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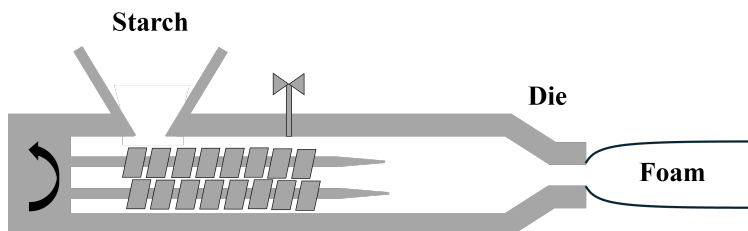
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THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Carbohydrate-based foam as green and biodegradable packaging material

From extrusion foaming to additive foam manufacturing



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SCUOLA POLITECNICA E DELLE SCIENZE DI BASE

DIPARTIMENTO DI INGEGNERIA CHIMICA, DEI MATERIALI E DELLA PRODUZIONE INDUSTRIALE

*La vittoria è personale quando è
personalizzata.
Alla fine un happy end.*

CARBOHYDRATE-BASED FOAM AS GREEN AND BIODEGRADABLE PACKAGING MATERIAL

FROM EXTRUSION FOAMING TO ADDITIVE FOAM MANUFACTURING

Ph.D. Thesis presented
for the fulfillment of the Degree of Doctor of Philosophy
in Industrial Products and Processes Engineering
by

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Candidate's declaration

I hereby declare that this thesis submitted to obtain the academic degree of Philosophiæ Doctor (Ph.D.) in Industrial Products and Processes Engineering is my own unaided work, that I have not used other than the sources indicated, and that all direct and indirect sources are acknowledged as references.

Parts of this dissertation have been published in international journals and/or conference articles (see list of the author's publications and conferences at the end of the thesis).

Napoli, February 10, 2025

Claudio Esposito

Abstract

This Ph.D. dissertation presents an in-depth study of the extrusion foaming of starch, with a focus on optimising die design and managing shape instability during the process. The research integrates experimental investigations and computational fluid dynamics (CFD) simulations to investigate how processing conditions, die geometry, and material properties influence the quality and stability of foamed extrudates. Focusing on starch, a renewable, bio-based, and biodegradable material derived from sources such as potatoes and corn, the research highlights the potential of starch-based foams as a sustainable alternative to fossil-based materials such as expanded polystyrene (EPS) and expanded polypropylene (EPP), which are commonly used in packaging and other industries. However, the extrusion of starch-based foams presents challenges related to moisture content and die swelling. The main challenge addressed is die swell, also known as the Barrus effect, which causes irregular swelling at the die exit, resulting in distortion and inconsistencies in the final product. To mitigate this problem, a fluid dynamics model was developed to predict the final shape of the extrudate by simulating die geometry, flow conditions, and material behaviour, significantly reducing trial-and-error iterations in die design. The simulations have been validated with experimental data, improving the accuracy of predictions of extrudate shape and foam behaviour. Through this integrated approach, the thesis provides valuable insights into the role of die design in improving the extrusion process and advancing the development of starch-based foams for various applications.

In addition, the research incorporates advanced 3D printing techniques to further explore foam structure and morphology. One of the key findings was the discovery of dual-orientation bubble morphology in 3D-printed foams, where bubbles are orientated both in the extrusion direction and radially. This behaviour, which is influenced by processing parameters such

as extrusion temperature, provides new insights into bubble formation and foam microstructure. The second finding relates to the 3D printing process for plant-based meat alternatives. In particular, the research demonstrates the potential of manipulating process parameters (printing velocity and temperature) to achieve a specific internal morphology in terms of bubble number and size. This allows material properties to be controlled through parameter adjustments, rather than relying on complex ink formulations, and has important implications for tailoring foam properties for specific applications in industries such as food, packaging, and materials science.

Keywords: Starch-foaming, die design, extrusion, shape instabilities, three-dimensional printing.

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Introduction

The environmental impact of conventional plastics has become one of the most pressing challenges of our time. Derived primarily from non-renewable fossil feedstocks, synthetic polymers such as polyethylene terephthalate (PET), polypropylene (PP) and polystyrene (PS) have revolutionised industry due to their durability, versatility and cost-effectiveness. However, their non-biodegradability and the enormous amount of plastic waste generated worldwide have led to alarming levels of environmental pollution, with millions of tonnes of plastic accumulating in landfills and oceans every year. This problem, coupled with the depletion of petroleum reserves, has driven the search for sustainable alternatives in line with the principles of the circular economy. Foams such as expanded polystyrene (EPS) are widely used in packaging due to their lightweight, structural diversity and versatility. While EPS is recyclable under certain conditions, its high carbon footprint, incompatibility with carton recycling systems and low recycling rates make it an environmentally unsustainable choice. In this context, bio-based and biodegradable materials such as starch offer a promising alternative. Starch-based foams can reduce reliance on fossil fuels, reduce greenhouse gas emissions and align with circular economy principles, especially if designed to integrate with existing recycling infrastructures. This PhD dissertation focuses on the development of carbohydrate-based foams as green and biodegradable packaging materials. Starch, a naturally occurring renewable and biodegradable polysaccharide, has been extensively studied for its potential as a sustainable alternative to conventional plastics. Through the application of heat, shear and plasticisers such as water, starch can be converted into thermoplastic starch (TPS), a versatile material suitable for producing lightweight, porous structures through foaming techniques. In particular, extrusion foaming is an established method for producing starch-based foams due to its scalability and the ability to incorporate functional additives, to enhance foam properties.

The work presented in this thesis is divided into six chapters. Each chapter covers a key aspect of the development and optimisation of starch-based foams. Chapter 1, provides an introduction and review of the state of the art, focusing on the structure and composition of starch, the conversion of starch to TPS, and the processes involved in the foaming of thermoplastics, including the role of extrusion and additives.

Chapter 2 examines the 3D printing of starch-based gels with the ad-

dition of proteins. Proteins act as functional additives to improve the mechanical and rheological properties of printed structures. This chapter examines the interplay between starch-protein composite properties, rheology and the resulting foam morphology and properties, demonstrating the potential for tailoring materials for specific applications.

Chapter 3 focuses on the additive manufacturing of foams with a unique double orientation morphology within the filament. This distinctive foam structure enhances mechanical properties and improves performance in packaging applications. The chapter discusses the processing parameters required to achieve this morphology and their correlation with the functional properties of the foam.

Chapter 4 examines the design of the extrusion die and the prediction of die swell using computational modelling in COMSOL Multiphysics. Die swell, a phenomenon in which the extrudate expands as it exits the die is a critical parameter that affects the final properties of the foam. Using computational fluid dynamics (CFD) simulations, this chapter provides insight into optimising die geometry to control die swell and improve foam quality.

Chapter 5 discusses the shape instabilities that occur during the extrusion foaming process, in terms of the non-desired final shape. These instabilities can significantly affect the quality and consistency of the final foam product. Through a detailed investigation of the underlying mechanisms, the chapter offers strategies for optimising die design to minimise instabilities and improve foam performance.

The conclusions, Chapter 6, provides an overall summary of the research findings, highlighting the progress made in understanding the processing -structure-property relationships of starch-based foams. The key contributions of this work to the development of sustainable packaging materials are underlined, along with the potential for future applications in biodegradable and recyclable packaging solutions. By combining experimental research, computational modeling and innovative manufacturing techniques, this thesis contributes to the advancement of carbohydrate-based foams as viable alternatives to conventional plastics. The results address critical technical challenges and provide a foundation for the development of materials that support global efforts towards sustainability and a circular economy.

Chapter 1

State of the Art

1.1 Starch and Thermoplastics material

The term "biopolymers" is defined as polymers that are synthesised through natural processes during the proliferation and development of all living organisms. Starches are complex carbohydrates that play a major role in the diet of humans and animals as a primary source of energy. They are polysaccharides composed of glucose units linked together in the form of two different molecular structures: amylose and amylopectin. The ratio of amylose to amylopectin varies among starch sources, with typical values ranging from 20 – 30% amylose and 70 – 80% amylopectin in most cereal starches. Amylose is a linear polymer consisting of glucose units linked by $\alpha(1\rightarrow4)$ glycosidic linkages. In contrast, amylopectin is a highly branched polymer containing both $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$ linkages [1], the molecular structures of the two polysaccharides is reported in the Figure 1.1.

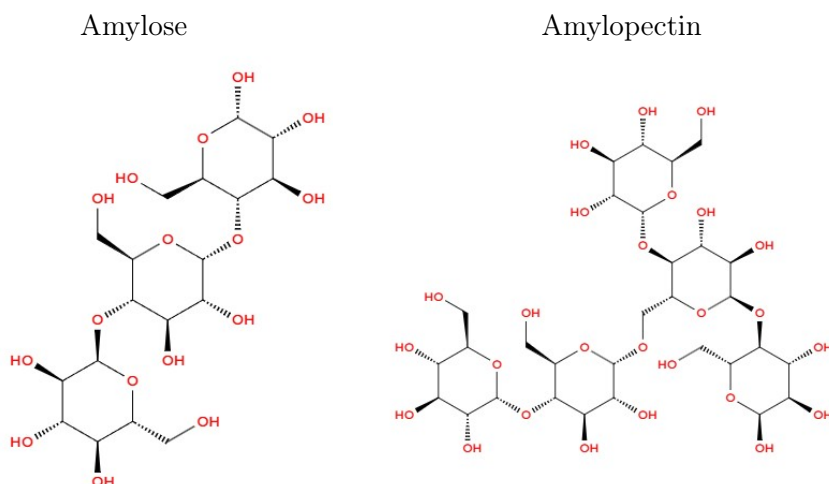


Figure 1.1. Molecular structures.

The arrangement of amylose and amylopectin within the structure of a starch granule is characterised by a high degree of order. In the presence of water, however, the arrangement of the two polymers becomes disordered upon heating. The loss of internal order occurs at varying temperatures, correlating with the specific type of starch in question. With

continued heating in water, the native granules expand and their structure is ultimately compromised. The general chemical formula for starch is $(C_6H_{10}O_5)_n$, where "n" is the number of glucose units, which can vary depending on the botanical source of the starch. This variability in composition and structure is crucial to understanding the diverse functional properties of starches in food science and technology.

The structural properties of starches are naturally linked to their functional properties, which include gelatinisation, retrogradation, and digestibility. Starch granules have different crystalline forms, which are mainly categorised into A, B and C structures. A-type starch, commonly found in cereal grains, shows strong diffraction peaks at approximately 15° , 17° , and 23° in X-ray diffraction patterns [2]. In contrast, B-type starch, typical of tuber starches such as potatoes, has peaks at around 5.7° , 17.3° , and 19.6° [2]. C-type starch, which has characteristics of both A and B types, is observed in certain sources such as cassava and some rice varieties.

The crystalline structure of starch granules is a key determinant of their thermal and rheological properties, which influence their behaviour during cooking and processing.[3] The motivation to utilise starch as a component of packaging materials can be traced back to the 1970s, a period during which there was a notable intensification in global awareness of environmental issues. [1]. In its native form, starch exhibits a semi-crystalline arrangement; in this configuration, the granules are rigid, making difficult to melt or flow under the action of heat, which is the main characteristic of a thermoplastic material. Plasticisation is therefore a key step; this process involves the addition of plasticisers, which are molecules that reduce the intermolecular hydrogen forces between amylose and amylopectin chains. Two of the main plasticisers used are water and glycerol. When starch is heated in the presence of plasticisers, it undergoes a process called gelatinisation. During gelatinisation, the starch granules absorb water and swell, causing the crystalline regions to break down and dissolve into a gel-like network, the process is synthesised in Figure 1.2 This transition makes starch more flexible and capable of being shaped under heat and pressure, a key characteristic of thermoplastic materials. In particular, the released amylose chains reorganise, forming a gel-like network, while amylopectin gives the material elasticity and flexibility. The ratio of amylose to

amylopectin significantly affects the mechanical properties and biodegradability of TPS. The conversion of starch into a thermoplastic material

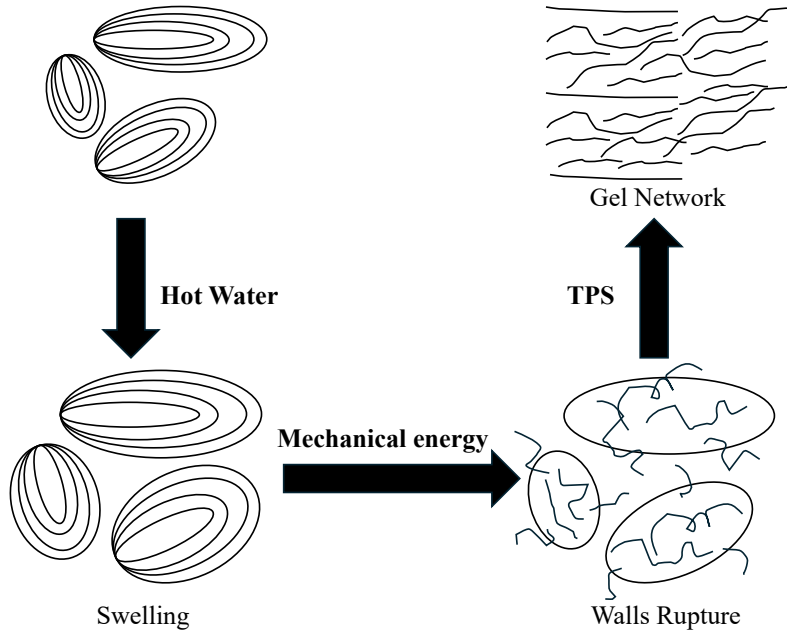


Figure 1.2. Starch crystals disruption and TPS formation

represents a significant advancement, facilitating its manipulation through conventional polymer processing techniques, including extrusion, injection, and compression molding. Thermoplastic starch offers distinctive benefits in single-use applications, including food packaging, agricultural films, and disposable containers. In terms of environmental impact, TPS is a superior alternative to other thermoplastic materials, such as polylactic acid (PLA), polyethylene terephthalate (PET), and polypropylene (PP), a materials classification is reported in the figure 1.3. These materials persist in the environment for prolonged periods, often centuries, whereas TPS decomposes within weeks or months under composting conditions, thereby significantly reducing its long-term ecological footprint.

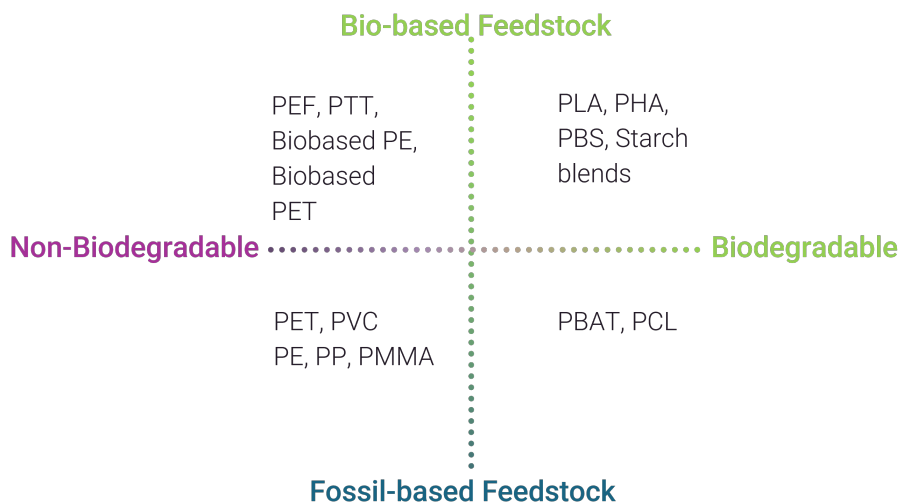


Figure 1.3. Classification diagram of materials.

Despite all the environmental benefits biopolymers have some cons, for example, PLA, derived from renewable resources like corn starch, is known for its excellent mechanical properties and biodegradability, making it suitable for a wide range of packaging applications. However, PLA's brittleness and sensitivity to moisture can limit its effectiveness in certain environments. PET and PP are favoured for their superior mechanical strength and thermal stability, but they are derived from non-renewable resources and pose significant environmental challenges upon disposal. TPS, while generally less robust than PET or PP, can be enhanced through blending with other biopolymers or additives to improve its mechanical properties and moisture resistance, thereby expanding its applicability in packaging solutions.

