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**3D Modelling of the viscous sintering of
superimposed layers of biopolymer-based
thermoplastic filaments**

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Chapter 1

Abstract

Key words: Additive manufacturing, biopolymers, FEM, numerical simulation, zein, AM-ME, Fused filament fabrication, Level set method, Heat transfer, Navier-Stokes equation.

Mots-clés : fabrication additive, biopolymères, MEF, simulation numérique, zéine, AM-ME, fabrication par dépôt de fil fondu, méthode Level Set, transfert de chaleur, équation de Navier-Stokes.

New materials such as biopolymers derived from vegetables are increasingly attractive for various applications, particularly in the biomedical, pharmaceutical, and food sectors. New methods for producing parts from these materials are required, and additive manufacturing is among the most common due to its simplicity, speed, and ability to produce complex shapes. To understand the behavior of a zein-based biopolymer—zein being a protein derived from maize—during an additive manufacturing process using fused filament fabrication, it was necessary to model the coalescence process between layers. A 3D model based on the Finite Element Method (FEM) and the Level Set method was developed to study the sintering process between four filaments of zein plasticized with 20 wt% glycerol. A second composition was also investigated: zein plasticized with 10 wt% glycerol and an active pharmaceutical ingredient (API), such as lidocaine and ibuprofen.

To validate the model, the results were compared with experimental data obtained at the SOLEIL Synchrotron [1]. A sensitivity study was conducted to examine the influence of parameters such as printing temperature, surface tension, and dynamic viscosity. The results showed that higher temperatures accelerate the coalescence process, whereas higher viscosity slows down the sintering, especially when the amount of glycerol decreases. This model can help guide the selection of the optimal material composition and printing parameters for the manufacturing process.

Les nouveaux matériaux tels que les biopolymères issus de végétaux suscitent un intérêt croissant pour diverses applications, en particulier dans les secteurs biomédical, pharmaceutique et alimentaire. De nouvelles méthodes de fabrication de pièces à partir de ces matériaux sont nécessaires, et la fabrication additive figure parmi les plus répandues en raison de sa simplicité, de sa rapidité et de sa capacité à produire des formes complexes. Afin de comprendre le comportement d'un biopolymère à base de zéine — la zéine étant une protéine extraite du maïs — lors d'un procédé de fabrication additive par dépôt de fil fondu, il a été nécessaire de modéliser le processus de coalescence entre couches. Un modèle 3D basé sur la méthode des éléments finis (MEF) et la méthode Level Set a été développé pour étudier le processus de frittage entre quatre filaments de zéine plastifiée avec 20 % p/p de glycérol. Une seconde composition a également été étudiée : zéine plastifiée avec 10 % p/p de glycérol et un principe actif pharmaceutique (API) tel que la lidocaïne et l'ibuprofène.

Pour valider le modèle, les résultats ont été comparés aux données expérimentales obtenues au synchrotron SOLEIL [1]. Une étude de sensibilité a été menée pour analyser l'influence de paramètres tels que la température d'impression, la tension superficielle et la viscosité dynamique. Les résultats ont montré que des températures plus élevées accélèrent le processus de coalescence, tandis qu'une viscosité plus élevée ralentit le frittage, surtout lorsque la quantité de glycérol diminue. Ce modèle peut aider à orienter le choix des paramètres d'impression pour le procédé de fabrication.

Chapter 2

State of art

2.1 Introduction

Additive manufacturing is commonly used today to produce objects and parts with complex shapes and in shorter time compare to the traditional manufacturing process. In particular, additive manufacturing, especially by molten Material Extrusion (AM-ME) allows the use of special materials such as biopolymers to build these parts. One of these biopolymers is plasticized zein, a storage protein extracted from maize. This protein, when plasticized with 20% glycerol in weight, can be extruded into filaments and has a similar behavior that can be compared with common polymers such as PLA and ABS. Thanks to the property of this material, it can be used in different application fields, such as biomedical, pharmaceutical and food sectors. The aim of this study is to analyze the viscous sintering process that occurs during a 3D printing manufacturing process. Sintering occurs due to the effect of heat, the particles of the system start to soften and coalesce. In a 3D printing this phenomenon typically happens between two adjacent layers of material. In order to simulate this phenomenon, a 3D simulation is developed to analyze the effects and importance of the key physical parameters of the system, such as the surface tension of the melt Γ , the temperature T , the dynamic viscosity η and density ρ . The model is based on an experiment carried out by INRAE at the Synchrotron SOLEIL. In that experiment, to simulate the coalescence during a 3D printing the authors placed 4 filaments of zein like superimposed layers on a pre-heated aluminium plate. An oven surrounded the four filaments, and it was set at 120°C, simulating the temperature conditions of the material during the 3D printing process. 3D scans were performed during the isothermal viscous sintering using dynamic X-ray microtomography to observe the variation of the central pore between the 4 filaments. The same configuration is used

in this numerical model, where three different simulation are performed:

- Thermal simulation: evaluation of temperature evolution over time in all the system
- Fluid simulation of a two-phase fluid: laminar flow simulation coupled with the Level set method: study the evolution of the fluid flow over time without the effect of the temperature
- Multiphysics simulation: A non-isothermal model where temperature effects are included and coupled with fluid dynamics

The main goal of the simulation is to understand the effect of the main drivers of the system in order to find the better combination of them in order to achieve an high quality of the manufacturing process. The effect of temperature, surface tension and dynamic viscosity have been studied. To compare the results between the numerical simulation and the experimental data, the focus was put on the evolution of the central pore of the four filaments. From this evolution it is possible to evaluate the sintering rate and to see the evolution by time of the sintering process.

2.2 3D printing process: Fused Filament Fabrication

Additive manufacturing process are now very common in many industrial application for multiple reason. One of the main advantages is the ability to quickly transition from 3D CAD model to the produced part. In the biomedical field it is possible to have a direct path from the 3D CAD files or scanned images to 3D printing components, resulting in the production of the final product. Another reasons about the diffusion of additive manufacturing process in biomedical domain is it the possibility to directly control the geometry and porosity of the finished part without using a mold (like the other technique used in the biomedical sector [2]). This capability is very important in the pharmaceutical sector, where it is a requirement to produce drugs with a specific porosity to control the release of active ingredients once ingested [3]. With AM, especially with ME process, it is possible to print the part with minimal waste of raw material compared with to other process where the material is in a powder state (like LPDF) and it is not necessary to heat the rigid part to achieve precise dimensions. Two serious issues present in the versatility and

simplicity of AM are: the printing machine command and the material's behavior during processing. The conversion of the numerical models to the printer control commands follows the generation of the mesh of the 3D structure of the final part and the division of it into parallel planes that simulated the layers during the manufacturing process. After the 3D CAD model built, there are many file format to chose to gives the surface of an object. The basic one is the STL file. This file is interpreted by the software built in the 3D printer, and it divides the model in a succession of multiple deposition planes, contours, the filling pattern, which once superimposed constitute the 3D finished part. Fused filament fabrication (FFF) is an additive manufacturing process based on extrusion of material to build parts. It is also known as fused deposition modelling (FDM). In these printers, material is heated, melted and pushed by a feed system that forced the material through a nozzle. The extruded material will flow at a constant pressure and constant rate and will also have a constant cross-section diameter. A series of motors are attached to heating elements to move it in a three-dimensional space to build the final part. FFF is a common manufacturing process due to its simplicity, speed and low cost [2]. However, challenges remain in achieving good mechanical properties and surface quality in the printed parts. During the process all the material is assumed to be in a molten state when it enters the convergent part of the die. The angle β of the nozzle in the convergent part is very close to 90° (Fig2.1). Thermoplastic polymers usually exhibit a shear-thinning behavior in molten state. To express the variation of their dynamic viscosity η with the shear rate $\dot{\gamma}$ (s^{-1}) the power law is used:

$$\eta = K \cdot \dot{\gamma} \quad (2.1)$$

where K is the consistency index ($\text{Pa} \cdot \text{s}^{-1}$) and n is the flowing index (with $0 < n < 1$ for pseudo-plastic materials such as thermoplastics molten). In the liquefier and the die (Fig2.1) a non-isothermal flow takes place, so the viscosity depends on the temperature when the $T \gg T_g$ where T_g is the glass transition temperature. The Arrhenius equation expresses this dependence:

$$K = K_0 \cdot \exp \left[\frac{E}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2.2)$$

where E is the activation energy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), R is the ideal gas constant and T_0 is the reference temperature. It can be the printing temperature set at the nozzle. Understanding how viscosity varies with the temperature is essential to analyze the deposition and adhesion behavior of the molten polymer [4]. Several material properties are involved in this process, such as surface tension, viscosity and

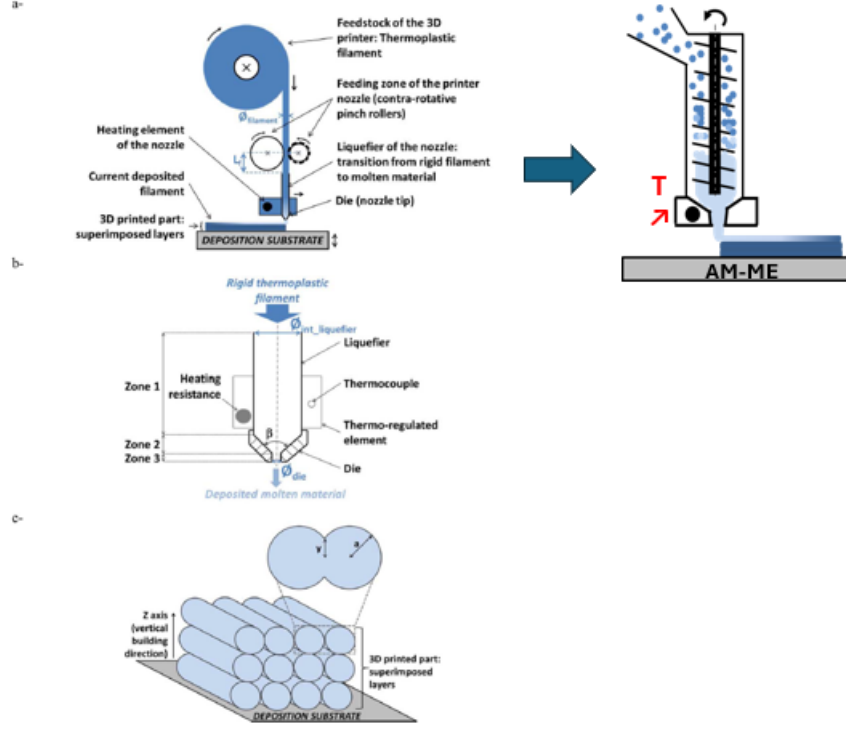


Figure 2.1: FFF Process [2]

density. During the printing process, the layer of material exits the nozzle and it is deposited onto the previous layer, where it fuses to obtain the 3D printed part. Now, the molten material is cooling to the ambient temperature. The linear deposition rate ($\text{m} \cdot \text{s}^{-1}$) is expressed like:

$$R_{\text{deposition}} = \frac{Q}{A} \quad (2.3)$$

where Q ($\text{m}^3 \cdot \text{s}^{-1}$) is the volume flow of the material and A is the area of the section of the deposited filament (m^2). It can be considered as an ellipse due to the spreading of the molten material:

$$A = \pi \cdot a \cdot b \quad (2.4)$$

where a is the semi-major axis of the ellipse (m) and b is the semi-minor axis (m). The distance between the nozzle exit and the deposition (h , in m) surface has to be larger than the nominal diameter of the deposited filament:

$$R_{\text{deposition}} < \frac{Q \cdot \pi}{h^2} \quad (2.5)$$

Viscosity η and surface tension Γ are used to describe the drop spreading between the molten material and the deposition surface by a capillary number:

$$Ca = \eta \cdot \frac{R_{deposition}}{\gamma} \quad (2.6)$$

If Ca increase, at a constant temperature, less material would spread. Notably, the surface tension of molten polymers (particularly biopolymers) is often poorly characterized. When the thermoplastic filaments is out of the die, it cools down and its viscosity increases. Below crossing the glass transition temperature, the filament reaches the solid state. The filaments will not have a circular section, but they will have an elliptic section. This particular section may create voids between layers of material. The number and size of these voids will have an effect on the surface quality of the final part. The mechanical properties of the final part are influenced by the material's mechanical strength, the bonding area between two hot welded deposited filaments and the number of voids[5].

2.3 Zein as material for 3D printing process

Fused Filament Fabrication allows the use of a wide range of material in additive manufacturing process, but some criteria about the material properties must be taken into account:

- Printing temperature T_p : It must be higher than the glass transition temperature T_g to have the material in a molten state, but less than the degradation temperature of the material T_d

$$T_g < T_p < T_d \quad (2.7)$$

- material rigidity: the material used in the feeding system must have a rigidity at room temperature close to the vitreous storage moduli in GPa.

$$E_{solid} \approx E_{vitreous} \geq 1 \text{ GPa} \quad (2.8)$$

- Sharpness of the solid-to-melt transition: This feature is important to reduce the dimensions of the feeding/die system. It is usually estimated by two characteristics of the material: the ratio between the moduli at room temperature and the glass transition temperature and the width of the solid-melt transition [6]

$$\frac{E_{vitreous}}{E_{rubbery}} \approx 1.10^3 \quad \Delta T_{vitr-rub} = 30 - 40K \quad (2.9)$$

The thermoplastics materials common used in the FFF process, such as ABS and PLA, they meet these criteria, but for biopolymer it depends of which types of biopolymer an source of the biopolymer [6].

