Model-based design and validation of food texture of 3D printed pectin-based food simulants

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ABSTRACT

A prime interest in 3D food printing consists of controlling the texture of food products by means of structure design. Analytical and finite element models were used to predict the texture properties of printed honeycomb structures. Structures with varying cell size were 3D printed using food-inks composed of three different pectin concentrations and characterized with micro-CT and compression analysis. Porosity and average wall thickness of the samples appeared independent of food-ink composition but structure deviations could be distinguished between actual printed structures and CAD designs. The comparison between the texture properties of printed structures and those predicted by analytical and FE modelling in function of porosity showed that both predicted and actual texture properties matched to the same decreasing trend with increasing porosity. Finally, a good fit of the analytical model to the measured Young's modulus was obtained by using the actual porosity of the printed structures, while the validated finite element model provides a means to design more complex structures. The results emphasize the importance of structure correspondence for reliable design of texture properties of printed food structures.

Keywords: additive manufacturing; cellular food; texture; 3D food printing; model-based design

1 INTRODUCTION

Food Layer Manufacturing, generally referred to as 3D food printing (3DFP), combines additive manufacturing (AM) with traditional food processing in order to create new food products with

new structures, textures and flavors taking into account consumer nutritional needs [1–5]. 3DFP follows the same concept than traditional AM technology; the object commonly designed with computer-assisted design (CAD) software, is built from the bottom up by assembling successive layers of powder, liquid, or sheets of edible material [6–8]. Among the existing AM techniques, extrusion deposition, fused deposition modeling, and laser-sintering are mostly used to build food structures [1,5].

In the last few years, the interest in 3DFP is extending and an increasing variety of food products suitable as “food-ink” for AM processing has been reported, including food having a low melting point [9–12], dough [1,13,14] and mashed or liquid foods containing gelling agents [15–21]. Most of these studies were focused on factors influencing the rheology and printability of food material. They also reported methodologies to optimize the printing settings in order to accurately manufacture simple and more complex food structures. So far, the personalization of printed food by means of customized formulations and desired texture properties has received little attention.

One main interest of 3DFP technologies consists of improving the appearance and texture of food products by controlling the food material at the meso- and micro-structure levels [22]. Texture control by means of 3D printing can be realised through two different manners; (i) the printing of materials having different textures together or, (ii) the printing of a material into a meso- structure with defined porosity [6]. Lipton et al. already demonstrated that texture properties of printed foam objects made of corn dough could be modulated by varying the infill porosity. By selecting appropriate printing setting, the porosity of the printed object was induced through viscous thread instability in the printing process itself [23]. Thus, the printing design file that includes building instructions and printing settings, is the key to manipulate the

shape, size and distribution of gas spaces influencing the food texture properties. Moreover, using knowledge of mechanical properties in relation to macro- and microstructures offers possibilities for controlling food texture based on the 3D product design. 3D printing would thus allow to print dedicated structures based on a structure design file that is a result of model-based analysis of the mechanical behaviour of food products. We proposed such approach recently without validation on actual printed structures [24].

Analytical models and finite element modelling (FEM) may be used to predict the mechanical properties of a 3D printed object based on mechanical properties of the materials and the structure of the object. Analytical models are available to predict mechanical properties of cellular solids by representing the cellular structure in different patterns such as hexagons in two dimensions or tetrakaidecahedron (14-faced polyhedron) in three dimensions [25,26]. However, most of those analytical models result in laborious and complex expressions if they are not based on a repetitive geometry. Unit cell geometries may simplify the analysis but may not provide a reliable representation of the real finite material. Gibson and Ashby developed a simplified analytical model correlating the properties of cellular structures based on the relative density and solid material properties, limited to a restricted range of structure configurations with high porosity including a hexagonal honeycomb patterns [27]. FEM, on the other hand, allows the analysis of an unlimited variation in structure designs incorporating local effects, such as imperfections, but is computationally more demanding [28]. Moreover, the actual geometry of particular samples can be modelled by combining FEM with imaging techniques such as micro-computed tomography [29,30].

The objective of this work was to design, print and verify 3D pectin-based food simulants having particular porous structures with dedicated texture perception. Hexagonal honeycomb structures

having variable cell sizes were designed for 3D printing and their mechanical properties were predicted by an analytical model and FEM. After characterization of the printed objects, their structure features were compared to those estimated by the design. Finally, the predicted texture properties were related to the actual texture of printed structures for model validation. This research intends to show a proof-of-principle that model-based food design can be combined with 3D food printing in order to create personalized foods.

