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Structuring wheat dough using a thermomechanical process, from liquid food to 3D-printable food material

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ABSTRACT

In extrusion printing, the printability of food materials depends on the rheology of the food under shearing when extruded, and at rest, post-deposition. Piloting food microstructure to provide rheological properties compatible with 3D extrusion printing is a major challenge. Microstructure, rheology, and printability of wheat-flour based materials with varying concentrations of flour, sugar, oil, and water were studied. Materials were obtained by heating and shearing doughs with a moisture content above 55% (wb). The processed doughs were structured as closely-packed particles made of swollen gelatinized starch granules glued in a denatured proteins network. These materials were easily extruded in self-supporting layers by a 3D food-printer and formed stable objects with precise dimensions. The water/flour ratio played a crucial role in the structure of the wheat materials, impacting the storage modulus (G'), tan δ and printability. This work highlights the importance of tan δ in predicting the ability of food materials to hold its 3D structure.

1. Introduction

The growing interest of researchers and industry in 3D food printing in the last five years led to advances in the technology and to the formulation of a variety of printable edible materials. Extrusion printing, which consists in forcing material through a die opening, was first used to print thermoplastics (Turner et al., 2014). Then, edible 3D objects made of food materials with a pasty texture were printed including wheat dough (Severini et al., 2016; Yang et al., 2018), mashed potatoes (Liu et al., 2017) and surimi paste (Wang et al., 2018). Studies of 3D printing of polylactic acid (PLA), a widely used thermoplastic in design and prototyping, revealed a correlation between the viscosity of a material and its ability to be printed (Bakrani et al., 2019). At room temperature, PLA is a solid-like material and can only be extruded when heated above its melting transition temperature (about 200 °C for semi-crystalline PLA) when its viscosity is lowered to about 2,000 Pa s (Bakrani et al., 2019). When deposited on the printing plate after extrusion, the material rapidly solidifies by going through the glass transition while cooling. To form an object in volume, the viscosity of the material must be high enough to form a self-supporting layer, *i.e.,* not deform under its own weight or the weight of subsequently deposited layers, until the transition to a solid state is achieved (Godoi et al., 2016). On the other hand, printing a high viscosity material requires considerable energy and can increase pressure inside the printer which then affects the printing flow rate. Printability defines the ability of the material to be extruded by the printer and to maintain its printed structure post-deposition (Godoi et al., 2016). Thus, shear-thinning fluids showing high viscosity at very low shear rates, but whose viscosity is several orders of magnitude lower during extrusion, could be compatible with 3D printing. Wheat flour dough was one of the first food material successfully 3D printed. To some extent, the doughs of cereal products combine the shear-thinning behavior required during the extrusion step of the printing process (Jiang et al., 2019). These properties are related to the organization of the wheat flour components in the dough combined with the structuring effect of proteins at room temperature obtained by kneading and, to a lesser extent, of the numerous starch granules dispersed within the dough. The organization of the gluten proteins depends mostly on the water content and the mixing process, and can lead to the formation of an elastic network of proteins in which starch granules are embedded (depending on the quality of the protein and the type of wheat) (Auger et al., 2008). So far, wheat flour has been added in the recipes of printable materials because of the ability of the compounds in the flour to bind water, and the ability of the proteins in the flour to interact and form a viscoelastic gluten

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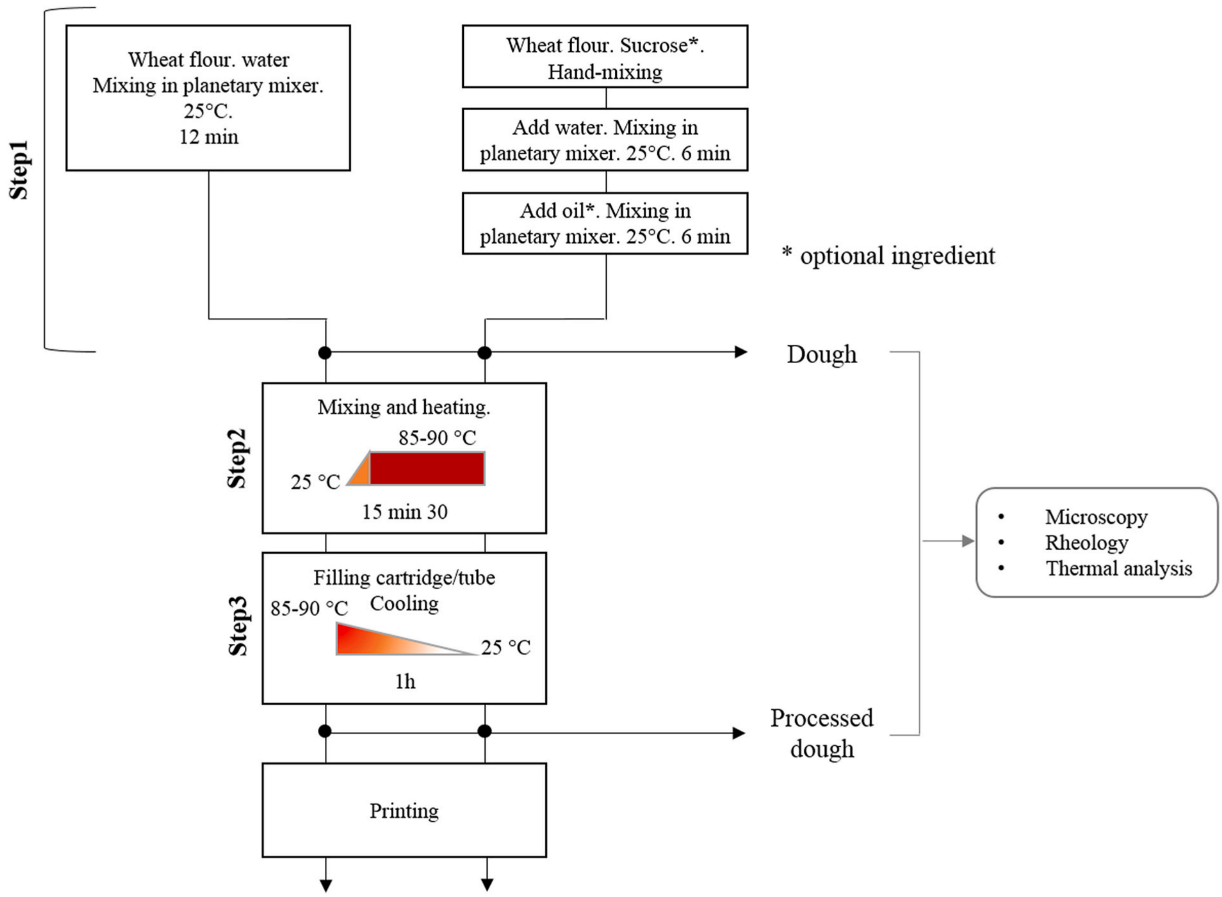


Fig. 1. *Experimental design to produce wheat flour-based printable material and characterization methods.*

network (Kim et al., 2019; Severini et al, 2016, 2018, 2016; Yang et al., 2018; Zhang et al., 2018). However, to our knowledge, no works have explored changes in the properties of the dough under heat treatment at water contents higher than 55 wt% for which no gluten network can be formed, whereas, the swelling of starch in such wheat doughs may provide an interesting path for the development of printable food materials.