1.2 Thermoplastic Foaming

The thermoplastic foaming method is a process whereby gaseous components, either physical or chemical blowing agents, are incorporated into thermoplastic polymers during the manufacturing stage, resulting in the

formation of a cellular or porous structure. They can find their application in the automotive [4], electronics [4], packaging [5], and medical fields [6], as they are lightweight materials compared to their bulky counterparts and have a high strength-to-weight ratio, excellent thermal and acoustic insulation, and energy absorption capabilities.[7, 8]. The gaseous component, known as the blowing agent, can be physical (e.g., carbon dioxide, nitrogen) or chemical (e.g., azodicarbonamide, sodium bicarbonate). These agents expand under heat and pressure, forming gas bubbles within the molten polymer matrix. The foaming process occurs through three critical stages: cell nucleation, cell growth, and cell stabilisation [9]. Of these stages, cell nucleation is a determining variable in setting the final structure and properties of the foam. The process of cell nucleation can be classified into two main types according to the distribution of the cells in the material: homogeneous nucleation and heterogeneous nucleation. A fundamental framework for understanding the mechanisms of the nucleation during the foaming process is provided by the Classical Nucleation Theory (CNT) [10], which describes nucleation as the formation of bubbles through the creation of a thermodynamic new phase (daughter phase) within the metastable phase (parent phase). The bubbles are capable of irreversibly growing into larger-sized nuclei[11]. The CNT considered these hypotheses and approximations[12]:

- The cells are spherical with a sharp boundary.
- All cell nuclei have the same bulk property.
- Considers the effect of pressure drop on cell nucleation and ignores the effect of pressure drop rates.
- Assumes an instantaneous pressure drop followed by instantaneous cell nucleation.
- The theory considers the bubble interface as an infinity plane.

In the CNT theory, physically, a metastable state corresponds to a local minimum of the free energy. Metastability means that the system in this state is stable, state A, to small fluctuations in the thermodynamic variables, but after a certain time will evolve to state C, corresponding to the global minimum of the free energy. This system has to overcome a barrier

to perform this transformation, representing a local maximum of the free energy. The latter corresponds to an unstable equilibrium state, state B, in which the system is unstable due to small fluctuations in the thermodynamic variables. A fluctuation is required to overcome the energy barrier, which causes the formation of a small quantity (cluster) of the new phase called the nucleus.

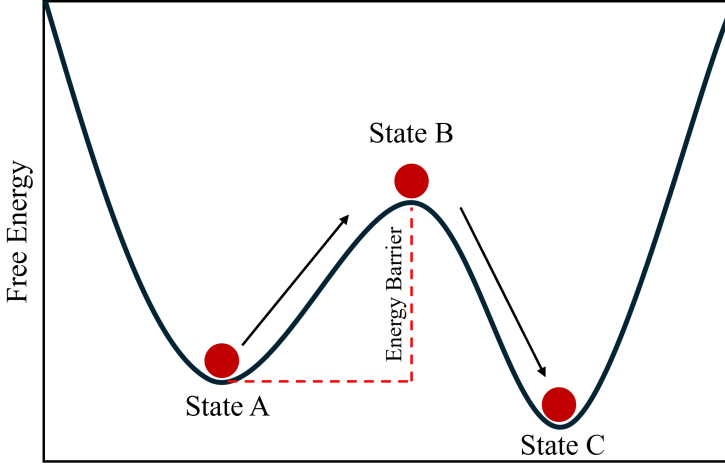


Figure 1.4. Bubbles states transition.

The energy barrier arises from the competition of two factors: the Volume Free Energy ($\Delta G_{FreeVol}$); which represents the energy gain from the reduction of gas supersaturation that favours the bubble formation, and the Surface Energy ($\gamma_{\alpha\beta}$) which is the energy cost of creating a new interface between the gas phase and the surrounding polymer matrix, that opposes to the bubble formation.

1.2.1 Homogeneous nucleation

According to the CNT, homogeneous nucleation occurs as a response to a change in pressure or temperature. As we can also see from figure 1.5, as the bubble radius R became smaller than the critical radius r^*

($R < r^*$), the nucleus was formed; when r^* it was reached, the energy barrier (ΔG) reaches a maximum value, and growth could start. The r^* also indicates the minimum dimension that a cell must have before growth to become a stable bubble. Equation 1.1, expression for the Gibbs free energy, describes the process of nucleus formation and growth, by taking into account the difference of the inner pressure of the cell and the pressure of the surroundings and the surface energy [12].

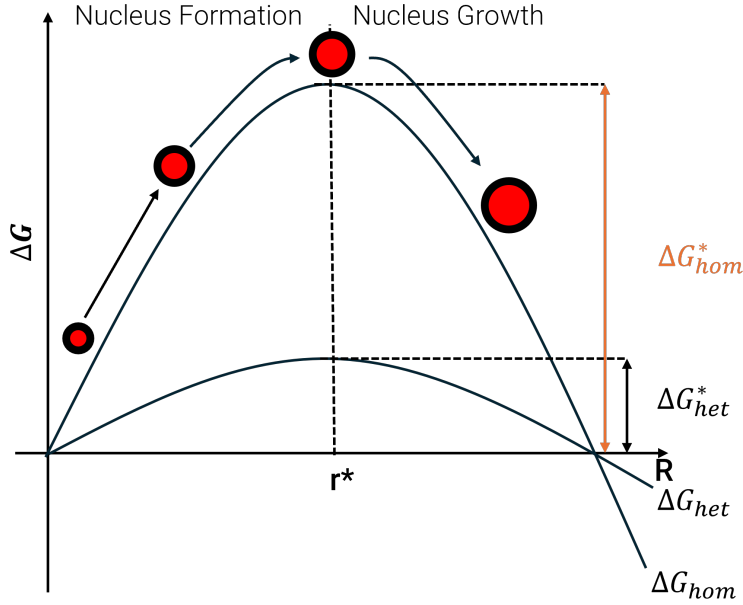


Figure 1.5. Bubble nucleation and growth in function of Gibbs free energy(ΔG).

$$\Delta G(R) = -\frac{4}{3}\pi R^3 \Delta P + 4\pi R^2 \gamma_{\alpha\beta} - \Delta V_{FreeVol} \quad (1.1)$$

where ΔP is the pressure difference between the internal and external of the nucleus, $\gamma_{\alpha\beta}$ is the interfacial energy, and $\Delta V_{FreeVol}$ the free volume related to the presence of additives (this term is zero in case of homogeneous nucleation). By imposing the derivative of both terms in eq. 1.1

equal to zero, the value of the critical radius can be found in terms of ΔP and $\gamma_{\alpha\beta}$ (1.2).

$$r^* = \frac{2\gamma_{\alpha\beta}}{\Delta P} \quad (1.2)$$

By substituting eq. 1.2 into eq. 1.1, the value of the Gibbs free energy barrier, ΔG_{hom}^* , can be found (eq. 1.3):

$$\Delta G_{hom}^* = \frac{16\pi\gamma_{\alpha\beta}^3}{3\Delta P^2} \quad (1.3)$$

1.2.2 Heterogeneous nucleation

Heterogeneous nucleation, which is not spontaneous, occurs when additives act as nucleation centres and lower the Gibbs free energy barrier. The lowering of the energy threshold is related to the dimensions of the additive particles and their surface topography. These factors can be inserted into the equation of this process by modification of the equations governing homogeneous nucleation with a shape factor $S(\theta)$ (eq. 1.5). Eq. 1.4 describes the Gibbs free energy barrier [12]:

$$\Delta G_{het}^* = \Delta G_{hom}^* S(\theta) \quad (1.4)$$

$$s(\theta) = \frac{1}{4}(2 + 3\cos\theta - \cos^3\theta) \quad (1.5)$$

The shape factor is a function of the contact angle Θ between the bubbles and the surface of the additive. This factor decreases as the contact angle increases (Fig. 8). Although eq. 1.5 refers to additives assumed to have a planar surface, nucleation often occurs in conical-shaped cavities with round-shaped standard nucleating agents. Therefore, the semi-conical angle β must be considered, leading to eq. 1.6.

$$s(\Theta, \theta) = \frac{1}{4}(2 - 2\sin(\theta - \beta) + \frac{\cos\theta\cos^2(\theta - \beta)}{\sin\beta}) \quad (1.6)$$

Although heterogeneous nucleation might seem to be more advantageous than homogeneous, it strongly depends on the additives, and a good cell structure is hard to achieve[8]. As a final step, once the foam structure has

formed, the stabilisation is performed by just lowering the temperature of the gas-polymer mixture and/or adding surfactants to lower the interfacial energy.

1.3 Extrusion

Extrusion is a versatile and widely used manufacturing process that involves the continuous shaping of materials by forcing them through a specially designed opening called a die. This technique has acquired considerable importance in several industries, particularly the plastics, food and pharmaceutical sectors, where it is used extensively to produce a wide range of products. These products include but are not limited to, films, sheets, profiles, tubes and fibers. The extrusion process is distinguished by its ability to produce products with consistent cross-sectional profiles, which makes it ideal for high-volume production. In the plastics industry, extrusion is fundamental to the production of items such as pipes, window frames and packaging materials. The food industry uses extrusion to produce cereals, pasta and various snack foods, while the pharmaceutical industry uses the technique to produce pellets, granules and certain drug delivery systems. The extrusion system consists of several key components, each of which plays a critical role in the overall process. The main components of a typical extruder are shown in Figure 1.6, which provides a schematic representation of the layout of the system and the flow of material through the various stages of the extrusion process.

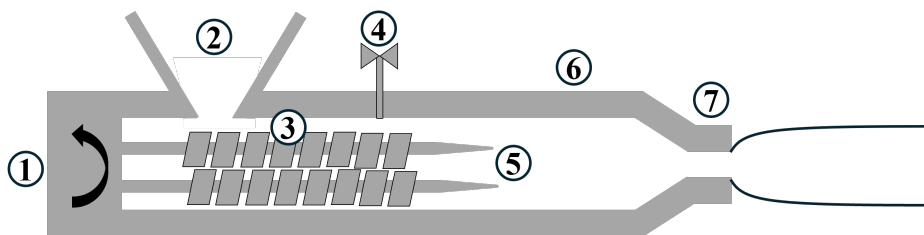


Figure 1.6. Extruder line components.

The main functions of the components shown in Figure 1.6 are listed below:

- ① **Motor:** Provides the necessary power to rotate the screws, driving the material through the system.
- ② **Hopper:** feed the raw material into the system, ensuring a continuous and controlled flow for consistent processing.
- ③ **Barrel:** A long cylindrical chamber that encloses the screws, facilitating material heating, mixing, and conveying.
- ④ **Blowing Agent Inlet:** Injects a blowing agent into the material to induce foaming or achieve a specific texture.
- ⑤ **Screws:** Spiral elements within the barrel that transport, melt, and mix the material as it moves through the extruder.
- ⑥ **Cooling/Mixing Part:** Facilitates proper cooling or further mixing of the material before it exits the die, often incorporating additional mixing elements.
- ⑦ **Die:** The final forming section at the end of the extruder that shapes the material into the desired shape.
- ⑧ **Extrudate:** The final product that is pushed out of the die, which is ready for further processing or use.

The extrusion process can be summarised in three stages, shown in Figure 1.7: 1) feeding and melting, 2) mixing and homogenisation, and the last stage, 3) shaping and cooling. The first stage begins with the feeding of raw materials, typically in the form of granules (pellets) or powders, into the hopper. The rotating screw or screws transport the material along a heated barrel where it is melted through a combination of thermal conduction and mechanical shear. In the second stage, the material is mixed to allow the uniform distribution of all ingredients, such as additives, fillers, plasticisers, or the blowing agent. In the last stage, the material is pushed out through a die which defines the final shape of the product. Upon exiting the die, the material is cooled using various methodologies, including air exposure, water bath, or oil bath immersion. The cooling phase is also critical, as ineffective temperature control or rapid cooling can cause shape instability, such as warping or uneven contraction. Such instabilities can

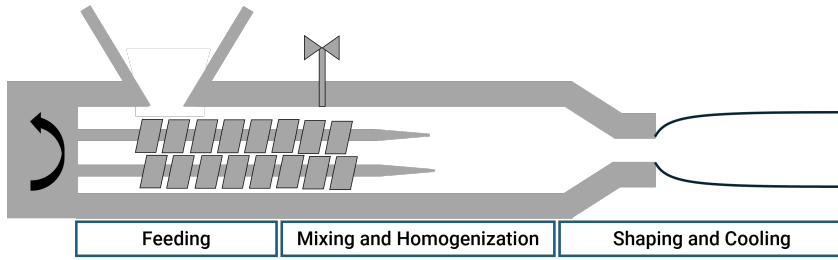


Figure 1.7. Extruder stages.

have a significant impact on the final dimensions and overall structural integrity of the material and a more detailed analysis of these instabilities is provided in paragraph 1.4.1. The versatility of extrusion allows for incorporating various additives, such as colourants, fillers, and blowing agents, which can modify the properties of the final product to meet specific application requirements.

1.3.1 Extrusion Foaming

A specialized application of extrusion is foaming extrusion, in the context of thermoplastic foaming, extrusion plays a critical role in producing lightweight, cellular materials. The foaming process involves the introduction of gas into the molten polymer matrix, resulting in a foamed structure that can significantly enhance the material's properties, such as thermal insulation, sound absorption, and mechanical cushioning. The Process of foaming extrusion is well reported in the section 1.2. The blowing agent used to introduce the gas phase in the polymer matrix can be classified into two categories: Physical blowing agent and Chemical Blowing agent. The most used materials used nowadays in foaming extrusion are mainly fossil-based, such as polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyethene terephthalate (PET). These materials exhibit favourable properties for foaming, such as high melt strength, good thermal stability, and compatibility with various blowing agents. However, the reliance on non-biodegradable fossil-based polymers raises environmental concerns, particularly regarding waste accumulation and carbon emissions. For these motivations have emerged the use of renewable alternatives to fossil-based

material, the starch-based thermoplastics, as mentioned in section 1.1.

1.4 Die Design

In extrusion, the material is forced out of the extruder through a special conduit, shaping the material in the desired profile, named die. Serves as a transition point where the molten material transforms into the final shape. The design of dies in extrusion processes is a fundamental aspect that significantly influences the efficiency, quality, and the dimensional precision of the final product, but not only aesthetic properties are affected; also mechanical properties are driven by the die. For these reasons, the design process involves a comprehensive understanding of the material properties, flow behaviour, and thermal dynamics during extrusion. An effective die design must account for the rheological properties of the material, including its viscosity and elasticity, which dictate how the material flows through the die. The die must ensure uniform material flow, minimise defects, and control the mechanical and thermal stresses within the material. In addition, in foaming extrusion, there is the introduction of another complex factor, foaming. So, the die must also facilitate the nucleation and the stabilisation of the bubbles always maintaining the desired product dimensions and mechanical properties. Four features of a die for extrusion are the baseline for designing: Entrance zone, converging zone, exit shape, and land length at the exit. Some other features can be added to the design according to the final application or according to the control of the process parameters, such as the pressure drop or the velocity of the molten polymer in the die, this feature can be a restriction before the die exit.

- ① The Entrance zone is important for the transition from the larger extruder barrel to the small conduit of the die. The design of this region is useful to minimize the turbulence, reduce the shear stresses and ensure the uniform distribution of the material.
 - ② The Converging zone is a transition zone from the larger upstream flow channel to the smaller one. The role of the converging zone is important in three factors: Shear control, Flow uniformity, and pressure control. A sharp converging angle can lead to high shear stress which can promote overheating or degradation of the material.
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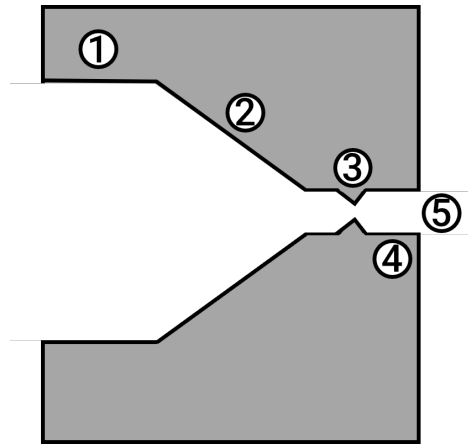


Figure 1.8. Schematic representation of the extruder die, highlighting its main components.

Regarding the flow uniformity a gradual converging zone can ensure the right material distribution across the profile, reducing the risk of dead zones. For the pressure, a controlled converging angle allows the generation of the necessary back pressure for processes that need high-pressure environments, such as foaming.

- ③ This feature, the restriction, is placed before the exit in order to modify the material's flow. This allows the control of the pressure because increases the back pressure, which is essential for ensuring uniform flow and helps in processes such as foaming. In addition, still in the foaming process, the restriction promotes the control of the bubble formation creating a region in which the shear and pressure are high. And also, helps in flow homogenisation by reducing velocity profile variation in the material.
- ④ The Land length refers to a straight, uniform section of the die, it is crucial to stabilise the material flow. Works as a pressure stabiliser because provides a region where the material pressure and flow become consistent. Allows the defects because works as a calibrator, helping in preventing common defects such as die swell, melt fracture

or uneven thickness.

- ⑤ The exit shape of a die is the region where the material assumes its final profile. The exit surface must mimic the cross-section of the desired geometry by taking into account the die swell. The well-designed exit must guarantee the uniform distribution of the velocity across the entire profile because also small variation of the velocity profile in the section can lead to distortion, warping or other defects. In addition, it is needed to take into account also the material thermal and viscoelastic behaviour, to ensure that the material stabilizes quickly to maintain dimensional accuracy.

