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Laurent Chaunier, Mélanie Thadasack, Anne-Laure Réguerre, Achraf Chebbi, Lucas Huttin, et al.. Experimental assessment and 2D-Modelling of the viscous sintering of superimposed filaments based on biopolymer. ESAFORM 2025, ESAFORM, May 2025, Paestum, Italy. pp.2-11, <10.21741/9781644903599-1>. <hal-05063496>

HAL Id: hal-05063496

<https://hal.science/hal-05063496v1>

Submitted on 19 May 2025

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Experimental assessment and 2D-Modelling of the viscous sintering of superimposed filaments based on biopolymer

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Keywords: Bonding, Image Analysis, FEM, Level Set, Protein, X-Ray Tomography, Zein

Abstract. Additive Manufacturing by Molten material Extrusion (AM-ME) of biocompatible and edible parts based on natural biopolymers, such as zein, a protein extracted from corn, opens prospects for applications in the pharmaceutical field. Cohesion between deposited layers requires filament spreading and diffusion of macromolecules at the interface. Viscous sintering has to be characterized and modelled in the case of zein, to better control its processing in the molten state. Sintering kinetics of polymer melts is generally assessed in an instrumented furnace and modelled using the Frenkel-Eshelby approach. It is based on the evaluation of the growth rate of the bonding neck between two circular parts, linked to the melt's surface tension (Γ), the driving force, and viscosity (η). It was recently completed by the acquisition of 3D scans by dynamic X-ray tomography (5.2 μm pixel size, 1 scan/s) on the ANATOMIX beamline of Synchrotron SOLEIL, to follow the hot-melt sintering of 4 filaments ($L_{\text{Filament}}=5$ mm, $\varnothing_{\text{Filament}}=2$ mm) disposed in two layers. The analysis of the reconstructed volumes leads to assess the decreasing size of the central pore during sintering. 2D modelling is carried out by FEM combined to Level Set with COMSOL Multiphysics®. It requires a simplification of the geometry according to an axial symmetry and an adaptive time-stepping. At 120 °C, a typical temperature to process plasticized zein, simulated and experimental sintering are similar, with a decrease rate of the central pore at about 1%/s. Increasing sintering rates are obtained as the temperature and surface tension increase.

Introduction

Additive Manufacturing by molten Material Extrusion (AM-ME) allows obtaining biocompatible, resorbable and edible parts from natural biopolymers, such as plasticized zein, a storage protein extracted from corn kernels. This leads to potential applications in the pharmaceutical or the biomedical field [1,2]. To control the cohesion between the deposited layers, based on the spreading of filaments and the diffusion of macromolecules at their interface, it is necessary to characterize and to model their viscous sintering, especially in the case of superimposed layers. Then, zein, plasticized by adding 20% glycerol, can be extruded as filaments at temperatures around 120 °C, the glass transition temperature of this material being about 45 °C [3]. In the molten state, the mechanisms underlying filaments sintering involve surface tension of the melt, Γ [N/m] (the driving force) and its viscosity, μ [Pa·s]. An experimental device was previously used for 2D monitoring of the fusion-bonding by visible light imaging using backlighting [4]. It made it possible to define and measure the bonding neck length during the hot-melt sintering of two

juxtaposed filaments. Between 120 and 130 °C, plasticized zein was found to exhibit thermo-rheological and surface properties similar to those of standard synthetic polymers used in AM-ME, with sintering abilities close to that of ABS at its 3D printing temperature [3,4].

These results needed to be refined to dissociate the flow of the molten material linked to its viscoelastic swelling (edge effect), from that really due to viscous sintering and avoiding surface interactions with the basement of the furnace. This cannot be achieved by 2D imaging [5], because of drop shadow potentially caused by backlighting of the filaments and the absence of a stable focal plane on filaments during the whole hot-melt sintering sequence. This can be improved by the acquisition of 3D scans during the isothermal viscous sintering of superimposed layers of zein-based extruded filaments by dynamic X-ray microtomography. For this purpose, a furnace was recently designed at INRAE and set up on the ANATOMIX beamline at synchrotron SOLEIL to characterize juxtaposed filaments sintering [2,6,7]. It has to be adapted to characterize the sintering of 4 superimposed filaments placed in stable manner, as two superimposed layers, when submitted to hot-melt sintering at high temperature. The analysis of 3D scans has to lead to the evaluation of fusion-bonding kinetics, as done more basically on two juxtaposed filaments [2,4]. The characterization has to be carried out in volume, especially by following the evolution of the collapse of the central pore, located at the middle of the four superimposed filaments submitted to sintering at 120 °C, a standard temperature to process plasticized zein. On the other hand, modelling the hot-melt sintering of thermoplastic zein has been also previously investigated by Finite Element Modeling (FEM) in the case of two juxtaposed filaments [8]. The 2D-FEM model, coupled to the Level Set (LS) method, leads to track the interface in the case of a two-phase flow of the molten model-biopolymer in air.