Wheat starch is a well-known food texturing agent (Rapaille and Vanhemelrijck, 1997) and a major component of wheat flour (between 70 and 80% of dry mass). Wheat starch is composed of glucose polymers, amylose, and amylopectin, organized in a semi-crystalline structure in the native starch granule. Under heat treatment and in presence of water, the starch absorbs the water from the medium, loses its semi-crystalline structure and swells. This phenomenon, which affects the structure of the granule, is referred to as starch gelatinization. Depending on the concentration of starch and on the heating parameters, the swollen starch granules may come into contact with one another. They then form a closely-packed system of granules that occupies a much larger volume than the one occupied by the continuous phase made of denatured gluten proteins that covers the starch granules (Bagley and Christianson, 1982; Hermansson and Svegmark, 1996).

The effect of the composition of the dough after the addition of texturizers, sugars and fat on the printability of wheat doughs has been studied by several authors (Kim et al., 2019; Yang et al., 2018). The addition of sucrose and fat are known to reduce the viscosity and elasticity of the dough at room temperature (Hesso et al., 2015; Maache-Rezzoug et al., 1998). Depending on the composition of the dough, upon heating, the addition of sugar and oil affects starch gelatinization kinetics (Abboud and Hoseney, 1984; Perry and Donald, 2002) and delays the swelling of the granules until higher temperatures are reached (Bean and Yamazaki, 1978). In the same process, the volume fraction of the starch granules may differ depending on the concentration of sucrose or oil, and consequently alter the properties of the heated dough.

If the system is sheared during heating, ongoing starch pasting and denaturation of the gluten network lead to the formation of a gel that is cut into numerous sticky particles. The rheology of closely-packed particulate systems is driven by the volume fraction, *i.e.,* the volume occupied by the particles, the spatial organization, the contact interactions, and the shape and the rigidity of the particles (Coussot and Ancey, 1999; Quemada, 1977). Rheology is most often characterized by a yield stress and shear-thinning behavior beyond this stress. At low shear rates, the rheology of a closely packed particle system is dominated by contact interactions, in other words, friction between the particles (Coussot and Ancey, 1999) and the spatial arrangement of the particles, which might be randomly close-packed or follow a pattern (Quemada, 2006). Under shearing, the stabilized particulate network has to be broken by the action of stress applied above the system yield stress to allow the system to flow with increasing hydrodynamic interactions, *i.e.,* the energy dissipated by viscous frictions between the medium and particles (Quemada, 1977). The state of the surface and the rigidity of the particles are important parameters in the rheology of concentrated suspensions, as they define contact interactions and the ability of the particles to deform and align with the flow with major effects on the shear-thinning behavior of the system.

The dough obtained after heating under shear can be compared with a system of closely-packed particles that stick together due to the denatured proteins that coat them. These particles are also rather soft due to the properties of the swollen starch granules and to the denatured protein network in which they are stuck. To date, this system has not been well characterized in the literature. Indeed, particles involved in concentrated food suspensions, such as starch paste or vegetable purees, may be deformable, but were previously not defined as being sticky

Table 1
Composition of doughs used in this study. The doughs are ordered according the ratio of water to flour. The ingredients are expressed as a percent, in g of ingredient/100 g of dough. The water/flour ratio is the ratio of the weight of added water to the weight of wheat flour.

Code number	Water/Flour (w/w)	Water content (%)	Added water (%)	Sucrose (%)	Oil (%)
0	1.12	60	52.8	0	0
1	1.35	60	54.0	6	0
2	1.43	65	58.8	0	0
3	1.67	60	55.0	12	0
4	1.68	55	50.5	12	7.5
5	1.76	65	59.9	6	0
6	1.83	70	64.7	0	0
7	1.86	65	60.2	0	7.5
8	2.25	65	60.9	12	0
9	2.34	74.6	70.1	0	0
10	2.34	60	56.4	12	7.5
11	2.55	70	67.5	6	0
12	2.61	65	61.5	0	15
13	3.10	65	62.0	18	0
14	3.41	80.7	77.3	0	0
15	3.41	65	62.2	12	7.5

(Leverrier et al., 2016; Rao, 2007). In another field of application, the stickiness of clay particles was made visible by slow dispersion of the particles under shearing, but clay particles are much more rigid than dough particles (Mongondry et al., 2005).

The aim of the present study was to develop a wheat-based material compatible with 3D printing extrusion, using the structuring properties of starch and proteins while heating under shearing. A lab-scale thermomechanical process was developed that enabled heat induced changes in the organization of starch and proteins to increase wheat dough viscosity. The roles of starch, protein, water and additional sucrose and oil in structuring were analyzed. The rheological properties of the resulting material were investigated and compared to its printability.

2. Materials and methods

2.1. Materials and preparation of printable food materials

Wheat-based printable materials were prepared by mixing all-purpose wheat flour (soft wheat), (Les fournils du Val de Loire, France) with deionized water, with the addition of commercial sugar (sucrose) (Saint-Louis) and sunflower oil (Cora). The water content of the wheat flour was 14.55 ± 0.01 g per 100 g flour (ISO 712:2009). Total protein content was 11.29 ± 0.04 g per 100 g dry flour (ISO 16634–2) (Qualtech, France) and ash content was 0.58 ± 0.01 g per 100 g dry flour (ISO, 18122). Powdered sugar and sunflower oil were stored in a dry place at room temperature and wheat flour was stored in airtight plastic buckets at −30 °C. All the ingredients were allowed to return to room temperature before use. The materials to be printed were obtained in the 3-step process described in Fig. 1.

The first step was mixing the ingredients for 12 min in a 5K45SS EOB CLASSIC planetary mixer fitted with a paddle (KitchenAid, USA) at room temperature at speed 4 (about 120 rpm). The second step was a thermomechanical process performed in a Thermomix (TM5, Vorwek, Germany) fitted with an anchor device for 15.5 min at speed 1 (100 rpm) while the temperature was increased from 25 °C to the set-point temperature of 85 °C or 90 °C. These process parameters were chosen after preliminary experiments and were set to allow heat-induced modifications of starch and proteins, without significant evaporation of water and hence drying of the dough. In the bowl, the heat was transferred in the dough from the bottom to the top. The third and last step consisted in filling the printing cartridge or tube using a pastry bag and leaving it to cool for 1 h at room temperature so the temperature of the processed dough reached about 25 °C before further measurements and printing.

A dough with 65 wt% water was chosen as reference. This water content allowed us to obtain a post heating viscosity that was compatible with lab-scale production. Changes in temperature and in the rheological properties during step 2 were studied by stopping the process at different times. The temperature of the dough was measured immediately after the process was stopped. The rheology was characterized after cooling the sample to room temperature.

In order to investigate the effect of ingredients on the 3D printing properties of the processed dough, three levels of sunflower oil, three levels of sucrose and six levels of water were tested. Water, sucrose, and oil concentrations were varied in the ranges 55–80.7 wt%, 0–18 wt% and 0–15 wt%, respectively (Table 1). The highest concentrations of oil (15%) and sucrose (18%) in the recipes we tested are the oil and sucrose contents found in existing products, such as laminated biscuits (Charun and Morel, 2001). All the compositions of the doughs are summarized in Table 1.

