applied sciences

MDPI

Support information

Simulations of extrusion 3D printing of chitosan hydrogels

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SI.1. Geometry and parameters of nozzle fluid flow in COMSOL simulation

The geometry is designed in a simulation of chitosan-based extrusion 3D printing by COMSOL Multiphysics software. The schematic geometry is split 2D axisymmetric using in a simulation. The schematic of the two-dimensional simulation (COMSOL 5.2a) for the extrusion-based 3D printing method will be given. The dimension of the main channel is $15\ mm$ in height, and in width $2\ mm$, and the side channel is $0.4\ mm$ in width. The dimensions of the channel were chosen to keep in mind the conditions for geometries that promote squeezing mechanism: (i) the width of the main channel should be smaller than its height, and (ii) the width of the inlet channel should be an equal index to the width of nozzle in the experimental test. The dispersed phase (chitosan ink) is extruded through the main channel and the continuous phase (air) is among the side channel. In this simulation, fluid chitosan hydrogel is set as the dispersed phase and the air is set as the continuous phase.

The continuity equation is settled to solve for the velocity and pressure parameters in the geometry. In COMSOL simulation fluids properties and boundary condition of two-phase flow are chosen by the user. The solution of geometry is obtained automatically in software. The COMSOL geometry of the nozzle of extrusion-based 3D printing is demonstrating in Figure S1. The nozzle geometry is kept constant n various simulations. However, the tip of the nozzle dimension with All other parameters including inlet and outlet pressure, fluid viscosity and density, and boundary conditions are kept constant. When the nozzle dimension is kept constant, the velocity and viscosity will be changed to study the effect of different velocities in a simulation of extrusion 3D printing. Resulted of these simulations were used to extract information on velocity and pressure profiles.

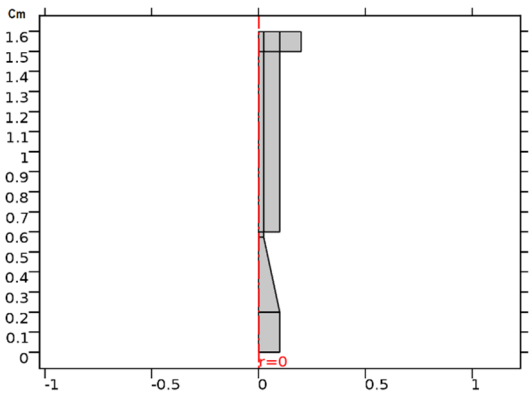

Figure S1. Geometry of nozzle of chitosan 3D printing in comsol.

We use the same parameters in the simulation of extrusion-based chitosan 3D printing methods. The parameters are given in Table S1. Where the density of ink is set as 1×10^3 $[kg/m^3]$ and 0.02×10^3 $[kg/m^3]$ and the density of air is 1.225×10^3 $[kg/m^3]$. And the viscosity of ink is 150×10^{-1} $[Pa.s]$ to 250×10^{-1} $[Pa.s]$and viscosity of air is 1.789×10^{-5} $[Pa.s]$, the surface tension coefficient is 0.07 $[N/m]$. Furthermore, the ink velocity was adjusted to 1 [m/s], 2 [m/s], 3 [m/s].

Table S1. Description of the parameters of simulation of 3D printing chitosan.

Name	Expression	Value
Density, Ink	0.02×10^3 $[kg/m^3]$	20 $[kg/m^3]$
Viscosity, Ink	250×10^{-1} $[Pa.s]$	25 [Pa.s]
Viscosity, Ink	200×10^{-1} $[Pa.s]$	20 [Pa.s]
Viscosity, Ink	150×10^{-1} $[Pa.s]$	15 [Pa.s]
Density, Air	1.225×10^3 $[kg/m^3]$.	0.071225 $[kg/m^3]$
Viscosity, Air	1.789×10^{-5} $[Pa.s]$	0.0001789 [Pa.s]
Surface tension coefficient	70×10^{-3}[N/m]	[N/m]

SI.2. Modifications on the meshes

Simulations were conducted in COMSOL Multiphysics to theoretically demonstrate extrusion formation of chitosan 3D printing methods. For this numerical simulation, physics-controlled meshes use the predefined finer size and free triangular. As we observe in **Figure S2** the meshed model used in the simulation. It used various types of meshes in a model that use in a numerical simulation study. The different size of mesh with the interface are shown in this figure where **Figure S2A** use finer physic-controlled and **Figure S2B** use normal physic-controlled. The size of the mesh can affect the thickness of the interface and calculation time of simulation. When the mesh size change from finer to normal, the simulation time is reduced from 24 hours to 8 hours accordingly. Although, the deviation results taken from the simulation aren't evident. When the local mesh refinement is used. The interface thickness depends on the biggest mesh in the system, resulting in the simulation model makes hard to convergence. Hence, it can use the homogenous meshes in simulation that big mesh size or normal physic is reduced calculation simulation time. The small mesh size of fine physic controlled is obtained longer time for calculation and hard to convergence model. Consequently, we have used the homogenous meshed with normal physic controlled in extrusion-based chitosan 3D printing as shown in **Figure S2B**.