The aim of the present work is to investigate the modelling of the isothermal viscous sintering of superimposed layers of biopolymer-based filaments, with an image analysis method set up to compare to experimental results obtained by dynamic X-ray tomography during sintering trials.

Material and methods

Raw materials and filaments extrusion. Zein (Ref. Z3625) and glycerol (Ref. G7893) were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). 20% glycerol (in weight) were added as standard plasticizer to the raw commercial zein, to obtain a powder blend. Then, filaments were extruded with a twin-screw micro-compounder (Haake Minilab, Thermo Scientific GmbH, Karlsruhe, Germany) equipped with a cylindrical die ($\varnothing_{\text{Filament}}=2$ mm) [3].

Dynamic X-ray tomography. The assessment of the hot-melt sintering of superimposed filaments was carried out using the microtomography station of the ANATOMIX beamline at Synchrotron SOLEIL [6,7]. A furnace (outer dimensions: 105x100x80 mm³), dedicated to microtomography at high temperature, was designed specifically for this purpose (Fig. 1) [2]. Four extruded filaments based on plasticized zein ($\varnothing_{\text{Filament}} = 2$ mm, $L_{\text{Filament}} = 5$ mm) were superimposed as two layers on the flat top of the sample holder ($\varnothing_{\text{Sample_holder}} = 10$ mm) made of PEEK and topped with an aluminum plate (Fig. 1b). To carry out viscous sintering trials under isothermal conditions, the furnace was preliminary heated up for 10 min at 120 °C, while kept in a position 20 cm above the samples and the X-ray beam. Then, the oven was lowered (in about 10 s) over the samples using a motorized translation, enabling tomography scanning of the superimposed filaments layers during their hot-melt viscous sintering. Fast tomography scan series were taken with a duration of 1.2 seconds for each full volume scan, 1000 projection radiographs per scan and a repetition rate around 1 scan every 6 seconds. This was achieved with a setup including a rotation stage (RT500s, LAB Motion Systems, Bekkevoort, Belgium) rotating continuously at 150°/s during the scan series, an indirect lens-coupled detector system with a single-crystal scintillator (lutetium aluminum garnet 300 μm thick, Crytur, Turnov, Czech Republic) and a set of Hasselblad photo optics in tandem geometry projecting the image from the scintillator onto the set of a rapid scientific CMOS camera (pco.dimax HS4, Excelitas PCO, Kelheim, Germany, physical pixel size

11 μm) with a magnification factor of 2.1, resulting in an effective pixel size of 5.2 μm . During the scan series, the image data were first recorded in the internal memory of the camera, then downloaded to the control system after completion of each scan series. With 36 GBytes of camera on-board memory and operating the camera with a region of interest (ROI) of 1600 \times 1600 pixels (corresponding to a field of view 8.3 \times 8.3 mm²), this enabled to acquire up to 28 scans per series, thus covering a process period around 160 seconds for each scan series.