2.2. Printing process and evaluation of printing quality

The hot processed dough was used to fill the cartridge (60 mL syringe, BD Plastipak, USA) that was plugged into a prototype 3D food printer designed by Dagoma (Roubaix, France). The printing process consists in the extrusion of the material stored in the cartridge by a piston. The syringe is held vertically on the printer axis parallel to the printer plate (X axis). It moves laterally and vertically (Z axis) while the printing bed moves on the Y axis orthogonal to the X axis. The piston is in contact with the surface of the material with the larger diameter of the syringe and moves toward the smaller diameter (or bottom of the syringe). The end diameter of the syringe is 3.7 mm, which defines the width of the smallest layer that can be printed using these parameters. The models to be printed were drawn on Tinkercad (online open access software, Autodesk, USA). The models were loaded in Cura software interface (version 2.6.2, Ultimaker, NL) in which the printer and material profiles were downloaded. The script for the nozzle and printer plate movements were created by the software under gcode format. The height of the deposited layer was 2 mm and of the width 3.7 mm. The height of the layer was reduced to increase adhesion between layers and the printing resolution. Depending on the object, the infill percentage varied from 100% (object is full) to 0% (only the external walls are printed). All printings were carried out at 25 °C at a printing speed of 5 mm/s (for walls and infill layers). Pictures of the printed objects were taken after printing. The dimensions of the object were measured using a caliper (Mitutoyo, Absolute Digimatic) immediately after printing and again 5 min later. The printing was assumed to be of good quality when (1) the extruded layer formed a continuous smooth line, (2) the dimensions of the object were similar to the dimensions of the digital model (with a tolerance of less than ± 20% of deviation, given the complexity of the printed structures) (Yang et al., 2018) and (3) the dimensions of the structure remained unchanged after 5 min of observation.

2.3. Thermal analysis (differential scanning calorimetry)

A power-compensated DSC calorimeter equipped with an autosampler (Q100 DSC, TA instruments, Newcastle, UK) was used. Temperature and enthalpy parameters were calculated using the melting transition of indium (T_0 = 156.6 °C; ΔH = 28.5 J/g). An empty sample pan was used as reference and nitrogen was used as the purge gas to cool the system down. Between 3 and 10 mg of product (dough or processed dough, Fig. 1) were weighed in aluminum pans. The samples completely covered the bottom of the pans. A few drops of water were added to the pans containing samples of processed doughs to allow further gelatinization in the processed doughs (final weight < 12 mg). The pans were then heat-sealed and left to rest at 4 °C for 10 h to let the water diffuse into the processed dough. The DSC protocol began by cooling the samples to 0 °C before heating them to 150 °C at 10 °C/min. Thermograms

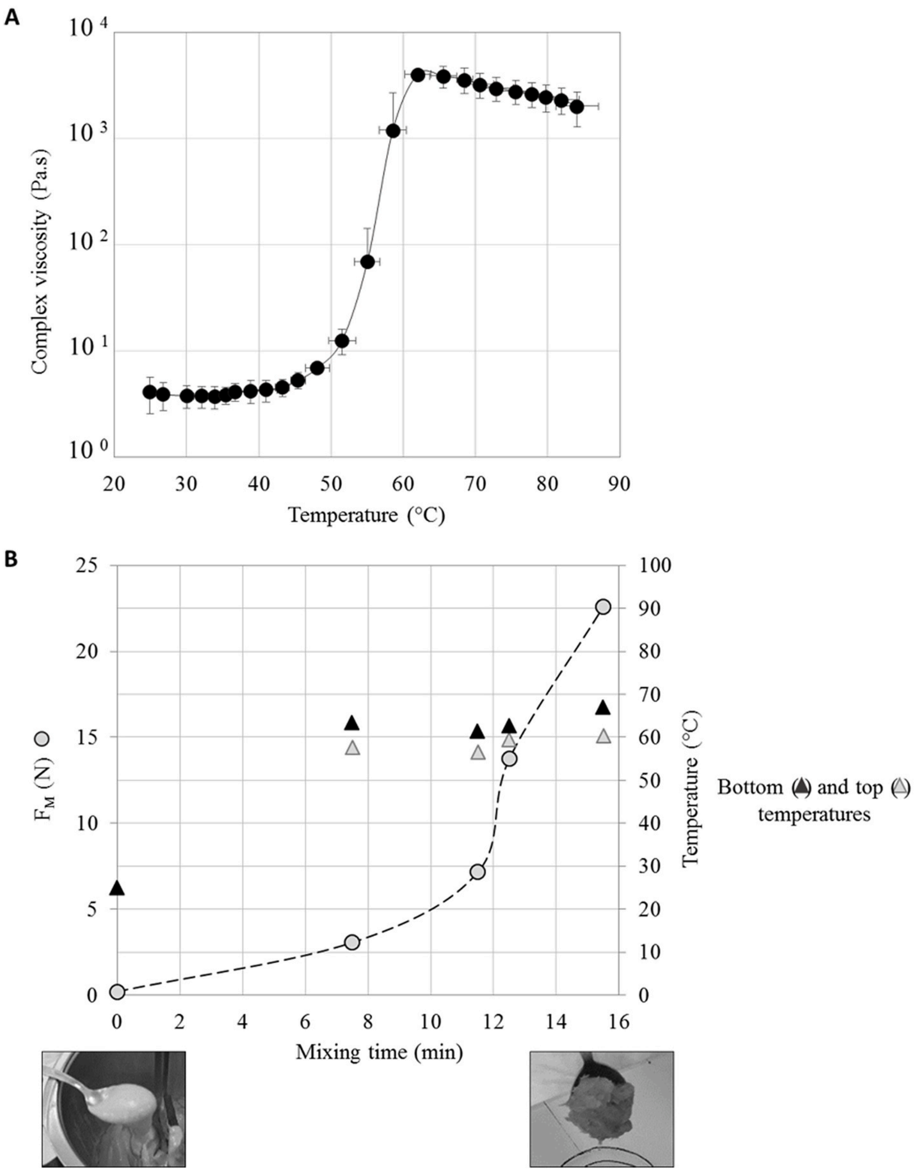


Fig. 2. Increase in complex viscosity and normal resistance force (F_M) of dough at 65 wt% of water upon heating. A. Complex viscosity at 1Hz (heating rate: 5 °C/min; 0.2% strain); B. F_M (after cooling) and temperatures at different mixing times.

were used to determine the temperature transition and enthalpy (ΔH) of starch gelatinization. T_{onset} is the temperature required to trigger gelatinization and T_{Max} is the temperature at which gelatinization is maximum. The enthalpies are converted from J/g of product to J/g of starch, considering that starch represents 70% on a wet basis of the wheat flour used. The degree of starch gelatinization in processed dough, G, is determined by the ratio of enthalpies measured in doughs and processed dough, ΔH_D and ΔH_{pD}, respectively (Eq. (1))

$$G = 100 \times \left(\Delta H_D - \Delta H_{pD}\right) / (\Delta H_D) \quad (1)$$

By convention, the starch was considered to be completely gelatinized when the indicator G was equal to 100% with a margin of 5%, *i.e.*, for all the values of G greater than or equal to 95%. For G < 95%, starch was defined as partially or not gelatinized, no distinction being made between the two.

2.4. Microscopy

Wheat starch granules were observed with an optical microscope (Olympus, Japan) at ×50 magnification under polarized and non-polarized lights. Samples of dough and processed dough weighing approx. 0.1 g were collected at different locations in the bowl and deposited on a slide. Using a 5-mL plastic Pasteur pipette, two drops of distilled water (about 0.2 mL) were placed on top of the samples to dilute the samples before the slide was covered with a cover slip.

The organization of the proteins in the material at 65 wt% of water was observed with a confocal laser scattering microscope (CLSM) (Leica TC SP8 Leica, Germany). Using 250 μm thick spacers, the material was put on the lamella and 2 μL of Dylight 488 was poured on top of the dough to label the proteins. The stain was excited using a laser with a wavelength of 488 nm and the emitted fluorescence was detected in the range of 496–576 nm. Pictures were taken at ×10 magnification.