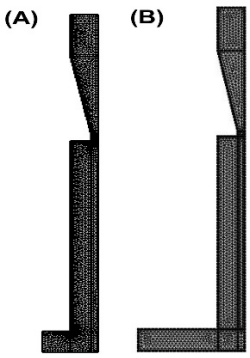

Figure S2. Different types of the meshes used in the simulation; (A) Default meshes with fine physic-controlled; (B) Default meshes with normal physic-controlled.

SI.3. Materials and Methods

in this research, we have used the chitosan powder with a degree of deacetylation (DD = 89%) from Ruji Biotechnology Co., Ltd. The Chitosan Aqueous solution was prepared by dissolving chitosan in an alkaline solvent. When chitosan is dissolved in an alkaline aqueous solution, the hydrogen bond of macromolecules and chitosan and alkali/urea is making complex formation at low temperature. As shown in Figure S3A, the hydrogen bond of the chitosan chain can't dissolve in alkali/urea solution at room temperature. After once freezing, the hydrogen bond could be destructed. So, the macromolecules of the chitosan chain and alkali/urea make a dissolution on chitosan as shown in Figure S3B. Hence, after the freezing-thawing process, the chitosan chain is dissolving in an alkaline aqueous solution. As the result the chitosan ink was obtained.

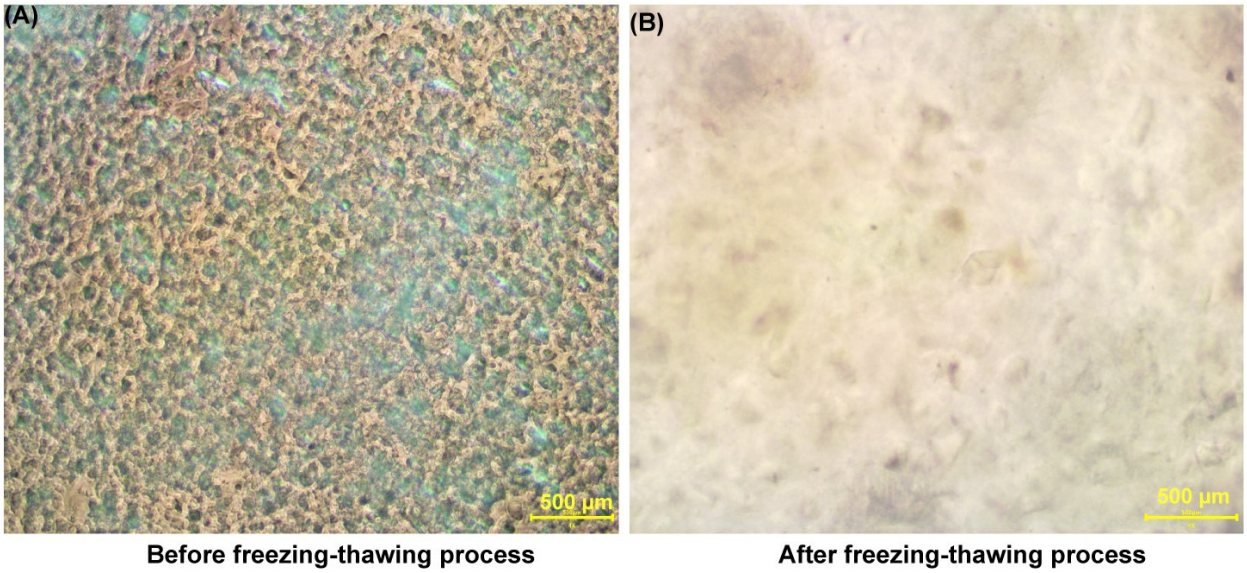

Figure S3. The phase of chitosan ink before and after freezing-thawing process.