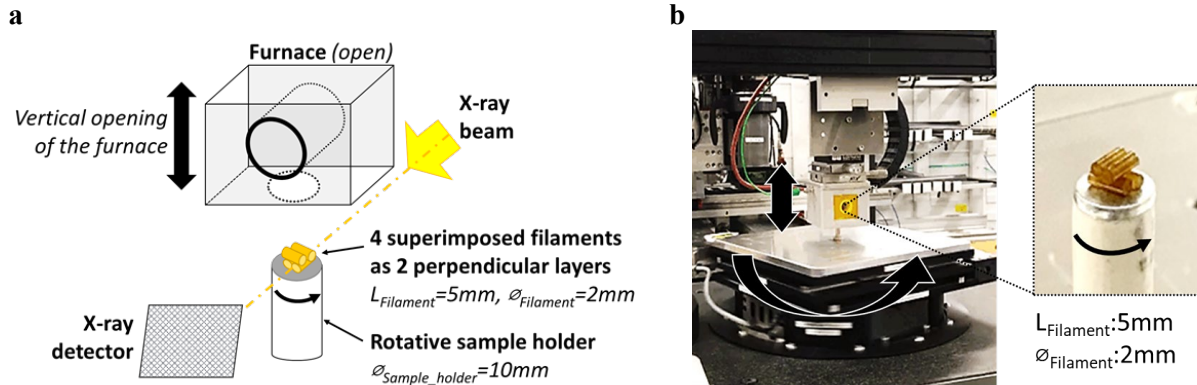


Figure 1 – (a) Schematic drawing of the experimental set up for dynamic X-ray tomography carried out during superimposed layers sintering at the ANATOMIX beamline of the Synchrotron SOLEIL. (b) Front view of the furnace (in lowered position, i.e., containing sample), with Kapton window and picture of the four superimposed filaments ($L_{\text{Filament}} = 5 \text{ mm}$, $\varnothing_{\text{Filament}} = 2 \text{ mm}$) placed on the rotative sample holder (aluminum plate, $\varnothing_{\text{Sample_holder}} = 10 \text{ mm}$) before lowering furnace.

Image analysis. The 3D reconstructed volumes were segmented to isolate the biopolymer-based filaments and dissociate them from the central cavity in 3D and in 2D (as side view of the reconstructed volume to compare to the 2D-FEM model of isothermal sintering; Fig. 2 and Fig. 3).

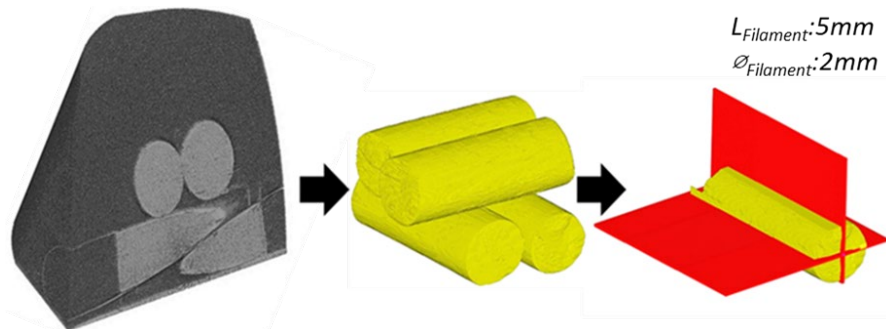


Figure 2 – Segmentation of reconstructed volumes obtained by fast synchrotron X-ray tomography (ANATOMIX beamline) to characterize sintering between 4 extruded zein-based filaments placed in two superimposed layers: Initial raw 3D rendering of the volume with the 2 layers (left); 3D rendering of the isolated biopolymer-based filaments after segmentation (center and right, in yellow); Determination of the vertical and horizontal planes (right, in red, here for a sole filament among the 4 considered in the sintering trials), to define the central porosity being progressively collapsed during filaments sintering.

The analysis of the reconstructed 3D-scans leads to a quantification of the decreasing volume of the central pore (located at the middle of the two superimposed layers) and then establishes its collapsing rate to characterize viscous sintering kinetics of the four thermoplastic filaments.