2.5. Rheological analysis

2.5.1. Back extrusion

The rheology of the processed doughs at large deformations was investigated using the back extrusion method in a texture analyzer (TaHD, Stable Micro System, UK). About 35g of material were poured into 40-mL plastic tubes and compressed by a piston (annulus gap of 1.5

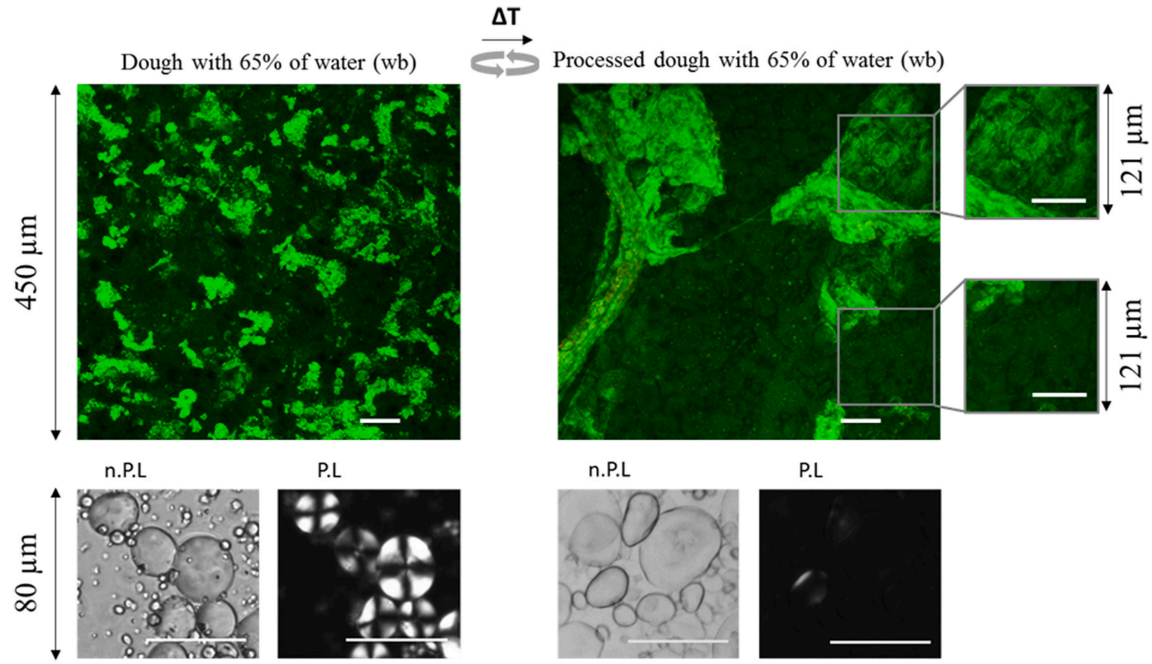


Fig. 3. Observations of the dough with 65% of water after mixing at room temperature (Step 1) and after thermomechanical processing and cooling (Step 3) by CLSM (magnification ×10; proteins are stained green) and viewed under polarized light (P.L) and non-polarized light (n.P.L) (magnification ×50). All scale bars are 50 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

mm) at a crosshead speed of 1 mm/s applied along the 35 mm of depth. The tubes were filled with the hot processed dough obtained in step 2 and cooled in the tube to room temperature. Because of the method artifact, the volume filling of the tubes was kept constant in all experiments. During compression, the normal force (N) increased quite linearly until it reached a plateau. The normal resistance force to the flow in the annulus gap (F_M) was defined as the mean value calculated between 10 and 20 mm of penetration in the sample, values for which the flowing stage (corresponding to the plateau) was obtained in all samples (Moussier et al., 2019). Measurements were made in triplicate on at least two different products.

2.5.2. Temperature and frequency sweep tests

Rheological measurements under dynamic oscillations were made using a dynamic stress rheometer Carri-Med CLS[2] 100 (TA Instruments, USA) fitted with a cone-plate geometry (diameter: 4 cm, angle: 4°and truncation: 106 μm). Dough samples were heated from 25 to 85 °C during temperature sweep tests performed at 1Hz, 5 °C/min and 0.2% of maximum strain amplitude. These conditions were chosen in the linear domain (identified by preliminary strain sweeps, data not shown). Frequency sweep tests conducted in the range 0.1–10 Hz, at 20 °C and 0.2% of strain showed that all the processed dough spectra were the same shape, with higher elastic modulus (G′) than loss modulus (G″) over the frequency range. Thus, results at 1 Hz allowed comparison of the samples.

3. Results and discussion

3.1. Characterization of dough and processed dough made of wheat flour and water

Fig. 2.A shows changes in the complex viscosity as a function of temperature for doughs with 65 wt% water. The viscosity decreased slightly from 25 to 40 °C, most probably due to a thermal agitation effect (Vanin et al., 2018). Then, between 55 and 65 °C, viscosity increased dramatically to 4,000 Pa s, in good accordance with the literature (Campos et al., 1997; Vanin et al., 2018). DSC measurements identified the temperature required to trigger starch gelatinization (T_{onset}) in this dough to be around 58 °C (±0.3 °C). Consequently, the increased viscosity is assumed to be caused not only by the absorption of the water and swelling of the starch granules, but also by protein aggregation between 50 and 85 °C (Leon et al., 2003). From 65 °C to 80 °C, viscosity decreased slowly to reach 2,025 Pa s. The slow decrease in the complex viscosity from 60 to 85 °C is hypothesized to reflect the softening of the swollen starch granules (Tsai et al., 1997). The final viscosity was rather close to the viscosity of melted PLA, suggesting that this heated dough has potential for 3D printing.

Back extrusion tests were carried out to monitor changes in dough texture during the thermomechanical process used for the production of printable material. Fig. 2B presents F_M and the temperature levels at the bottom and at the surface of the dough as a function of the processing time. A progressive increase in F_M from 0.2 to 7 N occurred from 0 to 11.5 min of thermomechanical treatment. After 11.5 min, F_M increased by a factor 2 in only 1 min to reach 14 N. At the end of the process, F_M was 22 N. Overall, the average temperatures at the surface and at the bottom of the bowl remained relatively stable over time and higher than the theoretical starch T_{onset} measured in the dough, corresponding to the beginning of starch gelatinization. The increased F_M was correlated with changes in the texture of the dough, which changed from liquid to pasty and sticky as shown in the pictures taken before and after processing (Fig. 2B).

When a suspension of starch and proteins was heated and mixed, shearing led to the formation of particles composed of swollen gelatinized starch embedded in a continuous gelled phase. The flow properties of the particle system were evaluated by measuring F_M when the particles were going through the gap during the back-extrusion test. The particles were invisible to the naked eye but were expected to be less than 500 μm.

The microstructure of the dough and processed dough with 65 wt% of water is shown in Fig. 3. The proteins in the dough formed unbound particles >50 μm in diameter. Mixing conditions and water content led to the production of unconnected swollen objects made of proteins (Auger et al., 2008; Masbernat et al., 2021). Starch granules were dispersed in the suspension as shown in diluted condition with