Among naturally occurring polymers, only few of them are melt-processable, which is a mandatory requirement for processing them by ME. Biopolymers are mainly derived from two major families of crops: starches [7] and proteins [8]. For starches, is possible to obtain the melt only with the presence of moisture, because the water molecules act as plasticizer and also the effect of water on the rheological behavior during the ME process is well known [9]. The final material can exhibit either rubbery or ductile behavior when it reaches the ambient temperature, depending on the plasticizer used. Add 23% of glycerol in weight to starch yields will give to the composition a rubbery state when it reaches room temperature. The elastic module E will be close to 13 MPa [10]. The plasticized starch now is melt-processable but it is not rigid enough to be used inside a 3D printing, especially in the feeding mechanism [11]. A second option is using proteins. The proteins present by default hydrophilic and hydrophobic characters because they have properties of their amino acid monomer. Most proteins required plasticizer to become melt-processable, to achieve good mechanical properties and to have a glass transition temperature higher than ambient temperature [12],[13]. A good candidate to reach a compromise among these requests is the zein. Zein is a storage protein derived from maize. Zein is an abundant resource since more than 800 million tons of maize kernels are harvested every year in the world. Commercial zein can hot-spun as a thermoplastic filament by extrusion. Add 22% of glycerol in weight, zein reach the required properties, like an high elastic module ($E > 1$ GPa) and a glass transition temperature higher than ambient temperature ($T_g \approx 60^\circ\text{C}$). Also the zein is edible, easier to be processable in the molten state and it is less sensitive to water than starch. Also, the melt viscosity η of zein changes from 0.1 to 1 kPa·s for T varying in the range 120-160°C with a shear rate $\dot{\gamma} = 160 \text{ s}^{-1}$ (a typical shear rate in the die nozzle of an ME printer) [14],[15]. Zein is a maize storage protein, it represents from 3 to 5% of the kernel dry weight and is part of the prolamin family. Zein is used in multiple application and in different fields [16]. It is used as a water barrier in the food and pharmaceutical industries, but also to produce degradable plastics that can be used to make scaffolds for cell growth [14],[15]. Zein is made by low-charge proteins, this means that their amino acid primary sequences have both hydrophobic and hydrophilic behavior. These proteins constitute amphiphilic polymers, that can thermoplasticized after adding plasticizers. An example of the use of zein like thermoplasticized polymer is to use zein to control the paracetamol release in extruded-molded caplets [17]. Entry deep inside the structure of the zein, and taking the example of Z22 (Fig2.2), is present

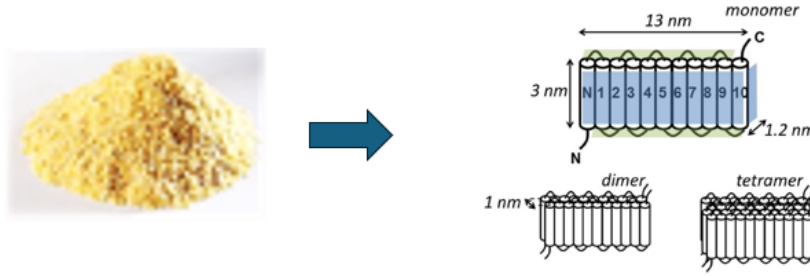


Figure 2.2: Zein (α -zein, Z22) prismatic structure (known as a “monomer”). Hydrophobic faces in blue; hydrophilic turn between α -helices in green [2]

a prismatic model ($13 \times 3 \times 1.2 \text{ nm}^3$) [18]. The vertical part sides give hydrophobic properties, and also the bonds between the repeat units are made by glutamine residues that present hydrophilic properties. This type of structure let the biopolymer to auto-assembly in solution and to interact with different plasticizers: that one with polar structures (such as water and glycerol) or amphiphilic structures (such as fatty acids) [19]. During the first steps of the extrusion in the 3D printer, it is noticed that the crosslinking occurred at high temperature. This phenomenon is due to thermal oxidation of cysteine sulfhydryl groups ($-\text{SH}$) such as disulfide bonds (S-S), that increases the stiffness of the material. This effect creates high molecular weight molecules, and the crosslinked structure of the material remains in the 3D printed part, when the temperature of extrusion is $T_{\text{extrusion}} = 130^\circ\text{C}$ [20], meanwhile the thermal decomposition occurs at $280\text{--}300^\circ\text{C}$ [21]. To understand better the behavior of zein at different temperatures and the influence of the plasticizer percentage, it is a good option to compare the zein with the other standard polymers used in ME extrusion process. PLA has a glass transition temperature around 50°C and endothermic transition from 130°C to 150°C where the material melts. Instead, ABS has an amorphous vitreous structure at ambient temperature; its glass transition temperature is between 90°C and 140°C . PLA and ABS have different mechanical behaviors but they both have high modulus than biopolymers at ambient temperature and a molten state that enabling them to flow when $T > T_g$. For the zein the situation changes depending on the percentage of plasticizer inside the composition. When only 10% of glycerol is added, there is no significant decrease of the modulus that do not let the material flow when $T > T_g$, mandatory feature to use it for 3D printing process [22]. If we increase the amount of glycerol in the composition, overcome 30% of glycerol, the zein will have lower mechanical properties compare to zein with 22% of glycerol. In fact, the optimal glycerol content for processing the material via 3D

printing is in the 20–25% range. Studying the decrease of the mechanical strength, the change of the structures and the relaxation mechanisms at high temperature, the printing temperature for thermoplasticizes zein is $T_{printing}=120^{\circ}\text{C}$. [2]

In this study, Z20Gly (20% of glycerol added) is used. At this concentration the zein has a rheological behavior very similar to the other standard polymers used in additive manufacturing process [23]. But also simulation with another formulation of zein is carried out. In addition to zein, 10% of glycerol and two Active Pharmaceutical Ingredient - Ionic Liquid (API-IL) [Lidocainium][Ibuprofenate] are blended [24]. This new composition is tested to be processed by hot melt extrusion. This two ingredients, Lidocaine and Ibuprofen, have been chosen because they can be easily dosed and processed also by thermo-mechanically process. They are able to constitute molecules which have better bioavailability and stability than solid forms. The therapeutic effects of both the ingredients are also kept after the extrusion process: it showed a progressive release of these active ingredients as obtained in simulated physiological conditions. It was possible, thanks to high affinity between zein and [Lid][Ibu] [25]. The zein-matrix, under thermomechanical treatment for 3 min at 130°C , keep its structural integrity as evidenced by thermal gravimetric analysis (TGA), and it reach the primary decomposition temperature above 250°C . Also, the matrix still have both anesthetic effect of Lidocaine and the analgesic effect of Ibuprofen [26]. To understand and to compare the behavior of the two different composition during an additive manufacturing process, different experiments are carried out but Chaunier et al.[27]: one to study the rheological properties of the zein plasticized with glycerol and API-IL in steady state flow under extrusion conditions. The second one examined the sintering properties of plasticized zein. In the final one the zein was 3D printed by hot melt extrusion and their porous structure were analyzed. In the first experiment they used a micro-compounder to reproduce extrusion process conditions and a conical twin-screw system was used; 7-8 g of material were introduced in the system at 130°C . The apparent viscosity η_a has been calculated:

$$\eta_a = \frac{\tau}{\dot{\gamma}_a} \quad (2.10)$$

where τ is the shear stress and $\dot{\gamma}_a$ the apparent shear rate. The results showed that for composition Z20GLY and Z10GLY10LI both present low initial viscosity and a large process window, that let the material to be used in 3D printing process (Fig 2.3). Consequently, for the following steps in the work, these two compositions have been used.

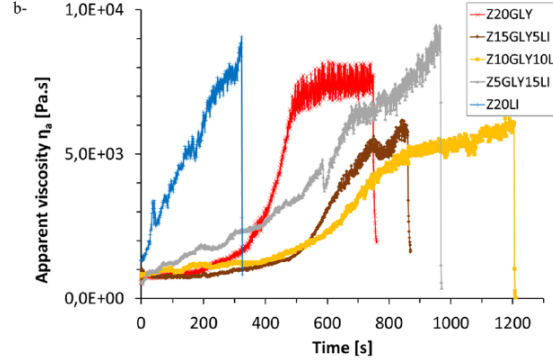


Figure 2.3: Apparent viscosity, η_a , of molten zein-based materials recirculating in the micro-compounder at 130°C [27]

To study the sintering abilities, the author analyzed the bonding angles between a couple of zein filaments. Two experiments were carried out, one using Z20GLY and one using Z10GLY10LI. In each experiments, two filaments were heated a different temperatures by an oven, and with an X-ray tomography they studied the bonding angles, i.e; the angles between the two filaments.

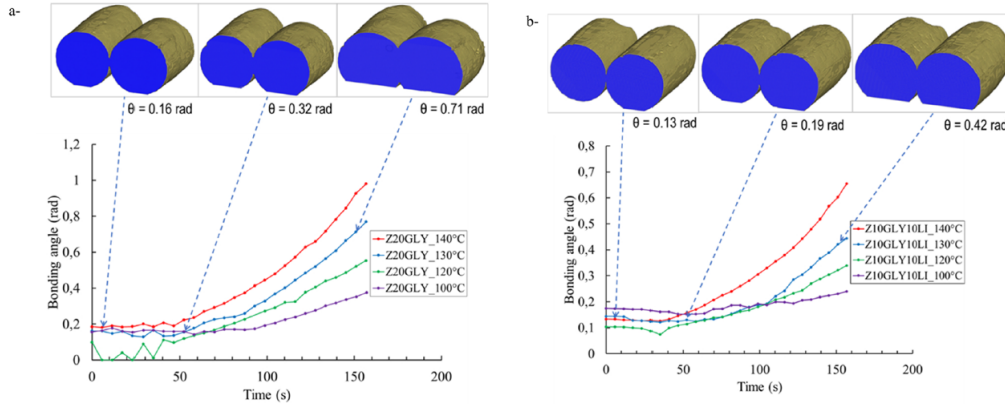


Figure 2.4: Sintering kinetics monitored via the evolution of the bonding angles assessed by dynamic X-ray tomography for Z20GLY (a) and Z10GLY10LI (b) [27].

In Fig. 2.4 it showed the difference behavior between the two materials; the curves are slope before to reach 50 s, then the sintering process begins. However, sintering progresses slowly because the molten state is reached only at a temperature close to 80°C. The sintering rates V [rad·s⁻¹] has been calculated, defined as the slope of the linear part of the curves in the range between 100 and 150 s. The material with [Lid][Ibu] presents lower rates compare to the one with only glycerol [28]. The ratio

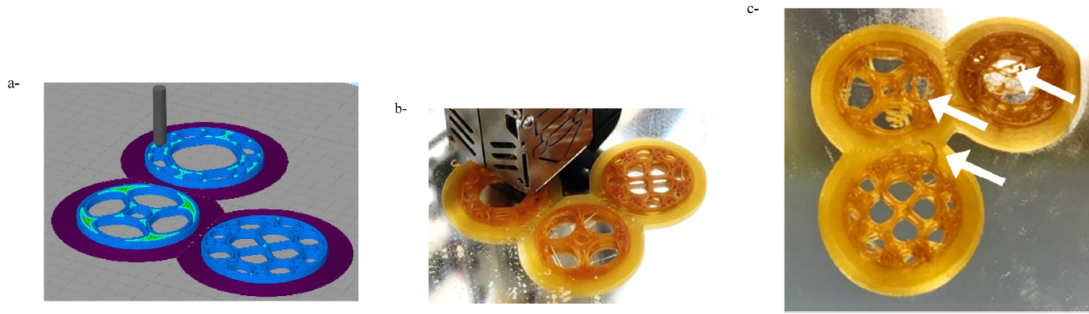
Table 3

Sintering rate of Z20GLY and Z10GLY10LI and their ratio at different temperatures (*beginning of the sintering phenomenon, slightly starting at 100 °C).

Temperature [°C]	V [rad.s ⁻¹]		Ratio: V _{Z10GLY10LI} / V _{Z20GLY}
	Z20GLY	Z10GLY10LI	
140	0.0093	0.0060	65%
130	0.0075	0.0047	63%
120	0.0050	0.0028	56%
100*	0.0032	0.0008	25%

Figure 2.5: *Sintering rate V [27]*

between the formulations for temperature above 100 °C has also been calculated. It showed how the sintering rate of Z10GLY10LI is much slower than Z20GLY (Fig. 2.5). In the final experiment it has been tested and observed that the sintering rate and the adhesion in the Z10GLY10LI is lower than in the Z20GLY formulation. Three different tablets have been printed with both formulations (they have been modelled with 50% infill density). With an X-RAY tomography the results have been checked: They showed that the tablets made by Z20GLY fitted the density requirement. Instead, the tablets made by Z10GLY10LI revealed poor adhesion (Fig. 2.6). For the last one formulation, it has been a second trial where the nozzle temperature was increased by 5°C and the extruded material flow rate was increased by 15%. It helps the printability of Z10GLY10LI. [27]

**Figure 2.6:** *Preview of melt deposition paths for 3D printing with different geometries (a), after 3D printing of Z20GLY (b) and Z10GLY10LI (c). Arrows indicate adhesion defects [27]*

2.4 Mathematical model and experiment to study the polymer sintering

To describe the polymer sintering between two filaments, the Frankel's model developed for ceramic material (later modified by Eshelby to satisfy the continuity equation) can be used. Sintering between two or more particles occurs through viscous flow and molecular diffusion of the polymer chains. These objects are modeled as spheres, with an initial radius a_0 [28]. Pokluda refined the Frenkel's model to better explain the sintering phenomenon, deriving it by balancing the surface tension forces with the viscous forces. In this model, the variation of radius during sintering is considered [29]. The work done by surface tension can be defined using the following equation:

$$W_s = -\Gamma \frac{ds}{dt} = \Gamma \frac{8\pi a_0^2 2^{1/3} \cos \theta \sin \theta}{(1 + \cos \theta)^{4/3} (2 - \cos \theta)^{5/3}} \frac{d\theta}{dt} \quad (2.11)$$

where Γ is the surface tension and s is the cross-section of the coalescence system. θ is the angle of coalescence between two spheres or filaments (Fig.2.7). This angle is given by:

$$\theta = \sin^{-1} \left(\frac{x}{a} \right) \quad (2.12)$$

The work of the viscous forces is defined as follows:

$$W_v = \int \int \int_V (\tau : D) dV \quad (2.13)$$

where V is the sintering domain volume, τ is the stress tensor and D is the deformation tensor. From (Eq. 2.13), the energy dissipation can be derived as:

$$W_v = 32\pi a_0^3 \eta \dot{\epsilon}^2 \quad (2.14)$$

where $\dot{\epsilon}$ is the strain rate.

Equating the dissipation energy (Eq.2.14) and the work of surface tension (Eq. 2.11) leads to a nonlinear differential equation governing the evolution of the coalescence angle:

$$\frac{d\theta}{dt} = \left(\frac{\Gamma}{\eta a_0} \right)^{-1} 2^{-5/3} \frac{\cos \theta \sin \theta (2 - \cos \theta)^{1/3}}{(1 + \cos \theta)^{1/3} (1 - \cos \theta)} \quad (2.15)$$

where η is the polymer viscosity. A parameter used to describe the coalescence is the typical viscous sintering time $t_{vs} = \left(\frac{a_0 \eta}{\Gamma} \right)$ [s]. One of the main drivers during

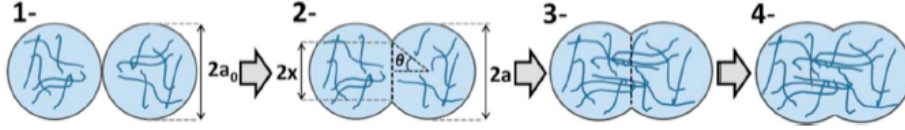


Figure 2.7: Fusion bonding steps at high temperature between two model circular thermo-plastic particles: 1- intimate contact, 2- apparition of a bonding neck, 3- neck growth due to polymer diffusion through interface and 4- randomization for long time [28].

the coalescence phenomenon is the surface tension Γ of the polymer melt, instead of the viscosity that has less impact [28]. However, applying Eq.2.15 to model bonding polymer filaments is questionable for two main reasons:

- Eq. 2.15 is used to describe the sintering kinetics between two spherical particles, not cylindrical filaments. For cylindrical filaments, the Hopper model is more suitable. Hopper's model does not use differential equations but instead uses geometrical description of the cross-section for two cylinders, approximated as an inverse ellipse of constant area. The governing equation that describes the system is:

$$\left(\frac{\Gamma t}{\eta a_0} \cdot \frac{1}{\sqrt{2}} \right) = \left(\frac{t}{t_{vs2}} \cdot \frac{1}{\sqrt{2}} \right) \cdot \left(\frac{x}{a_0} \cdot \frac{1}{\sqrt{2}} \right) \quad (2.16)$$

The factor $\frac{1}{\sqrt{2}}$ comes from the assumption that the two filaments after complete coalescence become a single cylinder of radius $a_f = \sqrt{2}$ [30].