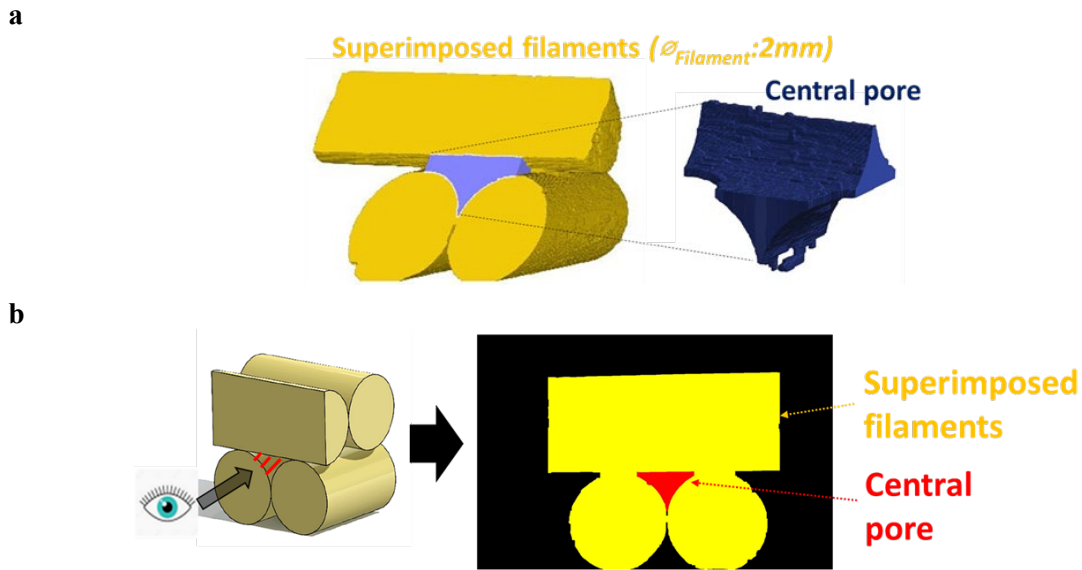


Figure 3 – (a) Analysis of 3D scan obtained by dynamic X-ray tomography after segmentation of the ROI, to separate biopolymer-based filaments from the central (tracking the evolution of the size of this pore will allow the assessment of filaments viscous sintering at high temperature). (b) Side view of 2 superimposed layers of thermoplastic filaments based on biopolymer, with the central pore presented in red (i.e., 2D experimental results to be compared to the 2D-FEM model of the filaments sintering).

FEM model, Level Set method and sensitivity study. The numerical simulation of superimposed filaments sintering is performed using a two-phase flow simulation with COMSOL Multiphysics® software (COMSOL Inc., Burlington, MA, US) [8]. Phase #1 is constituted by air and phase #2 by plasticized biopolymer (i.e., zein; Fig. 4). The software makes it possible to solve systems of differential equations with the coupling of physical phenomena by the Finite Element Method (FEM) on a geometry simplified by using the vertical axial symmetry of the four superimposed filaments. The integrated solver allows solving the equations and visualizing the results by a graphic post-processing.

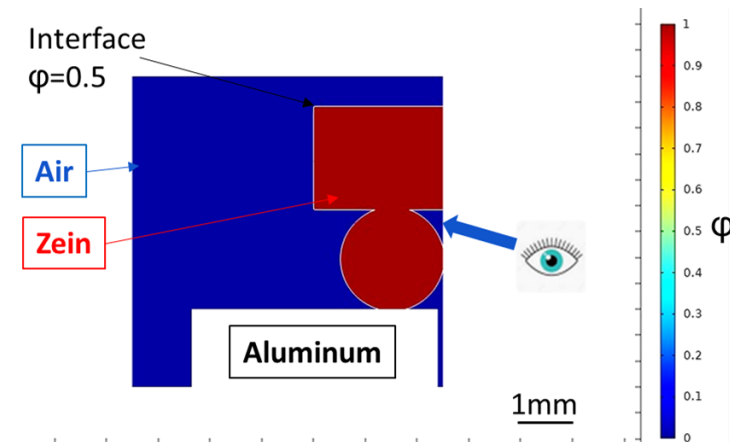


Figure 4 – Schematic illustration of the domain considered for the numerical modelling by FEM of superimposed filaments sintering as a two-phase flow ($\phi_{\text{Filament}}=2\text{ mm}$) and central pore presented as being focused on (Phase #1 = air; Phase #2 = plasticized zein).

The level set (LS) and Navier-Stokes (NS) equations are used to model the flow of the molten plasticized zein during its hot melt sintering under the effect of the surface tension as the driving force. The interface between the two immiscible fluids – zein and air – is monitored. A reduced

form can be given to the NS equation (Eqs. 1 and 2), because of inertial term being negligible at low velocity (*i.e.*, at low Reynolds number):

$$\rho \cdot \frac{\partial V}{\partial t} + \rho(V \cdot \nabla V) = \nabla \cdot [-pI + \mu(\nabla V + (\nabla V)^T)] + \rho \cdot g + F_{ST} + F, \quad (1)$$

and

$$\rho(V \cdot \nabla V) = 0, \quad (2)$$

with t , the time [s]; ρ , the density [$\text{kg} \cdot \text{m}^{-3}$]; V , the flow velocity [$\text{m} \cdot \text{s}^{-1}$]; P , the pressure applied to the fluid [Pa]; μ , its dynamic viscosity [$\text{Pa} \cdot \text{s}$]; g , the acceleration of the gravity field [$9.80665 \text{ m} \cdot \text{s}^{-2}$, or $\text{N} \cdot \text{kg}^{-1}$], F_{ST} the force resulting from the surface tension [N] and F all other body forces applied to the flowing fluid [N].