2 MATERIALS & METHODS

2.1 Design of honeycomb structures

A hexagonal honeycomb pattern was selected as a generic structure for ease of 3D printing. Moreover, a simple mathematical expression of the structure-texture relation is available for such patterns. Four honeycomb patterns were designed by varying the cell size which was defined as the edge of the equilateral hexagon cell. The cell sizes were selected based on the resolution of the printing process in order to avoid clogged pores. In order to predict the texture properties of printed structures through modelling, 3D volumes of honeycomb structures with different porosities were generated. First, a 2D honeycomb pattern was drawn using AutoCAD as computer-aided design software (AutoCAD; Autodesk, Cupertino, CA, SA) as shown in Figure 1. Then, the structure surface was created by thickening the honeycomb pattern to a constant value of 1.2 mm; the 3D volume was then obtained by surface extrusion. The properties of the designed structures are provided in Table 1. In this study, we defined the volume as the space that was occupied by the solid material. The porosity corresponded to the air fraction of the structure considering an inscribed prismatic volume as region of interest represented in Figure 1. Finally, the pore size was determined through the equivalent diameter considering the honeycomb cell voids inside the structure.

2.2 Analytical model

The analytical model used to predict the mechanical properties of honeycomb structures was described by Gibson and Ashby [27]. This model is based on standard beam theory and only considers that the structure deforms in a linear-elastic way leading to the axial deflection of cells under small strain compression in the in-plane direction. In this situation, the relative Young's modulus of a regular honeycomb structure (E/E^*) is proportional to the cube of the relative density (ρ/ρ^*) and is estimated by Eq. 1:

$$\frac{E}{E^*} = \frac{3}{2} \left(\frac{\rho}{\rho^*} \right)^3 \quad (1)$$

where E is the compressive Young's modulus of the cellular material and E^* is Young's modulus of the solid material. The relative density (ρ/ρ^*) is expressed in function of the material porosity (ϕ):

$$\frac{\rho}{\rho^*} = 1 - \phi \quad (2)$$

Note that this simplified model assumes that the relative density of the structure is lower than 0.3. Thus, this could not be adapted to all the designed structures. In this situation, more complex analytical expressions must consider the total deflection of the cells including the axial and shear deformation of the cell walls. Further details can be found in Gibson and Ashby (1982) [27].

2.3 Finite element model

The model was developed using the transient structural model of ANSYS 18.1 (ANSYS, Inc., Pennsylvania, USA). The CAD files of the honeycomb structures that were generated using AutoCAD were imported to ANSYS DesignModeler. A Young's Modulus of 63.5 kPa and

Poisson's ratio of 0.49 were applied as material properties, based on mechanical compression tests performed on 25 g/L low methoxylated (LM) pectin solid gels (see further) and considering the gel as incompressible material (the same material and concentration used to print object). We hypothesized that other concentrations of LM pectin gels had the same deformation behaviour than 25 g/L and hence, similar FEM results considering the relative Young's modulus. After conducting a mesh sensitivity study, the geometrical model was discretized using a maximum mesh size of 0.00025 m that gave more than 360,000 elements (Figure 2). The top surface of the structure where the load was applied was taken as a displacement boundary. The surface was displaced downwards using a vertical velocity of 0.1 mm/s (the same as in the deformation experiment). The bottom surfaces of the structure were taken as a fixed boundary. The model was solved using a time step of 1 s for a total time of 20 s that resulted an equivalent strain (ε) of about 0.1. The calculation was done using a 64-bit, Intel® Core™ i7-4790 CPU, 3.60 GHz, 32 Gb RAM, Windows 7 Professional computer. The equivalent Young's modulus of the designed cellular structure was calculated from the predicted reaction force on the displaced surface and deformation using the following equation:

$$E = \frac{\sigma}{\varepsilon} = \frac{F/A}{dL/L} = \frac{FL}{dL \cdot A} \quad (3)$$

where E is the engineering Young modulus in (Pa), σ is stress (Pa), ε is strain, F is reaction force (N), L is the initial length of the model (m), dL is the deformation (m) and A is the projected area of the model perpendicular to the applied load (m^2).

2.4 Materials and food-ink preparation

LM pectin was produced by alkaline saponification (pH 11) of high methoxylated pectin (Sigma-Aldrich P9135) by the protocol detailed in Vancauwenberghe et al [31]. The LM pectin had a degree of methoxylation of 20 ± 0.7 % which was determined by infrared spectrometry according to the method described by Kyomugasho et al. [32]. The gelation of LM pectin food-ink was generated through the crosslinking of Ca^{2+} ions between free carboxyl groups of the polygalacturonic acid chain of the pectin polymer and can be quantified by the stoichiometric ratio ($R = 2[\text{Ca}^{2+}]/[\text{COO}^-]$) [33,34]. The addition of CaCl_2 in the food-ink composition was required and adjusted according to the R ratio in the range [0.2 – 0.5] in order to ensure a partial crosslinking and obtain suitable flowability of the gels during printing [31].