Among the various die configurations, two primary types are commonly used in the industrial world: strand dies and slit dies. The strand die produces multiple small-diameter strands of extrudate. The shape of the holes could be round, square, or triangular. The material flows through each channel, and at the exit of the die, it is glued together due to the fact that the material is still melted in the centre. While slit dies are designed to produce wide, thin or thick sheets or films by shaping the molten material into a flat profile as it exits the die. In several applications, slit dies are preferred over strand ones due to their superior control of product quality and versatility. Also, the flat extrudate of a slit die cools more uniformly compared to individual strands, reducing the risk of warping, delamination, or incomplete solidification. For example, in foaming, it could occur that in strand dies foam, in the contact surface between each strand, there is the presence of non-foamed material or not well-foamed material. In addition, slit dies allow higher production rates as the material solidifies and is processed more rapidly compared to the smaller and individual strands from a strand die.

1.4.1 Foaming Extrusion Instabilities

The phenomenon of shape instabilities during extrusion is a critical area of research in materials science and engineering, particularly in the processing of polymeric and composite materials. The extrusion process is often plagued by various instabilities that can adversely affect the quality and consistency of the extrudate. Shape instabilities can manifest as

distortions, surface defects, or inconsistent dimensions, all of which can compromise the product's functionality and appearance. The common shape instabilities are: a) a not controlled die swell at the exit of the die; b) high shear rates near the die exit can cause surface roughness, sharkskin textures, or gross melt fracture; c) cooling or residual stresses can cause the extrudate to bend or curl; d) inadequate support during extrusion or cooling can result in large-profile extrudates deforming under their weight, causing buckling and sagging; e) in the case of thermoplastic foaming, inconsistent bubble nucleation or growth can lead to uneven cell structures or collapsed regions. The causes of these instabilities can be found in the viscoelastic nature of the polymers used, the flow dynamics inside the die due to dead zones, a high-pressure gradient, or a high shear rate. Also, die design (as shown in Section 1.4), post-extrusion cooling plays an important role in the stabilisation of the final shape of the product, and the last one can be related to the external mechanical influence such as pulling or stretching; also, gravity can play a role in the stabilisation. Detecting and monitoring instabilities during extrusion are also critical for maintaining product quality. Naue et al. developed a high-sensitivity system to detect pressure fluctuations within the die, which correlate with observable melt instabilities [13]. Such advancements in monitoring technology are essential for real-time adjustments during the extrusion process, allowing for immediate corrective actions to be taken when instabilities are detected. This proactive approach can significantly enhance the reliability of the extrusion process and improve the overall quality of the extrudate. In addition to the aforementioned factors, the material composition and the presence of additives can influence the stability of the extrusion process. Adesina et al. conducted a comparative analysis of various additives on the rheological properties of high-density polyethylene, finding that certain processing aids could mitigate melt instabilities and enhance productivity [14]. This suggests that the careful selection of materials and additives is vital for optimising the extrusion process and minimising the risk of defects. The processing conditions, such as temperature and pressure, are critical in influencing shape stability during extrusion. High processing temperatures can enhance the flow of the polymer but may also lead to thermal degradation or changes in molecular structure, which can compromise the integrity of the extrudate. Conversely, insufficient temperatures

can result in poor melt flow and increased viscosity, leading to difficulties in achieving the desired shape. The balance between temperature and reaction kinetics is crucial for maintaining the desired properties of polymers during processing, particularly in applications where the material undergoes significant thermal cycling or mechanical stress [15]. In foaming extrusion, the introduction of gas can also lead to challenges in maintaining dimensional stability. The foaming process can result in rapid expansion of the material, which may cause the extrudate to deform or collapse if not properly controlled. The significance of controlling the foaming process to mitigate issues related to die swell and shape retention has been highlighted in recent studies [16]. The viscoelastic properties of the polymer melt, combined with the dynamics of gas expansion, create a complex interplay that must be carefully managed to achieve stable foamed products. The selection of polymer materials also influences the occurrence of shape instabilities during extrusion. For instance, polymers with low melt strength may be more susceptible to deformation and instability during processing. The lack of entanglements in certain polymer blends can lead to challenges in maintaining shape during foaming and extrusion processes, emphasising the need for materials with appropriate rheological properties to ensure stability [17]. Additionally, the incorporation of additives or fillers can modify the flow behaviour and mechanical properties of the polymer, potentially enhancing its resistance to shape instabilities.

1.5 CFD in Die Design

Computational Fluid Dynamics (CFD) has emerged as a powerful tool in the design and optimization of extrusion dies. By simulating the flow of polymer melts through dies, CFD allows engineers to predict and analyse the behaviour of materials under various processing conditions. This predictive capability is essential for identifying potential issues related to flow uniformity, pressure distribution, and temperature gradients within the die, all of which can significantly impact the stability of the extrusion process. For instance, Zhang et al. demonstrated the application of an inverse design method for thin-wall hollow profiled polymer extrusion dies using FEM-CFD simulations, highlighting how variations in die geometry can influence pressure drops and flow characteristics [18]. Such insights are

invaluable for optimising die designs to minimise instabilities and improve product quality.

The sensitivity of die design features is another critical aspect addressed through CFD simulations. Mamalis et al. conducted a sensitivity analysis of numerical models for extrusion spider dies, revealing how specific design parameters can affect flow behaviour and temperature uniformity within the die [19]. By systematically varying these parameters, researchers can identify optimal configurations that enhance the stability of the extrusion process. This approach not only reduces the need for extensive physical prototyping but also accelerates the development of effective die designs.

In addition to traditional extrusion processes, CFD simulations are increasingly applied to foaming extrusion, where gas is introduced into the polymer melt to create a cellular structure. Yao et al. explored the dynamics of bubble growth in supercritical CO₂ extrusion foaming of polyethylene terephthalate, utilizing dynamic flow simulations to predict the behaviour of viscoelastic fluids during the foaming process [20]. Their findings underscore the importance of incorporating viscoelastic properties into CFD models to accurately capture the complexities of foaming extrusion and mitigate potential instabilities.

The design of extrusion dies for foaming processes requires careful consideration of the interactions between the polymer melt and the gas phase. The introduction of gas can significantly alter the flow characteristics of the polymer, leading to challenges such as uneven expansion and shape distortion. Gonçalves et al. highlighted the need for optimised die designs that account for the unique flow dynamics associated with wood-plastic composite profiles, emphasising the role of CFD in achieving effective design solutions [21]. By simulating the interactions between the polymer and gas, engineers can develop dies that promote uniform bubble distribution and minimise defects in the final product.

Moreover, the application of CFD in die design extends to the analysis of complex geometries and multi-material extrusions. The work of Cheng et al. demonstrated the utility of numerical simulations in optimising die structures for complex aluminium profiles, revealing how variations in die design can influence material flow and reduce the occurrence of defects such as die swell [22]. This capability is particularly important in industries where precision and consistency are paramount, as it allows

for the development of dies that can produce high-quality extrudates with minimal variability.

The integration of CFD with other numerical methods, such as the Finite Element Method (FEM), further enhances the predictive capabilities of die design simulations. For example, the combination of FEM and CFD has been employed to analyse the thermo-mechanical behaviour of materials during the extrusion process, providing insights into the effects of temperature and pressure on material flow and stability. This integrated approach allows for a more comprehensive understanding of the extrusion process, enabling engineers to optimise die designs for improved performance and reduced defects.

As the field of extrusion continues to evolve, the role of CFD simulations in die design will become increasingly critical. The ability to accurately model the complex interactions between materials, processing conditions, and die geometries will be essential for developing innovative solutions to address the challenges of shape instability. Researchers are continually refining CFD models to incorporate more sophisticated rheological behaviours, enabling the simulation of non-Newtonian fluid dynamics that are characteristic of many polymer melts [20]. This advancement will enhance the accuracy of predictions related to flow behaviour and stability, ultimately leading to improved die designs and higher-quality extruded products.

1.6 Foam Additive Manufacturing Scale-down

3D printing has been revolutionising the way to transform materials into functional objects by virtue of 1) incredible freedom of design compared with traditional techniques, 2) high sustainability due to waste minimisation, and 3) the possibility of mass customisation because, for moderate quantities of items, it is more economical than traditional techniques. [23] Among the numerous techniques for 3D printing, fused deposition modelling (FDM) or Fused Filament Fabrication (FFF) uses a continuous filament of a thermoplastic polymer to 3D print layers of materials. The filament is heated at the nozzle of the printer and extruded through a small opening on a platform or on top of previously printed layers. Many attempts have been made to produce 3D-printed foams with high poros-

ity and intrastrand micropores. [24, 25, 26, 27] Moreover, the complexity of 3D printing structures can be further enhanced through the utilization of 3D foam printing techniques [28, 29, 30]. The introduction of a micro-porous structure has the potential to enhance the specific mechanical properties and increase the possibilities of different texture of the final product. Is it possible to achieve a fine tuning of cell morphology in the printed strands by designing the operating conditions through the modelling of transport phenomena. Recently, three-dimensional (3D) printed foams with high porosity and intrastrand micropores have been produced using a newly developed technology known as in situ Foam 3D Printing or Foam Additive Manufacturing, FAM, which can induce cell nucleation and growth through solubilization of blowing agents in the filaments. [31, 32] This technology has several advantages: (i) higher printing velocity thanks to the plasticization effect due to gas solubilization; (ii) higher specific mechanical and thermal properties; (iii) more degrees of freedom to tune material properties attained by changing the extruded strand density.

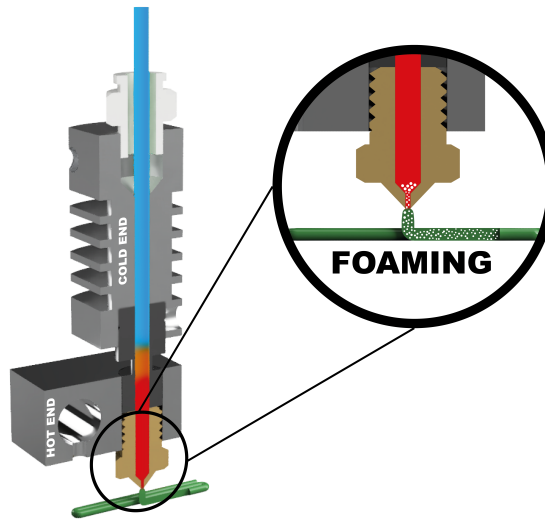


Figure 1.9. Schematic of a 3D FFF printer, integrating the foaming technique. The solid filament saturated with gas is shown in blue, the filament melting zone is highlighted in red, and the deposited filament with bubble formation at the nozzle exit is depicted in green.

Foam Additive Manufacturing (Foam AM) represents a significant advancement in the field of material processing, particularly because it can be used as a scale-down of traditional foaming extrusion processes. This innovative technique allows for the optimization of material properties and the conduction of high-throughput experiments; unlike the traditional extrusion setup, in this way, researchers can explore several process parameters. With this method also the cost is affected, making it a cost-effective and highly controllable method for producing complex structures.

1.6.1 Starch 3D Printing

Three-dimensional printing technology has revolutionised the manufacturing of materials, particularly in the field of biopolymers such as starch. Starch has garnered significant attention due to its biocompatibility, biodegradability, and potential applications in several sectors such as food industry [33], construction [34], clothing [35], drug delivery [36], scaffolds for tissue engineering [37] and in the packaging industry [38, 39]. This process consists of transforming these biopolymers into a printable material, commonly by direct ink writing (DIW) or fused deposition modelling (FDM). These two printing methods allow precise control of the morphology and structure of the final product, which is decisive for tailoring the properties of the final product to specific requirements.

The processing conditions employed in the production of 3D-printed starch materials have a significant impact on the structural and degradation characteristics of the resulting material. The extrusion process, in particular, can induce mechanical and thermal stresses that lead to the disruption of glycosidic linkages within the starch chains. This phenomenon is particularly prevalent in amylopectin-rich starches, where the structural integrity of the material may be compromised, potentially affecting its rheological properties and printability. [40]. It is fundamental to the optimisation of the performance of starch-based inks that these parameters be manipulated, given that the rheological behaviour has a direct impact on the quality of the printed structures [41].

Another important factor in these structures is the porosity of 3D-printed starch materials, is a significant factor that can influence their functionality. The creation of porous structures during the printing process can enhance the material's surface area, which is beneficial for appli-

cations [42]. The ability to control pore size and distribution is crucial for applications requiring specific mechanical properties and biological interactions in biomedical applications[43, 36]. The potential for obtaining porous structures during the 3D printing of starch materials is particularly noteworthy. The incorporation of porogens or the use of specific printing techniques can facilitate the formation of interconnected pores within the printed matrix. This is advantageous for applications in tissue engineering, where the porosity of scaffolds is essential for cell infiltration and vascularization [44]. Furthermore, the design of the printing path and the choice of printing parameters can be tailored to create hierarchical porous architectures, which can mimic the complexity of natural tissues [45]. In addition to enhancing mechanical properties, the introduction of porosity can also influence the degradation rate of starch-based materials. Porous structures may facilitate more rapid enzymatic degradation, which is beneficial for applications requiring controlled release of bioactive compounds [46]. The interplay between porosity, mechanical strength, and degradation behaviour is a critical area of research that can lead to the development of advanced materials with tailored properties for specific applications.

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Chapter 2

Porous Starch Structures

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Tailoring Texture and Functionality of Vegetable Protein Meat Analogues through 3D Printed Porous Structures

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2.1 Abstract

This study presents a comprehensive 3D printing process for plant-based meat alternatives, covering ink formulation, printing, and final product characterization. Traditionally, achieving desired food properties requires extensive exploration of ink components. Here, we demonstrate the potential of manipulating processing parameters instead of ink composition. Two structures were printed, differing only in extrusion temperature.

The printed structures exhibited a dimensional accuracy slightly below 100%. We investigated their behavior through simulated food production cycles, including freezing, thawing, dehydration, and rehydration. Rheological measurements revealed that protein denaturation caused a 20% increase in viscosity. Temperature-induced protein denaturation allowed to produce 3D printed samples with a fine porous structure, with pore sizes ranging from 50 to 450 μm .

Mechanical characterization showed that a single printing parameter (extrusion temperature) significantly impacts the final product mechanical properties, with an increase of about 50% in the maximum stress for denatured samples after rehydration.

This novel approach simplifies 3D-printed protein-based food production, establishing a link between processing parameters and the final product mechanical behavior.

Graphical Abstract

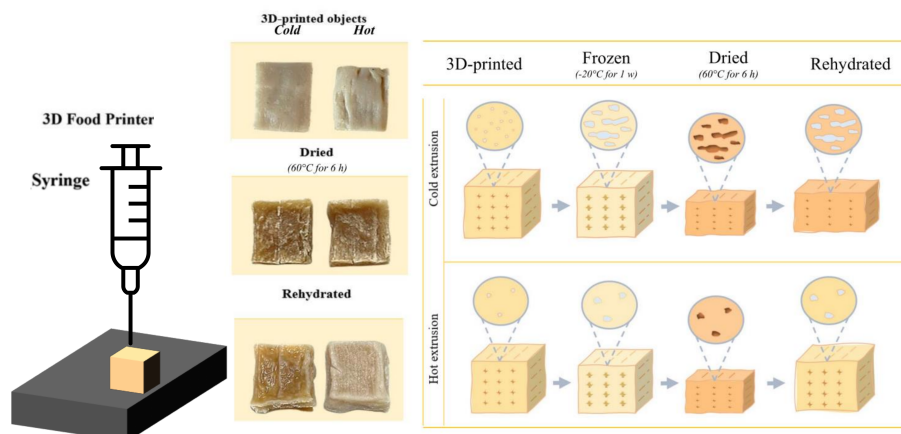


Figure 2.1. Graphical abstract.

2.2 Introduction

Most consumers have long embraced meat not only for its reputation as a high-quality protein source but also for its distinct taste and texture [1, 2]. However, excessive consumption of meat products can be detrimental to health due to their cholesterol and polyunsaturated fatty acid content, which may contribute to cardiovascular disease [3, 4, 5, 6]. Studies indicate that plant-based foods generally have lower greenhouse gas emissions compared to animal products, with beef and mutton being the highest emitters [7, 8, 9]. Researchers have observed that meat analogues exhibit faster digestibility than animal meat due to differing protein compositions [10]. These analogues aim to replicate the texture, flavor, color, and nutritional profile of meat.