- During AM-ME, viscous sintering is not the only main phenomenon that occurs, as explained by experimental [31] and modeling results [32]. These results and experiments show that the polymer chain interdiffusion at the interface between the filaments has a primarily role during the manufacturing process. It proceeds faster than viscous sintering kinetics described by Eq. 2.15 and is recognized as a key factor influencing the final bond adhesion quality [33].

In order to verify the results obtained by the Hopper's model, several experiments have been carried out [28]. This experiment is inspired by the approach that Bakrani Balani et al. used but with some modifications [34]. The aim of the experiment was to study the viscous sintering of two horizontally adjacent extruded filaments. The experimental setup was: an oven, containing two identical zein filaments blend with 20% of glycerol and a camera with an high image acquisition rate to follow the coalescence of the filaments. The values of the bonding neck angle θ obtained by

morphological analysis; in order to compare these values for different temperature, the slopes $d\theta/dt$ were calculated only for $t=35$ s. With the values of θ and $d\theta/dt$; it is possible to evaluate the characteristic time for viscous sintering t_{vs1} by using Eq. 2.12. To evaluate the same time t_{vs2} but by using the Hopper's model, it requires the calculation of the master curve [30]. From this curve, it is possible to obtain the value of θ and by using the following equation the values of t_{vs2} are evaluated:

$$\frac{d\theta}{d\left(\frac{t}{t_{vs2}}\right)} = t_{vs2} \cdot \frac{d\theta}{dt} \quad (2.17)$$

The results are compared in the following table. Excluding lower temperatures (80-100°C), the values of t_{vs1} and t_{vs2} are similar. This indicates that the assumption of modeling cylindrical sintering using Eq. 2.15 which was developed for spherical particles is quite reasonable.

Table 2.1: *Comparison of sintering parameters at different temperatures [28].*

T_{set} [°C]	θ_{final} [rad]	θ at $t=35$ s [rad]	$d\theta/dt$ at $t=35$ s [10^{-4} rad/s]	t_{vs1} Eq. (2.15) [s]	t_{vs2} (Hopper) [s]	$\frac{t_{vs1}}{t_{vs2}}$
80	0.39 ± 0.02	0.31 ± 0.07	3.0 ± 0.8	5233 ± 1460	3492 ± 974	1.5
100	0.73 ± 0.14	0.29 ± 0.03	28 ± 10.4	599 ± 222	369 ± 232	1.6
120	1.10 ± 0.10	0.54 ± 0.21	108 ± 53.5	77 ± 38	82 ± 41	0.9
125	1.19 ± 0.05	0.57 ± 0.05	294 ± 84.9	27 ± 8	29 ± 9	0.9
130	1.27 ± 0.01	0.48 ± 0.04	364 ± 46.2	26 ± 3	25 ± 3	1.0
140	1.33 ± 0.27	0.52 ± 0.11	625 ± 404.6	14 ± 9	14 ± 9	1.0

Another experiment has been carried out by Chaunier et al.(2025), where in this case 4 filaments of zein have been used. These filaments have been displaced like superimposed layers, two of them on the bottom, and other two on the top but positioned in an orthogonal way. A new furnace was designed to let possible the acquisition by a 3D scan of the coalescence of the four filaments. Another aim instead to study only the bonding kinetics of the system, was to study the collapse of the central pore. The central pore is located in the middle of the four filaments. The sintering temperature was set to $T=120^\circ\text{C}$ [1]. The materials and the methods used in the experiment were (Fig.2.8):

- four filaments of Z20GLY with a lenght $L=5$ mm and a diameter $\phi_{\text{filament}} = 2$ mm.
- furnace with dimensions: $105 \times 100 \times 80$ mm³
- Rotative sample holder made by PEEK and covered on the top by an aluminium plate $\phi_{Al} = 10$ mm

- Microtomography station of the ANATOMIX beamline at Synchrotron SOLEIL [35]

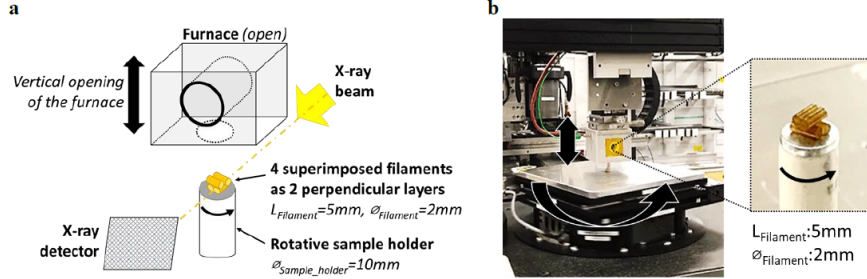


Figure 2.8: a) Schematic drawing of the experimental set up for dynamic X-ray tomography carried out during superimposed layers sintering at the ANATOMIX beamline of the Synchrotron SOLEIL (b) Front view of the furnace, and picture of the four superimposed filaments placed on the rotative sample holder [1]

In order to evaluate the collapse of the central pore, the 3D reconstructed volumes were segmented and a cut plane inclined was used. Several snapshots have been taken at different time steps, and they showed the decrease of the air volume due to the coalescence of the biopolymer filaments (Fig. 2.9).

2.5 Physics, coupling and numerical method to describe the polymer sintering

In order to simplify the study of the polymer sintering, numerical simulations with FEM were carried out to predict the behavior of the biopolymer during 3D printing process. These numerical simulations are inspired from the experimental trials made before. The model is a two-phase model made by Z20GLY for the filaments and hot air comes from the oven. The physics involved in the model are:

- Heat transfer: due to the effect of the oven, the filaments increase their temperature and reach the molten state. A convection-diffusion equation is included in the model (body sources are neglected, such as melting or crystallization).

$$\rho \cdot C_p \cdot \left(\frac{\partial T}{\partial t} + \mathbf{V} \cdot \nabla T \right) = \nabla \cdot (\lambda \nabla T) \quad (2.18)$$

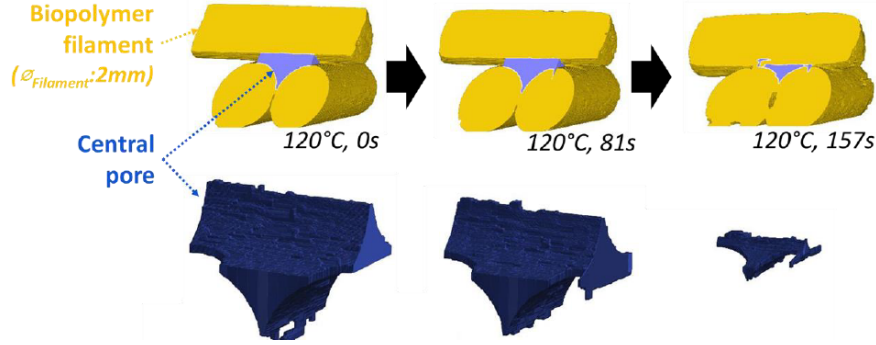


Figure 2.9: Real-time X-ray microtomography of 2 superimposed layers of thermoplastic filaments during their hot melt sintering at 120°C. Initial step (0 s), mid-time of the acquisition sequence (81 s) and final step (157 s) [1]

where T is the temperature ; λ is the thermal conductivity [$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$], C_p is the specific heat capacity [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$] and V is the fluid velocity [$\text{m}\cdot\text{s}^{-1}$]; ρ is the density [$\text{kg}\cdot\text{m}^{-3}$] and t is time [s].

- Laminar flow: to model the flow of the plasticized zein in the system the Navier-Stokes equation is used.

$$\rho \cdot \frac{\partial V}{\partial t} - \rho(V \cdot \nabla V) = \nabla \cdot [-pI + \eta(\nabla V + (\nabla V)^T)] + \rho \cdot g + F_{st} + F \quad (2.19)$$

A restricted form can be given because the inertial term is negligible due to the low velocity of the system and for the incompressibility of the system. $\rho(V \cdot \nabla V) = 0$. In Eq. 2.19 η is the dynamic viscosity [$\text{Pa}\cdot\text{s}$]; P the pressure applied to the fluid [Pa]; g the acceleration of gravity field [$\text{m}\cdot\text{s}^{-2}$], F_{ST} the force resulting from the surface tension [N/m^3] and F contains all the other body forces applied to the flowing fluid [N/m^3].

- Level set method: it is used to describe the interface between two different fluids, in this case zein and air. It updates the material properties according to macroscopic flow front position at each time-step. This means that the density, ρ , the viscosity η and the thermal diffusivity D are determined for each point of the mesh by these equations:

$$\rho = (1 - \varphi) \cdot \rho_1 + \varphi \cdot \rho_2, \eta = (1 - \varphi) \cdot \eta_1 + \varphi \cdot \eta_2, D = (1 - \varphi) \cdot D_1 + \varphi \cdot D_2 \quad (2.20)$$

Where φ is the volume fraction of the phase of interest. It is the one of the outputs of the two-phase flow simulation. Is is used to follow the coalescence and especially the air/biopolymer interface when φ reaches the value of $\varphi=0.5$ (It is $\varphi = 0$ for a domain full of air and $\varphi = 1$ for a domain full of zein). To study the evolution of this interface between the two phases, it is added to the Navier Stokes equation also the transport equation in Eq. 2.21:

$$\frac{\partial \varphi}{\partial t} - \nabla \cdot (V \varphi) = \gamma \nabla \cdot (\epsilon_{ls} \nabla \varphi - \varphi \cdot (1 - \varphi) \cdot \frac{\nabla \varphi}{|\nabla \varphi|}) \quad (2.21)$$

with γ the re-initialization factor [$\text{m} \cdot \text{s}^{-1}$] and ϵ_{ls} a factor that regulates the interfacial thickness [36].

With the presence of three different physic inside the model, it can be defined like a coupled model. Each physics depend of the other by a parameter or a variable. Fig. 2.10 shows all the coupling inside the model.

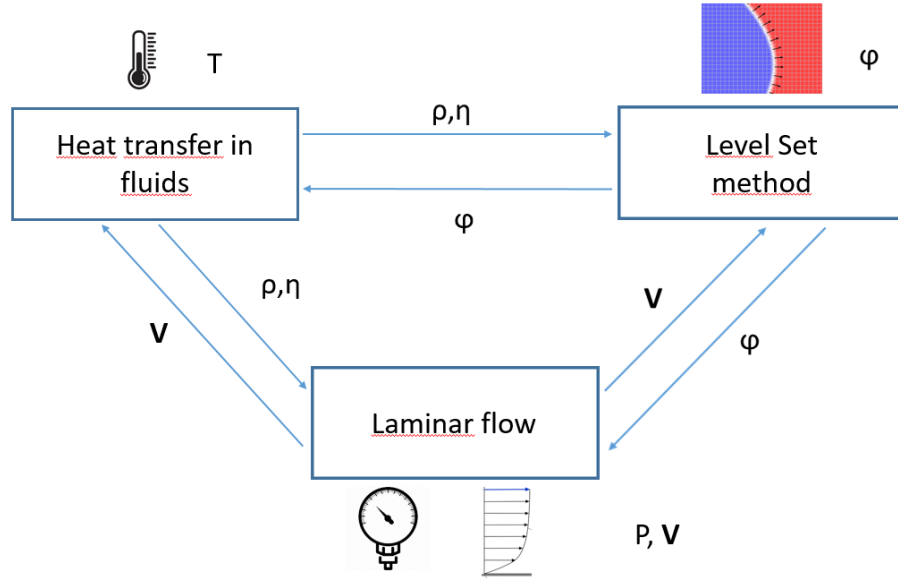


Figure 2.10: *Physics and coupling scheme*

Most of the material properties inside the model are temperature dependent, such as density and dynamic viscosity of the zein. The change of this properties due to temperature effect affects other physics, like laminar flow and level set method. The same append due to the advection term inside the heat equation that depends on the

velocity calculated in the Navier-Stokes equation. A 2D numerical simulation has been performed with COMSOL Multiphysics® software (COMSOL Inc., Burlington, MA, US). With this software it is possible to solve systems of differential equations with coupling of physical phenomena by FEM. A simplified 2D cartesian geometry is used but it does not represent exactly the real geometry since the top filament is represented as a slab and not a cylinder through this simplification. (Fig. 2.11)[1].

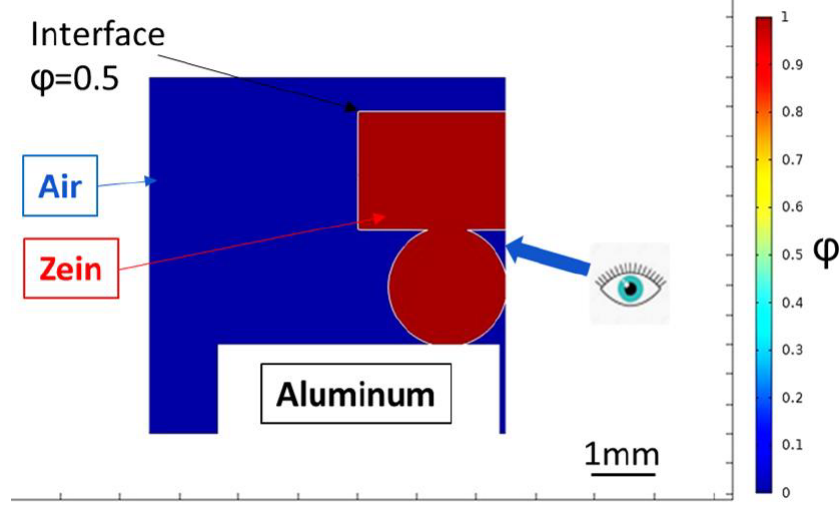


Figure 2.11: Illustration of the domain considered for the numerical modelling by FEM of superimposed filaments sintering as a two-phase flow ($\phi_{\text{Filament}}=2 \text{ mm}$) and central pore presented as being focused on (Phase 1 = air; Phase 2 = plasticized zein) [1].

The value of data are:

- Initial temperatures: $T_{\text{oven}}=120^{\circ}\text{C}$, $T_{\text{initial-zein}}=25^{\circ}\text{C}$
- Velocity: initial values set to $V=0 \text{ m/s}$
- Pressure: set to environment pressure $P=1 \text{ atm}$
- Air phase: its thermal conductivity is assumed at $\lambda_{\text{air}}=0.024 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $\rho_{\text{air}}=1.2 \text{ kg}\cdot\text{m}^{-3}$, $C_{p-\text{air}}=1 \text{ kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and $\eta_{\text{air}}=1 \times 10^{-5} \text{ Pa}\cdot\text{s}$
- Zein phase: $\rho_{\text{zein}}=1200 \text{ kg}\cdot\text{m}^{-3}$, $C_{p-\text{Zein}}$ increased when the glass transition temperature is overcome. It passes from $1.5 \times 10^3 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 20°C to $2.2 \times 10^3 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 130°C . The value of the surface tension, one of the main driver of the system is assumed at $30 \text{ mN}\cdot\text{m}^{-1}$. The thermal conductivity is assumed

$\lambda_{Zein}=0.26 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. The value of the dynamic viscosity η was taken from the following table [36]:

Temperature [°C]	t_{vs} [s]	$\eta_{220\text{Gly}}$ [Pa.s]
80	3492	1.1×10^5
100	369	1.1×10^4
120	82	2.5×10^3
125	30	8.9×10^2
130	25	7.5×10^2
140	14	4.3×10^2

Table 2.2: *Dynamic viscosity $\eta_{20\text{Gly}}$ evolution with respect to temperature [36].*

The results of the simulation show that the viscous sintering can be modeled. The numerical simulation carried out for 5 minutes where the temperature of the oven is equal to 120°C (Fig. 2.12).