The food-inks were composed of different concentrations of LM pectin and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Chem-Lab, cat. no. CL00.0317.1000). As described in our previous research [31], LM pectin was first dissolved in distilled water with 2 drops of red food colorant E122 (Vahiné®, France). The solution was stirred under magnetic stirring at room temperature (23 °C) for 3 h at least in order to ensure complete dissolution of pectin. Then, the appropriate volume of 50 mM CaCl_2 solution was added drop-by-drop to the pectin solution in order to reach the desired concentrations given by Table 2. The solution was kept overnight at 4 °C and used for 3D printing the day after. Just before printing, the food-inks were mixed for 10 min under 10000 rpm stirring (IKA® T25 Digital Ultra-Turrax, head size 18 mm).

After printing, the gelation of the printed object was completed by incubation into a CaCl_2 solution of 50 mM for 60 min.

2.5 3D printing and reference object

The 3D printing process described by Vancauwenberghe et al. [31], was based on extrusion deposition at room temperature (23 °C). The 3D printer prototype consisted of a 3D robotic system (CNC Bench 3D 4046, GoCNC.de, Germany), control software (WinPN-CN USB, Lewetz, Germany), a pressure system and an injection device. A syringe pump (Harvard Apparatus, Holliston, MA, USA) acted as a pressure system and provided a precise extrusion flow rate. The following printing setting were used: extrusion nozzle diameter of 0.838 mm, layer height of 0.838 mm, extrusion flow rate of 0.34 mL/min.

Cubes of 1.5 cm edge were printed as reference object for the three pectin concentrations. The object was designed and exported as STL file using AutoCAD. We used an open-source CAM software Slic3r (slic3r.org, consulted on February 2015) to generate the G-code file, providing the XYZ pathway instructions of the printer, from the CAD design. The infill velocity was fixed at 10 mm/s corresponding to the spindle speed during extrusion. The travel velocity was fixed at 200 mm/s which was the spindle speed of a jump between the end of one extrusion and the next. The perimeter related to the construction of the object wall was set at 2 and the infill pattern consisted to “honeycomb” pattern with an infill density of 85 %. Those slic3r settings ensured shape accuracy and complete filling inside the material without any additional pores induced by the 3D printing process [31].

2.6 G-codes of honeycomb structures

From the 2D honeycomb drafts, we created the G-code files necessary to print the structured objects. G-code is numerical control (NC) programming language instructing the CNC spindles of the 3D printer prototype. We used the computer-aided manufacturing (CAM) software FILOU NC12 (FILOU Software GmbH, Germany) to generate the G-code language providing the path

and velocity that the printhead should follow to draw one layer of the honeycomb pattern. To ensure a representative structure, the printing method consisted of the deposition of the same quantity of food-ink following the honeycomb pattern through the layers in order to obtain constant cell size and wall thickness. This was performed with a constant extrusion flow rate as its variation did not take place instantaneously in the extrusion system due to the visco-elastic properties of pectin food-inks.

Based on pre-experimental tests, we adopted the following printing strategy: at each layer, the printhead deposited the food-ink by following the printing path as shown in Figure 3. As a consequence, the printhead would pass some segments twice. In order to keep the same wall thickness over the design, two spindle velocities were set for single and double passages of the printhead. The velocities were first theoretically estimated by the volume balance between the extruded and deposited food-ink considering a cell wall thickness of 1.2 mm and neglecting the spreading of food-ink. After experimental adjustments, the velocity of single passage was set at 5 mm/s for the structures Cell3, Cell4 and Cell5 while it was 7 mm/s for Cell2 due to the higher number of cells which involved more double passages. The velocity of double passage was set at 15 mm/s for all structures. According to this printing strategy, the G-code of the first layer was written using the CAM software which gave the XY coordinates of the honeycomb pattern. Then, the spindle velocities were attributed considering single or double passage of the printhead. Finally, the height position of the printhead (Z axis) was moved 0.838 mm up before starting the deposition of the next layer. The instructions of the first layer were re-used to deposit the food-ink following the same XY path over a height of 15 mm.

2.7 X-ray micro-CT and image analysis

The day after 3D printing, X-ray computed tomography (CT) was performed to visualize the 3D macro- and microstructure of printed samples using a Skyscan 1172 (Bruker microCT, Belgium). The source current was set at 112 μA and the source voltage at 90 kV. The entire volume of samples was scanned at a pixel image resolution of 14.97 μm with an averaging of 3 frames for each rotation step of 0.3° over 180° . The stack of radiographic images of 1048 by 2000 was reconstructed using NRecon software (version 1.6.10.2, Bruker microCT, Belgium).