The innovative layer-by-layer stacking method inherent in three - dimensional printing (3DP) technology enables the creation of intricate structures not feasible through conventional manufacturing processes[11]. In the realm of food production, the fusion of 3D printing and digital cooking technology opens avenues for crafting novel food items with intricate

shapes, distinct textures, and enhanced nutritional profiles [12, 13, 14]. This integration allows for the replication of the fine structure of vegetable-based protein, closely approximating the texture of real meat [15]. 3D food printing holds significant potential in various applications, particularly within the healthcare sector. For instance, using fresh vegetables with minimal hydrocolloids, it can create safe, nutritious, and visually appealing dysphagic diets for patients, benefiting those with swallowing difficulties [16]. This technology has also been utilized to produce senior-friendly foods that are customizable and have optimal nutritional properties, addressing the specific dietary needs of the elderly [17]. Furthermore, 3D food printing offers the potential to revolutionize food provision for space missions, enabling the creation of a wide variety of customized foods in a confined area with limited resources, thereby enhancing the quality and variety of astronauts diets during long-term missions [18].

Moreover, the complexity of 3D printing structures can be further enhanced through the utilization of 3D foam printing techniques [19, 20, 21]. The introduction of a micro-porous structure has the potential to enhance the specific mechanical properties and increase the possibilities of different texture of the final product.

When compared to other manufacturing techniques 3D printing has several advantages for the production of food products [15, 22]. The emergence of novel materials, including edible hydrogels [23], plant-based proteins [15, 24], and cell-based meat [25], has broadened the scope for creating nutritious and environmentally sustainable food items through 3D printing. Plant-based proteins are the primary building blocks for 3D printed meat analogues due to their abundance, sustainability, and textural versatility [15]. Soy and pea protein isolates are popular choices for their gelling properties that mimic meat textures [26, 27]. Wheat gluten offers a distinct advantage in replicating chewy textures thanks to the formation of a gluten network [28], while chickpea and lentil flours with high protein content are gaining traction [29]. Mycoprotein, derived from fungi, is another promising option due to its complete protein profile and meat-like texture [30].

Numerous studies have investigated the fabrication of food products with significant porous structures [31, 32, 33]. In the domain of meat analogues, the incorporation of biosurfactants into soy protein-based ink has

been demonstrated to produce a fine porous structure, thereby enhancing mechanical properties [34]. Other research has focused on the development of complex microstructures in soy protein 3D printing samples to create plant-based fish analogues with similar textures [35] or to evaluate the impact of red cabbage on printability [36]. Yu et al. found that the addition of polysaccharides improved the printability of soy proteins, resulting in samples with a less porous structure compared to those without polysaccharides [37]. Polysaccharides helped form a stronger gel network [38] and increased the ink viscosity [39]. Moreover, polysaccharides improved gel elasticity by increasing both G' and G'' , indicating a more robust and tighter intermolecular network between protein and polysaccharides [40]. Common post-printing treatments, such as drying [41], freezing [42, 43], and rehydration [44, 45], can further alter the structure and preservation properties of 3D printed food products.

Few studies have focused on the effect of temperature on the porous structure. Liu et al. achieved a fine porous structure in 3D printed potato starch ink, reporting an increase in cell density and a decrease in cell size with temperature, attributed to increased chain mobility and decreased viscosity with rising temperature [46]. Similar results for starch ink indicated that pores became smaller and shallower as the temperature increased from 65°C to 85°C [47]. The impact of temperature on microstructure is also highly dependent on ink composition, as demonstrated by Chen et al. with the addition of sodium alginate to soy proteins [48]. Elevated temperatures can cause protein denaturation in heat-sensitive proteins like egg yolk, leading to increased storage and loss moduli, improved printing performance, and changes in microstructure [49].

A key challenge in 3D printed food is achieving sufficient mechanical strength, which relies on understanding the relationship between internal structure (microstructure) and the resulting texture [50]. Most protein-based prints suffer from low mechanical strength [51]. Derossi et al. intentionally printed samples with a fine internal microstructure, resulting in a decrease in Young's modulus with increased porosity [52]. It was also shown that an increase in porosity can significantly decrease the compression force of 3D printed cereal-based inks [32].

Currently, there is a limited understanding of the effect of critical printing parameters, such as temperature, on the internal porous microstructure

of 3D printed samples. Most studies investigating the microstructure of soy protein 3D printed samples do not consider the effect of temperature on porosity or ink properties. To the best of our knowledge, the impact of increased viscosity due to protein denaturation on the porous structure of 3D printed meat analogues has not been investigated yet. Furthermore, the precise relationship between the microstructure of 3D printed protein structures and their mechanical and textural properties remains poorly understood. Additional research is essential to tailor printing processes and formulations to achieve the desired textures and functionalities in 3D printed protein-based foods.

This study aims to fabricate porous protein structures using 3D printing technology. Our primary hypothesis is that structural changes in the protein matrix of meat analogues can be induced by controlling process temperature and promoting protein denaturation. We further hypothesize that these structural modifications will impact the behavior of the printed product during post-printing processes, such as freezing and drying. The resulting structural changes lead to a final product with a microporous architecture, advancing the understanding of microstructure formation in 3D-printed meat analogues. We investigated the influence of these micropores on the textural and mechanical properties of the printed samples in both dried and rehydrated states. Our findings contribute to understanding the fundamental principles linking sample microstructure and mechanical properties, paving the way for the engineering of hierarchical structures in 3D-printed meat analogues.

2.3 Materials and Methods

2.3.1 Materials

All materials utilized in ink preparation adhered to food-grade standards. Cellulose (CE) was procured from Arbocel® BWW40 (JRS PHARMA LP, USA). Potato starch (PN) with 17% moisture content was sourced from KMC (Brande, Denmark). Soy protein isolate (SPI) boasting 85% protein content was obtained from Bulk™ (Colchester, United Kingdom). Wheat gluten (WG) with a protein content of 75% was purchased from Bongiovanni srl (Cuneo, Italy).

2.3.2 Mixture preparation

In the formulation process for 3D printing material, SPI was dispersed in distilled water and mixed using a paddle stirrer equipped with six holes, generating radial flow ideal for stirring low to medium viscosity substances. WG was introduced to the SPI only after thorough dispersion in water to prevent immediate formation of protein networks. After conducting several pre-tests, the optimal consistency and printability were achieved with a SPI:WG ratio of 3 to 1. In our pre-tests with soy-protein and wheat gluten-based ink alone, we encountered multiple failures, resulting in unstable structures that could not sustain themselves. Starch and cellulose were added simultaneously to the mixture, which was then heated to 65°C while maintaining constant stirring at 400 rpm for 15 minutes to guarantee starch gelatinization. Subsequently, stirring was continued for an additional 30 minutes to ensure a homogeneous mixture, which was then allowed to cool. To prevent moisture loss, the inks were stored in disposable cups tightly wrapped with cling film prior to printing. The composition of the mixture is detailed in [Table 2.1](#).

Table 2.1. Weight percentages of mixture components.

Water	SPI	WG	PN	CE
79.10	13.37	4.46	2.23	0.84

A crucial requirement for the ink is its ability to be extruded from the nozzle stably and uniformly [26]. The composite printing ink with more closely bound water is more uniform, extrudes better, and exhibits some self-supporting properties after extrusion. In contrast, water not closely bound to the protein became free water under extrusion pressure during printing, which was evident in our tests without polysaccharides, where water visibly separated from the ink post-printing. Chen et al. examined the 3D-printing properties of protein inks mixed with various hydrocolloids and found that the control group without hydrocolloids had poor printing performance, with some samples failing to extrude and only unbound water being expelled [26]. We encountered a similar problem, underscoring the necessity of adding polysaccharides to our mixture.

2.3.3 3D printing

The mixture was deposited using a custom-made syringe-based extrusion 3D printer (3DRAG, Futura Elettronica, Italia; Ender-3 V2, Shenzhen Creality 3D Technology Co., China). The material was propelled through a nozzle at a constant pressure, driven by a motor connected to the plunger, while the nozzle followed a computer-controlled, predetermined path. The printing materials were loaded into a plastic syringe with a 1 mm nozzle. The printing parameters are reported in [Table 2.2](#). The printing velocity directly influenced both the duration and dimensional accuracy of the printed structures, requiring synchronization between the nozzle movement speed and the extrusion rate for precise deposition and accurate models. Low printing velocities could lead to paste accumulation and wavy lines with larger diameters, while excessively high velocities could cause filament dragging and breakage, resulting in discontinuous lines, broken layers, or no extrusion at all [15].

Nozzle size (mm)	Printing speed (mm/min)	Infill density (%)	Bed temperature (°C)
0.7	50	100	Room temperature

Table 2.2. Printing parameters for hot and cold extrusion.

The entire 3D printing process was programmed using MATLAB software. Two distinct printing protocols were employed: cold extrusion, conducted at room temperature, and hot extrusion, performed at 85°C. The hot extrusion temperature was chosen to be near the denaturation temperature of the utilized proteins. For hot extrusion, the printing ink was preheated to 85°C for 15 minutes with continuous stirring to ensure uniform temperature distribution throughout the material before printing. Henceforth, these protocols will be referred to as cold extrusion and hot extrusion, respectively.

The printed products were then compared. Following printing, all samples were stored in a refrigerator at −20°C for one week. This low-temperature freezing period helped maintain the samples shape, increased hardness due to water crystallization, and facilitated easier handling for subsequent analyses.

2.3.4 Rheological characterization

The rheological properties of the edible inks and printed samples were assessed using oscillatory tests with a dynamic mechanical analyzer (MCR 702, Anton Paar, Graz, Austria) employing a plate-plate geometry with a diameter of 25mm. The tests for the printed samples were conducted after printing a single layer of approximately 1 mm, allowing for easier insertion of the samples between the rheometer parallel plates. Measurements were conducted at 25°C. Amplitude sweep were conducted to identify the linear viscoelastic region (LVR) of a material. Frequency sweeps were performed to characterize the time-dependent behavior of the samples within the non-destructive deformation range, with a frequency range from 1 s⁻¹ to 200 s⁻¹. Tests were conducted with a strain amplitude of 0.3%. This strain amplitude was chosen after conducting an amplitude sweep, and it falls within the linear viscoelastic region (LVR). Each measurement was conducted in triplicate to ensure reproducibility.

2.3.5 Scanning Electron Microscopy (SEM)

SEM analysis was performed with an Hitachi Tabletop Microscope TM3000 (Deben, United Kingdom). The surface of each printed structure was observed at different magnification ranges, and to better visualize the inner morphology, the samples were cut across the radial section and the longitudinal section. Image analysis was performed using ImageJ software and MATLAB image processing toolpath to evaluate pore morphology.

2.3.6 Shape fidelity

Length and height measurements were used to determine the dimensional accuracy and shape stability of printed samples. Dimensional accuracy (DA) was calculated by measuring the length, width, and height of each printed sample, and comparing them to the CAD model measurements according to [Equation 2.1](#):

$$DA (\%) = \left(1 - \left| \frac{D_0 - D_t}{D_t} \right| \right) \cdot 100 \quad (2.1)$$

where D_0 represents the initial measurement of the 3D printed sample at print time and D_t represents the defined dimension from the CAD model. A parallelepiped geometry with dimensions of 40 mm in length, 15 mm in width, and 6 mm in height was used for the computer-aided design (CAD) model. Whereas, shape stability (SS) was calculated by measuring the length, width, and height of the printed sample according to [Equation 2.2](#) [13].

$$SS (\%) = \frac{H_1}{H_0} \cdot 100 \quad (2.2)$$

where H_0 represents the initial height of the sample and H_1 represents the height of the sample after the desiccation and rehydration steps.

2.3.7 Moisture content

The moisture content MC was analyzed by means of the moisture analyzer (MA40, Sartorius, Göttingen, Germany). Around 2 grams of samples were cut into tiny pieces (≈ 3 mm) after they were thawed, placed on the balance, and heated to 105°C for 18 min [53]. Four replicas were made. MC was calculated using [Equation 2.3](#):

$$MC = \frac{W_w - W_d}{W_w} \cdot 100 \quad (2.3)$$

where W_w stands for wet weight and W_d stands for dry weight [53]. It is important to note that moisture is not just water: it is a wider term that includes anything that evaporates from a substance when heated, e.g., solvents, flavorings, fats, and other substances. The dry matter that remains after moisture analysis is commonly referred to as total solid (TS) [54].

2.3.8 Rehydration rate

The rehydration rate RR ([Equation 2.4](#)) was determined using a standard analytical balance.

$$RR (\%) = \frac{M_2}{M_1} \cdot 100 \quad (2.4)$$

where M_2 represents the weight of rehydrated material and M_1 represents the weight of the dry material. The purpose of rehydration is to obtain an appearance and taste very similar to animal meat by contacting the dried samples with liquid [44]. The rehydration rate was measured according to the method of [45] with some modifications. The samples used for the moisture content analysis were then subjected to a rehydration test. Then, they were placed in a sieve in tray filled with lukewarm water for rehydration and the weight was measured and recorded every 2 minutes until the equilibrium was reached, and no more water was absorbed.

2.3.9 Texture analysis

Texture profile analysis (TPA) of the printed objects was performed using a TA.XTplus Texture Analyzer (Stable Micro Systems, Surrey, United Kingdom). Compression tests were chosen to measure various attributes such as bite force, chewiness, hardness/tenderness, springiness, and adhesiveness. Tenderness, an essential attribute of meat and food in general, is quantified as a sensory characteristic that significantly contributes to mouthfeel. Along with texture, juiciness, and taste, tenderness shapes the overall quality perceived by consumers.

The tests followed the method outlined by Liu Y. et al. [55], with some modifications. After undergoing freezing and thawing, samples were sliced into squares measuring 20 mm × 15 mm × 6 mm. These slices were analyzed both vertically and horizontally to assess the organization of protein within the fiber structure. Comparisons were also made with rehydrated samples. In this scenario, both hot and cold-extruded samples, already cut into squares, were dried in an oven at 60°C for 6 hours and then soaked in water for 1 hour before testing. Hot-extruded samples exhibited faster rehydration. For the compression test, the parameters included a 5 kN load cell, a smooth 10 cm cylinder probe, a test speed of 1 mm/s, a trigger force of 0.1 N, and an 80% strain.

2.3.10 Mechanical properties

The mechanical properties of cold and hot-extruded 3D-printed objects were evaluated using a tensile testing machine (ZwickRoell Z010, Ulma, Germany) with a 5 kN load capacity. The tensile test direction is parallel

to the printing direction to ensure consistent testing conditions. Extension tests were performed until the samples visibly failed, indicated by the force dropping to zero. Each test was conducted at least three times.

From the tensile data, force-extension graphs were generated, enabling the calculation of key properties such as tensile strength, tensile strain, and Young's Modulus. These properties represent the material's behavior when subjected to external forces. To minimize stress concentrations induced by the loading grips, dog bone-shaped specimens were prepared for the tension tests. These specimens were securely positioned within the clamps, and a traction force was applied to initiate the testing process.

2.4 Results

2.4.1 Rheological measurements

The rheological properties of the ink used for 3D printing are shown in 2.2a and 2.2b. Regardless of the mixing procedure, the ink exhibits shear thinning behavior, which is associated with enhanced printability [49]. The viscosity data have been fitted using a generalized Newtonian power-law model $\eta = K\dot{\gamma}^{n-1}$, and the corresponding parameters are documented in Table 2.3. As indicated in Table 2.3, the power law exponent remains consistent across both mixed inks and printed samples, suggesting a similar shear thinning behavior. Shear thinning is commonly observed in fluids with suspended particles or long-chain molecules, and several studies have documented shear thinning behavior in various food based inks [31, 35, 37, 36]. These studies report a consistency index ranging from 20 to 1000 Pa $\cdot$ sⁿ and a flow index between 0.05 and 0.2.