The conservation of mass is solved by the continuity equation (Eq. 2). At each point of the mesh used for FEM, the density, ρ (Eq. 3), the viscosity, μ (Eq. 4), and the thermal diffusivity, D (Eq. 5), at each point of the mesh are determined:

$$\rho = (1 - \varphi) \cdot \rho_1 + \varphi \cdot \rho_2, \quad (3)$$

$$\mu = (1 - \varphi) \cdot \mu_1 + \varphi \cdot \mu_2, \quad (4)$$

and

$$D = (1 - \varphi) \cdot D_1 + \varphi \cdot D_2, \quad (5)$$

with ρ_1 and ρ_2 , the densities; μ_1 and μ_2 , the dynamic viscosities and D_1 and D_2 , the thermal diffusivities of each phase of the two-phases flow (zein and air). Then, the volume fraction is one of the outputs of the two-phase flow simulation to follow sintering and especially the air/biopolymer interphase at $\varphi = 0.5$ (N.B. $\varphi = 0$ for a mesh element filled with air, in blue on the Fig. 4, and $\varphi = 1$ for a mesh element filled with the biopolymer).

The melt flow velocity is considered zero when the cylinders (*i.e.*, the extruded filaments based on zein) are in contact with the basement of the furnace (aluminum plate of the experimental device). The monitoring of the interface between the two phases is carried out by the LS method by solving the following transport equation added to those of NS. It allows describing fluid flow in a continuous medium following Eq. 6:

$$\frac{\partial \varphi}{\partial t} + \nabla \cdot (V\varphi) = \gamma \nabla \cdot (\varepsilon_{IS} \nabla \varphi - \varphi \cdot (1 - \varphi) \cdot \frac{\nabla \varphi}{|\nabla \varphi|}) \quad (6)$$

with φ being the volume fraction [-]; γ , the re-initialization factor [$\text{m} \cdot \text{s}^{-1}$] (maximum rate of melt in two-phase flow) and ε_{IS} , regulating the interfacial thickness.

To avoid an artificial rise of pressure in the central and bottom cavities due to the 2D representation, small air outlets were implemented as boundary conditions in these regions. To take in consideration the heat transfer during the simulation, a convection-diffusion equation (Eq. 7) is added to the model:

$$\rho \cdot C_p \cdot \left(\frac{\partial T}{\partial t} + V \cdot \nabla T \right) = \nabla \cdot (\lambda \nabla T) \quad (7)$$

with T being the temperature ($T_{\text{oven}}=120 \text{ }^\circ\text{C}$ and $T_{\text{initial_zein}}=25 \text{ }^\circ\text{C}$); V , the flow velocity, the coupling term with NS equations; λ , the thermal conductivity [$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$] and C_p , the specific

thermal capacity [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$]. Concerning air (*i.e.*, Phase#1), its thermal conductivity is assumed at $\lambda_{\text{Air}}=0.024 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $\rho_{\text{Air}}=1.2 \text{ kg}\cdot\text{m}^{-3}$, $C_{p_Air}=1 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and $\mu_{\text{Air}}=1.10^{-5} \text{ Pa}\cdot\text{s}$.

The density of the plasticized zein is assumed at $\rho_{\text{Zein}}=1200 \text{ kg}\cdot\text{m}^{-3}$. C_{p_Zein} , previously determined by DSC, increases when exceeding the glass transition temperature from $1.5\cdot 10^3 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, at 20°C , to $2.2\cdot 10^3 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, at 130°C [4,8]. The basic surface tension of plasticized zein melt is assumed at $30\text{mN}\cdot\text{m}^{-1}$. The thermal conductivity and diffusivity, as well as the decrease of melt viscosity with temperature (from about $1.1\cdot 10^5 \text{ Pa}\cdot\text{s}$ at 80°C to about $4.3\cdot 10^2 \text{ Pa}\cdot\text{s}$ at 140°C) were taken from recent literature [8].

A sensitivity study is carried out to dissociate the impact of different parameters of the 2D-FEM model: (i) Temperature (ranging from 100°C to 130°C); (ii) Viscosity (with an applied factor increasing from $\times 0.1$ to $\times 2$); and (iii) Surface tension (applied factor ranging from $\times 0.5$ to $\times 2$).