We analyzed the reconstructed images using CTAn software (Bruker microCT, Belgium) to determine the volume (V), porosity (ϕ), thickness distribution (δ) and pore size (d_{eq}) distribution. The sliced images were treated with a median filtering and an automatic thresholding by the Otsu method [35]. Finally, morphological operations, including sweep, closing with a radius of 2 pixels and opening with a radius of 3 pixels, were performed to remove speckles. The porosity and thickness distributions were provided by 3D analysis into a prismatic region of interest that was inscribed to the sample border as defined in section 2.1 (Figure 1). The average object thickness (δ_{av}) was defined by the parallel plate model [36]:

$$\delta_{av} = \frac{2}{S_{Obj}/V_{Obj}} \quad (4)$$

where S_{Obj}/V_{Obj} is the surface to volume ratio of the solid object.

Then, the honeycomb cells were isolated by inverting the binarized images using bitwise and border kill operation. An individual object analysis was performed on every 50 slices in order to establish 2D pores size distribution by considering Area-equivalent circle diameter (d_{eq}) of the honeycomb cells.

In addition, the 3D volume rendering and pore distribution were visualized using Avizo software (version 9.0.1, VSG, France). The volume rendering of pores, obtained by inverting the thresholding, was superposed to the volume surface of the object.

2.8 Mechanical characterization

After the CT scans, the printed samples were physically characterized by force-deformation measurements using a TA.XTPlus texture analyzer device (Stable Microsystems, Godalming, UK). The compression test was performed using a cylindrical metal compression plate of 75 mm diameter at a speed of 0.1 mm/s with a maximal strain of 80 % and load force of 0.5 N. All the samples having honeycomb structure were compressed in the in-plane direction (X1, see Fig. 1) as shown in Figure 4.

The engineering Young's modulus E was calculated by the slope of the linear part of the stress-strain curves using Eq. 3. The linear part was estimated by the line of best fit obtained from the stress-strain curve with a coefficient of regression superior than 0.95. This corresponded in the strain region $\varepsilon = [0.05 - 0.20]$. For all samples, the change of area was considered negligible up to $\varepsilon = 0.20$.

2.9 Statistics

For the three food-ink compositions, the cube object and the four honeycomb structures were 3D printed in 5 replicates which were characterized using micro-computed tomography (CT) and compression measurements. For all measurements, the mean value $\pm$ standard error was calculated. The mean and variance were respectively analyzed through t -test and p -test at confidence level of 95 % in order to highlight the significance and independence of the investigated parameters on measured properties.

245

246 3 RESULTS AND DISCUSSION

247 3.1 Dependence of Young's modulus on porosity

248 Relative Young's moduli of honeycomb structures were predicted using the analytical model
249 (E/E^*_{An}) and FEM (E/E^*_{FEM}) and are represented in Table 3. E/E^*_{An} was obtained using the
250 porosity of the designed structures given in Table 1 and Eq. 1 while E/E^*_{FEM} resulted from the
251 deformation simulation performed on the CAD generated geometries as illustrated in Figure 5.
252 The FE model gave close results to the analytical model; the relative Young's modulus of the
253 honeycomb structures followed a downward trend with increasing cell size that was proportional
254 to porosity. It shows that structure-based texture design is possible and allows to create objects
255 with a ten-fold range in E-modulus using the same material.

256 The coefficient of determination (r^2) was calculated in order to analyze the level of
257 correspondence between the results obtained by the analytical model to those predicted by FEM.
258 As the r^2 was 0.96, we concluded that the analytical model and FEM gave equivalent predictions.
259 Thus, both models can be used to predict mechanical properties of honeycomb structures. Note
260 that FEM is most suitable to design structures of low porosity and predict their properties as the
261 model incorporates all deformations caused by the compression. Moreover, the analytical model
262 was restricted to honeycomb patterns of high porosity while the FE model can be used for a large
263 variety of structures.

264 3.2 3D printing and characterization of the printed samples

265 For the three food-ink compositions, the reference cube and four honeycomb structures were
266 successfully 3D printed and characterized. Figure 6 shows the internal and external aspect of

printed objects made of 25 g/L pectin and compares micro-CT image cross-sections to the honeycomb design (objects composed of 15 and 35 g/L pectin not shown). All honeycomb structures were printed respecting the design pattern and resulted in discernable pores. Nevertheless, small visual deviations from the initial design were notified; all printed structures had rounded corners and pores in comparison to the designed structures, especially for the structures of 2 mm cell size which had some clogged pores. This deviation was due to spreading of the food-ink and resolution of the printing width as already reported in a previous study [13,31]. The cube structure that was printed as reference contained some trapped air bubbles while it was expected to be totally filled. The air entrapment could have happened during the food-ink preparation as the honeycomb structures also contained small trapped bubbles in their walls. Note that the presence of entrapped air into the food-ink was not considered in the further discussion as it represents less than 2 % of the food-ink volume according to the porosity of the printed cubes given in Table 4.