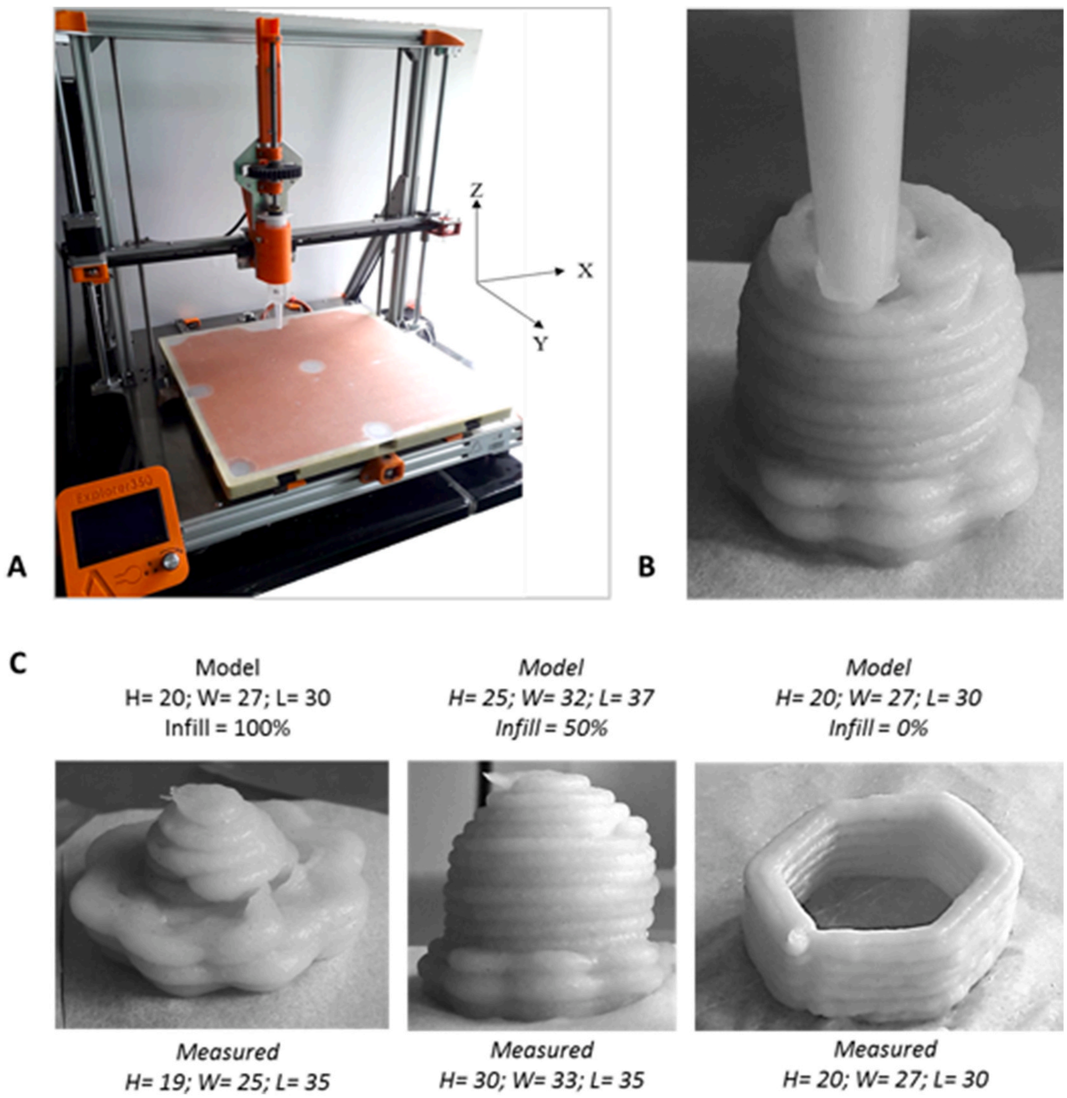


Fig. 4. Pictures of 3D printed objects made of processed dough containing 65 wt% of water after thermomechanical processing and cooling. A. 3D printer; B. Printing in progress; C. Examples of printed objects. The height (H), length (L), width (W) and infill percentage of the models are given in mm and % above the pictures. The dimensions (mm) measured after printing are given under the pictures.

non-polarized light microscopy (n.P.L) (Fig. 3). Large and small starch granules with diameters ranging from 1 to 45 μm were identified, in good agreement with the literature (Raeker et al., 1998). Under polarized light, starch granules showed the Maltese cross attesting to the semi-crystalline organization of the macromolecules in the native starch granule (French, 1972).

After the thermomechanical treatment, the wheat flour proteins formed large connected objects in addition to the continuous filler present between the starch granules. With sufficient hydration during heat treatment, the denaturation of proteins starts with reversible unfolding of glutenins followed by the formation of disulfide bonds in the glutenins, resulting in the formation of insoluble protein aggregates containing both gliadins and glutenins (Domenek et al., 2003). When mixing and heating were combined, the dense aggregates of protein particles connected to each other to form larger strands that were stretched by shearing (Fig. 3). The presence of proteins between the starch granules is shown by the green stain observed on the surface of starch. This observation confirms the hypothesis proposed by Mann et al. (2014) that denatured gluten aggregates act like weakly interconnected fillers in the starch network when a dough with 40 wt% of water is heated.

The photo taken under n.P.L shows swollen granules, whose contours are thin and blurred. The photo taken at the same location under polarized light shows a black background. The loss of crystallinity and the moderate swelling indicate that starch granules gelatinized during the heat treatment, yet the gelatinization appears to be only partial: observation of the microscopic pictures under polarized light shows some granules with crystalline parts near the surface. In the close-up CLSM pictures of the processed dough (Fig. 3, on the right), starch granules are embedded in the protein aggregates and are in contact with other granules.

These results are evidence that the process modified the state of both starch and proteins by enabling the starch to swell and gluten protein to aggregate. After the process, the swollen starch granules occupied a large proportion of the processed dough and the denatured proteins formed a continuous matrix between the starch granules and long proteins strands, the latter can reach 500 μm in length. Similarly to the more dilute heated dough studied by Champenois et al. (1998), the denatured protein strands formed areas that prevented contact interaction between granules and delimited cohesive dough particles composed of some swollen starch glued in denatured proteins. These particles occupied all the volume and were sticky. They formed a closely-packed network. Therefore, the rheological properties of the processed dough are hypothesized to be determined by the interactions and mechanical

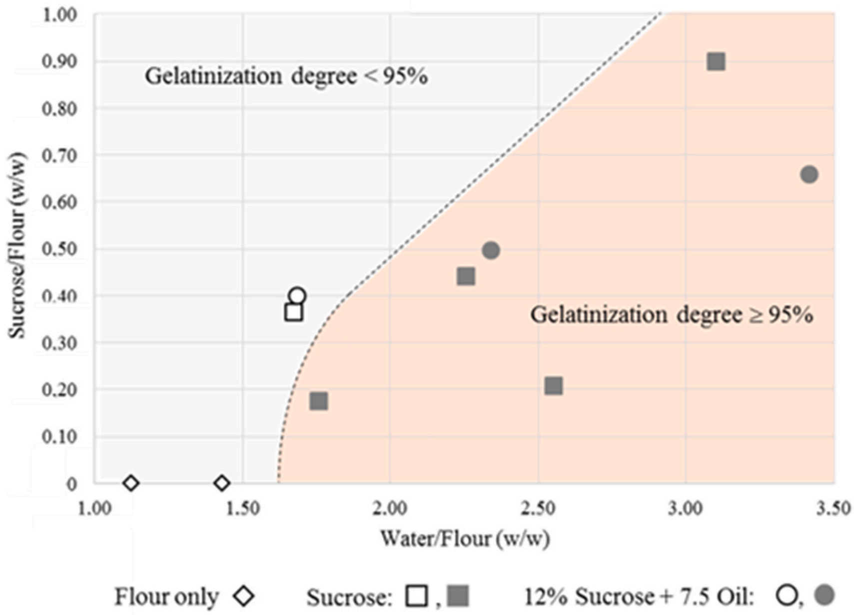


Fig. 5. Degree of starch gelatinization in processed doughs with the addition of different quantities of sugar (from 0 to 18 wt%), oil (0 or 7.5 wt%) and water (from 55 to 70 wt%). Black symbols, G ≥ 95%; empty symbols G < 95%. The dotted line is the estimated water/flour ratio above which starch gelatinization in the processed dough was complete.