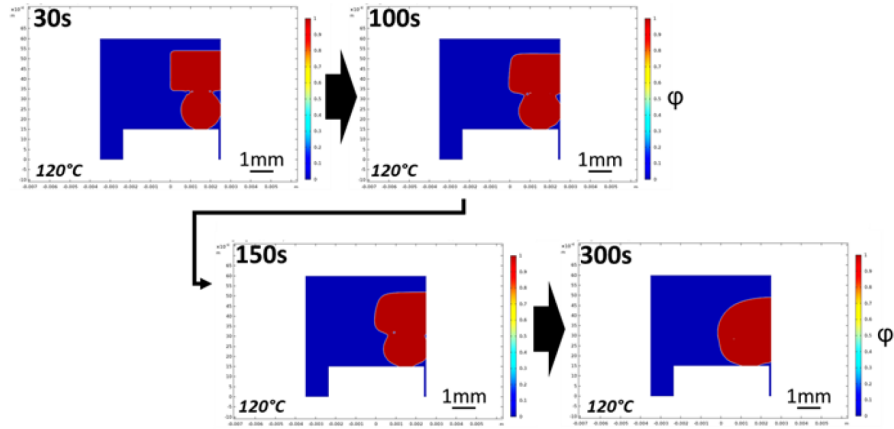


Figure 2.12: *2D FEM results: air presented in blue and zein in red [1].*

Using a surface integral function in COMSOL, it was possible to evaluate the air inside the central pore and its evolution in time. The results were first compared to the ones obtained from the experiment trials, then a sensitive study has been done changing the value of the oven temperature from 100°C to 130°C (Fig. 2.13) [1].

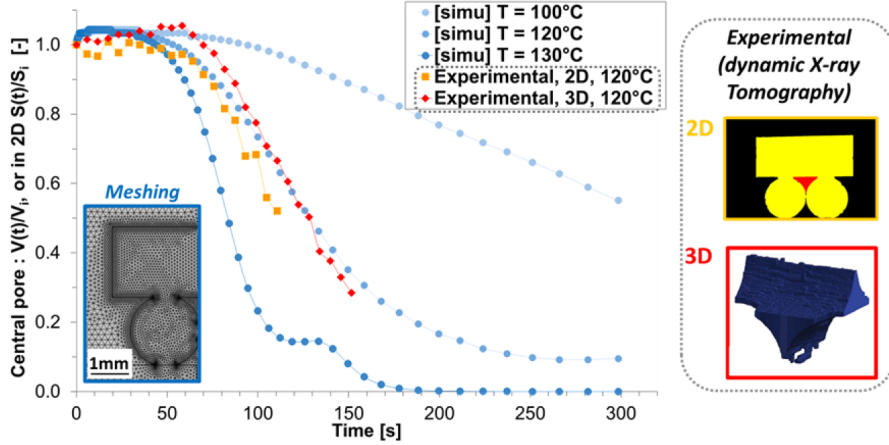


Figure 2.13: *Experimental results in 2D and 3D and the results of the 2D FEM simulation at different oven temperatures (100°C, 120°C and 130°C) concerning the evolution of the normalized central pore volume [1]*

The 2D simulation showed a good agreement with the experimental ones for the central pore evolution. But it is possible to observe that a singularity (plateau) is present during the simulation at 130°C after 100 seconds of simulation. This is due to a numerical problem comes from the 2D simulation. For this reason was necessary to perform a 3D numerical simulation, in order to have a model closer to the reality and to have a visual results of the coalescence process. With this simulation it will be possible to understand better the effect of each physics and each parameters inside the model.

2.6 Conclusion and objectives

The main conclusion from the literature review is that the physics involved in polymer sintering are well known and described. Experimental transient Xray scans have been realized and show a non linear decay of the central pore size. A previous 2D cartesian FEM modelling and simulation has shown good trends and agreed well with experiments, though the model's geometry is too simplified and required boundary conditions' adjustments to properly run the simulation and expell the air trapped in the central pore. Finally, because of future pharmaceutical uses there is a need to make sensitivity analysis on process parameters (oven temperature) and material parameters (viscosity). Therefore, the objectives of this study are :

- built a fully coupled transient multiphysics 3D sintering model that includes heat transfer, fluid flow with surface tension effects.
- optimize the domain size by comparing the simulation results of full 3D domain versus quarter-size 3D domain
- validate the model with the experimental results and compare with the previous 2D model
- run sensitivity analysis to optimize the process for other application such as pharmaceuticals.

The thesis is organized as follows. First the heat transfer submodel is built and results are analyzed. Then the submodel coupling fluid flow, surface tension effects and Level Set is described and the results are discussed. The last section will cover the description of the fully coupled model and the sensitivity analysis. Finally a conclusion and perspectives are given.

Chapter 3

3D Model: Thermal simulation

To study a coupled problem like this one, a numerical simulation can be useful to understand better the parameter and the effect of these on the physics. A specific software is used to carry out this simulation: COMSOL Multiphysics® v6.2. This software allows to build and mesh the 3D geometry of the system and to implement the physics that describes the problem. To understand better the influence of each physics and how to set it, each physics was studied first independently. The first one was the thermal simulation in order to investigate the effect of the heating inside the domain and to evaluate the temperature field evolution.

3.1 Geometry

The geometry of the model was built directly in the software (Fig.3.1). First the aluminium plate was built, with a diameter of $\phi_{al} = 10$ mm and a thickness $h = 1.5$ mm. Then the four filaments of the zein were built. The filaments of zein have a diameter of $\phi_{zein} = 2$ mm and a length $L = 5$ mm. During the experimental trial at Synchrotron Soleil, the aluminium was preheated until it reaches 80°C. So, when the four filaments of zein were positioned on it, due to the increase of temperature, they fused a little bit together. The neck forms on common sides of the filaments, and between the top and the bottom filaments. It was evaluated that the initial bonding neck is equal to $b = 0.35$ mm. To build this bonding neck, the cylinders were divided in 4 parts, because the cylinder at the bottom has two contact areas with the other on the top. This contact area has a width $w = 0.35$ mm (equal to the bonding neck) but a length of $l = 0.55$ mm in order to avoid any kind of interpenetration between the filaments. Then, the oven was modeled like a cube, in order to surround all the filaments, with a side of $s = 6$ mm (Fig.3.1).

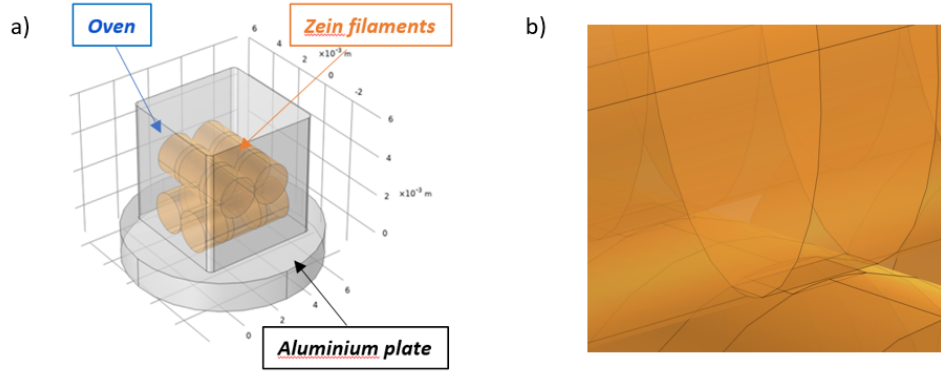


Figure 3.1: a) 3D geometry of the system, b) Filaments contact area

Such a large 3D geometry, increases a lot the computational time of the simulation. In order to reduce it, it was decided to chose two vertical symmetry plane in order to study only a quarter of the domain. These symmetry boundaries were implemented in each physics. In Fig.3.2 it is possible to see the new domain.

3.2 Physics and material properties

3.2.1 Governing and constitutive equations

The first physics implemented was the Heat transfer. This physics was chosen to study the thermal effect coming from the oven and to evaluate the temperature field inside the oven. To implemented this the physics *Heat transfer in fluids* was used. This because inside the model there is air, that has to be evaluated like a fluid. The governing equation that models the heat transfer in COMSOL Multiphysics is:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q + Q_p + Q_{vd} \quad (3.1)$$

where the first term it the transient term, the second one is the advection term, and the last one is the conduction term. Q is an internal source term, Q_p is the work done by pressure force and Q_{vd} is the source by the viscous force (all the source term are neglected). The constitutive equation for the heat flux, according the Fourier's law was used:

$$\mathbf{q} = -k \nabla T \quad (3.2)$$

where k is thermal conductivity and T is the temperature. The reference temperature was set it $T_{ref} = 25^\circ\text{C}$. This temperature is used for the evaluation of the reference

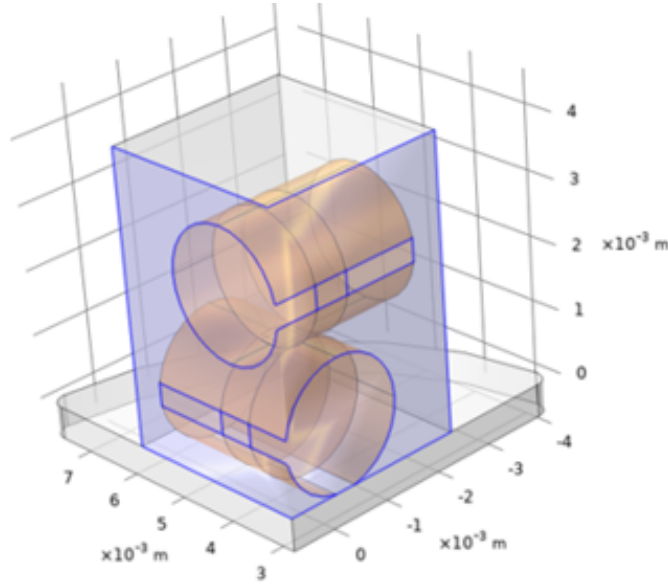


Figure 3.2: *Quarter of the domain with symmetry planes in blue*

density ρ_{ref} . The variable of the thermal problem is T . When this variable is set, it means that all the material properties and the other parameters that are temperature dependent will be function of this variable.

3.2.2 Material properties

For the material properties, it was possible to set them by default thanks the COMSOL library, and others were set as a function of the temperature. In COMSOL Multiphysics, when a specific physics is implemented in the system, the software by default choses the material properties useful to solve the problem. To study only the thermal problem, the material properties selected from COMSOL were:

- density ρ [kg/m^3] for Aluminium, zein and air
- Ideal gas constant R [$\text{J}/(\text{kg} \cdot \text{K})$] for the air
- Thermal conductivity k [$\text{W}/(\text{m} \cdot \text{K})$] for all
- Thermal capacity at constant pressure C_p [$\text{J}/(\text{kg} \cdot \text{K})$] for all

For the air, the Ideal gas constant is a specific value of $R = 287.05 \text{ J}/(\text{kg} \cdot \text{K})$, but k and C_p are function of temperature. For the aluminium, the maximum temperature reached in the system is too low to describe it like a molten flow, so its material properties are constant. The thermal capacity at constant pressure is equal to $C_{p,Al}=900 \text{ J}/(\text{kg} \cdot \text{K})$, the thermal conductivity $k_{Al}=238 \text{ W}/(\text{m} \cdot \text{K})$ and the density $\rho_{Al}=2700 \text{ kg}/\text{m}^3$. The zein's material properties are temperature dependent, expected for the thermal conductivity $k_{zein}=0.26 \text{ W}/(\text{m} \cdot \text{K})$ [36]. The other material properties, like density and thermal capacity at constant pressure, are temperature dependent. To describe these properties, a continuous equation is used and that follows the phase change of the zein when the temperature glass transition is overcome [37]. For the density the equation Eq.3.3, was used:

$$\rho(T) = \rho_{liq} + (\rho_{sol} - \rho_{liq}) \cdot \frac{1}{1 + \exp(\rho_{coef,melt} \cdot (T - T_g))} \quad (3.3)$$

where $\rho_{liq}=1100 \text{ kg}/\text{m}^3$ and $\rho_{sol}=1200 \text{ kg}/\text{m}^3$ are the value of the zein in solid state and when it overcomes the glass transition temperature $T_g=42^\circ\text{C}$. The $\rho_{coef,melt}=0.1 \text{ K}^{-1}$ [37].

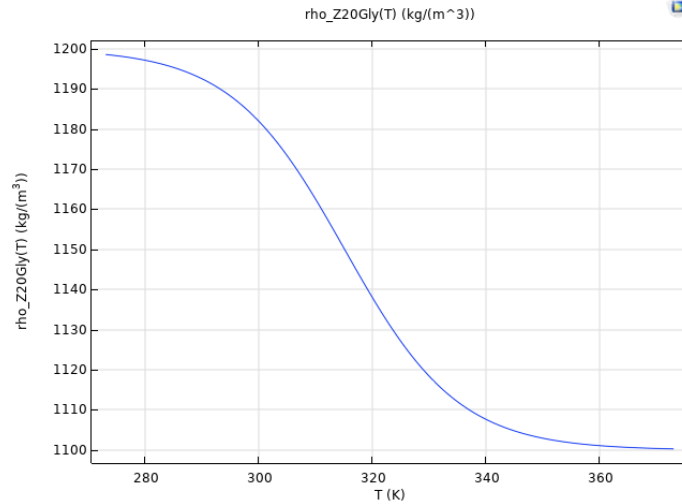


Figure 3.3: $\rho = f(T) : f(t)$ is the function described in Eq.3.3

For the thermal capacity the same function was used:

$$C_p(T) = C_{p,sol} + (C_{p,sol} - C_{p,liq}) \cdot \frac{1}{1 + \exp(-C_{p,coef,melt} \cdot (T - T_g))} \quad (3.4)$$

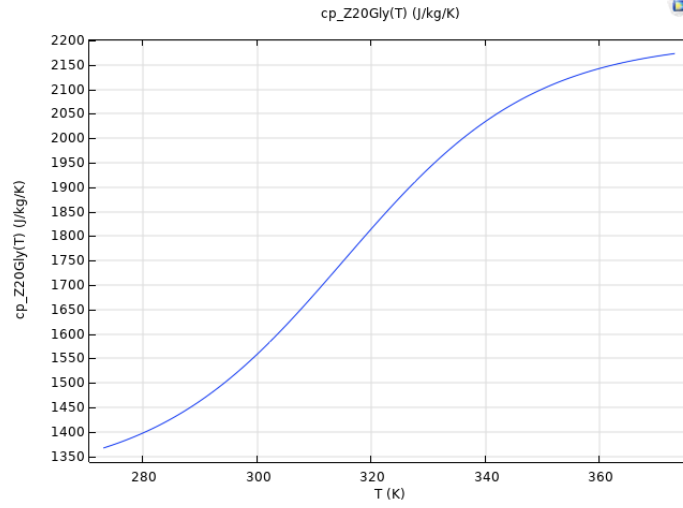


Figure 3.4: $C_p = f(T)$ where $f(T)$ is Eq.3.4. There is an increase of the thermal capacity until a the value of $C_{p,liq}=2200$ [J/(kg· K)]

where $C_{p,sol} = 1300$ [J/(kg· K)] and $C_{p,liq} = 2200$ [J/(kg· K)]. The $C_{p,coeff,melt} = 0.06$ K⁻¹ [1].The evaluation of the thermal capacity is:

3.3 Initial values, boundaries condition and mesh

3.3.1 Initial values

The initial values of the system were set like the one of the experiments. The initial value of the model for the thermal simulation were:

- $T_{air} = T_{oven} = 120^{\circ}\text{C}$ the temperature of the air was set equal to the oven one
- $T_{in,zein} = 25^{\circ}\text{C}$ is the initial temperature for the zein filaments
- $T_{al} = 80^{\circ}\text{C}$ is the initial temperature of the aluminium plate due to the fact the during the experiment at Synchrotron Soleil, the aluminium plate was preheated at 80°C in order to increase the sintering rate [1]

For the thermal simulation, there is not movement of the material, only the air has a behavior like fluid, the zein filaments and the aluminium plate are considered like solid.