From visual inspection (Figure 6), the wall thickness of the honeycomb structures appeared regular, suggesting that the deposition strategy based on single and double printhead passages was appropriate to print these structures. The structure thickness distributions (δ) as a function of volume fraction (V_f) are represented graphically in Figure 7. All distributions covered the same range of values regardless the cell size of the designed structures which confirmed the observations. The food-ink composition seemed to affect the structure thickness distribution; its range was comprised in the interval [1.2 – 2.5 mm] for the objects made of 15 and 25 g/L pectin while it appeared thinner with less variation for the object made 35 g/L pectin ($1 \text{ mm} < \delta < 2 \text{ mm}$), at least for the less porous structures. This difference was probably due to the food-ink spreading which was related to the food-ink viscosity [31,37]. The food-ink composed of 35 g/L

pectin had the highest viscosity and thus, allowed the printing of a more rigid structure which was less subjected to food-ink spreading [19,38]. The spreading effect was particularly observed for the structure having 2 mm cell size and made of 15 g/L pectin which had small volume fractions and thickness values up to 4.5 mm. Finally, the most open structure with the largest cell size, resulted in narrower thickness distributions which may be related to less food-ink overspreading during the printing because of a higher porosity or lower number of cells in the structure influencing the portion of single and double deposition of material.

The average object thickness (δ_{av}) was estimated according to the parallel plate model (Eq. 4) in order to obtain a representative average cross-sectional wall thickness of the printed honeycomb samples (see Table 4). According to the statistical tests, the average object thickness appeared significantly higher for the structures having 2 mm cell size due to the resolution of the printing width in addition to some clogged pores that were detected by visualizing the CT cross-section images. For the other structures, the average wall thickness tended to slightly decrease with cell size in agreement with the observations of the structure thickness distribution.

From the 2D analysis of honeycomb cells, we calculated the pore size distribution by means of equivalent diameter (d_{eq}) and normalised it dividing it by the total number of pores analyzed through the cross-sectional CT images of samples (N_{tot}). We excluded the pores smaller than 650 μm from the distribution which corresponded to trapped air bubbles in the food-ink, in order to consider only pores induced by 3D printing. Figure 8 shows the pore size distributions of all printed objects and the average and deviation of equivalent diameter are given in Table 4. The average pore diameter of the printed objects increased linearly with cell size in agreement with the designed structures, which confirms the good reproducibility of the printing process. At fixed cell size, the pore size distributions covered the same range regardless the food-ink composition.

Although the pores size distributions of structures made of 35 g/L pectin appeared narrower than those of objects made of 15 and 25 g/L pectin, the average pores size remained statistically equivalent for the three food-ink compositions per cell size. The narrower pore size distribution of samples made of 35 g/L pectin was correlated to the structure thickness which was influenced by the food-ink spreading. Thus, the structure made of 35 g/L pectin resulted in more regular pores. The pore size distribution of structures having 5 mm cell size appeared broader than distributions of other structures and presented several modes suggesting that the honeycomb cells may be different in size. Similarly to the observations for the structure thickness, changing the cell number of the structure caused small deviations linked to the porosity or the cell number in the honeycomb pattern.

Although small variations of wall thickness and pore size distributions were caused by the food-ink composition, the variation of the average wall thickness and pore diameter with the food-ink composition remained statistically insignificant. These structural features were, therefore, independent of the food-ink composition. However, the volume of honeycombs made of 15 g/L was consistently lower than that of objects made of 25 and 35 g/L pectin that had similar volumes. This difference was probably due to too high Ca^{2+} concentration in the printed objects made of 15 g/L pectin which can cause the syneresis of LM-pectin gel [39–44]. Syneresis corresponds to a slow shrinking of a polyion gel upon the increase of the crosslinking ion concentration. It can also be visualized as a release of water from the gel involving a decrease in its volume dimensions [45,46]. Considering that the final Ca^{2+} concentration in the printed samples rose up to the CaCl_2 concentration of the post-treatment solution (50 mM), the final stoichiometric ratio after incubation would result in a value of 2, 1.2 and 0.85 for the printed samples made of 15, 25 and 35 g/L pectin, respectively. As syneresis increases with the

336 stoichiometric ratio [33,47,48], the printed objects composed of 15 g/L pectin were more
337 susceptible to this effect, resulting in a smaller volume.

