Molecular Gastronomy Meets 3D Printing: Layered Construction via Reverse Spherification

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Abstract

The potential use of additive manufacturing (AM) techniques for processing of food can span from satisfaction of basic necessities to high-end cuisine and fine dining. The purpose of this study was to explore how AM, specifically extrusion-based layer-wise deposition, can be combined with the reverse spherification technique that is widely used in molecular gastronomy. First, by manual extrusion, we identify suitable recipes and ingredient concentrations to form freestanding features in a liquid bath. Subsequently, a desktop extrusion is adapted for the deposition of a calcium solution into an alginate bath first as a two-dimensional (2D) pathway and then as three-dimensional (3D) geometry by layer-wise deposition. The 2D geometries are measured and compared to a nominal geometry, to elucidate how tool speed and extrusion rate influence form and dimensional accuracy. We demonstrate that motorized extrusion-based AM can be combined with reverse spherification to form stable objects by gelation of fruit-based solutions. In addition, a wider set of manual experiments shows the possibility of combining different flavors and the creation of complex multilayer and multiflavor objects. Additional studies on the deposition precision are required to optimize the process of creating a full 3D geometry. This study shows that 3D printing via reverse spherification can bridge the gap between culinary art and AM technology, and enable new capabilities for creation of dining experiences. This is a step toward the digital design and manufacturing of unique edible objects with complex flavors, textures, and geometries.

Keywords: 3d printing, molecular gastronomy, spherification, food

Introduction

“Food is a biological need, a vital necessity, without food no one can survive.”1 With this statement Lyman highlights the importance of food for human beings, however, there is much more in food than mere nutriment. Food is the fuel to perform daily tasks and regulate human biorhythm. Food is also the third largest expense of an average U.S. family, amounting to 6602 USD spent annually and representing 13% of their income.2 The industrialization of food production has transformed how humans perceive, access, and experience food.3 For example, with the introduction of mass-produced meals, people started cooking less, compromising the quality of their meals with easy-to-get and low-cost food.3

In this context, additive manufacturing (AM) has the potential to change the way food is manufactured and experienced by promoting different levels of customization, for example, based on nutrition, texture, and/or geometry,4,5 along with high quality and freshness. The combination of food and three-dimensional (3D) printing originated in 2007 with the use of a Fab@Home system, based on the fused deposition modeling (FDM) process, to print chocolate, cheese, and sugar glazing in 3D.6 Since then, interest in combining AM with food has grown considerably.7–9 For example, Coelho has proposed concept scenarios for the future kitchen, where daily meals will be prepared with a 3D printer inspired by the Star Trek’s replicator.3 Another example is represented by the European project Performance,10 which addresses the needs of people with mastication problems by designing a 3D printer capable of producing appealing meals with the consistency of soft puree. In 2013, NASA began a project aiming to develop food printers for long-term space missions, using dehydrated food as ingredients.11 Extensive research on food and 3D printing is...
carried out by the nonprofit Dutch research institute TNO\textsuperscript{12} and Cornell University.\textsuperscript{6,13,14} Another aspect is the use of AM for the customization of food products, from chocolate sculpture\textsuperscript{15,16} to sugar candies\textsuperscript{17} and ice cream.\textsuperscript{18} Printing of food can also address issues such as material waste\textsuperscript{19} and the incorporation of alternative nutrients such as insects.\textsuperscript{20}

One exciting area for the exploration of AM with food is molecular gastronomy,\textsuperscript{21} which investigates the physical and chemical transformations of ingredients that occur in cooking,\textsuperscript{22} especially in the alteration of food textures, crafting of edible pieces of art, and the generation of innovative ways of experiencing flavors. Molecular gastronomy is becoming increasingly used in fine dining.\textsuperscript{23,24} One widely used molecular gastronomy technique is reverse spherification (Fig. 1), which is a process of encapsulating a flavored liquid into edible calcium–alginate spheres, by a technique of reverse gelation.\textsuperscript{25} On contact of the calcium juice solution with an alginate bath, a thin gel membrane is formed, encapsulating the flavor.\textsuperscript{26,27} Reverse spherification is used especially for encapsulating alcoholic liquids and products rich in calcium, such as dairy. Often it is used with juices as well.