For hot mixing at 85°C, measurements indicate a higher viscosity compared to ink prepared at room temperature. The impact of temperature on viscosity is complex; in some cases, it can decrease viscosity due to enhanced mobility of macromolecular chains at higher temperatures [48, 47, 46]. However, protein denaturation is often responsible for viscosity increases [49]. The observed viscosity can be attributed to both protein denaturation and water evaporation. To isolate the effect of protein denaturation, we rehydrated the hot-mixed samples with the amount of water lost during evaporation. As shown in 2.2a, the rehydrated ink

exhibits approximately 20% higher viscosity than the cold-mixed samples, highlighting the significant impact of protein denaturation. As shown in

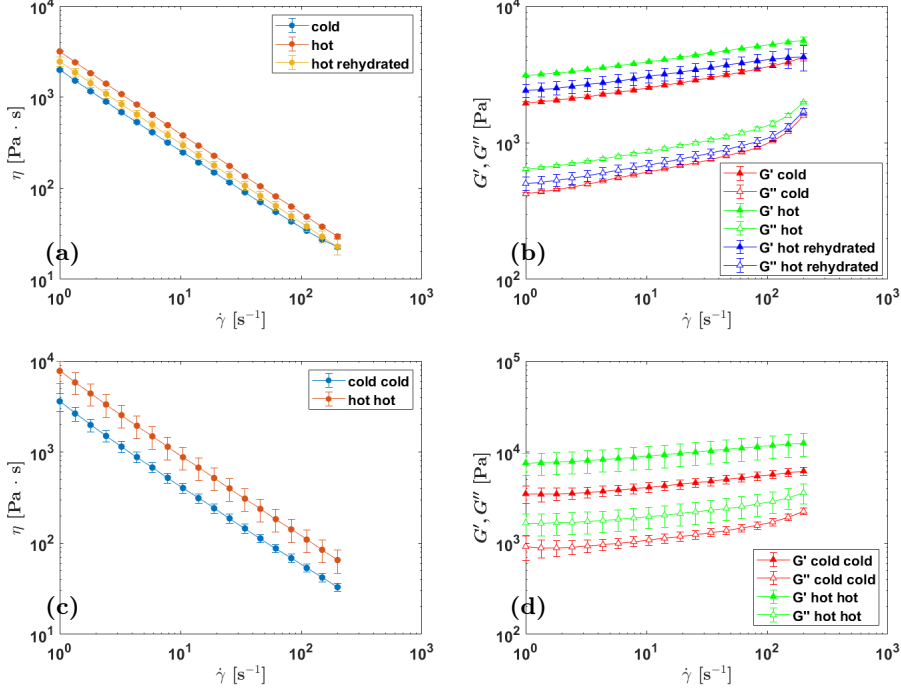


Figure 2.2. (2.2a and 2.2b) Complex viscosity, storage modulus, and loss modulus as a function of shear rate for ink prepared with cold (room temperature) and hot mixing (85°C). For comparison, rehydrated ink after hot mixing is also shown. (2.2c and 2.2d) Complex viscosity, storage modulus, and loss modulus as a function of shear rate for samples printed at room temperature after cold mixing, and at 85°C after hot mixing.

2.2b, the rheological tests reveal that the ink exhibits a solid-like behavior ($G' \geq G''$), which enhances resistance to collapse after printing [49, 47, 48]. Both G' and G'' increase with the mixing temperature, which can be attributed to temperature-induced protein denaturation [49]. The behavior of rehydrated ink falls between that of the hot- and cold-mixed inks. 2.2c and 2.2d present the results of rheological tests performed on inks after 3D printing extrusion. The differences in viscosity, G' , and G'' between

Sample	K (Pa · s ^{n})	n
cold mixed ink	2.0×10^3	0.11
hot mixed ink	3.2×10^3	0.092
rehydrated hot mixed ink	2.4×10^3	0.096
cold mixed, cold printed	3.5×10^3	0.051
hot mixed, hot printed	7.7×10^3	0.064

Table 2.3. Power-law fitting parameters for inks and printed samples at different conditions.

the cold and hot extruded samples are even more pronounced than after initial ink preparation. This suggests that extruding the samples at 85°C may further induce protein denaturation and water evaporation.

2.4.2 Printing performance and shape fidelity

Despite showing different degrees of dimensional accuracy and stability, all samples successfully achieved the intended shape. Printing parameters were adjusted according to the dimensions of the CAD model, with a consistent printing velocity of 1000 mm/min. No significant die-swell, which could compromise shape fidelity due to sample elasticity [56, 57], was observed at the nozzle exit. Samples produced using hot extrusion printing appeared slightly smoother and more uniform compared to those printed at ambient temperature. The successful printing results are shown in Figure 2.3. As evident from the cross-section image, the filaments fused together, resulting in a printed structure with indistinguishable individual filaments.



Figure 2.3. From left to right: 3D-printed object top view, side view and cross-section. CAD dimensions: 40 mm $\times$ 15 mm $\times$ 6 mm.

Dimensional accuracy was assessed using Equation 2.1, which compared the disparities between the length, width, and height of the CAD model and those of the printed object. In Figure 2.4, both cold and hot-extruded samples achieved a dimensional accuracy exceeding 90% for each dimension. The dimensional accuracy achieved here is similar to that obtained with other meat analogues in other studies for each dimension [58, 59, 60].

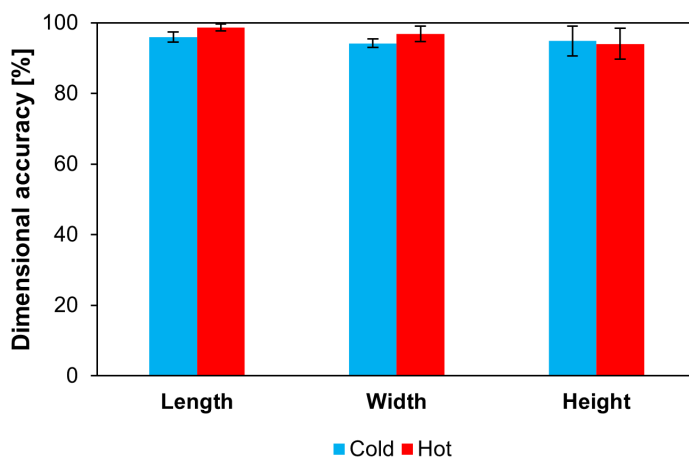


Figure 2.4. Dimensional accuracy for samples printed in cold and hot conditions.

2.4.3 Macro and micro structure of 3D printed samples

The printed objects were stored at -20°C for one week. Following this, the frozen 3D-printed objects were dried at 60°C for 6 hours, a common procedure to enhance the shelf life of food products. This drying process induced changes in the samples' shape, which are detailed in the following paragraph. Subsequently, the cold and hot-extruded samples were rehydrated to assess the reversibility of the drying process. Figure 2.5 illustrates the immediate qualitative changes observed during the different processes the printed structures underwent, including alterations in color, height, and overall morphology.



Figure 2.5. Macroscopic structure evolution of the 3D-printed samples (cold-extruded on the left and hot-extruded on the right of each column) from left to right: 3D-printed objects; dried samples at 60°C for 6 h; rehydrated objects for 1 h in lukewarm water.

Equation 2.2 quantifies shape stability by comparing the dimensions of printed objects before and after desiccation and rehydration. Cold and hot-extruded objects showed significant variation only in height after desiccation, as illustrated in 2.6a, with no notable differences in length or width. This suggests that these processes primarily affected height without causing noticeable shrinkage in other dimensions. 2.6b shows that hot-extruded samples tend to recover their initial height after rehydration, whereas cold-extruded samples exhibit a slight decrease in height. SEM microscopy was utilized to investigate the samples micro-structure in both extrusion conditions. Figure 2.7 showcases SEM images of both radial and longitudinal cross-sections for each sample after the desiccation step.

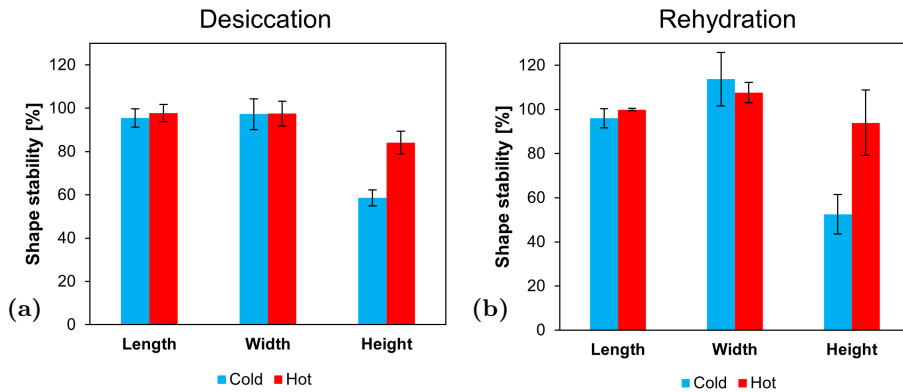


Figure 2.6. Shape stability after desiccation (2.6a) and rehydration (2.6b) processes. The blue bars refer to the cold-extruded samples; the red bars refer to the hot-extruded samples. The remarkable difference in height between the two samples can be attributed to the different pore density that affects the rehydration process.

Observations from the radial cross-section reveal a significant contrast in porosity between the cold and hot-extruded samples. The cold-extruded samples display higher porosity with numerous non-circular pores. The pores are often interconnected, resulting in the presence of relatively large vacancies in the protein matrix. As shown in Figure 2.8 this pattern is present both in the radial and longitudinal cross-sections. The hot-extruded samples display a large number of small pores ($\approx 50 \mu\text{m}$), with a higher presence of smaller pores compared to the cold extruded samples. Furthermore, there are several cracks on the surface with a length of about $200 \mu\text{m}$. In the case of cold extrusion, the pores in the longitudinal cross-section have a higher eccentricity than for hot extrusion, respectively 0.97 ± 0.01 and 0.77 ± 0.02 .

2.4.4 Water absorption capacity

Table 2.4 presents the results of the moisture content analysis, revealing a slight difference in volatile compounds the samples after the desiccation step. Moisture content is higher for cold-extruded samples than for the

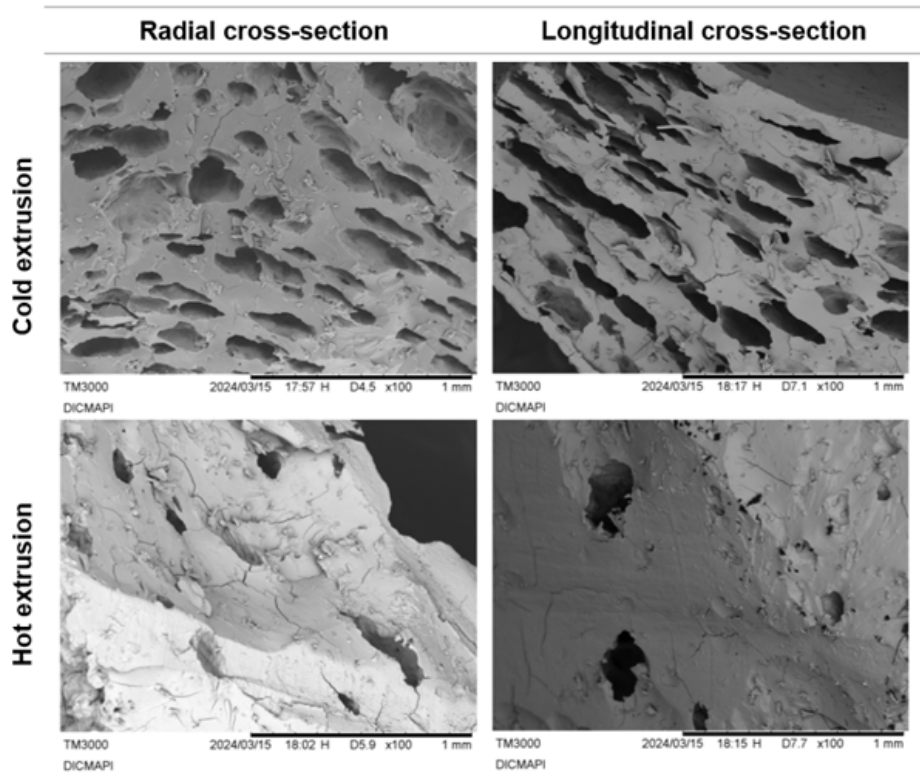


Figure 2.7. SEM micrographs of radial cross-section, and longitudinal cross-section of thawed and dried 3D printed products, for cold and hot printed samples.

hot-extruded one.

Sample	W_w (g)	W_d (g)	MC (%)	TS (%)
Cold extrusion	2.09 ± 0.07	0.64 ± 0.09	69.58 ± 4.05	30.42 ± 4.05
Hot extrusion	2.07 ± 0.07	0.70 ± 0.05	66.09 ± 1.91	33.91 ± 1.91

Table 2.4. Results from the moisture content analysis. From left to right: wet weight (W_w), dry weight (W_d), moisture content (MC), total solid (TS).

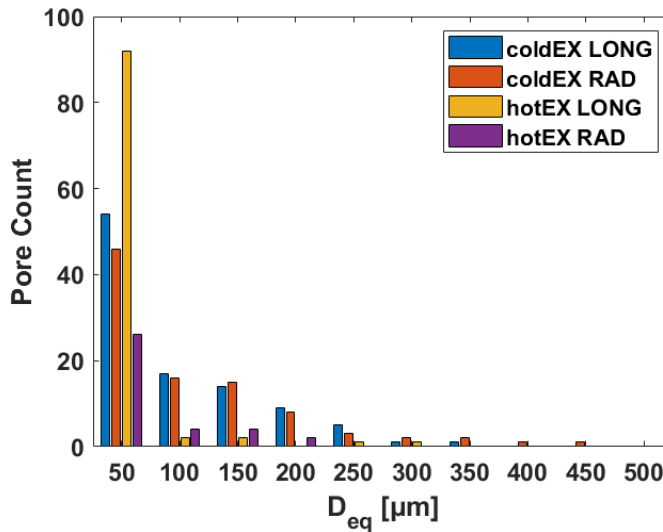


Figure 2.8. Pore size distribution of hot and cold extruded samples in longitudinal and radial cross sections.

The amount of absorbed water is also recorded during the rehydration step for both samples. Analysis of the measurements indicated that compared to their initial dry weight, the samples experienced a weight increase of 313.5% for cold extrusion and 344% for hot extrusion, attributable to absorbed water (Figure 2.9). Notably, cold-extruded samples demonstrated a higher rehydration rate than their hot-extruded counterparts, reaching a plateau around 7 min, whereas the hot-extruded samples plateaued around 26 min.

2.4.5 Textural and mechanical properties

Previous investigations on the structural characteristics of textured vegetable proteins (TVPs), revealed that these properties are primarily determined by processing conditions, moisture content in the feed, and the composition of materials used [53]. Pons M. et al. explained the meaning of the main characteristics that food possesses, and how to measure them via textural properties [61], such as: *hardness*, *springiness*, *co-*

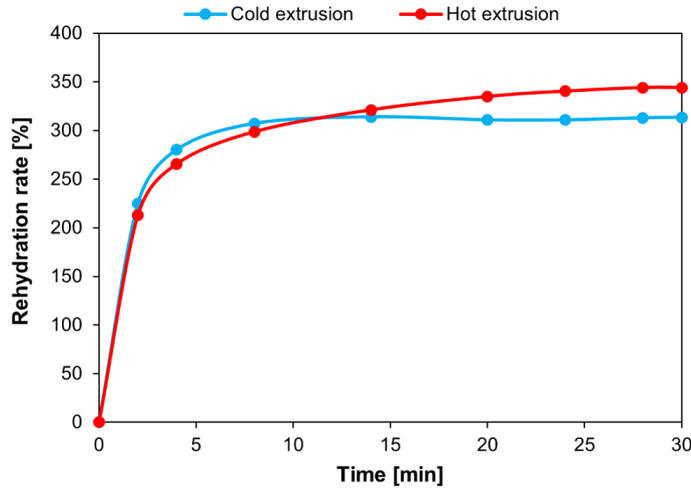


Figure 2.9. Comparison between the rehydration rate of cold and hot-extruded 3D printed objects evaluated with Equation 2.4.

hesiveness, adhesiveness, gumminess, and chewiness. Analyzing the force behavior during two compression cycles it was possible to measure all these properties (Table 2.5). The hot-extruded printed objects were too brittle to withstand the second compression cycle at a degree of compression of 80%, as illustrated in Figure 2.10. Typically, gel-type systems experience complete rupture of the gel sample at compressions exceeding 70-80%.

Texture Profile	Cold-extruded	Hot-extruded	Cold-extruded rehydrated	Hot-extruded rehydrated
Hardness (N)	59.75 ± 3.95	39.19 ± 7.23	71.14 ± 0.08	2.37 ± 0.61
Springness (mm)	3.68 ± 0.20	(Too brittle)	2.97 ± 0.41	(Too brittle)
Cohesiveness	0.88 ± 0.06	(Too brittle)	0.97 ± 0.04	(Too brittle)
Gumminess (N)	52.72 ± 7.15	(Too brittle)	68.98 ± 3.14	(Too brittle)
Chewiness (N)	193.22 ± 15.50	(Too brittle)	205.5 ± 37.61	(Too brittle)

Table 2.5. Compression test results of cold/hot-extruded and rehydrated cold/hot-extruded samples. Note that both samples showed no adhesiveness.

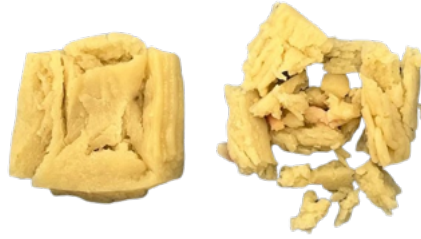


Figure 2.10. On the left the cold-extruded object after the first compression cycle; on the right the hot-extruded object after the first compression cycle. The hot-extruded one completely breaks down and was not suitable for the second compression cycle.