338 Structural deviations were noticed by comparing the predicted structure features (Table 1) with
339 the measured structure properties obtained by the micro-CT analysis (Table 4). The deviations
340 from predicted properties were expressed as a coefficient of variation and were positive when the
341 measured property was higher than the prediction and negative while the measured property was
342 lower (Table 5). Due to food-ink spreading during 3D printing combined with gel shrinking after
343 post-treatment, the average wall thickness, porosity, pore size and volume of printed objects
344 often deviated considerably from predicted structure designs. The porosity and average pore size
345 deviations appeared to vary similarly but in opposite direction than the average wall thickness
346 which was an obvious result as these structure features are correlated. The printed structures
347 tended to coincide more in the case of structures with large cell size, as the measured average
348 wall thickness decreased when the cell size increased.

349 When the average wall thickness of the printed samples was larger than the estimated wall
350 thickness, we would expect their volume to be larger than the designed volume. However, this
351 expectation was not met as all printed samples had a negative deviation from the predicted
352 volume, especially for the printed objects made of 15 g/L pectin. This observation confirmed that
353 gel syneresis and shrinking occurred for the three food-ink compositions, to a higher extent for
354 low pectin concentration objects. At this stage of the research, it seems that the correspondence
355 of the printed structure with the design also depends on parameters such as the pectin
356 concentration, cell size and honeycomb pattern.

3.3 Validation of modelled texture properties

The Young's modulus of the pectin gel material was set equal to the average Young's modulus of the printed reference cubes. Experimental data and prediction models were compared on the basis of the relative Young's modulus of the printed honeycomb samples (E/E^*). In Figure 9, the relative Young's modulus of honeycomb samples (empty symbols) are plotted together with the analytical predictions given by Eq. 1 (dashed line). The measured data fitted the analytical model with a coefficient of determination of 0.88 regardless of food-ink composition. This suggests that the honeycomb pectin structures were mainly subjected to bending deformations of cell walls [26]. In future research this should be confirmed by comparing the model to a more complex model incorporating axial and shear deformations. The deviation between measurements and model predictions increased with decreasing porosity as is clear from the results for honeycomb structures with a 2 mm cell size.

The geometrical features of the honeycomb designs (Table 1) were used to predict their relative Young's modulus by means of the analytical model (red filled triangles in Figure 9) and the FEM (black filled triangles). The values systematically deviated from the measured ones, likely due to porosity differences between the actual printed honeycombs and the corresponding designs. By considering the average actual porosity of the printed samples in the analytical model, the predicted relative Young's modulus fitted the experimental results much better (green filled diamond in Figure 9). This indicates that the spreading and shrinking of the printed structures that affect their porosity need to be taken into account in order to predict their Young's modulus based on their CAD designs. This could be incorporated into the design by modelling the gel solidification process using a multiphase rheological model or by using a simpler statistical regression model to relate deviations of the volume, average pore size and wall thickness

deviation due to the printing process to the pectin concentration and cell size. We attempted the latter but obtained a low coefficient of determination ($r^2 < 0.7$) and lack of fit with a p -value lower than 0.5. Without a multiphase rheological model of the printing process itself it remains difficult to predict the mechanical properties of the printed objects accurately.

4 CONCLUSIONS AND PERSPECTIVES

This study demonstrated that food objects with pores of different sizes can be successfully 3D printed using food-inks made of varying LM pectin concentration to result in a range of different porosities. The Young's modulus of the printed object, as a proxy of texture, depends on both the Young's modulus of the gelled food-ink as well as the porosity of the printed object.

We designed four honeycomb structures with significantly different mechanical properties that were verified experimentally afterwards. The average wall thickness of printed samples appeared to vary with designed structure properties including cell size of the honeycomb pattern. The printed pectin structures displayed several deviations from the designed structures which resulted from food-ink spreading during the printing process and volume shrinking after post-treatment due to syneresis of pectin gel.

The Young's modulus predicted by the analytical model and FEM calculations confirmed the same decreasing trend with increasing porosity that was observed for actual printed structures. Thus, analytical models and FEM analysis could be a promising tool to predict textural properties of food having designed structures. However, the accuracy of the model predictions depend on the accuracy of the printed structure. We found that using the actual porosity of printed objects improved considerably the correlation between model and measurement. For texture design of 3D printed objects it is imperative to use printing processes that result in

402 minimal deviations between the designed and actual 3D geometry of the printed object. Further
403 research should address modelling the actual 3D printing process using a multiphase rheological
404 model. Moreover, the design of more complex printed structures should be considered next
405 having variable pore size distributions and using a larger variety of food-inks.

