, Zhao, Cui, & 436 437 Liu, 2020). In this way, the printed cylinders were evaluated in relation to its textural parameters (Table 3). Results showed there was no significant difference in the cohesiveness, 438 439 springiness, and chewiness values of printed samples. On the other hand, the increase of the 440 heating period caused a significant (p<0.05) increase on hardness. According to Yang, Zhang, 441 Prakash, & Liu (2018b), higher G' indicates stronger mechanical strength often accompanied by greater hardness, behavior also observed in our results. The modified starches resulted in 442 printed samples with less adhesiveness. According to Anukiruthika, Moses, & 443 Anandharamakrishnan (2020), less adhesive "inks" flow more easily through the nozzle, 444 contributing to the 3D printing process. In this way, DHT extended the possibility of textures 445 of printed samples based on wheat starch hydrogels. 446

About reproducibility, the hydrogels based on modified starches showed lower weight and higher height than hydrogel based on control starch. The diameter did not show a significant difference among the treatments. Moreover, by comparing the standard deviation, we observed lower values for DHT_4h, indicating this treatment formed hydrogel were more reproducible 3D printing.

Finally, comparing this study with the previous of our group (Maniglia et al., 2020), we can observe that the same physical modification, DHT, showed different effects for each starch source, affecting the final printability characteristic. The modified cassava starch was more depolymerized, suffered oxidation, and showed gel firmness much higher than the native one, when compared with the changes here reported for wheat starch. Modified wheat
starch showed a reduction in syneresis, which is important for 3D printing application. In this
way, our results provide information on the benefits DHT modification can bring to each
source, mainly focusing on the application of 3D printing.

460

461 **4.** Conclusion

This work investigated the use of dry heating treatment (DHT) as a tool to improve the 462 printability of hydrogels ("inks") based on wheat starch. DHT caused a slightly expansion of 463 granule size; however, it did not alter the shape of the starch granules nor their surface. DHT 464 did not change the functional groups of the starch, indicating a negligible oxidation. However, 465 slight depolymerization of starch was observed, in special in the middle size molecules, as 466 well as a reduction of the crystalline zones in starch granule. The hydrogels based on the 467 468 modified starches showed lower apparent viscosity during pasting and greater structural strength at rest. The longer duration of DHT processing, higher was the firmness of the 469 hydrogels, and more reduced was the syneresis. The changes promoted by DHT in wheat 470 starch, in special in 4 h treatment, resulted in hydrogels with better printability and 471 reproducibility in 3D printing. 472

In this study, we demonstrated that the DHT is a simple alternative to improve the properties of wheat starch, as well as extend the texture possibilities of printed samples based on wheat starch hydrogels. Finally, this study shows the possibilities to expand the potential application of this starchy source.

477

478 Declaration of Conflict of Interest

479 The authors declare no conflict of interest.

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Fig. 1. The picture of 3D printer with the main parts: the extruder motor, syringe (cartridge) with the nozzle (movement in z direction), heating control, and mobile platform (movement in x and y directions).



Fig. 2. (A) Granule size distribution (B) Specific diameters (D[4,3], D[3,2], d0.1, d0.5, d0.9 - vertical red bars are the standard deviation) of the control and modified starches by dry heating (DHT_2h and DHT_4h):



Fig. 3. Photographs from light microscopy (40×) using (A) nonpolarized and (B) polarized light of the control and modified starches by dry heating (DHT_2h and DHT_4h).



Fig. 4. (A) Vibrational spectra in wavenumber interval between (A) 4000 until 900 cm⁻¹) and between (B) 1200 until 900 cm⁻¹ of the control and modified starches by dry heating treatment (DHT_2h and DHT_4h).



Fig. 5. Molecular size distribution of the control and modified starches by dry heating (DHT_2h and DHT_4h).



Fig. 6. (A) DSC thermograms and (B) XRD of control and wheat starch treated by dry heating (DHT_2 and DHT_4 h).



Fig. 7. (A) RVA curves, (B) oscillatory stress sweep analysis (G': storage modulus and G'': loss modulus), (C) Gel firmness, and (D) the energy required in a puncture assay of the control and the wheat starch treated by dry heating (DHT_2 and DHT_4 h).



Fig. 8. The 3D printed hydrogels (star, heart, and cylindrical shapes) based on control wheat starch and modified wheat starch by dry heating treatment (DHT_2h and DHT_4h).