Cold-extruded samples exhibited greater hardness (59.75 N) compared to hot-extruded samples (39.18 N). Additionally, rehydration significantly affected the textural attributes of both cold and hot-extruded printed objects. The hardness of the hot-extruded rehydrated sample decreased dramatically by approximately 95%, whereas the hardness of the cold-extruded variant increased by about 15%. Differences in cohesiveness were noted between the two cold-extruded samples, both before and after rehydration, with the latter displaying superior resistance to internal deformation compared to the former, while chewiness and gumminess values suggest the rehydrated samples require more effort to chew. These textural attributes provide insight into the material behavior during consumption. The measured hardness values, ranging from 10 to 100 N, are consistent with previous findings reported in the literature [62, 63].

Each sample was cut into dog-bone shapes trying to maintain the same surface area ($6.3 \times 10^{-6} \text{ m}^2$) for the tensile tests (Figure 2.11). During the test, all samples failed in a similar way, with strands breaking in the middle region.



Figure 2.11. Picture of dog-bone cut specimen for testing.

The results of the tensile extension experiments are illustrated in [Figure 2.12](#). The cold extrusion printed samples withstood a maximum stress of 1.4 kPa and exhibited a maximum strain of 16.12%, whereas the hot extrusion printed samples endured a stress of about 0.3 kPa with a maximum strain of 4%. This indicates an approximately 350% increase in maximum stress and of 300% in maximum strain from hot to cold extrusion.

The rehydrated samples exhibited distinct behavior. After 20 minutes of soaking, the cold-extruded samples experienced a reduction in tensile stress by around 40%, but their maximum strain increased significantly by 400% compared to the non-rehydrated samples. On the other hand, the hot-extruded samples showed considerable improvements in both tensile stress (approximately 300%) and maximum strain (approximately 50%) following rehydration.

[Figure 2.13](#) shows the Young's Modulus of the samples. Among non-rehydrated samples, cold extrusion produced the stiffest material, with a Young's Modulus of 17.7 kPa, followed by the hot-extruded sample at 12 kPa. Interestingly, the trend reversed after rehydration. The hot-extruded rehydrated sample became the stiffest (10 kPa), exceeding the cold-extruded rehydrated sample (5.5 kPa).

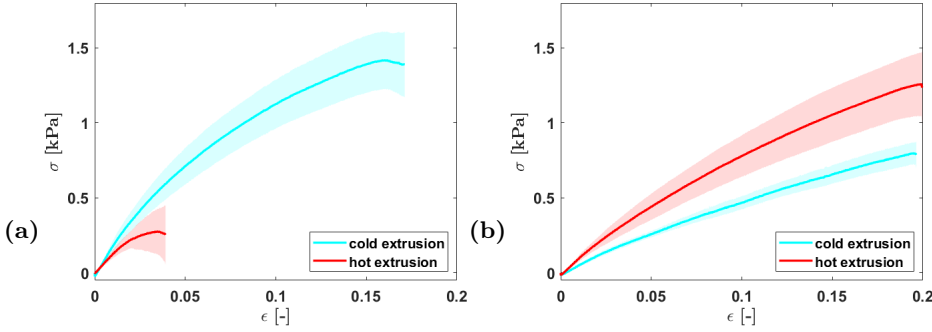


Figure 2.12. Tensile stress as a function of strain for: (2.12a) printed samples after thawing and defrosting; (2.12b) printed samples after thawing, defrosting and rehydration.

2.5 Discussion

This study reveals that a mere adjustment in processing temperature results in final products with markedly distinct internal structures. Cold extrusion yields an internal morphology characterized by numerous large pores, contrasting with the hot-extruded sample, which exhibits few large holes and several tiny ones. The formation of ice crystals during the freezing stage likely contributes to this porous structure, disrupting the fibrous structure of the protein [43, 65, 42, 66, 67, 68]. Moreover, the subsequent desiccation process might further enlarge these pores due to shrinkage of the protein matrix.

The two procedures employed in this study differ solely in mixing and extrusion temperatures. In the hot extrusion method, the temperature matches the denaturation temperature of the protein under investigation, whereas in the cold extrusion, it remains significantly lower. Protein denaturation typically increases the viscosity of the protein system [69, 49] as demonstrated in Figure 2.2, hence, in the hot extrusion scenario, the system viscosity surpasses that of the cold process. Higher viscosity impedes ice crystal growth and water aggregation [70]. In certain applications, elevated viscosity is attained through the addition of antifreeze components, which decelerate water migration onto the crystal plane and crystal nu-

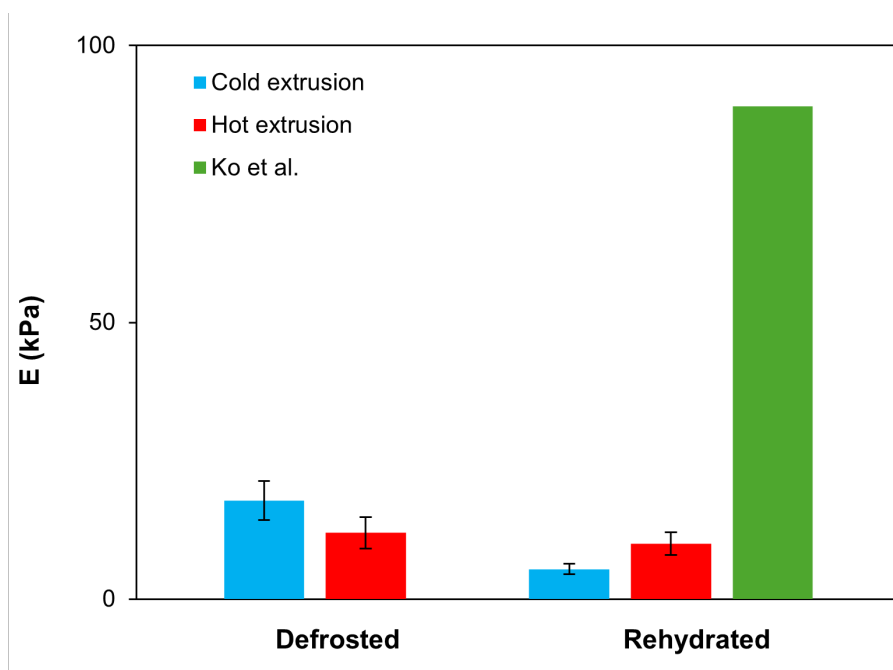


Figure 2.13. Young's Modulus of: printed and thawed samples after defrosting on the left; defrosted and rehydrated samples on the right. In green the comparison with the data in literature on a commercial sample [64].

cleation rate [71, 72]. Higher viscosity may also impede pore enlargement during the desiccation process due to reduced chain mobility [47, 48].

Moreover, the moisture content in the 3D printed sample may influence crystal growth. As indicated in Table 2.4, moisture content diminishes with protein denaturation (hot extrusion). As a result, the size of crystals decreases in conditions of low moisture content. This is expected since protein unfolding reduces water solubility, exposing hydrophobic groups to the surrounding environment [73].

The schematic evolution of each sample interior, depicted in Figure 2.14, traces the key stages of our experimental process from the immediate post-printing phase. Initially, the 3D printed structure is immediately frozen, prompting the growth of ice crystals within the protein matrix. Notably,

larger crystals form in cold extrusion scenarios, while smaller ones emerge in hot extrusion settings. Subsequent desiccation induces sample shrinkage due to water loss, resulting in the formation of a porous structure. Upon rehydration, this process reverses, leading to an increase in sample height.

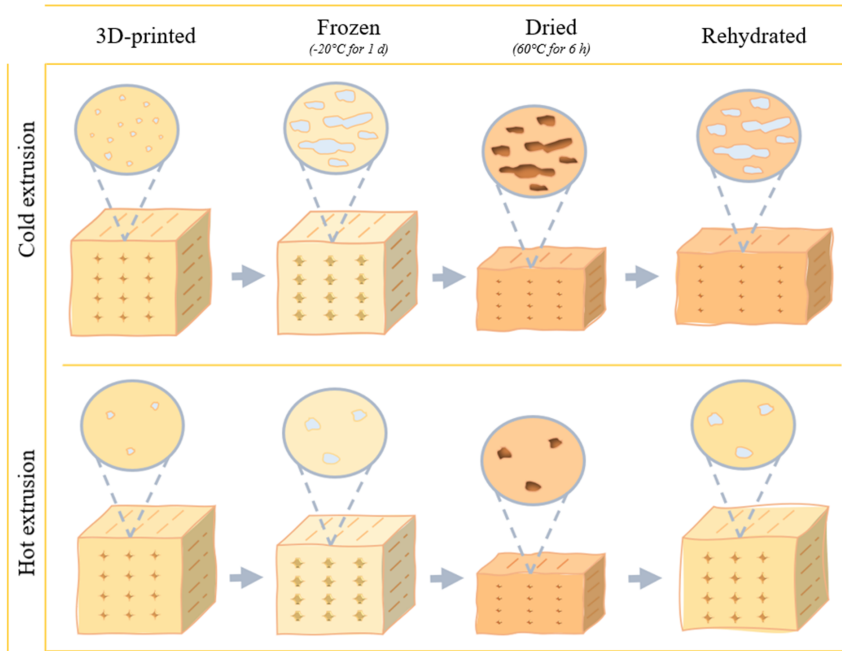


Figure 2.14. Schematic of the inner structure evolution upon different thermal processes.

The drying step (Figure 2.6) significantly impacted the sample height. Cold-extruded samples showed greater shrinkage, likely due to the collapse of their porous structure under their weight as water evaporated, which is consistent with the observed high pore eccentricity in these samples. Hot-extruded samples, with inherently fewer pores, exhibited less pronounced shrinkage. Variations in initial moisture content also influenced height reduction, with higher water content leading to greater shrinkage.

Water uptake during rehydration did not significantly alter the height of cold-extruded samples. Large, interconnected pores allowed water to

readily fill these spaces instead of dispersing uniformly, resulting in uneven distribution (Figure 2.9). These large pores also facilitated faster rehydration. However, the lack of smaller pores hindered water retention due to diminished capillary forces, leading to a lower final water content.

Conversely, hot-extruded samples readily absorbed water into their smaller pores and cracks. Capillary forces, stronger with decreasing pore size, likely contributed to water retention within this structure. This explains the partial height recovery and higher water content observed in hot-extruded samples after rehydration. However, smaller pores may also lead to slower rehydration kinetics as water molecules navigate narrower channels.

The observed microstructural differences may explain the variation in textural and mechanical properties. Cold-extruded samples exhibited higher hardness compared to hot-extruded counterparts (Table 2.5). This behavior might be attributed to the inhomogeneous water distribution within cold-extruded samples, where water may preferentially occupy voids left by melted ice crystals, leaving the surrounding protein matrix drier and potentially harder. Conversely, hot-extruded samples exhibited a more uniform water distribution throughout their structure, potentially leading to increased softness.

This disparity becomes even more pronounced upon rehydration. Following desiccation and rehydration, water becomes even more concentrated within the large pores of cold-extruded samples compared to immediately after thawing, further increasing inhomogeneity. In contrast, the uniform structure of hot-extruded samples facilitates optimal water distribution after rehydration, potentially explaining the observed decrease in hardness and the brittle behavior during compression testing (fracture upon compression initiation). This aligns with the lighter color observed in rehydrated hot-extruded samples compared to the darker color of cold-extruded ones, as depicted in Figure 2.5.

Tensile tests were performed on thin dog-bone samples (approximately 1 mm) formed by a single layer of mixture. This thinness may have led to faster water loss during thawing compared to thicker samples used for compression tests. In cold-extruded samples, this might have resulted in more water remaining in the large pores, leading to higher overall moisture content before the test compared to hot-extruded samples, where a more

homogeneous water distribution facilitated drying. This may explain the fragile behavior of hot-extruded samples in tensile tests, exhibiting lower load tolerance and limited elongation before fracturing compared to cold-extruded ones (2.12a).

Rehydration reversed this trend (2.12b). Cold-extruded samples displayed a decrease in maximum force before rupture, while hot-extruded samples showed an increase. However, final elongation upon rehydration increased for both groups. We attribute this reversal to the distinct water distribution patterns within the rehydrated structures. Uneven water distribution in cold-extruded samples might lead to slight softening, resulting in higher elongation but reduced load capacity. Deeper water penetration into the protein matrix of hot-extruded samples induces a more significant softening effect, contributing to the observed increase in maximum elongation and, consequently, the force recorded before breakage.

There is limited literature available for comparing the mechanical properties of 3D printed meat analogues, as existing studies typically do not address samples with a relatively high moisture content coupled with a porous structure. Derossi et al., in their extensive investigation, examined the compression resistance of wheat flour samples printed with large holes (6 mm). They found that an increase in density led to an increase in the maximum load upon compression. Additionally, they reported a decrease in moisture content with a decrease in sample density, suggesting that water content might also influence the mechanical behavior upon compression of the samples [74]. In another study, Derossi et al. assessed the dependence of Young's modulus on moisture content, discovering that Young's modulus decreases as moisture content increases [52]. This finding is consistent with our data (Figure 2.13), where rehydrated samples exhibit a lower Young's modulus than thawed and defrosted samples.

The data presented in Figure 2.13 indicates a significantly higher Young's modulus compared to all other samples [64]. Although the order of magnitude is similar, the distinct formulation and processing parameters used in their commercially produced product likely resulted in different mechanical properties. However, since the Ko et al. study does not disclose the specific formulation, we can only hypothesize that the higher modulus may be due to the inclusion of additional components. Future research could focus on examining how specific formulation ingredients and processing parameters

affect the mechanical properties of soy protein-based materials.

2.6 Conclusion

This study established a complete 3D printing process for plant-based meat alternatives, encompassing ink preparation, printing of regular-shaped samples, and morphological and textural characterization of the final products. We investigated the behavior of these structures through a mimicked food production cycle, including freezing, thawing, dehydration (desiccation), and rehydration. Scanning electron microscopy (SEM) revealed that cold extrusion generated a highly porous structure with larger pores compared to hot-extruded samples after freezing, thawing, and dehydration.

This difference can be attributed to temperature-induced protein denaturation. Higher extrusion temperatures increase the mixture viscosity [49, 26], hindering ice crystal growth during freezing and pore enlargement during dehydration. The highly porous cold-extruded structures exhibited greater hardness upon compression and better response in tensile tests compared to the denser hot-extruded structures. However, upon rehydration, the situation reversed, with the denatured protein structure in hot-extruded samples displaying improved mechanical tensile properties [52]. Notably, samples with smaller pores displayed faster water uptake and maintained better shape stability after dehydration and rehydration cycles.

This study presents a novel exploration into manipulating processing temperatures to induce structural changes in 3D printed protein meat analogues. Building upon existing research [46, 47], the study highlights significant variations in mechanical properties, suggesting that adjusting printing temperature can optimize final product characteristics for specific applications. This approach offers a promising foundation for material modelling without necessitating changes to the printing ink composition. Future investigations should delve into molecular-level interactions among ink components and further refine printing parameters such as speed, flow rate, and extrusion temperature to achieve targeted material properties effectively.

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Chapter 3

Additive Manufacturing Foams

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Orientation-Graded Morphologies in Microcellular Foams through Additive Manufacturing

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3.1 Abstract

We present experimental findings and modelling insights into the expansion of bubbles within a Newtonian fluid, observed during an advanced process integrating additive manufacturing and physical foaming techniques to fabricate complex microcellular foams with orientation-graded morphologies. A physical and sustainable blowing agent (CO_2) is solubilized into a biopolymer (PLA) that is 3D-printed through a cylindrical nozzle, and, at the nozzle outlet, the blowing agent foams inside the polymeric strand due to pressure drop or/and temperature rise. The experimental results show that, by engineering the temperature gradient at high printing velocities, corresponding to values of the Graetz number (i.e., the ratio of heat diffusion time and residence time inside the printer hot-end) larger than one, the microcellular foamed strands have a microstructure characterized by anisotropic bubbles oriented along two different directions. The microbubbles at the center of the strands are stretched in the extrusion direction, whereas those in the periphery are stretched radially. A foam morphology with microbubbles having two different orientations, smoothly changing within the cross-section, has never been reported before. We investigate the formation mechanism of such a morphology by simplified modelling and numerical simulations. Simulation results support the experimental findings and rationalize the effects of the Graetz

number on the microcellular foamed strands and on the expansion of gas bubbles in a Newtonian fluid, suggesting that the different orientations of the bubbles are due to the combined effect of high Graetz number and the radial expansion of the strand.