3.3.2 Boundary conditions

The boundaries condition inserted in the model are different for the two geometries that were studied, the full domain and a quarter of domain.

For all the domain, the boundary conditions are two:

- Heat flux imposed on the oven faces. (Fig.3.5)
- Thermal insulation imposed on the aluminium plate face, except for the part of the face shared with the oven. (Fig.3.6)

The heat flux was necessary to let the temperature increase over time in the model. With this configuration there is a continuous heat flux on the model. To imposed this heat flux, a flux was implemented in Eq.3.5 for fluids:

$$\begin{aligned} -\mathbf{n} \cdot \mathbf{q} &= q_0 \\ q_0 &= h(T_{ext} - T) \end{aligned} \tag{3.5}$$

where h is the heat transfer coefficient for fluids. It was set $h = 1000 \text{ W}/(\text{m}^2 \cdot \text{K})$, and the external temperature was equal to the oven temperature $T_{external} = 120^{\circ}\text{C}$. The heat flux is imposed like a normal flux on each faces selected. The thermal

insulation condition on the external faces of the aluminium plate doesn't let the heat exchange with the environment, following the equation:

$$-\mathbf{n} \cdot \mathbf{q} = 0 \quad (3.6)$$

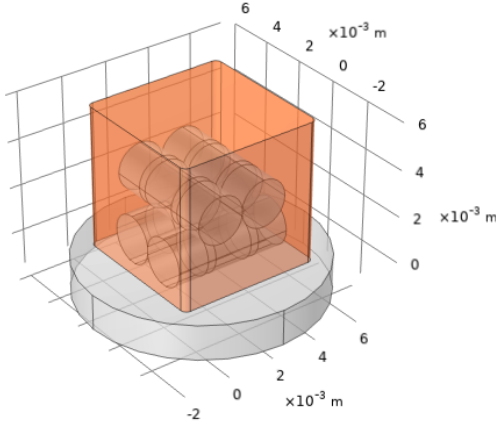


Figure 3.5: *Heat flux BC on the oven faces*

For the study about the quarter of the domain the boundaries condition were the same, expect for those faces of the oven shared with the symmetry plane (Fig.3.7). In these two faces, were imposed a symmetry condition following the same equation of thermal insulation (Eq.3.6) was imposed.

3.3.3 Mesh

In numerical analysis, mesh is a discretization of the geometric domain into smaller subdomains known as elements. A mesh is a collection of elements, (e.g., triangles, quadrilaterals in 2D, or tetrahedral, hexahedral in 3D) used to approximate the geometry and support numerical computation. These elements share nodes (points), where the solution is typically computed or interpolated [38]. In the model, the type of element used was a tetrahedral one, and the size of the mesh has been chosen in order to have a good accuracy of the results but also to not increase a lot the computational time. For the thermal simulation, the computational time are usually

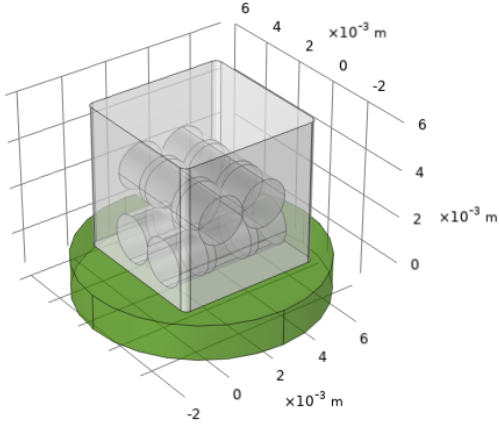


Figure 3.6: *Thermal insulation BC on the external aluminium faces*

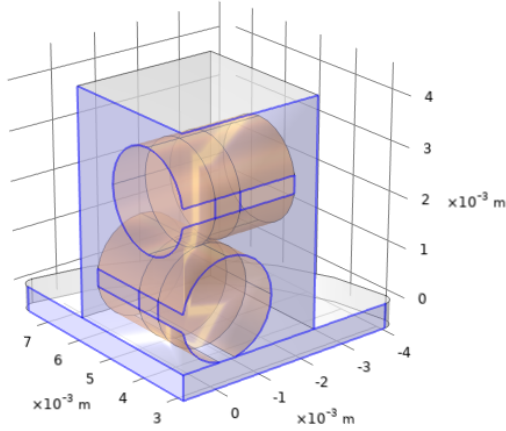


Figure 3.7: *Symmetry condition as BC to study a quarter of the domain*

low, (around 3 minutes), so after some trials it was possible to use a finer mesh. For the full domain simulation, it has been chosen a physics controlled mesh (the size of the mesh were set default by the software), but for one quarter of domain simulation it was used a user controlled mesh (size of the mesh set by the user). The Table 3.1

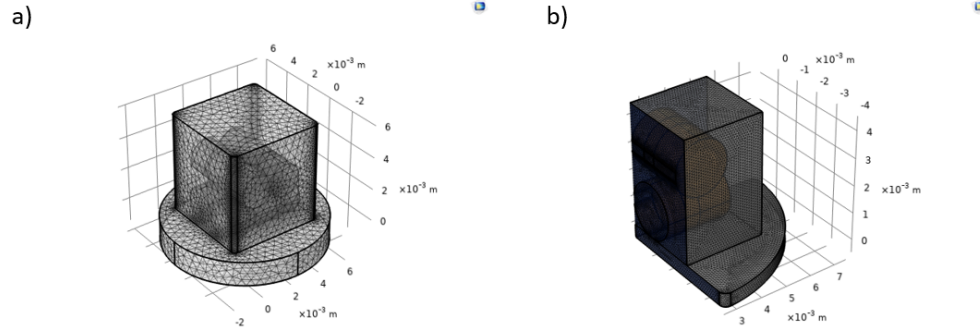


Figure 3.8: a) *Mesh full domain*, b) *Mesh a quarter of domain*

presents the value of the mesh parameters for each configuration:

Mesh parameters [unit]	Quarter of domain	Full domain
Type of mesh	User controlled	Physics controlled
Maximum element size [m]	1E-4	5.5E-4
Minimum element size [m]	5E-5	4.0E-5
Maximum element growth rate [-]	1.13	1.4
Curvature factor [-]	0.3	0.4
Thin regions resolution [-]	0.3	0.7

Table 3.1: *Mesh parameters for Full and Quarter Domain*

It was decided to use a finer mesh for the quarter of domain simulation because it was a smaller domain compared to the other one, but the difference in the results are low. Fig.3.8 shows the mesh for both domains.

3.4 Study and results

3.4.1 Study

For the thermal simulation, only the *Time dependent study* has been used, because to have results to compare with the experimental ones, the simulation was run for 5 minutes (300 s). The time steps of the data storage were chosen by a time law:

$$0, 10^{\text{range}(\log_{10}(0.1), \frac{1}{40}, \log_{10}(\text{TimeMax}))} \quad (3.7)$$

This law describes the system with several time steps at the beginning and less in the last minutes of simulation. This is due to the coalescence process, that evolves more in the first 150 s and less in the last part.

3.4.2 Results

For the results, the focus was set to evaluate the temperature field in the system. It was necessary to understand if the thermal problem was set well compared to the behavior of the zein in the reality. In the reality, zein reaches the molten flow when the temperature of the filaments is close to 100°C, and it happens after 100 s. In the Fig.3.9 and 3.10 it is possible to evaluate the temperature field of the system. The results showed how the conduction effect between the aluminium plate and the filaments has a priority effect, the filaments reach first the equilibrium with the aluminium plate. After there is the convection effect due to the effect of the oven. Also the figures show a small difference between the full domain and the quarter of domain. In the quarter of the domain the filaments reach the maximum temperature ($T_{oven}=120^{\circ}\text{C}=393\text{ K}$) before in the full domain simulation. This is due the difference of the mesh but also for the difference of the geometry. The results show that the heat transfer was implemented correctly. The temperature field is similar between the two different domains and, more importantly, with the real case, where the filaments reach the molten flow after 60 seconds. To save computational cost, it was decided to use only one quarter of the domain for the next two simulations.

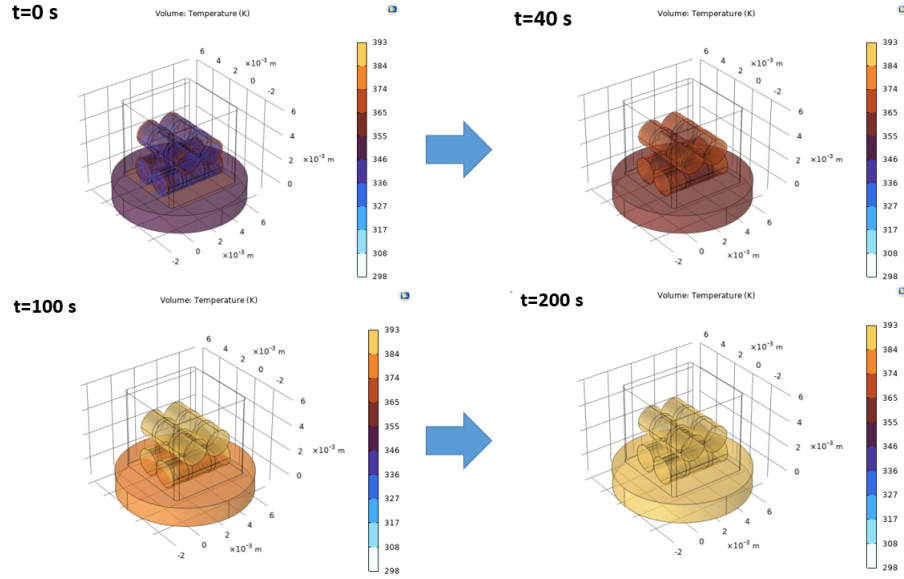


Figure 3.9: Full domain temperature field, evaluated at 0 s, 40 s, 100 s, 200 s, at $T_{oven} = 120^\circ\text{C}$

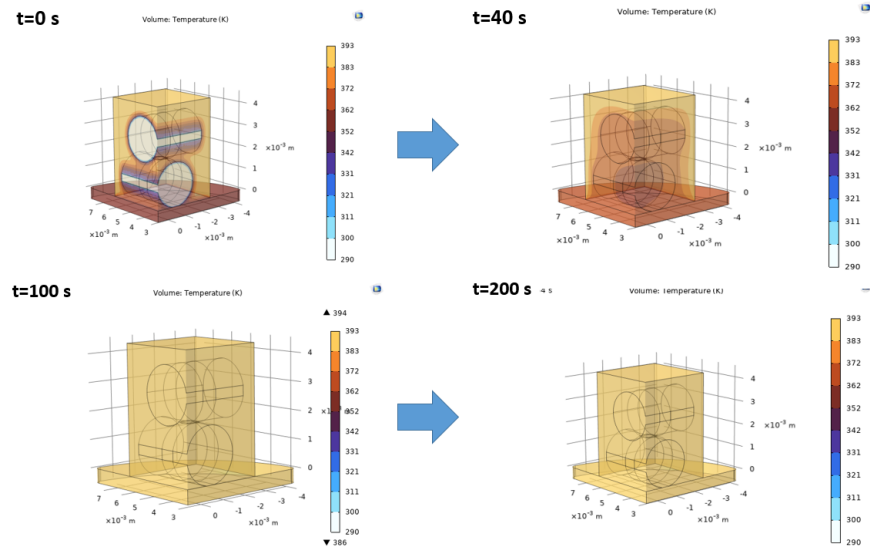


Figure 3.10: Quarter of domain temperature field, evaluated at 0 s, 40 s, 100 s, 200 s, at $T_{oven} = 120^\circ\text{C}$

Chapter 4

3D Model: Fluid flow and Level Set method simulation

The second physics implemented in the model is the fluid flow and the level set method. These two physics were necessary to describe the molten state flow of the zein filaments. Fluid flow was implemented through the *Laminar flow* physics. Laminar flow has been chosen because the velocity inside the model is low: there are not inlets or outlets for the air, since the air is static inside the oven and the velocity of the molten flow is low. The laminar flow resolves all the Navier-Stokes equation accounting four viscous forces, the gravity and the surface tension.

The *Level set method* was used to track and describe the moving interface between the two phases inside the model: air and zein. In this physic, the system was studied as a single fluid with two distinct phases. Each phases is described with a volume fraction function, ϕ . Since, Laminar flow and Level Set method are two different physics, they were coupled in the numerical model through the multiphysics feature called *Two – Phases Flow, Level Set*. This simulation makes it possible to verify whether the boundaries condition have been implemented in the right way.

4.1 Geometry

The fluid flow simulation, due to the presence of the molten flow, requires more computational time compare to the thermal simulation. To reduce computational cost, only one quarter of the domain was studied(Fig.3.2).