Samples	To (°C) Tp (°C) Tf		Tf (°C)	ΔH (J/g)
Control	47.99 ± 0.28^{a}	$58.05 \pm 0.10^{\circ}$	74.32 ± 0.56^{a}	9.85 ± 0.12^{a}
DHT_2 h	47.43 ± 0.37^{a}	58.30 ± 0.06^{b}	74.65 ± 0.62^{a}	9.89 ± 0.28^{a}
DHT_4 h	47.23 ± 0.43^{a}	59.85 ± 0.10^{a}	74.42 ± 0.35^{a}	7.57 ± 0.10^{b}

Table 1. Gelatinization properties of the control and modified starches by dry heating(DHT_2h and DHT_4h) (average ± standard deviation).

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

To = onset temperature, Tp = peak temperature, Tf = final temperature and Δ H = enthalpy.

DHT_2h: wheat starch dry heating treated for 2 h. DHT_4h: wheat starch dry heating treated for 4 h.

Table 2. Pasting parameters from RVA and parameters from oscillatory stress sweep analysis of the control and modified starches by dry

heating (D)	HT_2h and	l DHT_4h)	$(average \pm standard)$	l deviation)
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Samples	PAV (mPa.s)	TAV (mPa.s)	RBD (%)	FAV (mPa.s)	RSB (%)	PT (°C)	G´ (Pa)	G ~ (P a)	б 0,G' (Ра)
Control	2250.40±40.92 ^a	1378.43±18.30 ^a	37.36±1.09°	2757.50±14.95 ^a	40.71 ± 0.72^{a}	73.53 ± 0.32^{b}	175±25 ^c	$33.4 \pm 2.2^{\circ}$	12.74±0.05 ^c
DHT_2 h	2017.00±30.15 ^b	1172.80±22.30 ^b	40.45±0.82 ^b	2257.00±70.21 ^b	31.91±0.49 ^b	73.68±0.38 ^b	257±32 ^b	40.1±1.6 ^b	26.37±0.20 ^b
DHT_4 h	1820.72±22.17 ^c	1034.02±10.12 ^c	43.93±0.65 ^a	1927.50±82.73°	18.73±0.42 ^c	74.53 ± 0.25^{a}	430±14 ^a	88.9±4.5 ^a	54.56 ± 0.08^{a}

Peak Apparent Viscosity (PAV), Through Apparent Viscosity (TAV), Relative Breakdown (RBD), Final Apparent Viscosity (FAV), Relative Setback (RSB) and Pasting Temperature (PT), Storage modulus (G'), Loss modulus (G''), Yield stress ($\sigma_{0,G'}$)

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

DHT_2h: wheat starch dry heating treated for 2 h. DHT_4h: wheat starch dry heating treated for 4 h.

 Table 3. Texture parameters and reproducibility of the starch hydrogels printed in cylinder shape. The hydrogels are based on control and modified starches by dry heating (DHT_2h and DHT_4h) (average ± standard deviation)

Starch hydrogels	Texture					Reproducibility		
	Hardness (N)	Adhesiveness (N.s)	Cohesiveness (-)	Springiness (-)	Chewiness (-)	Weight (g)	Diameter (mm)	Height (mm)
Control	$0.68 \pm 0.08^{\circ}$	-1.67±0.01 ^a	0.41 ± 0.01^{a}	0.81 ± 0.03^{a}	0.27 ± 0.01^{a}	15.38 ± 0.36^{a}	2.50 ± 0.16^{a}	2.08 ± 0.08^{b}
DHT_2h	0.82 ± 0.03^{b}	-2.16±0.15 ^b	0.41 ± 0.01^{a}	0.84 ± 0.04^{a}	0.27 ± 0.01^{a}	14.74±0.34 ^b	2.58±0.16 ^a	2.34±0.11 ^a
DHT_4h	1.03 ± 0.05^{a}	-2.23±0.23 ^b	0.41±0.02 ^a	0.82 ± 0.04^{a}	0.32±0.03 ^a	14.81±0.18 ^b	2.48 ± 0.08^{a}	2.36±0.11 ^a

a - c: different letters in the same column indicates significant difference among samples, as revealed by Tukey's test, p < 0.05 DHT_2h: wheat starch dry heating treated for 2 h. DHT_4h: wheat starch dry heating treated for 4 h.

DHT improved the 3D printability and extended the texture possibilities of wheat starch hydrogels