Graphical Abstract

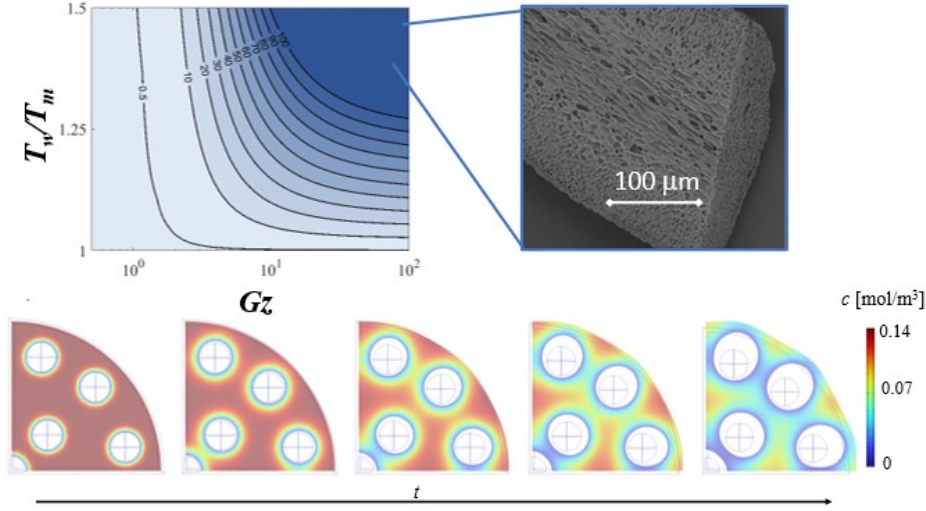


Figure 3.1. Graphical abstract.

3.2 Introduction

Natural lightweight materials, such as bamboo and beeswax honeycomb, exhibit intricate hierarchical structures meticulously designed to optimize specific properties or perform particular functions.[1] For example, natural cellular structures excel in stiffness-to-weight ratio, energy absorption[2, 3], thermal insulation[4], and magnetic resistance[5] compared to their dense counterparts. In human bones, a fine design of cell orientation and size allows to have highly anisotropic mechanical properties with the lowest possible weight. Butterfly wings feature a foamed hierarchical structure that brilliantly reflects energy while maintaining exceptional lightness, enabling flight[6]. Engineering applications have of-

ten been inspired by natural cellular materials, e.g., to optimize crash energy absorption[7], noise control, and sound damping[8], or to build lightweight construction[9], heat exchangers[10], and purifiers[11]. Microcellular foam fibers, with their unique combination of properties, such as lightweight, flexibility, and high porosity, offer a wide range of potential applications. For example, foamed fibers can be used in textiles and apparel as lightweight, insulating fabrics for clothing and outdoor gear or soft, comfortable filling materials for pillows, cushions, and blankets. On the other hand, the structures obtained by piling microcellular foam fibers can be employed in the automotive, medical and aerospace industry: as instance, in the automotive industry, they can be used as interior components (i.e., seat cushions, headrests, armrests, and door panels for comfort and weight reduction), sound insulators (e.g., under-hood and interior components to reduce noise pollution), and filters (air filters for improved cabin air quality). In additive manufacturing, many efforts have been made to produce cellular or mesh structures by extruding bubble-free polymeric strands in layers, where macroscopic porosity is generated by the gaps among the strands. The porous structure is then directly linked to the printing resolution, which results in a limited interstrand porosity. For instance, one of the most recent additive manufacturing techniques, i.e., two-photon polymerization, can achieve an interstrand porosity as small as 200 nm[12]. Despite reaching nanoscale porosity, this technique suffers from extremely long printing times for small volumes and is limited to millimeter-sized objects. Recently, three-dimensional (3D) printed foams with high porosity and intrastrand micropores have been produced using a newly developed technology, known as *in situ* Foam 3D Printing or Foam Additive Manufacturing, FAM, which can induce cell nucleation and growth through solubilization of blowing agents in the filaments[13, 14]. This technology has several advantages: (i) higher printing velocity thanks to the plasticization effect due to gas solubilization; (ii) higher specific mechanical and thermal properties; (iii) more degrees of freedom to tune material properties attained by changing the extruded strand density. The approaches proposed in the open literature, however, are seldom capable of attaining a fine control of the anisotropy of the bubbles, indeed a factor that, if overcome, would allow the production of objects with improved properties and promote wider adoption of additive manufacturing foam

applications. In extrusion-based additive manufacturing processes, it is well-known that, as the polymer is heated solely by conduction from the liquefier barrel, its rather low thermal conductivity, combined with the typically low residence time in the extruder hot-end, leads to large temperature gradients in the extruded strands[15]. Temperature gradients in the liquid flowing in the nozzle are a known source of problems as they might induce discontinuous flow conditions[16], irregular crystallization[17] or, in the case of FAM, nonuniform foaming[18]. In this paper, we demonstrate that what is believed to be a source of problems in the application of additive manufacturing to structured microcellular foamed strands is instead a possible route to the development of very interesting morphologies. We show that this seeming limitation can be a key factor in achieving strands with novel and potentially promising complex cell morphologies, opening the possibility of fully exploiting the rich design space offered by micro- and nanocellular complex structures. In fact, we engineered the development of proper thermal gradients inside extrusion-based AM (i.e., a Fused Filament Fabrication (FFF) printer) to achieve fine-tuning of cell morphology in the printed strands. We show that the presence of strong thermal gradients within the strand, when properly controlled, brings to the formation of a novel and innovative foamed structure with bubbles oriented in two different directions, a cell organization that we define “double morphology” (DM). By properly designing the printing velocity and the wall temperatures, we produced strands with DM with polylactic acid, PLA, i.e., a biodegradable and biobased polymer, blown with CO₂. We first report the experimental results, proving the ability to end up with such morphology and identifying the required operating conditions, then, by modelling the heat transfer and with the aid of a simplified bubble growth model, we generalize the approach to (hopefully) a wide variety of polymers.

3.3 Materials and Methods

PLA (grade NW4043D from NatureWorksLLC) was used in this study and its physical properties can be found in previous work by Tammaro et al[14]. PLA pellets were dried overnight at 60°C in an oven under vacuum conditions before any manipulation. A PLA filament (with a di-

ameter of 1.75 mm) was produced using a Composer350 extruder (from 3DEVO company, The Netherlands), whose process parameters, are given in previous work by Tammaro et al[14]. The extrusion process employed a screw rotation speed of 5 rpm, while the extruder zones were maintained at 150, 180, 200, and 190°C, respectively. A fan speed of 500 rpm was utilized at the die exit to facilitate rapid cooling of the polymer melt. A stable and consistent diameter of the filament was produced by cooling down the polymer in a water bath positioned at the extruder exit. The blowing agent, CO₂, was supplied by AirCos (Italy). A Prusa Research I3MK3S FFF 3D printer was then used to foam the filament. The foams were characterized to determine their bulk density, ρ , cell dimensions, and cell population density. The bulk density was measured according to ASTM D7710 by using an analytical balance (Mettler Toledo, Columbus, OH). To measure cell dimensions and ρ_b , the samples were first sectioned with a razor blade in liquid nitrogen and then coated with gold using a sputter coater. The cellular structure of the foams was investigated by using a scanning electron microscope (SEM, Hitachi TM 3000 SEM, Japan). The SEM images reported in this work were taken from randomly chosen cross-sections of the foamed samples. The cell dimensions were measured according to ASTM D3576 choosing lines in different directions on the analyzed cross sections. The cell density, ρ_b , was measured according to ASTM D792 choosing random cross sections. In particular, the cell population density was calculated $\rho_b = \frac{\rho_p}{\rho} \left(\frac{n}{A} \right)^{3/2}$, where ρ_p is the density of the solid sample and n is the number of cells in the area A of the SEM micrograph. Each foaming experiment was repeated at least three times to estimate the experimental error in cell characterization. The thermal behavior of PLA mixtures was investigated by means of a differential scanning calorimeter PerkinElmer DSC 8500 equipped with an IntraCooler III as refrigerating system. Dry nitrogen was used as purge gas at a rate of 30 mL/min. In order to calculate the crystallinity degree, the foamed strands were heated at 10°C/min from 0 to 200°C. To obtain precise heat capacity data from the heat flow rate measurements, each scan was accompanied by an empty pan run and calibration with sapphire. The crystalline weight fraction (w_c) of the materials was determined, after construction of the appropriate

baselines, from the first heating ramp, as

$$w_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta_c^0} \times 100 \quad (3.1)$$

where ΔH_m , ΔH_{cc} , and ΔH_c^0 are the melting enthalpy, the heat of cold crystallization (from 90 to 120°C), and the heat of crystallization of 100% crystalline PLA, equal to 111 J/g³⁹. Three replications were made for each sample in order to obtain an average value. The microcellular foams were mechanically characterized by a commercial microtensile tool from Hitachi, Japan, model 200N. The samples were fixed on the tool by gluing them on removable jaws. Each sample was subjected to tensile stress with constant displacement speed up to 30% deformation. The mean values and the standard deviation of the tensile strength, σ_{max} , were calculated over 11 samples. The measurements were conducted 1 week after the foam printing process to allow the escape of all the blowing agent. The process used to produce the microcellular foamed strands consists of the following stages: 1) solubilization of the blowing agent in the filament to be foamed, 2) control of the concentration profile of the blowing agent in the filament, 3) foaming at the exit of the printer nozzle, 4) stabilization of the foamed filament, 5) deposition of the foamed. All the experiments were performed at a fixed concentration of CO_2 in the filament equal to 8wt%. The sorption and desorption occurred offline, in a high-pressure vessel at controlled pressure (i.e., 20 bar) and temperature (i.e., room temperature equal to 25°C). The time of solubilization (4 days) of the filament was chosen much bigger than the characteristic diffusion time of CO_2 in PLA ($t = \frac{R^2}{D}$, $D = 20h$, where R is the radius of the filament, and D is the diffusivity of the blowing agent, equal to about $10^{-7} m^2/s$)^[5]. In order to quantify solubilization and desorption, two dimensionless times are defined: $\overline{t_{sol}} = \frac{t_{sol}}{\frac{R^2}{D}}$ and $\overline{t_{des}} = \frac{t_{des}}{\frac{R^2}{D}}$ where $(\overline{t_{sol}})$ and $(\overline{t_{des}})$ are the solubilization and desorption times (both at room temperature, 25°C). In this work, we investigate filaments solubilized with $\overline{t_{sol}} \gg 1$ and $\overline{t_{des}} \ll 1$, meaning that the blowing agent impregnates the entire filament section uniformly. The pressure vessel is a standard autoclave used for solubilization equipped with a pressure sensor, a temperature sensor and two automatic valves for inlet and outlet of the blowing agent, as detailed by Tammaro et al.^[19].

3.4 Results

The results are divided into the following three subsections: 1) Experimental campaign, 2) Heat transfer model, and 3) Bubble growth model. The first subsection, Experimental campaign, reports the results of the experiments made by FAM under different operating conditions. Microcellular foamed strands are characterized and process conditions in which the novel cellular double morphology is found are identified. The second and the third subsections present modelling results that can explain the experimental observations and can be used as a guide to the selection of the proper operating conditions to produce microcellular foamed strands with DM with different polymers.

3.4.1 Experimental campaign

A schematic description of the experimental setup is shown in Figure 3.2 a-b and the equipment is shown in Figure 3.2 c-d: the solubilized filament is pushed by the gears of the motor to pass through the cold-end (kept at ambient temperature) and the hot-end (kept at constant wall temperature through a PID control). These two zones are connected by a thermal bridge of 5 mm. In the nozzle, the demixing of the polymer/ CO_2 solution happens and micron-size bubbles nucleate inside the printed strand. The experiments were performed by printing in air at ambient conditions, with a nozzle placed about 10 cm above the printing plate to avoid any exit pressure that could build up in the strand in the region between the nozzle and the platform, and thus, to avoid any consequent deformation of the cellular morphology inside the strand. To keep the effect of the gravity force on the extruded strand at a minimum, we fixed the distance of the printing plate at 10 cm, so that the Galileo number, Ga , which is the ratio of gravity force and viscous force, $Ga = \pi(gLR_s^2\rho)/\eta \ll 1$, where g , L , R_s , ρ , and η are the gravitational acceleration, the total length and the radius of the strand, its density and viscosity, respectively. An extensive experimental campaign was carried out to investigate the effects of the feed rate, v_{in} (the velocity of the filament through the printer hot-end), and the hot-end wall temperature, T_w , on the morphology of the printed strands. In particular, to promote the formation of temperature gradients within the cross-section of the strand, we varied T_w between 440 and 560

K and v_{in} between 1 and 150 mm/s.

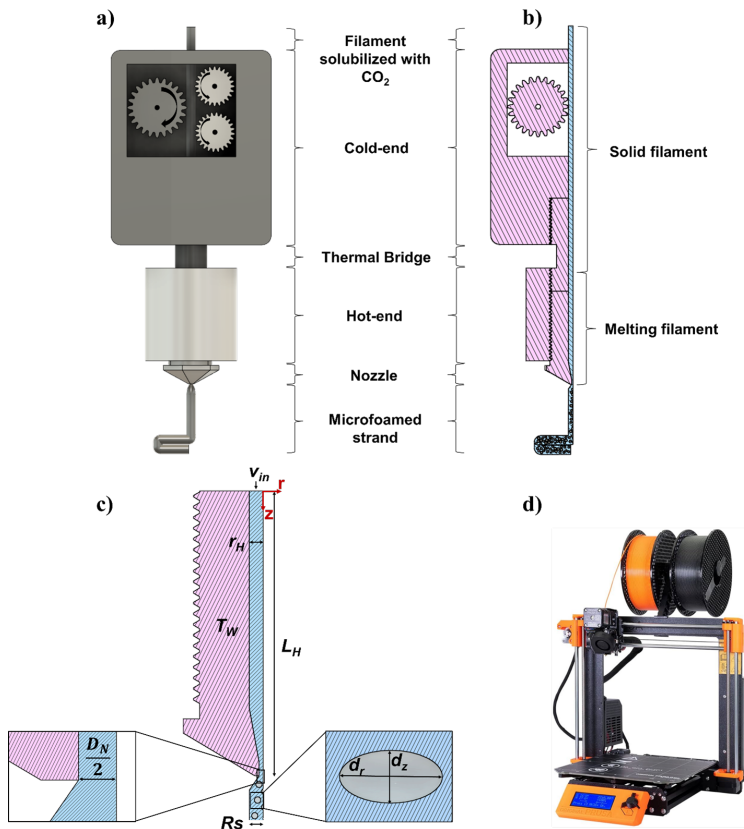


Figure 3.2. schematization of the additive manufacturing foam process. a) Sketch of the experimental setup; b) section of the experimental setup showing the change of state of the filament during printing; c) magnified view showing bubble formation at the exit of the nozzle; d) equipment used in the current work

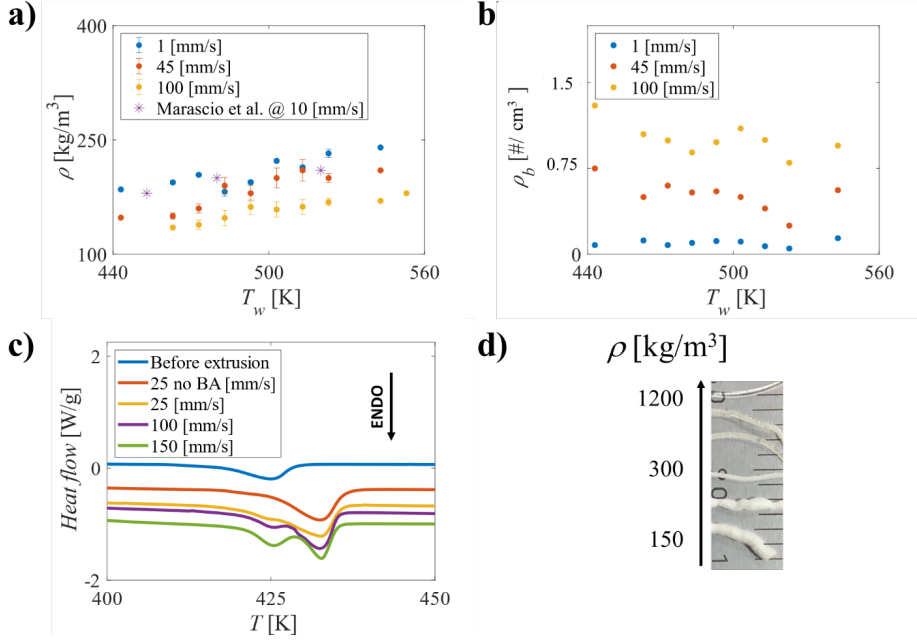


Figure 3.3. Study on the effects of printing velocity on 3D microcellular foamed strands. a) ρ as a function of T_w at three values of v_{in} and comparison with literature results; b) ρ_b as a function of T_w at the same three values of v_{in} as in panel a; c) effect of v_{in} on the melting behavior (formation of a double peak of melting); d) images of the foams produced in this work.