The adaptation of 3D printing methods to the spherification process used in molecular gastronomy could enable the design of new food experiences and custom tailoring of flavor and geometry. Moreover, the use of 3D printing can enable new artistic capabilities in cooking and extend the customization principles to the industrial culinary sector. The objective of the article is to investigate the suitability of direct-write extrusion as a means of building edible objects via reverse spherification. Starting with manual techniques and then following with the adaptation of the spherification process to direct-write extrusion, we develop a workflow for layer-by-layer construction by extrusion of calcium juice mixtures into an alginate bath and study the influence of key process parameters on the precision and stability of printed features. Extrusion allows continuous deposition of liquids having a wide range of viscosities, as opposite to the dropwise deposition of inkjet technology, which is limited in the viscosity of fluids that can be printed.\textsuperscript{28,29} We show that well-defined linear features can be made using direct-write extrusion into the alginate bath, but that formation of multilayer features is complicated by the sinking of the deposited material into the bath. We overcome this complication by fabricating multilayer, multiflavor constructs on a gelatin substrate and discuss how this could be implemented in an automated manner.

Materials and Methods

Recipes

A list of the ingredients and their proportions is shown in Table 1. The ingredients used for the final experiments are homemade orange juice and calcium gluconate lactate ((Ca(C$_6$H$_{11}$O$_7$)$_2$) for the calcium solution, and sodium alginate (CO$_2$Na) mixed with distilled water and xanthan gum for the bath. The orange juice is extracted manually by squeezing fresh oranges. The extract is then sieved twice through a fine mesh to remove seeds and pulp. The juice should be as homogeneous as possible to ensure a constant flow and a higher resolution of the printed part.

To prepare an exemplary solution, 125 g of orange juice is vigorously mixed with 1% of Ca(C$_6$H$_{11}$O$_7$)$_2$ and 0.13% xanthan gum for about 2 min with a hand mixer. At the same time, on the side, 500 g of water is mixed for 5 min with 0.5% of CO$_2$Na and 0.2% of xanthan gum, which serves to thicken the solution and increase its viscosity. This will facilitate the deposition process in the following step; the thicker substrate will keep the extruded juice from floating excessively on the surface of the bath. After being mixed, the solutions are placed inside a desiccator with the respective container and a vacuum pump is used to suck out the air to remove the excess of air bubbles caused by the mixing. Subsequently, the solutions are kept in the refrigerator overnight to allow complete hydration of the molecules.

Test setup

A custom setup built on a modified Printrbot\textsuperscript{30} is used for computer-controlled motion of the deposition nozzle in three
axes while modulating the flow rate of the calcium solution into the bath using a syringe pump. The heated extruder of the Printrbot was removed and replaced with a custom adapter, prototyped by the FDM process in ABS material (Fig. 2), for the fitting of two male Luer locks (3.17 mm ID, 3.68 mm OD) that serve as a connection between a Tygon tube and a tapered nozzle. Two sizes of tapered nozzles are used for the experiments: 0.8 and 0.58 mm ID. The opposite end of the tube is connected to a 10-mL syringe. The machine is interfaced with the software Printrun.

To evaluate the deposition precision of the calcium solution in the alginate bath, a simple two-dimensional (2D) geometry was traced, consisting of three segments, each 15 mm long, as shown in Figure 5a. Using this pattern, the
juice was extruded at six different rates starting from 15 mL/h (first value where a significant extrusion is registered) and an increase of 5 mL/h until the 40 mL/h was reached. For each extrusion rate, four different tool speeds are tested: F300, F400, F500, and F600 mm/min.

Experiments with each combination of parameters were repeated twice and a picture of each print was taken with a USB microscope immediately after deposition. The microscope is set at *300 mm of distance with the focus parallel to the build plate of the printer (see below the Image Analysis section). Pictures taken are analyzed with SPIP 6.4.1.

For printing 3D structures, a dual extrusion setup was used to alternate the deposition of one layer of calcium solution and subsequently a layer of alginate solution around the geometry. To compensate for the growth of the part, the layer of alginate is deposited along the perimeter of the 3D structure without covering its top surface. The flow rate of the calcium solution and alginate solution is regulated by two independent syringe pumps, respectively, 35 mL/h (calcium solution) and 46 mL/h (alginate). A picture of the setup is shown in Figure 2. A well plate is prepared with a thin uniform layer of alginate solution (~1 mm) at the bottom. A custom Gcode with a cube of 30 × 30 × 30 mm with a linear infill is generated. Layer thickness is set to 1.5 mm. A tool speed of 300 mm/min is used.