4.2 Physics and materials properties

4.2.1 Governing and constitutive equation

The *Laminar flow* was implemented by solving the Navier-Stokes simulation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] + \mathbf{F} + \rho \mathbf{g} \quad (4.1)$$

where the first term represents the transient contribution, then second is the advection term following by the effect of the pressure p , the viscous stress tensor $\mathbf{K}$ (arising from dynamic viscosity), the effect of surface tension included in the body force term $\mathbf{F}$ and the effect of the gravity. Usually, forces induced by surface tension are not applied in the volume of a domain since they are supposed to act on surface. Because of the choice to model the sintering with a single fluid domain and a level set the surface tension will act as a body force within the domain at the interface between the air and zein. To ensure mass conservation for an incompressible fluid, mass conservation writes:

$$\nabla \cdot \mathbf{u} = 0 \quad (4.2)$$

For the level set method the equation implemented is:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \gamma \nabla \cdot \left(\epsilon_{ls} \nabla \phi - \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right), \quad (4.3)$$

The most important parameters in Eq.4.3 are:

- ϕ : it is the volume fraction function that describes the additional scalar field to the modeling domain. The value of ϕ vary from 0 and 1, and the transition of the fields is quite abrupt in space, thus giving a good resolution of the two phases.
- γ : the reinitialization parameter that describes the moving interface of the fluid. If the value is too small, it can lead to numerical instabilities, if the value is too large the interface movement is not captured correctly. A good way to set this value is to equal it to the maximum velocity inside the model.
- ϵ_{ls} : this parameter controls the interface thickness. Like for the reinitilaization parameter, if this value is too small, it can lead to numerical instabilities, too high can not captured correctly the interface. A common way is to set this parameter equal to the maximum element size of the mesh [39].

4.2.2 Material properties

The material properties useful for the fluid flow simulation are only dynamic viscosity and the density. For the dynamic viscosity the value has been taken from the experimental trials made by Chaunier et al. [36] and presented in Table 2.2 and interpolated in (Fig 4.1): The material properties included in this simulation, are temperature

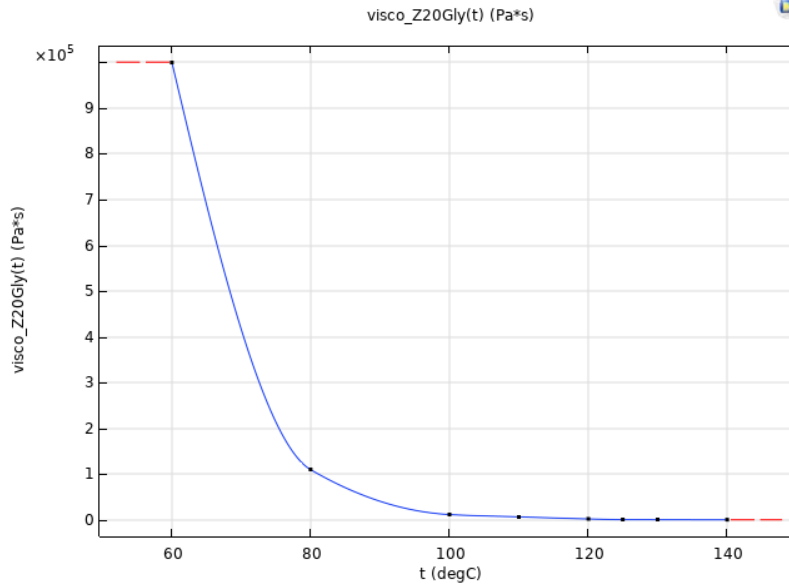


Figure 4.1: *Interpolation of the dynamic viscosity with a piecewise cubic function*

dependent. So the temperature of the oven was set equal to $T_{oven} = 120^\circ\text{C}$.

4.3 Initial values, boundaries condition and mesh

4.3.1 Initial values

In a Laminar incompressible flow the variables are two, pressure and velocity. The fluid is considered incompressible, and there is a little changes of the pressure inside the model that drives the flow. The reference pressure in the system was set equal to $p_{ref} = 1$ atm. The initial condition for the pressure is equal to 0 atm. For the initial velocity it was set equal $v = 0$ m/s. The aren't any inlet or outlet in the model or any type of external input to let the air/zein moving. The movement of the zein is lead by surface tension, heat and dynamic viscosity.

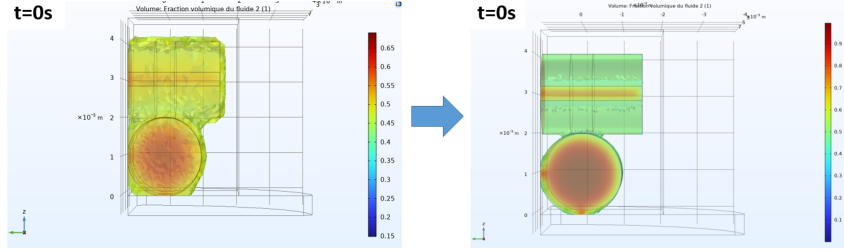


Figure 4.2: Effect of parameter interface thickness ϵ_{ls} , left $\epsilon_{ls} = 1.5 \times 5 \times 10^{-4}$, right $\epsilon_{ls} = 1.5 \times 1 \times 10^{-4}$

In the level set method the initial were set the initial value for the volume fraction function ϕ . This function is equal 0 when the volume fraction is only air, and equal to 1 when the volume fraction is only zein. The value for the reinitialization parameter was set $\gamma = 0,01$ m/s, like the maximum velocity inside the model, and the parameter interface thickness $\epsilon_{ls} = 1.5 \times h_{max}$ m where $h_{max} = 5 \times 10^{-4}$ m is the maximum element size of the mesh. But after several trials, the results shows that the interface is not well represented with this value of ϵ_{ls} (Fig.4.2). So it was decided with some trials to use $\epsilon_{ls} = 1.5 \times 1 \times 10^{-4}$ m .

4.3.2 Boundaries condition

The boundaries condition implemented inside the model are different between Laminar flow and Level Set method. This boundaries have been properly chosen to ensure that any loss of mass was presented inside the model. The domain of the model is still one quarter of the domain, so the two vertical symmetry BC are still present like in Chapter 3.

For the *Laminar flow* a *Wall* condition was implemented. This feature models the faces like solid walls and as default characteristic the No slip has been chosen. This precisely BC imposes that fluid velocity relative to the wall velocity is zero. For a stationary wall that means that $\mathbf{u} = 0$ [40].

For *Level set method* *Noflow* condition was chosen. It represents boundaries where there is no flow across the boundary and it follows the Eq.4.4 [41]:

$$\mathbf{n} \cdot \left(\epsilon_{ls} \nabla \phi - \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \right) = 0 \quad (4.4)$$

For both the two physics another boundaries condition called wetted wall was implemented at the bottom surface. This condition is used for the walls that are in

contact with the fluid interface and let it moves along the wall. In order to ensure the conservation of mass wetted wall enforces the no-penetration condition $\mathbf{u} \cdot \mathbf{n}_{wall} = 0$ and adds a tangential stress on the form:

$$\mathbf{K}_{nt} = -\frac{\eta}{\beta} \mathbf{u} \quad (4.5)$$

where β is the slip length. Due to the presence of the surface tension, wetted wall add another boundary force to enforce contact angle:

$$\mathbf{F}_\theta = \sigma \delta(\mathbf{n}_{wall} \cdot \mathbf{n} - \cos \theta_w) \mathbf{n} \quad (4.6)$$

where θ_w is the contact angle between the fluid interface and the wall[42]. It is possible to see the configuration in Fig. 4.4

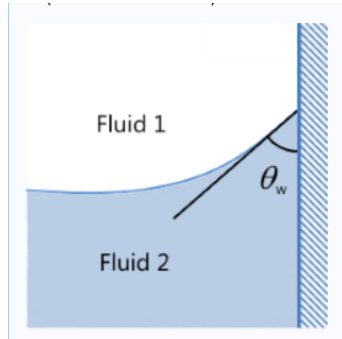


Figure 4.3: Contact angle θ_w [42]

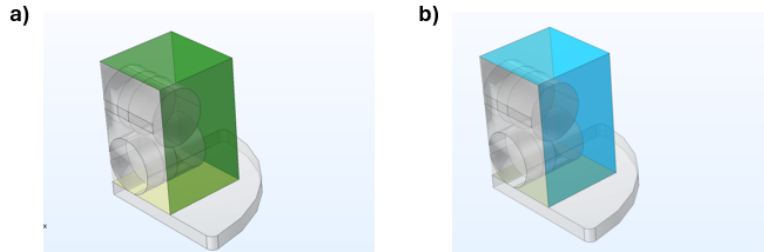


Figure 4.4: Boundaries condition for fluid flow simulation a) Laminar flow, in dark green Wall condition, in light green wetted wall. b) Level Set method, in blue no flow condition, in light green wetted wall.

4.3.3 Mesh

The mesh chosen in the fluid flow simulation is a Physics controlled mesh with a normal mesh size. In Tab.4.1 the mesh parameters are presented:

Table 4.1: *Element size parameters used in the COMSOL simulation*

Parameter	Value
Maximum element size	5.01×10^{-4} m
Minimum element size	9.01×10^{-5} m
Maximum element growth rate	1.5
Curvature factor	0.6
Resolution of narrow regions	0.5

4.4 Multiphysics

To link together the *Laminar flow* and *Level set method* was necessary to implemented the multiphysics feature. *The Two-Phase Flow, Level Set* were used. This feature was necessary to define in the model the density and dynamic viscosity of each phase of fluid used in the Laminar Flow interface. It also defines the surface tension on the interface in form of a volume force used in the momentum equation. It is possible with this feature to enable the Level set method to use the velocity field calculated from the Laminar flow to describe the moving interface. This features add more equation in the system:

$$F_{st} = \sigma \delta \kappa n_{int} + \delta \nabla_s \sigma \quad (4.7)$$

Eq.4.7 is needed to model the effect of surface tension at the fluid-fluid interface. The term inside this equation are: $\sigma=0.03$ N/m is the value of the surface tension, δ is the interface delta function, k the curvature of the interface, $\mathbf{n}_{int}$ is the normal vector to the interface and $\nabla_s \sigma$ is the surface gradient of surface tension

$$\kappa = -\nabla \cdot \mathbf{n}_{int}; \quad \nabla_s = (I - \mathbf{n}_{int} \mathbf{n}_{int}^T) \nabla \quad (4.8)$$

Equations (4.7) and (4.8) help to calculate the shape of the interface and how it curves.

$$\rho = \rho_1 + (\rho_2 - \rho_1)\phi \quad (4.9)$$

$$\eta = \eta_1 + (\eta_2 - \eta_1)\phi \quad (4.10)$$

Equations (4.9) and (4.10) smoothly interpolate the dynamic viscosity and the density across the fluid interface and they depend on the value of the volume fraction ϕ . η_1 and ρ_1 are the values for the air material properties and η_2 and ρ_2 for the zein.

4.5 Study and results

4.5.1 Study

It was necessary to implement two studies for the Fluid flow simulation, due to the presence of two-phases flow:

- Phase initialization study: this first step is dedicated to solving for the reciprocal interface distance. In the case of two-phase flow, the distance determined in the initialization step is the distance to the phase interface. The settings for this study are the same as for the Time Dependent study[39].
- Time dependent study: this second step was necessary to study the evolution in time of the moving interface. The same law time was used as in Eq.3.7.

4.5.2 Results

The goal of the simulation was to investigate the evolution in time of the shape of the two filaments and if the conservation of mass is well ensured. In Fig.4.5 it is possible to evaluate the evolution of the filaments of zein in time. There is a collapse of the zein filaments, and they merge together and reach a final shape like a sphere, and there is no flow of material outside the domain. The two physics are implemented correct and it is possible to couple them with the heat transfer in the last simulation.

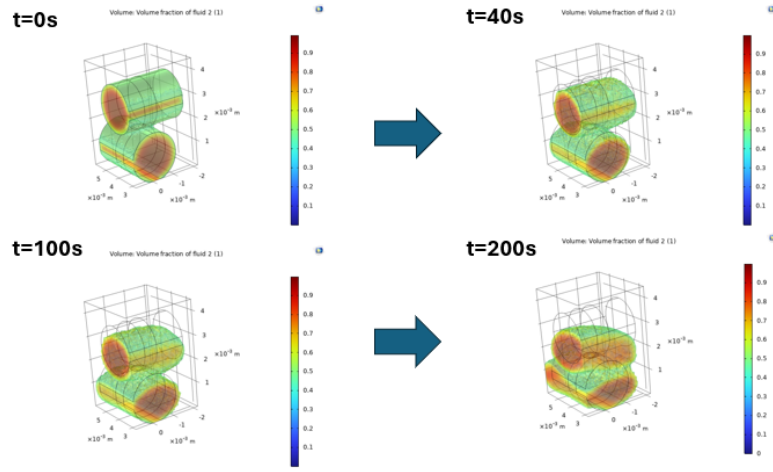


Figure 4.5: *Results of fluid flow simulation, coalescence process in four time steps 0 s, 40 s, 100 s, 200 s*

Chapter 5

3D Model: Fully coupled simulation

The fully coupled simulation is the final step to model the coalescence process of the 4 filaments of zein. In this simulation all the physics (heat transfer, laminar flow, level set) were implemented together. This simulation gives the final results about the sintering process, and with them it is possible to compare the model results with the experimental ones obtained at Synchrotron SOLEIL.

5.1 Physics, materials properties, initial values, boundary conditions

All the three physics studied in the previous simulation, they implemented together in the model:

- Heat transfer
- Laminar flow
- Level Set

The material properties have to be inserted like variable of the volume fraction function ϕ due to the presence of a two-phases flow:

- Thermal conductivity $k = k_1 \cdot ls.V f_1 + k_2 \cdot ls.V f_2$ where k_1 and k_2 are the values for the air and the zein and $ls.V f_1, ls.V f_2$ are the volume fraction functions for air and zein

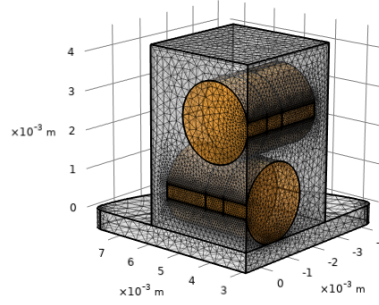


Figure 5.1: *Physics controlled mesh for the coupled simulation*

- Heat capacity at constant pressure $Cp = Cp_1 \cdot ls.Vf_1 + Cp_2 \cdot ls.Vf_2$
- Ratio of specific heats γ , $\gamma_1=1.4$ for the air and $\gamma=1$ for the zein.

For the initial condition they are the same like in the previous simulation, the one that changes is the initial values of the temperature for the fluid:

$$T_{in} = T_{oven} \cdot ls.Vf_1 + T_{zein} \cdot ls.Vf_2 \quad (5.1)$$

Also the reinitialization parameter was different, it was chosen equal to the maximum velocity inside the system, $\gamma = 4 \times 10^{-5}$ m/s. Geometry and boundary conditions are the same of the previous simulation. One quarter of domain was studied, with the two vertical symmetry planes in order to decrease the computational cost. The boundary conditions applied to the cube faces are:

- Heat transfer: Heat flux
- Laminar Flow: Wall condition
- Level Set method: No flow condition

For the mesh, like in the fluid flow simulation a Physics controlled mesh with a Normal size has been chosen (Fig.5.1).

5.2 Multiphysics

To couple the heat transfer with the fluid flow simulation, an additional feature was necessary. In the system, there is a flow of material due to the combined effects of surface tension and dynamic viscosity, the latter being temperature-dependent. This effect leads to a *Nonisothermal flow* as the temperature within the system changes. The *Nonisothermal flow* was implemented. This feature let to simulate fluid flow where the fluid properties depend on temperature and when it is combined with Laminar flow interface, it solves conservation of energy, mass and momentum in fluids and only conservation of energy in solids[43]. This feature link together the Heat transfer in fluids and the Laminar flow. The Boussinesq approximation was not used because it returns error.