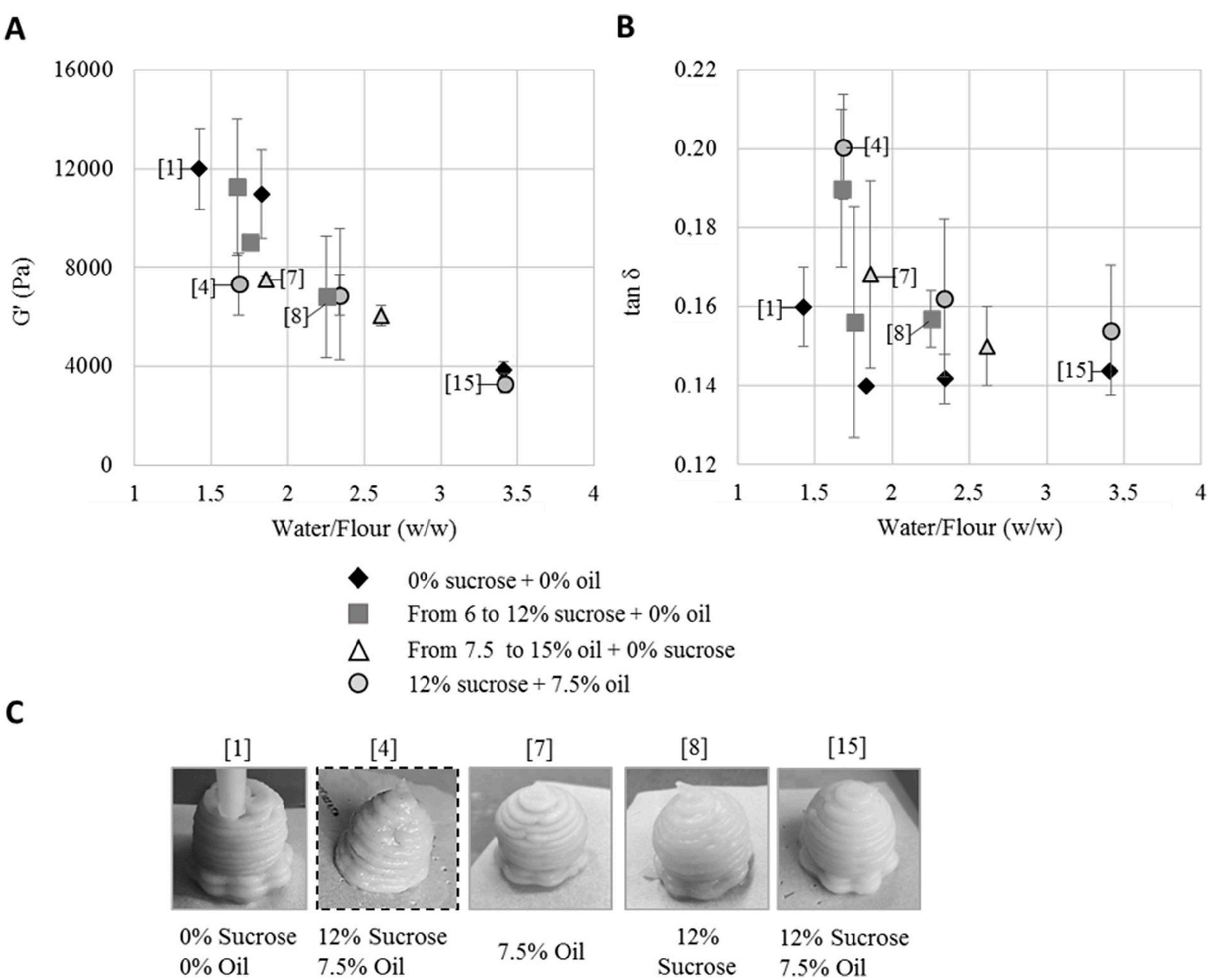
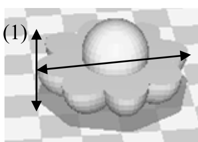
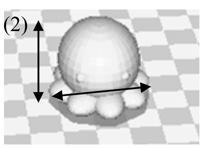
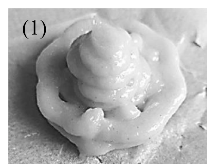
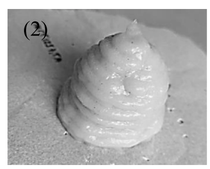
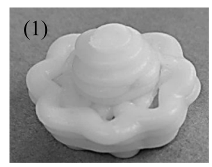
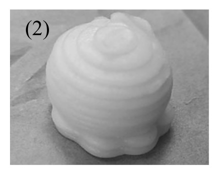
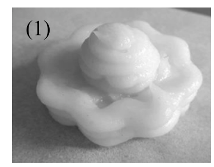
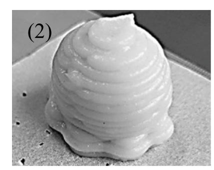


Fig. 6. Storage modulus (A) and tanδ (B), at 1Hz (0.2% of maximum amplitude strain, 20°C), versus measured water/flour ratios of processed doughs and pictures of printed objects with different proportions of flour/water, sucrose and/or oil (C). The picture framed by the black dashed line is an example of unsatisfactory printing.

Table 2
Water/flour ratios, storage modulus, tan δ (1 Hz, 0.2% of strain, 20°C) and printability of processed doughs including 12 wt% of sucrose and 7.5 wt% of sunflower oil with different total water contents ranging from 55% to 65 wt%.

	55% of water (wb)	**60% of water (wb)**	**65% of water (wb)**
Code number	[4]	[10]	[15]
Storage Modulus (Pa)	7337	6545	3310
tan δ	0.20	0.16	0.15
Water/Flour (w/w)	1.68	2.34	3.41
Printing: Pictures H = 20  W= 35 H = 25  W= 32	 	 	 
Dimensions Height (H) and width (W) after printing (mm)	(1) : H = 24; W = 26 (2) : H = 30; W = 26	(1) : H = 23; W = 32 (2) : H = 26; W = 30	(1) : H = 20; W= 36 (2) : H = 30; W= 32

properties of these sticky dough particles, that in turn, depend to a great extent on the state of the starch and gluten.

The processed dough at 65 wt% of water was printed with a 3D food printer prototype (Fig. 4A). Pictures of the printed objects are shown in Fig. 4 (B and C) and their dimensions compared to the corresponding models, showing from 0 to ± 17% deviation in length or height, which can be considered satisfactory given the complexity of the printed structure (Yang et al., 2018).

These dimensions remained unchanged 5 min after printing. Thus, with the printing conditions used here, the rheological properties of the processed dough were compatible with 3D food printing. Its stickiness could be an advantage for 3D food printing, increasing adhesion between the deposited layers, which is an important parameter in controlling the quality and mechanical properties of printed objects (Chaunier et al., 2018; Vancauwenberghe et al., 2017).

3.2. Impact of adding water, sucrose and oil on the printability of the processed dough

The characteristic gelatinization temperatures (T_{onset}, T_{Max}) measured by DSC for doughs before the heating step increased with increasing sucrose content, in agreement with the literature (Abboud and Hoseney, 1984; Perry and Donald, 2002). The degree of starch gelatinization (G) was calculated. As the proportion of water and sucrose versus starch influence the characteristic gelatinization temperatures, Fig. 5 presents the different points positioned with respect to both the water/flour and sucrose/flour ratios. Interestingly, two areas with different gelatinization degrees are defined: one with $G \geq 95\%$, the other one with $G < 95\%$.

Dough with a water/flour ratio below 1.5 and with no sucrose led to in incomplete starch gelatinization. The result was the same with a water/flour ratio of 1.68 with a sucrose/flour ratio of 0.40, probably due to the increase in T_{onset} and T_{max}. At higher water/flour ratios, whatever the sucrose/flour ratio, gelatinization was complete due to the larger amount of water available for starch gelatinization.