**Image analysis**

Features measured on the 2D geometry for the precision deposition are the length of the three segments (A, B, and C in Figure 5) measured by taking the farther out point to the opposite extreme of the segment (Fig. 5b) and the width of the three segments (D, E, and F in Figure 5). The widths instead are taken in an arbitrary point of the section of each segment, approximately in the middle; the left lower angle amplitude (G in Figure 5) measured at the center of the intersection between segment A and C. Since each experiment is made twice, the measurements are taken in all the pictures and then the values are averaged, plotted, and finally compared.

Time dependency of the gelation reaction based on calcium concentration is investigated by mixing two different quantities of calcium in the juice (Table 1) and then let two spheres, with a 20 mm diameter, to sit in the alginate bath for 4 min, taking a top-view picture with the USB microscope every 10 s. The diameter of the sphere is measured with two perpendicular cross sections, on the x- and y-axis.

**Results**

First, manual experiments were performed to determine suitable recipes for direct-write reverse spherification and to explore the stability of features that were made by direct dispensing of the juice into the bath. We found that this manual process can enable creation of a variety of interesting shapes such as those shown in Figure 3, and discussed later. After that, the 3D printer was constructed to explore the suitability for printing in the same manner as a single strand in FDM processes.

During the manual experiments (Fig. 3), the juice-calcium solution is laid down slowly and carefully onto the surface of the bath, using a pipette. Deposition of additional material causes the previous material to sink downward into the bath. On contact with the bath, gelation occurs exclusively on the outside perimeter of the pattern that has been deposited, yet not in between layers, thereby allowing the creation of a 3D geometry with a monolithic liquid interior.

After manual deposition of several layers of liquid (i.e., repeating the same manual deposition path several times), the formed part sinks due to its own weight, and a gel film forms over the top surface. This causes the flavored liquid (here,
juice-calcium mixture) to be encapsulated completely in 3D, terminating the process or enabling stratification of flavor into distinct layers. Manual agitation can also be used to submerge the deposited material and seal the top by gelation. After completion, the geometry then is removed from the bath with a perforated spoon and rinsed in distilled water, which fully stops the gelation reaction.

To develop guidelines for tailored geometries, it is necessary to understand the kinetics of gelation occurring at the juice–bath interface. For this, we laid a circular area of juice into the bath, and via image analysis measured its diameter versus time as it "grew" due to gelation. As shown in Figure 4, the diameter increases, and the growth rate is proportional to the concentration of Ca present in the solution. Under the same test conditions, the solution with higher Ca content (5 g) grows at a rate that is twice as large as the Ca with a lower content (2.5 g), and both growth kinetics are sublinear suggesting that penetration is diffusion limited. The thickening of the membrane could represent a problem for the sensorial experience of the diner; in this regard, the gel membrane should be as thin as possible. Therefore, knowing that both concentrations gave stable membranes we chose the lower concentration of Ca for carrying out the printing experiments.

FIG. 6. Plots of length A, length B, width D, and angle G of the 0.58 mm ID nozzle as a function of the deposition rate in respect of the tool speed. The dimensions are defined in Figure 5. Color images available online at www.liebertpub.com/3dp

FIG. 7. Automated multilayer deposition using the 3D printer. (a) Deposition of the geometry perimeter with juice-calcium mixture, (b) deposition of infill with juice-calcium mixture, (c) deposition of the second layer with juice-calcium mixture. Color images available online at www.liebertpub.com/3dp
Having proven the basic concept of manual direct-write spherification, we used the 3D printing machine to first understand how to control the dimensions of a continuous deposition path, analogous to traditional extrusion printing. The results are shown in Figure 5, using the 2D nominal geometry.