5.3 Results and discussion

5.3.1 Issues

The study implemented are the same as the fluid flow simulation. When the first trials were made the model showed two issues:

- Conservation of mass was not respected.
- No movement of the interface during the simulation

For the first issue, the conservation of mass was calculated by a volume integral following the Eq.5.2:

$$m = \int_V \rho_{zein} \cdot ls.V f_2 dV \quad (5.2)$$

where ρ_{zein} is the density of the zein in kg/m^3 . A mass loss exceeding 10% was observed. This problem comes from a numerical problem due to a default settings in *Level set method* feature. It was set by default in *Non conservative form*, that only conserves the integral of the level set function approximately. With the *Conservative form* gives the exact numerical conservation of the integral of ϕ . In Fig.5.2 it is possible to observed the conservation of mass before and after the application of the *Conservative form*. It shows a mass decrease of less than 10%, which is only due to the reduction in density during the heating of the filaments

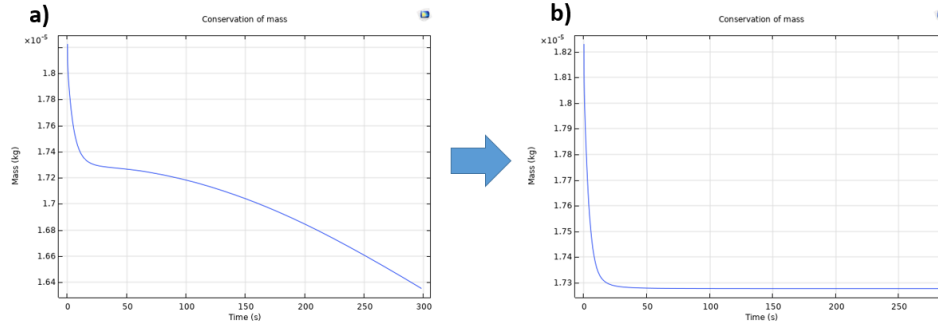


Figure 5.2: *Evaluation of mass in the system: a) with Non conservative form, b) with Conservative form*

The second issue was observed when after 140 seconds of simulation, the sintering process between the two filaments didn't happen. In Fig.5.3 it is possible to understand how the filaments started the sintering process, but it the interface did not move. This simulation was run for only 141 seconds as a test. Also the evaluation of

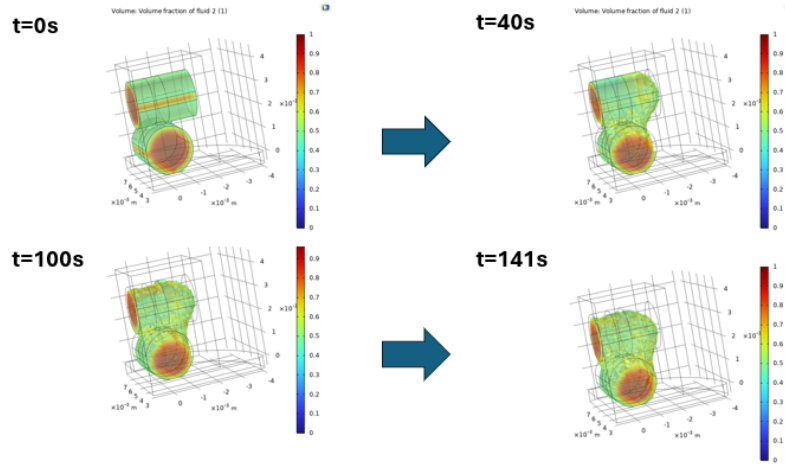


Figure 5.3: *Incomplete sintering process, four snapshots at 0 s, 40 s, 100 s, 141 s, at $T_{oven}=120^{\circ}C$*

the central pore by time (Fig.5.4) showed how the coalescence took more time compared to the experimental one when the coalescence after 150 second was already finished. To evaluate the evolution of the central pore over time, a volume integral was computed in the region of interest. To compare this value with the experimental

one, the volume value at each time steps was normalized with the volume value at the initial step. The results showed how slow the sintering process was in the 3D simulation compare to the experimental one.

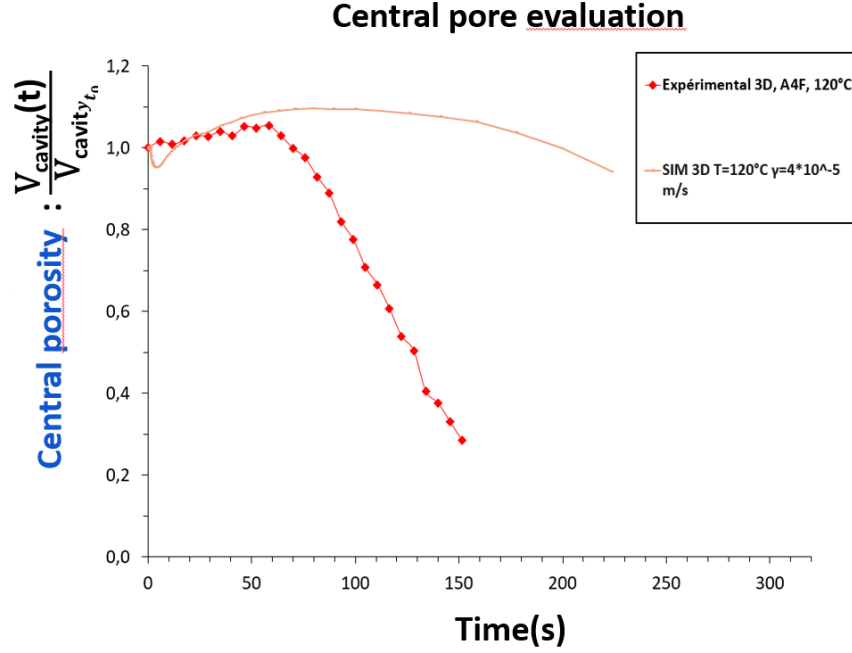


Figure 5.4: *Central pore evaluation, in red the curve obtained from Synchrotron Soleil experiment, in orange the result obtained from the simulation*

After several trials, trying to understand where the problem come from, it was decided to change the value of the reinitialization parameter γ . In Fig.5.5 it is observed how the coalescence process is faster when the reinitialization parameter increases. With a higher value of the reinitialization parameter, the two-phases flow moves and fill the central pore. But with a constant value of γ , the simulation doesn't respect the reality. With $\gamma = 5,5 \times 10^{-5}$ m/s the coalescence happend earlier than in the experiment. To avoid this problem and to fit better the experimental data, it was decided to study the velocity graph within the system (Fig.5.6). The velocity inside the system changes in time, with an increase until two minutes, and then a decrease. This trend of the curve describes well the behavior of the sintering process, after two minutes the sintering process slows down, and the mobility of the molten flow decreases due to the effect of the proteins agglomeration and makes the material stiffer. It was decided to set the value of the reinitialization parameter γ like function of the average velocity inside the system, using the function called $spf.U$, because the

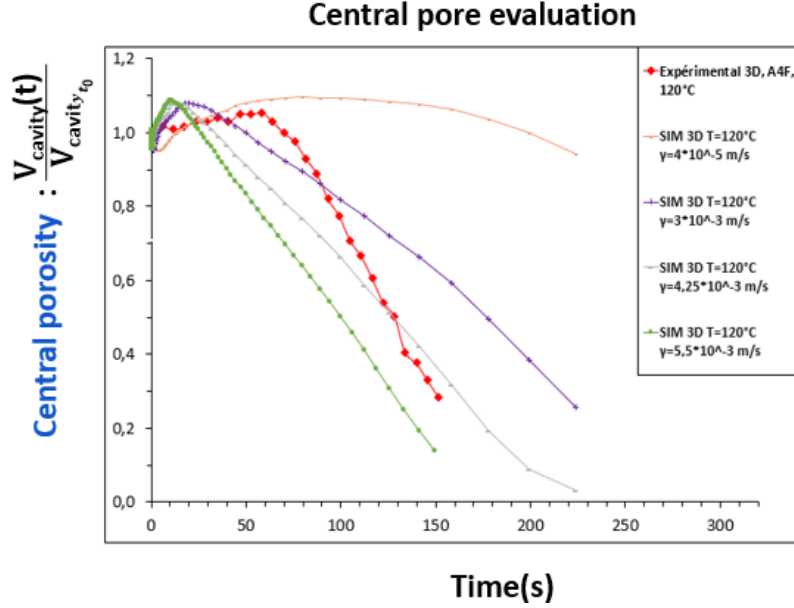


Figure 5.5: Influence of reinitialization parameter on the sintering process. Value of γ : 4×10^{-5} (orange), 3×10^{-3} (purple), $4,25 \times 10^{-3}$ (grey), $5,5 \times 10^{-3}$ (green)

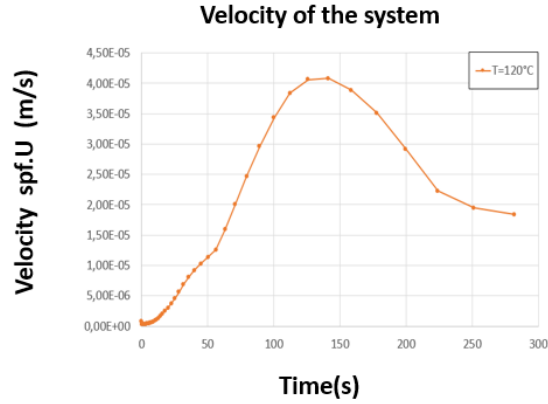


Figure 5.6: Maximum value of the velocity in the model at $T_{oven} = 120^\circ C$

velocity inside the system changes with the value of the parameter of the model, like temperature and dynamic viscosity. But this velocity has a value lower than the maximum velocity of the system. To reach a good value for γ to let the interface move, a scaling factor call $Fvel$ was applied so as to increase the value of the velocity. To find this in a properly way, a sensitivity study has been made while increasing

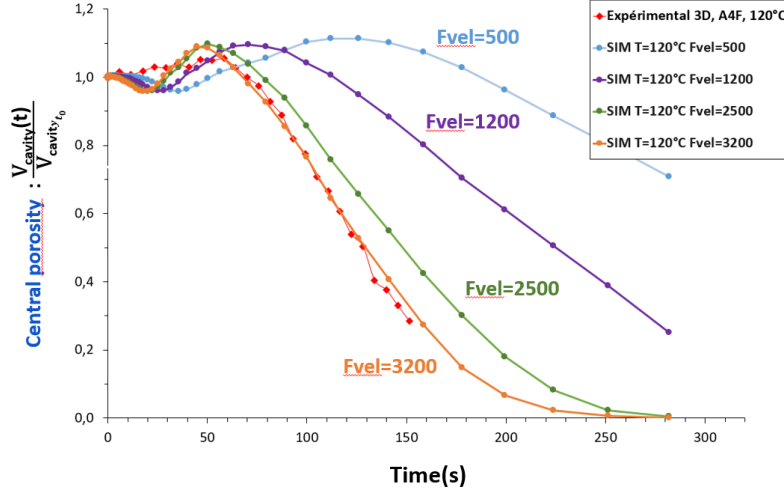


Figure 5.7: Central pore evolution with different value of $Fvel$: 500, 1200, 2500, 3200

this factor until the curve fitted the experimental one. In order to implemented this function without error, an *if* function was used. The initial value for the velocity was set equal to $V = 0$ m/s, but this value cannot be use for the reinitialization parameter γ , it has to be different from zero at every time steps. To resolve this issue, the following condition was implemented was implemented:

$$\gamma = if(t < 1 \text{ s}, 7 \times 10^{-4}, Fvel \cdot spf.U) \quad (5.3)$$

where the if condition returns that before the first seconds of simulation, γ has a constant value, and after it set equal to the velocity function scaled by the factor $Fvel$. In Fig.5.7 it is possible to see the results of this sensitivity study and the value of $Fvel$ that best fitted the experimental curve was $Fvel = 3200$.

5.3.2 Results

The results observed from Fig.5.8 describe the sintering process and the collapse of the central pore when the temperature of the oven was set equal to $T_{oven} = 120^\circ\text{C}$. The trend of the experimental curve has a decrease in the first 40-50 seconds, due to numerical instability for a coarse mesh, then there is an increase of the central pore, like in the experimental trial, and this one is an effect coming from the competition between surface tension and dynamic viscosity. When the dynamic viscosity is high, the material does not flow, and—if the surface is non-wetting—surface tension pushes the molten phase away from the central pore. Once the fluid reaches the

molten state, the viscosity decreases and coalescence process takes place. To validate

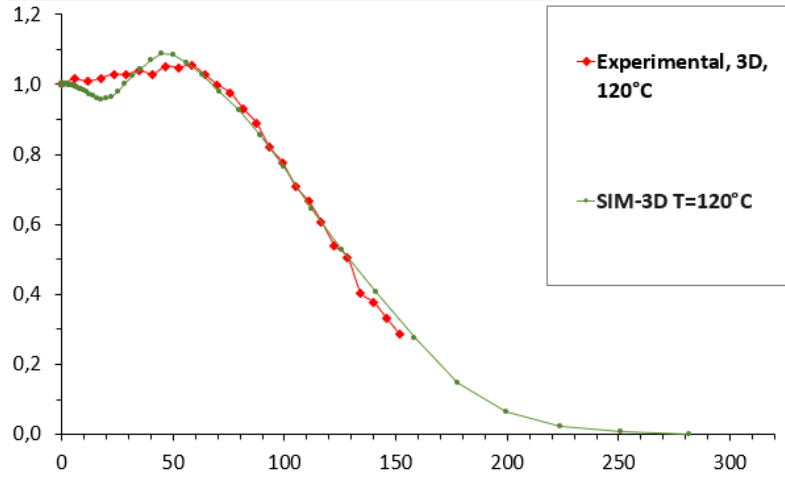


Figure 5.8: *Central pore evaluation at $T=120^{\circ}\text{C}$, curve obtained with a volume integral over a specific subdomain*

the results it was necessary also to observed the final shape of the filaments and the central pore. It is possible to see them in Fig.5.10 and in Fig.5.9. The filaments reach a final shape similar to a sphere. Also the evolution of the central pore is similar to the one in Fig.2.9.