Results and discussion

2D FEM coupled to the Level Set method allows the following of the two-phase flow during the numerical simulation of the hot melt sintering of superimposed biopolymer-based filaments (Fig. 5).

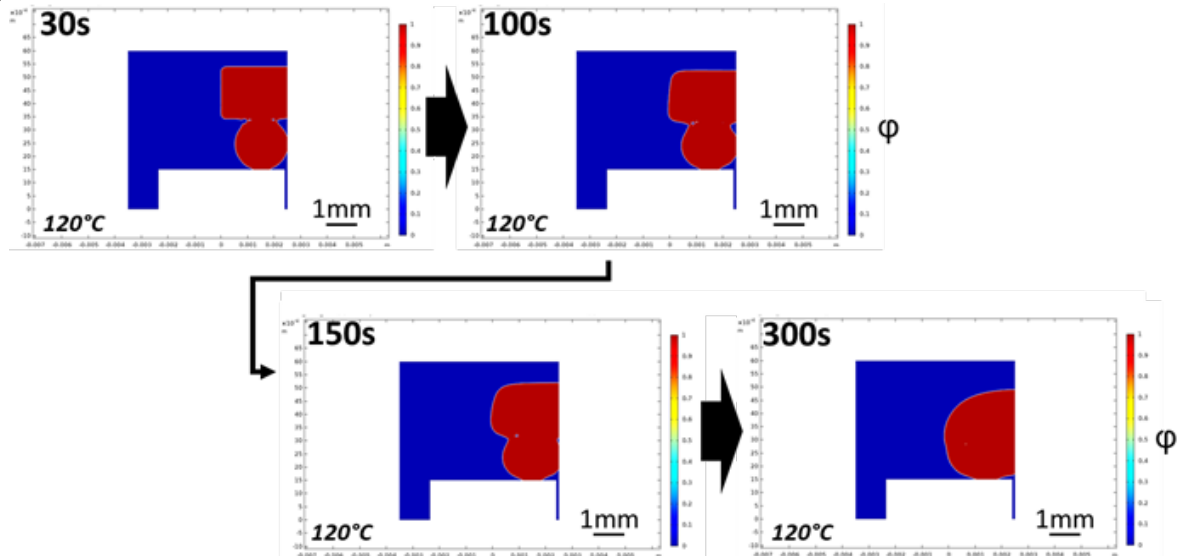


Figure 5 – Results of 2D FEM as a two-phase flow mapping (air presented in blue and zein in red) obtained by the Level Set method at 120°C for 5 minutes simulation of viscous sintering.

As in the experimental trial, similar evolution of the shape is obtained at 120°C , a standard temperature to process the model-biopolymer (*i.e.* plasticized zein) in the molten state. Indeed, the sintering leads to a progressive collapse of the central pore (located at the middle of the 2 layers), by four superimposed filaments drawing closer together from their initial state of rigid filaments due to the surface tension of zein-based melt obtained at high temperature (Fig. 5 and Fig. 6).

On the other hand, the impact of the simulated gravity leads to a progressive vertical melt flowing and sagging of the molten filaments, as during experimental trials followed up by X-ray tomography in the instrumented furnace.

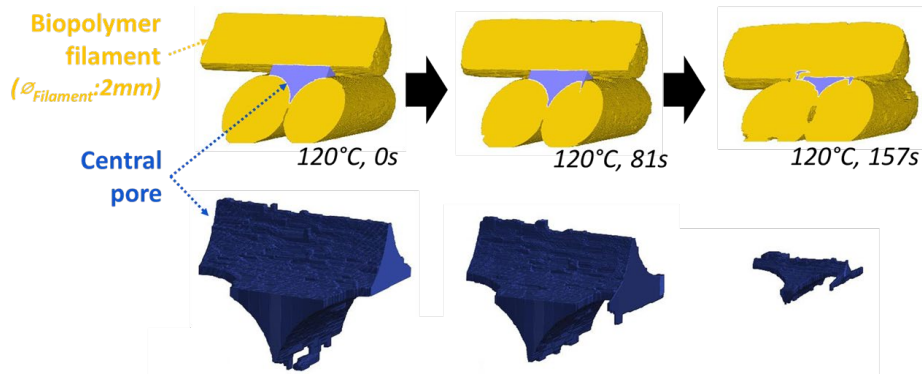


Figure 6 – Real-time X-ray microtomography of 2 superimposed layers of thermoplastic filaments during their hot melt sintering at 120 °C: Initial step (0 s), mid-time of the acquisition sequence (81 s) and final step (157 s). Biopolymer-based filaments presented in yellow and central porosity in light blue (zoom presented at the bottom line of the figure for the same three successive acquisition steps).