Non-gelatinized or partially gelatinized starch granules are more rigid than gelatinized ones. The higher the degree of gelatinization, the softer the starch granules and probably also the dough sticky particles.

Changes in the storage modulus and tanδ of the processed doughs are shown as a function of the water/flour ratio (Fig. 6A and 6.B, respectively). G′ decreased with an increase in the water/flour ratio, as reported by other authors in starch-concentrated pastes (Hansen et al., 1990). As G' is measured at low deformation, in concentrated particulate systems made of deformable particles, it reflects particle rigidity (Adams et al., 2004; Fridrikh et al., 1996). In the present study, it can be attributed to the greater softness of the starch granules, but also of the protein strands and of the glue between the starch granules due to a lower rate of protein aggregation.

It seems that at water/flour ratios above 2.0, adding sucrose and or oil to the dough has no effect. Water content was the most important factor in terms of softening. On the other hand, at water/flour ratios below 2.0, the G′ of doughs containing oil was significantly lower than that of doughs containing no oil, which means that oil has a softening effect by itself. This is in good agreement with the results obtained by Agyare and co-authors (2004) in a less hydrated heated dough including shortening. When the dough containing oil was heated, the size distribution of the oil droplets changed and the droplets merged to form a layer of fat around the starch granules (Hesso et al., 2015), which could facilitate slippage between starch granules. The effect of sucrose by itself on G' with this water/flour ratio is less clear. Tanδ values were all in the range 0.14–0.17 except for dough containing 12 wt% sucrose, which had higher values (0.19 and 0.20). All doughs with tanδ lower than 1, showed a solid-like behavior. It appears that high sucrose content leads to less structured systems with higher energy dissipation. With the water/flour ratio used here, starch was not completely gelatinized, and the softness of the main starch granules was medium. Thus, the protein strands and glue are probably the structures that are most affected by high sucrose content.

The printing quality of the objects printed using most of these doughs was satisfactory even if the range of their G′ values was rather wide (3.8–12 kPa) (Fig. 6C). This result is in good agreement with the literature (Liu et al., 2017; Zhang et al., 2018), in which G′ values in the range 4–27 kPa were positively correlated with shape retention and high resolution of 3D printed objects. However, in this study, the printing quality of doughs containing 12 wt% of sucrose was average (Fig. 6C, [8]) and that of doughs containing both 12 w% sucrose and 7.5 w% oil was even worse even though their G′ values were within the G' range of other printable doughs. Interestingly, their tanδ was significantly higher (0.19 and 0.20, respectively).

The printing quality thus appears to be higher for processed doughs with tanδ in the range 0.14–0.17. To check this hypothesis, values of G′, tan δ and shapes of 2 objects are reported and compared in Table 2 for 3 doughs containing 12 wt% of sucrose and 7.5 wt% of oil and 3 different water concentrations. Despite the higher G', the only one with poor printability quality was the dough with a tanδ of 0.20. Tan δ seems to be a relevant additional indicator to predict the printing quality of such doughs.

4. Conclusion

A thermomechanical process was successfully developed to produce wheat flour based printable material. The combination of mixing and heating led to the formation of closely-packed dough particles made of swollen starch granules glued in denatured proteins. Logically, the proportions of water, sucrose and oil affected the mechanical properties of these concentrated particulate systems. The water/flour ratio was found to mainly affect particle rigidity. At the lower water/flour ratio, the oil reduced G′ due to slippage, while sucrose increased tanδ due by modifying the structure of the protein aggregates. For a wheat flour dough with a G' in the range 3–10 kPa, a tanδ in the range 0.15–0.17 appears to be a relevant criterion to predict good printability.

Credit author statement

Masbernat Laurena: Investigation, Methodology, Validation, Writing – original draft, Visualization, Berland Sophie: Conceptualization, Methodology, Validation, Leverrier Cassandre: Methodology, Validation, Moulin Gabrielle: Investigation, Methodology, Michon Camille: Conceptualization, Supervision, Validation, Funding acquisition, Project administration, Almeida Giana: Conceptualization, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

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

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References

Abboud, A., Hoseney, R.C., 1984. Differential scanning calorimetry of sugar cookies and cookie doughs. Cereal Chem. 61, 34–37.

Adams, S., Frith, W.J., Stokes, J.R., 2004. Influence of particle modulus on the rheological properties of agar microgel suspensions. J. Rheol. 48, 1195–1213. https://doi.org/10.1122/1.1795193.

Agyare, K., Xiong, Y., Addo, K., Akoh, C., 2004. Dynamic rheological and thermal properties of soft wheat flour dough containing structured lipid. J. Food Sci. 69, 478–487.

Auger, F., Morel, M.-H., Lefebvre, J., Dewilde, M., Redl, A., 2008. A parametric and microstructural study of the formation of gluten network in mixed flour–water batter. J. Cereal. Sci. 48, 349–358. https://doi.org/10.1016/J.JCS.2007.10.006.

Bagley, E.B., Christianson, D.D., 1982. Swelling capacity of starch and its relationship to suspension viscosity-Effect of cooking time, temperature and concentration. J. Texture Stud. 13, 115–126.

Bakrani Balani, S., Chabert, F., Nassiet, V., Cantarel, A., 2019. Influence of printing parameters on the stability of deposited beads in fused filament fabrication of poly (lactic) acid. Addit. Manuf. 25, 112–121. https://doi.org/10.1016/j.addma.2018.10.012.

Bean, M.M., Yamazaki, W.T., 1978. Wheat starch gelatinization in sugar solutions.I. Sucrose: microscopy and Viscosity effects. Cereal Chem. 55, 936–944.

Campos, D.T., Steffe, J.F., Ng, P.K.W., 1997. Rheological behavior of undeveloped and developed wheat dough. Cereal Chem. 74, 489–494. https://doi.org/10.1094/CCHEM.1997.74.4.489.

Champenois, Y., Rao, M.A., Walker, L.P., 1998. Influence of gluten on the viscoelastic properties of starch-gluten pastes and gels. J. Sci. Food Agric. 78, 127–133. https://doi.org/10.1002/(sici)1097-0010(199809)78:1<127::aid-jsfa99>3.0.co;2-k.

Charun, E.P., Morel, M.-H., 2001. Quelles caractéristiques pour une farine biscuitière ? Influence de la dureté des blés et de la composition biochimique des farines sur leur aptitude biscuitière. Ind. Des. Cereales n°125, 2–16.

Chaunier, L., Guessasma, S., Belhabib, S., Della Valle, G., Lourdin, D., Leroy, E., 2018. Material extrusion of plant biopolymers: Opportunities and challenges for 3D printing. Addit. Manuf. 21, 220–233. https://doi.org/10.1016/j.addma.2018.03.016.

Coussot, P., Ancey, C., 1999. Rheophysical classification of concentrated suspensions and granular pastes. Phys. Rev. E 59, 4445–4457.

Domenek, S., Morel, M.-H., Redl, A., Guilbert, S., 2003. Rheological investigation of swollen gluten polymer networks: effects of process parameters on cross-link density. Macromol. Symp. 200, 137–146. https://doi.org/10.1002/masy.200351014.

French, D., 1972. Fine structure of starch and its relationship to the organization of starch granules. J. Japanese Soc. Starch Sci. 19, 8–25.

Fridrikh, S., Raquois, C., Rezaiguia, S., 1996. Rheological behaviour of concentrated suspensions of soft spheres. J. Chim. Phys. Phys. Chim. Biol. 93, 941–959.