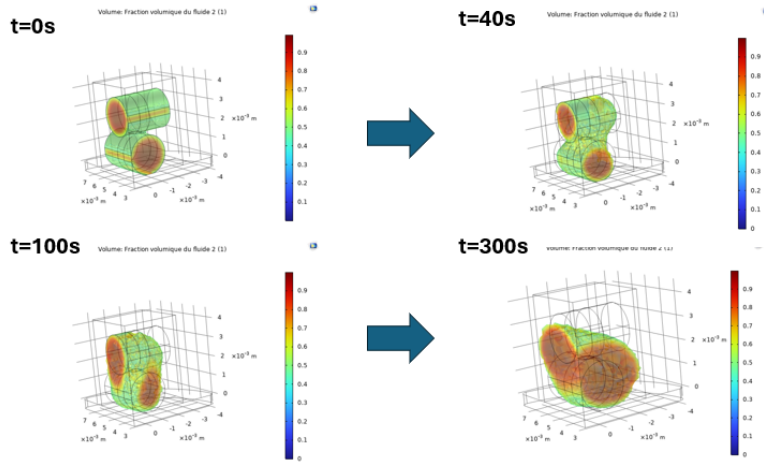


Figure 5.9: *Coalescence process of the two filaments in four time steps: 0 s, 40 s, 100 s, 300 s*

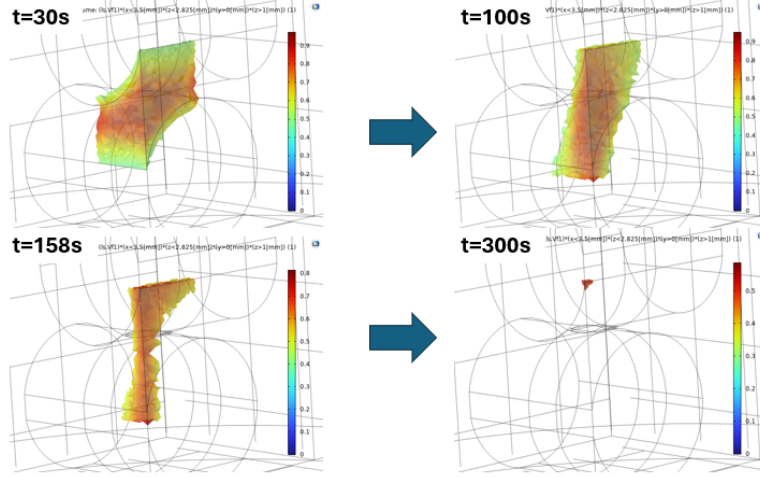


Figure 5.10: Central pore evolution in four time steps: 30 s, 100 s, 150 s, 300 s

To analyze the effect of the parameters, like temperature, dynamic viscosity and surface tension, sensitivity analysis were carried out. First, the impact of a temperature change from 100 to 130°C inside the model was evaluated. In Fig.5.11 one can see how the temperature impacts the velocity of the sintering process. When the temperature of the oven is set equal to $T_{oven} = 130^{\circ}\text{C}$, the velocity of the model increases and the dynamic viscosity decreases more than when the temperature is set to 120°C. These effects lead to a faster sintering process. In contrast, when the temperature of the oven is $T_{oven} = 100^{\circ}\text{C}$ the velocity is so low that the computer was not able to finish the simulation even after 3 days of calculation. The simulation stopped at around 100s, but it is possible to see from the trend the sintering process is slower.

The sensitivity study about the effect of the viscosity was split in two parts. In this simulation, the temperature of the oven was fixed equal to $T_{oven} = 120^{\circ}\text{C}$, and the dynamic viscosity η was changed. In the first one the focus was set to understand the behavior of the second composition of zein, with 10% of glycerol and two Active Pharmaceutical Ingredient - Ionic Liquid (API-IL). Using the value in Fig.2.5, a sensitivity factor was set to increase the value of the dynamic viscosity η by 70% compared to the standard composition. The results indicate that viscosity significantly influences the velocity of the sintering process, with higher viscosity lead to slower coalescence. The second part focused to have an overview of the viscosity effect by decreasing and increasing it with three different sensitivity factors: 0.1, 0.5, 2. The results in Fig.5.13 showed a different trends, a decrease of the sintering rate

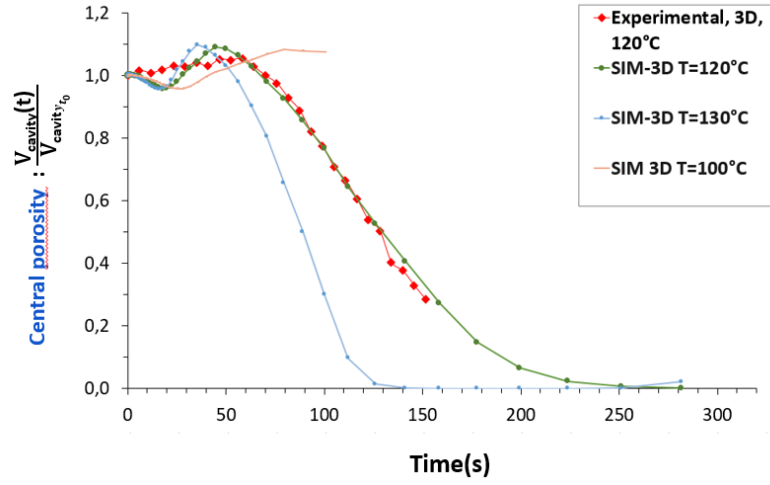


Figure 5.11: Sensitivity study with three different temperature: 100°C orange, 120°C green, 130°C blue

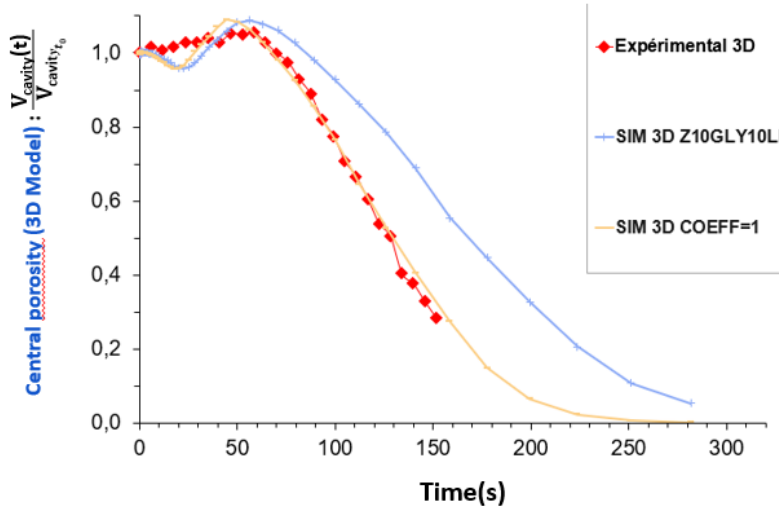


Figure 5.12: Evolution of central pore of the two composition of material: in orange Z20 and in blue Z10GLY10LI

when the value of η are very low and an increase of it when the factor is equal to 2.

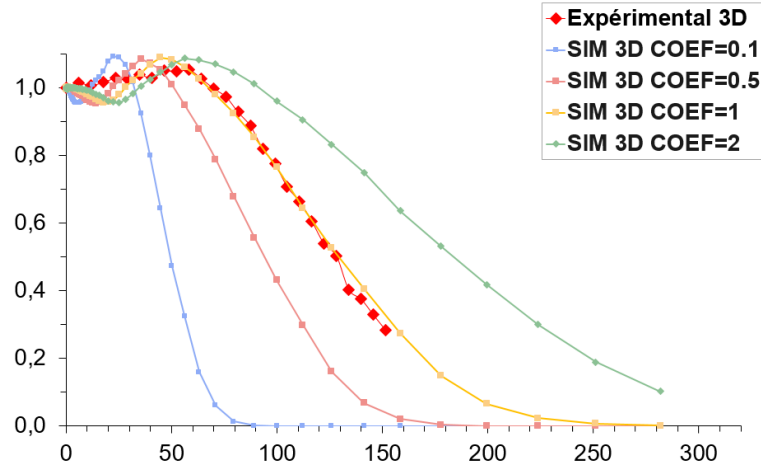


Figure 5.13: *Central pore evolution with different value of dynamic viscosity, scaling by three different factors: 0.1, 0.5, 2. Temperature of simulation $T = 120^{\circ}\text{C}$*

Another sensitivity analysis was conducted about the effect of the surface tension. It was decided to use three different factors, to increase and decrease the value of surface tension $\Gamma = 30 \text{ mN/m}$ at the constant temperature of $T = 120^{\circ}\text{C}$.

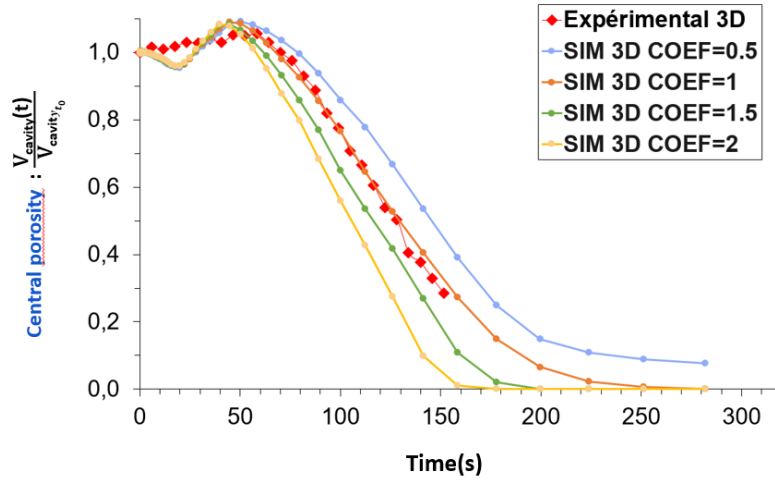


Figure 5.14: *Central pore evaluation with different value of surface tension, scaling by three different factors: 0.5, 1.5, 2. Temperature of simulation $T = 120^{\circ}\text{C}$*

In reality, the value of surface tension can vary depending on the composition

(e.g., the ratio of polar to non-polar components or the presence of plasticizers), as well as on the temperature (since Γ decreases with increasing T). However, in common practice, the surface tension is typically close to $\Gamma = 30$ mN/m. It was necessary to perform this test in order to verify the reliability of the model in a sensitivity study. The results shown in Fig.5.14 are consistent, since the collapsing rate increases with increasing surface tension, as Γ is the driving force of sintering.

A simulation was also performed in the presence of gravity, in order to evaluate its main effect on the physics of the system. In Fig.5.15 it can be observed that gravity influences the collapse of the central pore. The coalescence process takes more time, but the sintering rate is similar to the simulation with gravity. Surface tension remains the main driving force of the system, but the presence or not of the gravity have not a relevance impact in filling the central pore, making the results nonlogical.

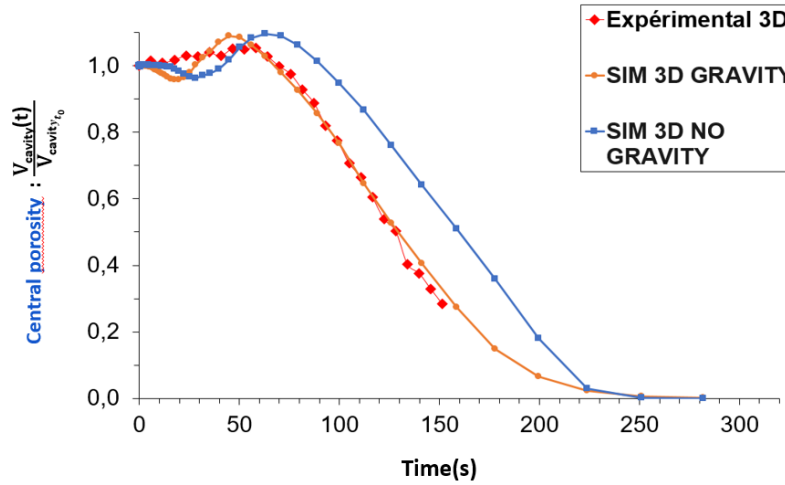


Figure 5.15: *Central pore evaluation at $T=120^{\circ}\text{C}$ with gravity and without.*

Similar results were obtain in the simulation without surface tension. Coalescence took longer and the sintering rate was different, but not very far from the baseline simulation (Fig.5.16). These results can be compared with the no-gravity case, and they show that surface tension has a greater effect then gravity. In fact, the sintering process without surface tension did not reach completion, and the central pore was not fully filled.

All these simulations could also be carried out using the full domain. The results would be essentially the same, thanks to the imposed symmetry condition.

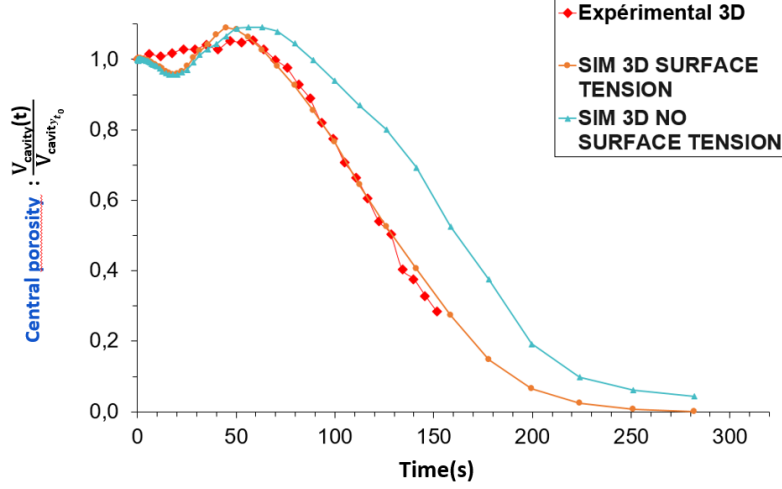


Figure 5.16: Central pore evaluation with and without surface tension Γ active at $T_{oven} = 120^\circ\text{C}$

5.3.3 Discussion

The results obtained from the simulation are useful for understanding the effect of each parameter on the process. Temperature is one of the main drivers of the system: higher temperatures increase the sintering rate and enhance the coalescence process. The opposite behavior occurs with changes in dynamic viscosity. An increase in η reduces the sintering rate and prolongs the overall process. In the case of machine settings during FFF, when using a more viscous composition—such as one containing 10% active pharmaceutical ingredient—it is necessary to increase the process temperature to ensure good adhesion between layers. This model makes it possible to study the combined effects of different parameters and to identify the optimal combination for achieving high manufacturing quality. The goals initially stated in this thesis have been achieved. A fully coupled transient 3D model, including heat transfer, fluid flow, surface tension effects and *Level Set* has been built, tuned and provided results. The validation, relying on experimental data and a former 2D cartesian study, has been performed. It showed that the numerical 3D solutions for central pore size evolution agrees well with the experimental response and the 2D cartesian solution as well. Both full size 3D domain and quarter size 3D domain exhibit similar solutions. Therefore for numerical efficiency one can use a quarter size domain. With a 3D model, the boundary and initial conditions can be implemented accurately and reflect more precisely the experiments. The effect of the reinitialization parameter in the *Level Set* method was also investigated. This parameter is very important

in the simulation, as its implementation is required both from a theoretical and a practical perspective in order to achieve reliable results. The sensitivity analysis for oven temperature and material's viscosity was studied and allow to optimize future application dealing with pharmaceuticals. The effect of surface tension was investigated to assess the suitability of the model in the sensitivity analysis. The effect of gravity was also studied, and its importance for the simulation was observed

For future perspectives, with all these results, it will be possible to gain an overview of all the driving forces of the system and their relative importance. Finally future work would also deal with more complex filament deposition scenarios. Geometries of depositions could include more filaments, different angles of depositions from a layer to another or even different filaments' diameter for instance. The results obtained from such geometries could help designing the best pharmaceutical pills.

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