The evolution of the size of the pore is presented normalized to its initial value to compare experimental results obtained in 3D and in 2D (*i.e.*, 3D seen as a side view, Fig. 3), to the results obtained by numerical simulations (FEM model in 2D with coupling to the Level Set method).

After a steady initial step during about 50 s to 1 min, the hot melt sintering begins and a linear phase at constant decrease rate of the central pore’s size is experimentally measured for the reference temperature, $T=120\text{ °C}$, at about 1%/s of collapsing rate (Fig. 7). These results are similar concerning the evolution of the surface of the central porosity in 2D (as evaluated from successive side views of the experimental characterization), its volume (experimental in 3D) and the simulation at the same temperature (FEM in 2D, at $T_{\text{Simulated}}=120\text{ °C}$). Furthermore, the sensitivity study, carried out for simulations obtained with 2D FEM, leads to faster sintering when increasing temperature from 100 °C to 120 °C and finally 130 °C, mainly because of the decrease of melt viscosity induced by temperature increase [4,8].

The sintering rate of molten filaments is faster and the collapse of the central porosity in the middle of the superimposed filaments is increased from about 0.2%/s, at $T_{\text{Simulation}}=100\text{ °C}$, to 2%/s at $T_{\text{Simulation}}=130\text{ °C}$.

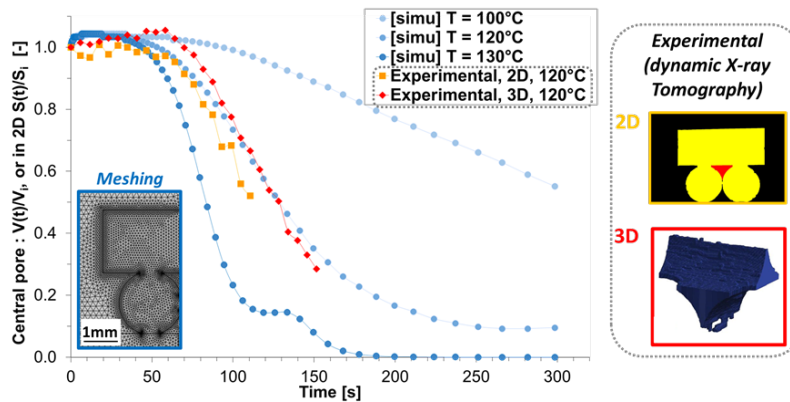


Figure 7 – Experimental results in 2D and 3D obtained at 120 °C concerning the evolution of the central pore size between 4 superimposed thermoplastic filaments (illustrations as inserts: X-ray tomography in 2D – side view, with central pore in red – and 3D – focus on the isolated central porosity of 2 superimposed layers of filaments, in dark blue – at the beginning of the hot melt sintering sequence acquired on the ANATOMIX beamline of Synchrotron SOLEIL) and results of the sensitivity study of the 2D FEM model in the case of temperature increasing from 100 °C, 120 °C to 130 °C (in blue on the chart – focus on 2D-FEM meshing –).

To investigate the sole effect of viscosity, dissociable from temperature in simulation, a sensitivity study is applied to the 2D FEM model coupled with the LS method at 120 °C for 4 levels of viscosity. When increasing the viscosity from a factor x0.1 to x2, based on reference value issued from literature [8], the collapsing rate of the central pore decreases from about 3%/s to 0.5%/s. As expected, melt viscosity limits sintering rates and its impact on kinetics leads to an increase of the fusion-bonding rates of thermoplastic filaments at lower viscosity level (Fig. 8a).

As the driving force of fusion-bonding, the evolution of the hot melt sintering kinetics is also impacted by surface tension. Indeed, a slight decrease of sintering rate is obtained in this case when decreasing the coefficient applied to surface tension from x2 to x0.5 (reference value set at 30mN·m⁻¹), with pore collapsing rate decreasing from 1.1 to around 0.7%/s (Fig. 8b). The effect of variation of the surface tension is proportionally less important than the one of the melt viscosity on the whole sintering phenomenon.