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Figure 1

Honeycomb pattern
CAD drafting

Cross-section surface
In-plane view

Design structure
CAD file

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 1 Design of honeycomb structure. From the CAD draft, the cross-section surface was generated using a wall thickness of 1.2 mm and was extruded to a 3D structure. The structural features, including cell size, wall thickness, volume (in purple) and porosity (in blue), are represented in the cross-section view of the structure.

Figure 2 Typical simulation domain, mesh and boundary condition for the finite element model of honeycomb structure.

Figure 3 The G-code of one layer was first generated using CAM software; the printing path of one layer considered continuous deposition of food-ink and allowing single or double passages. Then, the G-code was adjusted adding the printhead velocity depending on the single or double passage and the layering.

Figure 4 Orientation of the samples during the compression.

Figure 5 Compression simulations of the honeycomb structure having a cell size of 2 mm (Cell2) and 5 mm (Cell5) using FEM.

Figure 6 Cross-section design (row 1), photographic image (row 2), X-ray CT image slice (row 3) and volume rendering (row 4) of the reference and four honeycomb structures made of 25 g/L pectin (P25). Scale bar of micro CT images = 10 mm.

Figure 7 Mean thickness distribution (δ) of the printed objects expressed as volume fraction (V_f) for the printed object composed of 15 g/L pectin (black), 25 g/L pectin (purple) and 35 g/L pectin (blue) having the honeycomb structures (a) Cell2, (b) Cell3, (c) Cell4 and, (d) Cell5.

Figure 8 Size distribution of air pores based on equivalent diameters (d_{eq}) of the printed objects as a function of the relative frequency (N/N_{tot}) for the honeycomb structures (a) Cell2, (b) Cell3, (c) Cell4 and, (d) Cell5 made of composed of 15 g/L pectin (black), 25 g/L pectin (purple) and 35 g/L pectin (blue).

Figure 9 Comparison of the relative Young's modulus of the printed honeycomb structure using analytical model and FEM regardless of the food-ink composition. The measured data are represented by the empty marks: black squares, magenta circles and blue triangles for the printed structures made of 15 g/L, 25 g/L and 35 g/L pectin, respectively. The analytical model is represented in dash line including points corresponding to the predictive results calculated based on the porosity of the CAD designs (red filled triangles) and the actual average porosity of the printed samples (green filled diamonds). The simulation results of the FEM using the CAD files as object geometry are represented by the black filled triangles.

Table 1

Table 1. Dimensions and structure properties of the designed honeycomb structures.

Label	cell size mm	Number of cells	Wall thickness mm	Pore size mm	Dimension of inscribe prismatic volume mm x mm x mm	Volume mm ³	Porosity %
Cell2	2	18	1.2	2.4	17.37 x 15.08 x 15	2235.12	43.11
Cell3	3	8	1.2	4.2	16.35 x 16.7 x 15	1747.91	57.32
Cell4	4	8	1.2	6.0	21.39 x 21.98 x 15	2383.05	66.20
Cell5	5	5	1.2	7.8	26.45 x 18.55 x 15	2087.35	71.64

Table 2

Table 2. Bio-ink compositions and their stoichiometric ratio R.

Label	LM pectin g/L	CaCl ₂ mM	R $2[\text{Ca}^{2+}]/[\text{COO}^-]$
P15	15	11	0.48
P25	25	12.5	0.33
P35	35	15	0.28

Table 3. Relative Young’s modulus of honeycomb structures predicted using analytical model (E/E^*_{An}) and FEM (E/E^*_{FEM}).

Structure	E/E^*_{An}	E/E^*_{FEM}
Cell2	0.28	0.29
Cell3	0.12	0.14
Cell4	0.06	0.09
Cell5	0.03	0.04

Table 4**Table 4.** Mechanical and structure properties (average $\pm$ standard error) of the 3D printed objects including the Young's modulus (E), the porosity (ϕ), the object volume (V), the average object thickness (δ_{av}), the equivalent diameter of the printed pores (d_{eq}) and the total number of pore analyzed in 2D through the height of the sample (N_{tot}).