In the test pattern, higher speeds reduce lengths and widths of the segments and increase the amplitude of the angle G between segment A and C. Gathering information on the angle amplitude allows us to understand how sharp geometries and corners can be made. The amplitude of the angle G varies with the deposition parameters. The surface tension of the two liquids in contact makes the liquid on the surface, hence the juice-calcium mixture, to float. Because of this and due to the change of direction on deposition, the two segments A and C tend to move away from each other, distorting the pattern as it is printed. This effect is reduced for higher flow rates. Figure 6 shows that for flow rates of 30–35 and 40 mL/min, the angle is slightly wider than nominal geometry but it is not affected by the deposition speed in a significant manner. On visual inspection and then confirmed by the measurements, segment A appears to be shorter than the segments B and C, likely due to the sudden change in direction of the tool between the preload and the segment A. This shows a need to couple the flow rate to the motion rate of the printed head to achieve high-accuracy printing and to learn how the width of the printed feature is influenced by the local reaction kinetics on contact with the bath. From the experiments emerged that, in general, the parameters that allow a deposition closer to the nominal geometry are lower flow rates at higher motion speeds. The nozzle with the smallest diameter (0.58 mm ID) is preferable as it has a more controlled flow when the deposition flow rate is lower. In comparison, the results gained with the use of the larger nozzle (0.8 mm) are similar to the ones shown in Figure 8 but with overall larger values.

Next, we explored multilayer deposition with the 3D printer. First a thin layer of alginate is deposited with a designed nozzle, followed by a layer of calcium. The 3D geometry is built by alternating the deposition of calcium solution with alginate until the geometry is completed (see the Materials and Methods section). In this way, the level of the alginate rises as the part builds up. However, during printing we found that due to the gelation process occurring very quickly on the sides of the deposited bead of Ca solution on the bath, it was not possible to deposit a uniform square planar layer. In addition, the forces carried by the extruded Ca material separated the beads on deposition. For this reason, we were not able to deposit more than three consecutive stable layers (Fig. 7). This suggests the need for further investigation of the influence of the parameters and on the deposition control of 3D structures. Options for the potential improvement of the printing process are reduction of nozzle diameter, the use of a coaxial nozzle instead of a single nozzle, and the introduction of a controller for the independent adjustment of the flow throughout the print.

Additional experiments were performed manually to demonstrate the capability to pattern multiple flavors in a designed manner, by adding different types of juices in layers to create visually interesting patterns. This is done using a similar technique to the one illustrated above for the deposition of 3D structures. The use of a gelatin-coated build surface is introduced to the experiment to prevent the geometry from drifting in the bath. The gelatin is positioned to cover a portion of a flat bottom perforated rinsing spoon (Fig. 8). The holes are sealed on the outside with a hydrophobic film. A layer of alginate (to cover the gelatin) is distributed uniformly. Layers of different Ca solutions are stacked, alternating the deposition of additional alginate to compensate for the vertical growth of the geometry, but always leaving the top side uncovered to prevent the reaction to occur. On completion of the geometry, an additional layer of alginate is added to the surface to cover the top part as well (Fig. 8b). The hydrophobic film is removed and the alginate is allowed to drain (Fig. 8c). The tool is then submerged in a bowl of distilled water to stop the reaction and free the geometry from alginate leftovers. The result is spheres with added features that are possible exclusively with layered deposition. Automation of this process would facilitate the digital production of any designed shape, and it could be done in a more precise, stable, and fast way than by hand. In addition, the technique would allow for the combination of different flavors, in a predesigned amount, allowing the exploration of new tasting experiences for the diner, while providing an interesting visual effect as well.

Conclusions and Outlook

We have shown that it is possible to use direct-write extrusion to fabricate custom 3D geometries from a calcium solution into an alginate bath, via the process of reverse
spherification used widely in fine dining. This has the potential to create custom flavor configurations and geometries, and enable digital design of edible objects that encapsulate these flavors. The achievement of shapes that are closer to nominal values necessitates the adjustments of tool speed and deposition rate parameters in relation to the forces applied by the deposited material, during extrusion, on the surface of the alginate bath. As an alternative, the investigation of droplets, instead of beads, of materials is considered as a valuable option for further investigation. In addition, the use of nozzles of different sizes, especially smaller, and coaxial needles, represents an interesting way to proceed to accomplish the ultimate goal of making more complex 3D structures via reverse spherification.

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References


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