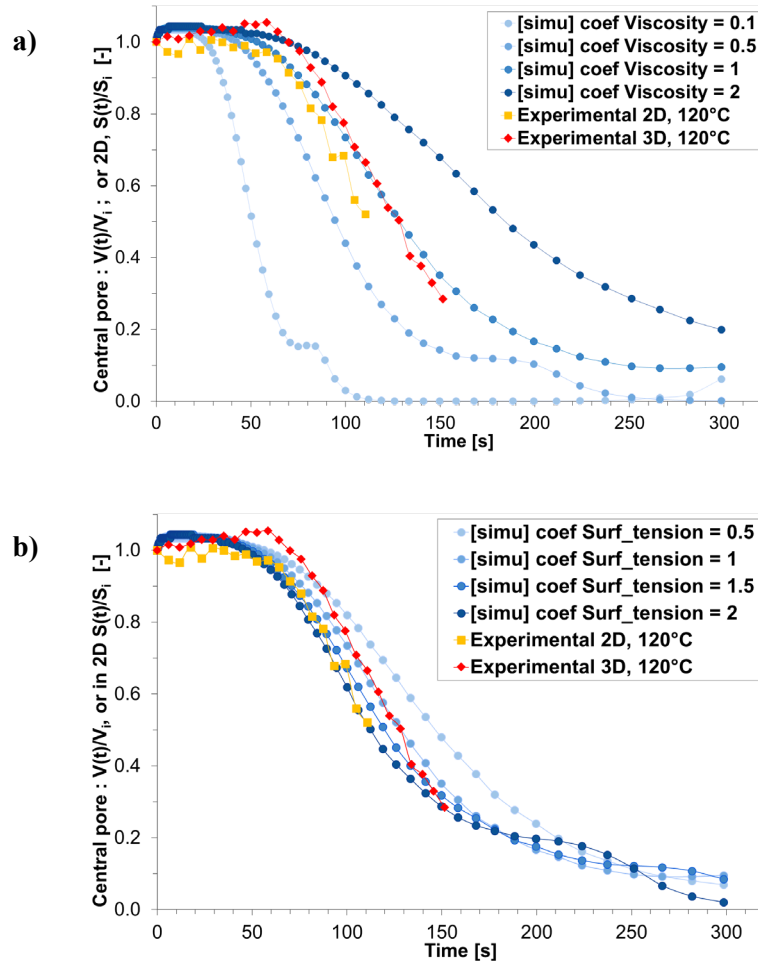


Figure 8 – Experimental results obtained at 120 °C during hot-melt sintering sequence acquired on the ANATOMIX beamline at Synchrotron SOLEIL and presented as the evolution of the central pore size of superimposed thermoplastic filaments in 2D (side view, curve in yellow on the chart) and 3D (whole reconstructed scan, curve in red). Sensitivity study of the FEM model at 120°C concerning: (a) viscosity (ranging from factor x0.1 to x2) and (b) surface tension (ranging from factor x0.5 to x2).

Conclusion

Dynamic synchrotron X-ray microtomography, at scan times around 1 s and a repetition rate around 10 scans per minute, with a pixel size of 5.2 μm , allowed the characterization of the hot melt sintering of superimposed biopolymer-based filaments layers.

A 2D FEM model coupled to the Level Set method was used to simulate filaments viscous sintering with melt surface tension as the driving force. By monitoring the collapse of the central pore during fusion-bonding of filaments layers, the sintering kinetics can be assessed and the experimental results compared with the simulations.

At 120 °C, a typical temperature for processing plasticized zein, the experimental data are similar to the simulated ones. A sensitivity study has confirmed the tremendous influence of temperature increase on the sintering rate, particularly because of decreasing melt viscosity. An effect of melt surface tension on sintering rate is also shown, albeit more moderate than the effect of temperature.

This work opens prospects concerning the modelling in 3D of layers sintering, for which more important computing resources will be necessary.

Acknowledgments

The authors acknowledge SOLEIL for providing synchrotron radiation facilities (project no. 20220020) and would like to thank Guillaume Daniel for assistance in using beamline ANATOMIX. ANATOMIX is an Equipment of Excellence (EQUIPEX) funded by the *Investments for the Future* program of the French National Research Agency (ANR), project *NanoimagesX*, grant no. ANR-11-EQPX-0031.

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