SI.4. Printing methods of Chitosan Hydrogel

In this experiment, chitosan 3D printing device consist of the following parts: cartridge and nozzle, temperature controlling unit, printing platform, and fixture. The Cartridge is made of stainless steel with an outer diameter of 4 centimeters with a syringe embedded inside with the tip of 3 micrometers. Temperature controller sensors are mounted on the nozzle and the printing bed is used to keep the nozzle and bed at the desired temperature so that the printing device can be used in an ideal condition. Two outputs are connected to relays so that, they can control the heating process. As the temperature sensor measures changes in temperature, this will in return, cause changes in the operational amplifier's voltage. After temperature comparison is made and the set temperature is achieved, it will cause the relay to turn off and stop the heating process. As the temperature sensor measures changes in temperature this will in return, cause changes in the operational amplifier's voltage. After temperature comparison is made and the set temperature is achieved, it will cause the relay to turn off and stop heating process. A heat exchanger is used in order to heat the feed water to set the right temperature for bed and the Chitosan ink. Further, a cartesian printer system is used because of the simplicity in movement and control. The nozzle set up is mounted on the intersection of linked arms. By controlling the arms, movement control can be achieved precisely.

All printings were carried out using a customized 3D printer (EFL-BP-6800, Suzhou Intelligent Manufacturing Research Institute, Suzhou, China)

Hardware:

Regardless of printer type, linear motion is the essential mechanism in the printing process. Knowing that the hot end is moving in three-dimensional space, all the movements can be broken down into linear motion. The most common way to drive linear motion is using a leadscrew because of the self-locking ability and significant push force while a stepper motor is used to convert electrical energy to first rotational movement and then to linear motion.

The mainframe has consisted of one carriage driven by a stepper motor that moves in the X direction with a nozzle mounted on which can move in the Z-direction perpendicular to the printing bed so that the pre-defined height set for moving layers is achieved. Printing platform bed movement is in the Y direction driven by a leadscrew and an electrical motor. The printer is equipped with a temperature controller for both nozzle and platform bed. The DIW 3D printer is controlled via a RepRap compatible motherboard.

Software:

The software components and system are discussed. We use Repetier-Host V2.00 software for slicing STL files to layers that using for printing models. Due to it is appropriate using for the user as well as easy access to the printer. The layered schematic CAD files of the five-pointed star and tensile specimens 'model after slicing is shown in **Figure S4A**.

Therefore, the Repetier-Host program converts the STL files to G code. It was able to control the extrusion rate and speed of printing. The Slicer settings and machine commands (G-code) is an adjustment for extrusion chitosan-based 3D printing. The slicer setting is adjusted by individual changing of the Cura engine program. The slicer program permits the specifying position of the material support structure, part

orientation, and layer height for the generation of G-code. G-code is shown to understand how the slicer settings controlled the printing system. The G code is including format of G1 X(x1) Y(y1) Z(z1) E(e) F(f). Thus, the G1is a command of starting printing. G28 is moving an axel to the position of home. The X, Y, and Z are defining nozzle positions. The E is showing filament length and F is the extrusion speed of filament. Hence, the chitosan-based ink extrude when the G code sends to the printer. While the bed temperature control with the printer device for printing crosslink. Ultimately, the scaffold is printed with proper structure as shown in **Figure S4B**.

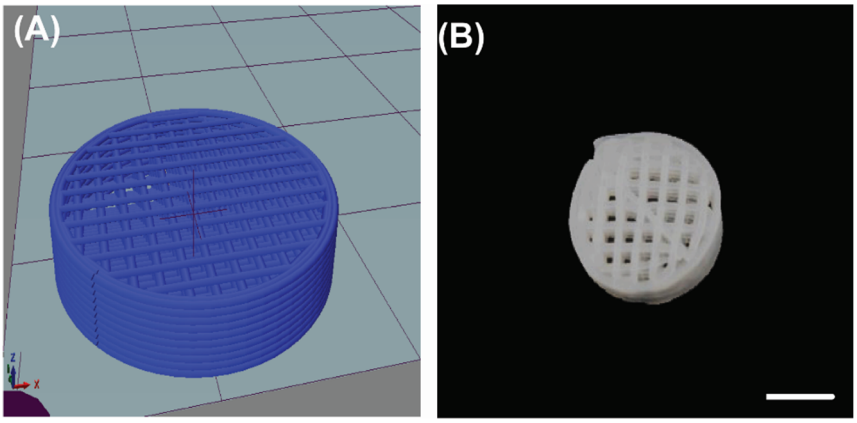

Figure S4. (A) Sliced layer by layer profile of samples;(B) Optical image of a printed cylinder scaffold (Scale bar: 2 mm)