Food-ink	Structure	E (kPa)	ϕ (%)	V (mm ³)	δ_{av} (mm)	d_{eq} (mm)	N_{tot}
P15	Cube	31.69 $\pm$ 3.84	1.57 $\pm$ 0.73	2242.01 $\pm$ 60.14	na [§]	na	na
	Cell2	14.22 $\pm$ 1.12	28.99 $\pm$ 3.11	1596.29 $\pm$ 50.59	1.75 $\pm$ 0.25	1.67 $\pm$ 0.38	1172
	Cell3	4.87 $\pm$ 1.14	46.76 $\pm$ 3.55	1314.52 $\pm$ 140.73	1.39 $\pm$ 0.12	3.35 $\pm$ 0.41	616
	Cell4	3.21 $\pm$ 0.57	56.21 $\pm$ 1.75	1724.39 $\pm$ 52.66	1.28 $\pm$ 0.12	5.03 $\pm$ 0.49	596
	Cell5	1.55 $\pm$ 0.45	65.23 $\pm$ 1.79	1388.60 $\pm$ 71.88	1.21 $\pm$ 0.06	6.85 $\pm$ 0.61	352
P25	Cube	63.43 $\pm$ 2.11	1.22 $\pm$ 0.26	2614.97 $\pm$ 208.76	na	na	na
	Cell2	39.83 $\pm$ 3.33	27.52 $\pm$ 1.44	2009.27 $\pm$ 198.44	1.76 $\pm$ 0.18	1.69 $\pm$ 0.34	1382
	Cell3	17.54 $\pm$ 2.25	41.41 $\pm$ 2.09	1637.40 $\pm$ 158.20	1.51 $\pm$ 0.14	3.32 $\pm$ 0.33	496
	Cell4	11.75 $\pm$ 0.93	53.79 $\pm$ 2.86	2238.56 $\pm$ 236.91	1.43 $\pm$ 0.14	5.15 $\pm$ 0.38	566
	Cell5	5.15 $\pm$ 0.65	63.15 $\pm$ 0.72	1649.05 $\pm$ 54.04	1.28 $\pm$ 0.02	6.94 $\pm$ 0.52	378
P35	Cube	118.58 $\pm$ 12.10	1.80 $\pm$ 0.15	2722.65 $\pm$ 66.40	na	na	na
	Cell2	75.87 $\pm$ 5.65	31.63 $\pm$ 2.46	1979.95 $\pm$ 47.16	1.48 $\pm$ 0.12	1.84 $\pm$ 0.32	1446
	Cell3	35.11 $\pm$ 5.75	43.44 $\pm$ 1.66	1661.08 $\pm$ 54.87	1.36 $\pm$ 0.07	3.55 $\pm$ 0.31	633
	Cell4	14.32 $\pm$ 0.42	54.66 $\pm$ 0.77	2159.01 $\pm$ 52.24	1.22 $\pm$ 0.02	5.49 $\pm$ 0.34	624
	Cell5	11.58 $\pm$ 1.43	62.92 $\pm$ 0.75	1889.14 $\pm$ 66.02	1.34 $\pm$ 0.07	7.07 $\pm$ 0.49	386

[§]Not applicable

Table 5**Table 5.** Relative deviation of the structure features of the printed object to their design value expressed in percentage: thickness ($\Delta\delta_{av}/\delta_{av}$), pore size ($\Delta d_{eq}/d_{eq}$), porosity ($\Delta\phi/\phi$) and volume ($\Delta V/V$). A deviation is positive when the measured property is higher than the predicted property and negative when it is lower.

Food-ink	Structure	$\Delta\delta_{av}/\delta_{av}$ (%)	$\Delta d_{eq}/d_{eq}$ (%)	$\Delta\phi/\phi$ (%)	$\Delta V/V$ (%)
P15	Cube	na [§]	na	na	-34 ± 2
	Cell2	46 ± 21	-29 ± 5	-33 ± 9	-29 ± 2
	Cell3	16 ± 10	-21 ± 6	-18 ± 9	-25 ± 8
	Cell4	7 ± 10	-17 ± 4	-15 ± 3	-28 ± 2
	Cell5	0.6 ± 5	-13 ± 1	-9 ± 3	-33 ± 3
P25	Cube	na	na	na	-23 ± 6
	Cell2	47 ± 15	-29 ± 6	-36 ± 4	-10 ± 9
	Cell3	26 ± 11	-22 ± 1	-28 ± 5	-6 ± 9
	Cell4	19 ± 12	-15 ± 1	-19 ± 6	-6 ± 1
	Cell5	7 ± 2	-12 ± 1	-12 ± 1	-21 ± 3
P35	Cube	na	na	na	-19 ± 2
	Cell2	24 ± 10	-23 ± 4	-32 ± 8	-11 ± 4
	Cell3	13 ± 6	-16 ± 2	-23 ± 4	-5 ± 5
	Cell4	2 ± 2	-9 ± 1	-17 ± 2	-9 ± 4
	Cell5	12 ± 6	-10 ± 1	-11 ± 1	-9 ± 4

[§]Not applicable