Godoi, F.C., Prakash, S., Bhandari, B.R., 2016. 3d printing technologies applied for food design: status and prospects. J. Food Eng. 179, 44–54. https://doi.org/10.1016/j.jfoodeng.2016.01.025.

Hansen, L.M., Hoseney, R.C., Faubion, J.M., 1990. Oscillatory probe rheometry as tool for determining the rheological properties of starch-water systems. J. Texture Stud. 21, 213–224. https://doi.org/10.1111/j.1745-4603.1990.tb00476.x.

Hermansson, A.M., Svegmark, K., 1996. Developments in the understanding of starch functionality. Trends Food Sci. Technol. 7, 345–353. https://doi.org/10.1016/S0924-2244(96)10036-4.

Hesso, N., Loisel, C., Chevallier, S., Marti, A., Le-Bail, P., Le-Bail, A., Seetharaman, K., 2015. The role of ingredients on thermal and rheological properties of cake batters and the impact on microcake texture. LWT - Food Sci. Technol. (Lebensmittel-Wissenschaft -Technol.) 63, 1171–1178. https://doi.org/10.1016/j.lwt.2015.04.041.

Jiang, H., Zheng, L., Zou, Y., Tong, Z., Han, S., Wang, S., 2019. 3D food printing: main components selection by considering rheological properties. Crit. Rev. Food Sci. Nutr. 59, 2335–2347. https://doi.org/10.1080/10408398.2018.1514363.

Kim, H.W., Lee, I.J., Park, S.M., Lee, J.H., Nguyen, M.H., Park, H.J., 2019. Effect of hydrocolloid addition on dimensional stability in post-processing of 3D printable cookie dough. LWT 101, 69–75. https://doi.org/10.1016/j.lwt.2018.11.019.

Leon, A., Rosell, C.M., De Barber, C.B., 2003. A differential scanning calorimetry study of wheat proteins. Eur. Food Res. Technol. 217, 13–16. https://doi.org/10.1007/s00217-003-0699-y.

Leverrier, C., Almeida, G., Espinosa-Mu noz, L., Cuvelier, G., 2016. Influence of particle size and concentration on rheological behaviour of reconstituted apple purees. Food Biophys. 11, 235–247. https://doi.org/10.1007/s11483-016-9434-7.

Liu, Z., Zhang, M., Bhandari, B., Yang, C., 2017. Impact of rheological properties of mashed potatoes on 3D printing. J. Food Eng. 220, 76–82. https://doi.org/10.1016/j.jfoodeng.2017.04.017.

Maache-Rezzoug, Z., Bouvier, J.M., Allaf, K., Patras, C., 1998. Effect of principal ingredients on rheological behaviour of biscuit dough and on quality of biscuits. J. Food Eng. 35, 23–42. https://doi.org/10.1016/S0260-8774(98)00017-X.

Mann, J., Schiedt, B., Baumann, A., Conde-Petit, B., Vilgis, T.A., 2014. Effect of heat treatment on wheat dough rheology and wheat protein solubility. Food Sci. Technol. Int. 20, 341–351. https://doi.org/10.1177/1082013213488381.

Masbernat, L., Berland, S., Almeida, G., Michon, C., 2021. Stabilizing highly hydrated wheat flour doughs by adding water in two steps. J. Cereal. Sci. 98, 103179. https://doi.org/10.1016/j.jcs.2021.103179.

Mongondry, P., Tassin, J.F., Nicolai, T., 2005. Revised state diagram of Laponite dispersions. J. Colloid Interface Sci. 283, 397–405. https://doi.org/10.1016/j.jcis.2004.09.043.

Moussier, M., Huc-Mathis, D., Michon, C., Bosc, V., 2019. Rational design of a versatile lab-scale stirred milk gel using a reverse engineering logic based on microstructure and textural properties. J. Food Eng. 249, 1–8. https://doi.org/10.1016/j.jfoodeng.2018.12.018.

Perry, P., Donald, A., 2002. The effect of sugars on the gelatinisation of starch. Carbohydr. Polym. 49, 155–165. https://doi.org/10.1016/S0144-8617(01)00324-1.

Quemada, D., 2006. Modélisation rhéologique structurelle : dispersions concentrées et fluides complexes. Lavoisier.

Quemada, D., 1977. Rheology of concentrated disperse systems and minimum energy dissipation principle - I. Viscosity-concentration relationship. Rheol. Acta 16, 82–94. https://doi.org/10.1007/BF01516932.

Raeker, M.Ö., Gaines, C.S., Finney, P.L., Donelson, T., 1998. Granule size distribution and chemical composition of starches from 12 soft wheat cultivars. Cereal Chem. 75, 721–728. https://doi.org/10.1094/CCHEM.1998.75.5.721.

Rao, M.A., 2007. In: Rheology of Fluid and Semisolid Foods Principles and Applications. In: Barbosa-Cánovas, G. V (Ed.), Food Engineering Series. Springer, Boston, M.A https://doi.org/10.1007/978-0-387-70930-7_5.

Rapaille, A., Vanhemelrijck, J., 1997. Modified starches. In: Thickening and Gelling Agents for Food. Springer US, Boston, MA, pp. 199–229. https://doi.org/10.1007/978-1-4615-2197-6_10.

Severini, C., Azzollini, D., Albenzio, M., Derossi, A., 2018. On printability, quality and nutritional properties of 3D printed cereal based snacks enriched with edible insects. Food Res. Int. 106, 666–676. https://doi.org/10.1016/j.foodres.2018.01.034.

Severini, C., Derossi, A., Azzollini, D., 2016. Variables affecting the printability of foods: preliminary tests on cereal-based products. Innovat. Food Sci. Emerg. Technol. 38, 281–291. https://doi.org/10.1016/J.IFSET.2016.10.001.

Tsai, M.L., Li, C.F., Lii, C.Y., 1997. Effects of granular structures on the pasting behaviors of starches. Cereal Chem. 74, 750–757. https://doi.org/10.1094/CCHEM.1997.74.6.750.

Turner, B.N., Strong, R., Gold, S.A., 2014. A review of melt extrusion additive manufacturing processes: I. Process design and modeling. Rapid Prototyp. J. 20, 192–204. https://doi.org/10.1108/RPJ-01-2013-0012.

Vancauwenberghe, V., Katalagarianakis, L., Wang, Z., Meerts, M., Hertog, M., Verboven, P., Moldenaers, P., Hendrickx, M.E., Lammertyn, J., Nicolaï, B., 2017. Pectin based food-ink formulations for 3-D printing of customizable porous food simulants. Innovat. Food Sci. Emerg. Technol. 42, 138–150. https://doi.org/10.1016/j.ifset.2017.06.011.

Vanin, F.M., Lucas, T., Trystram, G., Michon, C., 2018. Biaxial extensional viscosity in wheat flour dough during baking. J. Food Eng. 236, 29–35. https://doi.org/10.1016/j.jfoodeng.2018.05.007.

Wang, L., Zhang, M., Bhandari, B., Yang, C., 2018. Investigation on fish surimi gel as promising food material for 3D printing. J. Food Eng. 220, 101–108. https://doi.org/10.1016/j.jfoodeng.2017.02.029.

Yang, F., Zhang, M., Prakash, S., Liu, Y., 2018. Physical properties of 3D printed baking dough as affected by different compositions. Innovat. Food Sci. Emerg. Technol. 49, 202–210. https://doi.org/10.1016/j.ifset.2018.01.001.

Zhang, L., Lou, Y., Schutyser, M.A.I., 2018. 3D printing of cereal-based food structures containing probiotics. Food Struct. 18, 14–22. https://doi.org/10.1016/j.foostr.2018.10.002.