The measured strand density is shown in Figure 3.3a as a function of T_w at three different v_{in} -values (see legend). The density increases monotonically as a function of T_w and decreases with v_{in} . It is worth of noting that, for a standard extrusion process the plot of the density as a function of the extrusion temperature has a bell shape[20]. Our data are in good agreement with those reported by Marascio et al.[21]. Based on the existing literature[22], however, the strong dependence of the density on v_{in} was unexpected for a classical extrusion process. It is expected that the printing velocity influences the pressure in the nozzle, and, consequently, the so-called pressure drop rate, PDR , is usually defined as the ratio between the total pressure drop in the duct and the average residence time of the fluid in

it[23]. Considering a constant flow rate at the inlet of the duct, $PDR \propto v_{in}^2$, as detailed by Tammaro et al.[23]. Several authors[24, 25, 26, 27]report that, in foam extrusion, the PDR has minimal effects on the foam density, thus we speculate that the observed dependency of the density on v_{in} could be due to the possible non-uniformity of the temperature profile in the cross- section of the extruded strand. The presence of a significant temperature gradient inside the nozzle under specific operating conditions has been confirmed by numerous experimental studies[14, 15, 16]. Indeed, during 3D printing, strong radial temperature non-uniformity is usually encountered, and their magnitude depends on the printing velocity[16]. The higher the printing velocity, the lower the average temperature of the extruded strand; hence, foaming takes place in a liquid at higher viscosity and with a lower gas diffusivity, thus determining a decrease of the density by promoting setting mechanisms (such as crystallization) inside the foam and avoiding gas depletion through the boundaries. We further discuss the temperature non-uniformity in more detail in the next section, where the temperature profiles corresponding to our experimental conditions are estimated through modelling and numerical simulations. Another possible effect on the density of the foams is the gas lost during the passage of the material in the hot-end. In this work, we decided to neglect this effect because the residence time of the polymer in the hot-end (i.e., few seconds) is always much smaller than the characteristic diffusion time of CO_2 (i.e., few hours). No evidence of degradation, including colour change or smoke, was observed during the heating process. We attribute this to the polymer brief residence time in the heater and the minimal surface area exposed to the environment (i.e., water or oxygen). The measured cell densities of the strands are shown in Figure 3.3b as a function of T_w at the same values of v_{in} as in panel (a). The bulk density ρ_b is almost constant with T_w , but it increases by several orders of magnitude as v_{in} goes from 1 to 100 mm/s. Also in this case, we believe that this result is mainly due to the temperature non-uniformity described before that manifest at high v_{in} . A way to indirectly prove the actual relevance of temperature non-uniformity is to characterize the microcellular foamed strands at the nozzle exit by means of differential scanning calorimetry (DSC), as reported in Figure 3.3c. The percentage of crystallinity (measured according to the protocol detailed in Tammaro et al.[19]) increases with the feed rate, passing from 7 to 12 and,

then, to 15% for v_{in} equal to 25, 100, and 150 mm/s, respectively. The sample extruded at a low feed rate of 25 mm/s without a blowing agent (5%) exhibits lower crystallinity. The crystallinity of the sample referring to the filament after the solubilization and before the extrusion is 28% that is more crystalline than the produced strands. Interestingly, two melting peaks are clearly visible in samples produced at high printing velocity (see the yellow and violet lines in Figure 3.3c-d, corresponding to $v_{in} = 100$ and 150 mm/s, respectively), which mark the presence of two families of crystals[28]. We argue that those two families include: I) crystals created during the CO_2 absorption that have survived, flowing in the colder central zone, up to the nozzle, and II) crystals created during the foaming and during the fast cooling of the microcellular foamed strand outside the nozzle. Within this description, we argue that, at printing velocities larger than 45 mm/s, only partial melting occurs in the internal zone.

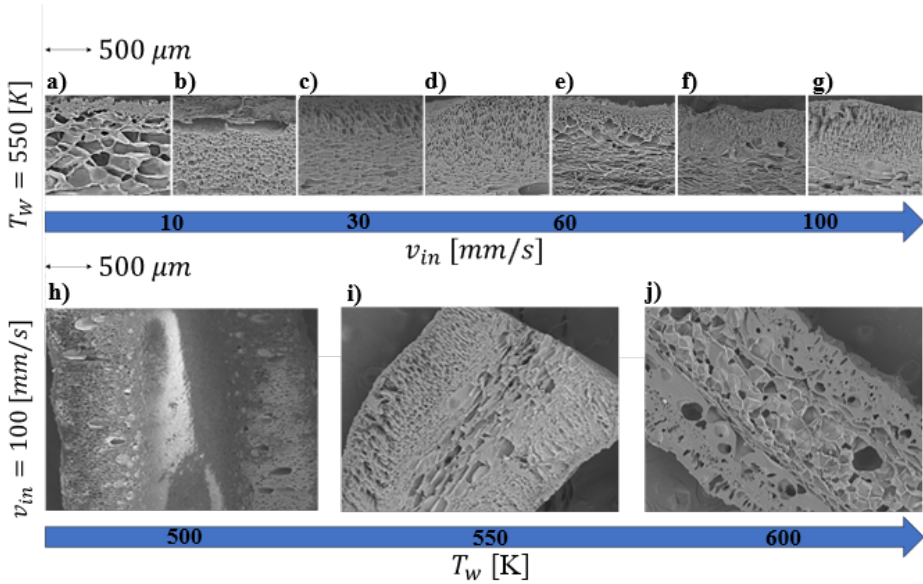


Figure 3.4. SEM analysis of the additive manufacturing foam strands. Top row: microcellular foamed strands obtained at $T_w = 500K$ and seven different values of v_{in} ; bottom row: microcellular foamed strands obtained at $v_{in} = 100$ mm/s and three different values of T_w .

Figure 3.4 shows SEM pictures of longitudinal sections of strands obtained at different values of v_{in} and T_w . The upper row, Figure 3.4a-g, shows the results at $T_w = 550$ K for various v_{in} -values. The bubble morphology significantly changes in terms of bubble size and orientation in the microcellular foamed strands. At very low v_{in} , such as 1 mm/s, the cells are coarse and slightly oriented in the extrusion direction, whereas, at $v_{in} > 10$ mm/s, the strand shows a peripheral layer of bubbles oriented differently with respect to those at the centre. The morphologies observed by varying T_w at $v_{in} = 100$ mm/s are shown in the second row, Figure 3.4h-j. At low T_w , the core of the strand is barely foamed, showing few very small cells; at intermediate T_w , the strand shows a clear change in morphology from the core to the peripheral region; finally, at high T_w , the bubbles close to the strand axis are surrounded by an external layer of cells that resembles a collapsed structure with a low density of cells and a broad cell size distribution.

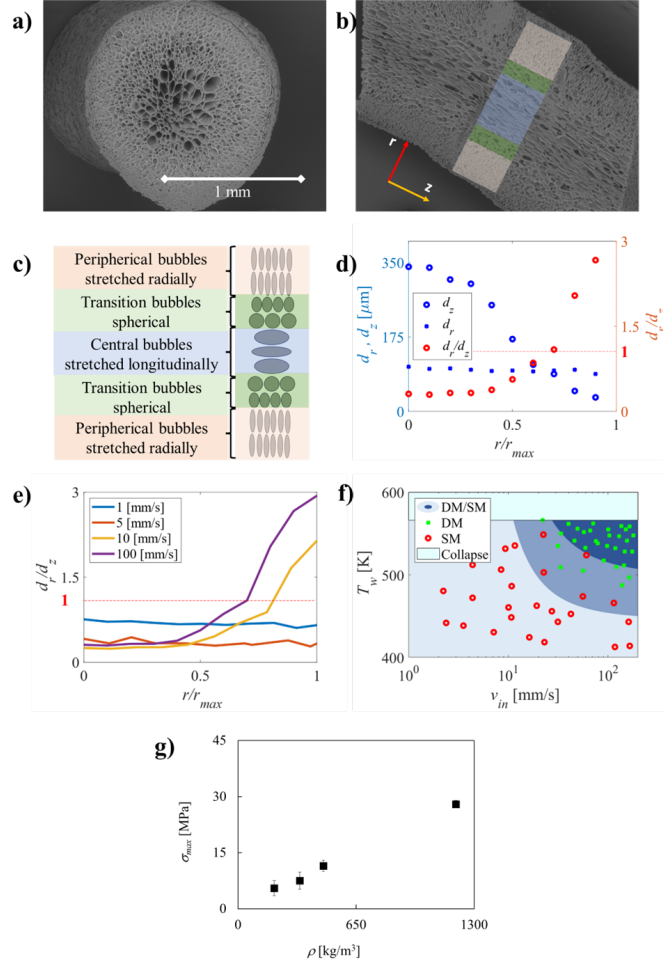


Figure 3.5. definition of the double morphology (DM). Cross-section (a) and longitudinal section (b) of a microcellular foamed strand with DM obtained at $T_w = 525$ K and $v_{in} = 100$ mm/s; c) schematic description of the double cell orientation, having cells oriented in the extrusion direction in the core and cells oriented radially in the periphery of the strand, within a smooth transition zone between them; d) radial profiles of cell dimensions across the longitudinal section of a strand with DM obtained at $T_w = 550$ K and $v_{in} = 100$ mm/s ($r_{max} = 1.2$ mm); e) cell size ratio radial profiles across the longitudinal section of a strand with DM obtained at $T_w = 500$ K and four values of v_{in} ; f) map of the morphologies obtained starting from a homogeneously saturated filament by tuning temperature and velocity; g) mechanical strength as function of the foam density.

It is interesting to notice that at large printing velocity and “intermediate” wall temperature (Figure 3.4i), a complex foam morphology is produced, consisting of “ellipsoidal” cells with two different orientations, as shown in detail in Figure 3.5a-b. The typical cross and longitudinal sections of a microcellular foamed strand are reported in Figures 3.5a and 3.5b, respectively, where it is apparent that bigger cells are present in the strand core and smaller ones in its periphery. The longitudinal section reveals the variation of the cell orientation along the radial direction of the strand: cells in the core (highlighted with a light blue colour in Figure 3.5b) are stretched in the extrusion direction (i.e., the z direction), whereas cells in the periphery (light red colour in Figure 3.5b) are stretched radially (i.e., the r direction); between these two zones, a transition region is present, which is characterized by almost spherical cells (in light green in Figure 3.5b). A schematic representation of the distribution of cell orientations on the strand longitudinal cross-section is shown in Figure 3.5c. To the best of our knowledge, this is the first observation of a foam morphology with coexisting cells having two different orientations, which we name “double morphology” (DM). This peculiar morphology resembles the macro/micro-morphology of the woodpecker’s beak and cranial bone[29]. Figure 3.5d reports the radial profiles of cell dimensions along the z -coordinate (dz) and r -coordinate (dr) as a function of the dimensionless radial position $r^* = \frac{r}{r_{max}}$, where r_{max} is the maximum radius of the microcellular foamed strand. The ratio $a_f = \frac{dz}{dr}$ is an anisotropy factor passing through the unit value for a spherical bubble. For $r^* \leq 0.5$, $a_f < 1$, i.e., the cells are oriented along the extrusion direction; on the other hand, for $r^* > 0.6$, the ratio a_f goes above 1, meaning that the cells are oriented in the radial direction, in between almost spherical cells are present. Hence, the DM is signalled by the passage across unity, i.e., sphericity, of the radial profile of the ratio a_f . Figure 3.5e shows a_f as a function of r^* at $T_w = 500\text{K}$ and four different v_{in} -values. At $v_{in} = 1$ and 5 mm/s (blue and red lines), a_f is almost constant and below 1 over the entire section of the strand, corresponding to a rather uniform morphology with cells elongated along the extrusion direction. On the other hand, at $v_{in} = 10$ and 100 mm/s (yellow and violet lines), a_f passes through the unit value at r^* around 0.5, corresponding to the formation of the DM. In particular, at the highest printing velocity, the ratio a_f becomes larger than 1 closer to the strand

axis and reaches a larger value at the strand periphery, thus, we can conclude that the DM is found above a critical v_{in} -value and that, at larger printing velocities, the bubble anisotropy in the radial direction becomes significantly more important. The results of the entire experimental campaign performed by varying T_w and v_{in} are summarized in Figure 3.5f, where green asterisks indicate conditions in which the DM was observed, and red circles indicate situations without DM. The cyan zone in Figure 3.5f represents the range of temperatures in which a collapse of the foam morphology is observed. The background color of Figure 3.5f qualitatively indicates conditions where the DM is present, with darker areas characterized by a more definite DM. It is evident that the DM occurs only at high v_{in} and within a range of T_w between 470 and 570K. The speed threshold above which both orientations are present in the strand decreases as T_w increases. So far, we have loosely spoken of “high” velocities or “high” wall temperatures, but a sounder evaluation requires a nondimensional quantification of the relevant factors that determine the formation of different morphologies. As we believe that such features descend from the presence of temperature non-uniformity in the extruded strand, it is useful to evaluate the Graetz number, defined as the ratio of heat diffusion time with residence time inside the printer hot-end, i.e., $Gz = \frac{\tau_{diff}}{\tau_{res}}$. This dimensionless group provides a measure of the relative magnitude of heat transfer by convection and conduction: when $G \ll 1$, the polymer flowing along the hot-end is expected to reach a uniform temperature close to the temperature of the metal wall, whereas, at $Gz \gg 1$, a non-uniform temperature radial profile is expected, with a colder zone at the center and a hotter zone in the periphery. The heat diffusion time inside the hot-end can be estimated, in our case, as $\tau_{diff} = \frac{r_H^2}{\alpha} \approx 10s$, where r_H is the heater radius (equal to 1 mm in our device, see Figure 3.2) and α is the thermal diffusivity of PLA (around $0.1 \text{ mm}^2/s$ based on the literature[22]). The characteristic residence time inside the hot-end is $\tau_{res} = \frac{L_H}{v_{in}}$, where L_H is the heater length (15 mm in our device, see Figure 3.2). In our operating conditions, by tuning v_{in} , τ_{res} ranges between 0.1 and 20 s. Consequently, our 3D printing process was carried out with $Gz \in [0.7, 100]$. The formation of a DM was found only at $Gz \gg 1$, i.e., in the presence of a clear temperature non-uniformity. The connection among v_{in} , Gz and flow rate is given in Table 3.1. The strand mechanical strength, σ_{max} , was measured

Value	v_{in}	Gz	Flow rate mm^3/s
MIN	1	0.7	2.4
MAZX	150	100	360

Table 3.1. the minimum and maximum values of v_{in} , Gz and flow rate.

over the entire range of densities obtained, Figure 3.5g. As expected, σ_{max} monotonically increases with the density and the σ_{max} -value of the “less foamed” sample, i.e., at the highest ρ , is in good agreement with the ultimate tensile strength of PLA reported in the literature [30].

3.4.2 Heat transfer modelling and simulation

The effect of Graetz number on the temperature profile in the PLA strands in the hot-end of the 3D printer was investigated through finite-element numerical simulations of the relevant transport phenomena. To this end, we used the commercial software COMSOL Multiphysics V6.1[31]. The mathematical model of the system is composed of the mass, momentum, and thermal energy balance equations for the PLA flowing from the thermal bridge to the nozzle exit (see Figure 3.2) under assumed steady-state conditions. The rheological behaviour of the fluid can be considered Newtonian since the Weissenberg number, $Wi = \lambda \bar{u} / (2r_H)$, measuring the ratio of the fluid relaxation time, λ , and the process characteristic time, $2r_H / \bar{u}$, with $\bar{u}$ the filament inlet characteristic velocity, is in the order of 10^{-3} (by taking $\lambda = 0.01$ s[32], namely, the relaxation time of PLA at the lowest temperature considered in the experiments, $T_w = 453$ K and $\bar{u} = 0.15 \times 10^{-3}$ m/s). The Reynolds number inside the nozzle is estimated as $Re = \rho v_{in} D_N / \eta$, with $\rho = 1200 \text{ kg/m}^3$ the fluid density, $v_{in} = 0.15$ m/s the maximum printing velocity, $D_N = 2 \times 10^{-3}$ m the heater diameter, and $\eta \simeq 2000$ Pa·s the fluid viscosity at 180°C , yielding $Re = 1.8 \times 10^{-4}$, so inertial terms in the momentum balance equation are negligible. Constant density (incompressibility) and thermal conductivity of the fluid are also assumed. Hence, the model reads

$$\nabla \cdot \mathbf{u} = 0 \quad (3.2)$$

$$\nabla \cdot [-p\mathbf{I} + 2\eta(T)\mathbf{D}] = 0 \quad (3.3)$$

$$\rho c_p \mathbf{u} \cdot \nabla T = k \nabla^2 T + \boldsymbol{\tau} : \nabla \mathbf{u} \quad (3.4)$$

with ∇ the “nabla” operator, $\mathbf{u}$ the fluid velocity, p the pressure, $\mathbf{I}$ the identity tensor, $\mathbf{D} = [\nabla \mathbf{u} + \nabla \mathbf{u}^T]/2$ the rate-of-deformation tensor, c_p the fluid specific heat, T the temperature, k the fluid thermal conductivity, and $\boldsymbol{\tau} = -p\mathbf{I} + 2\eta(T)\mathbf{D}$ the Newtonian stress tensor for an incompressible material. According to the literature [33], the viscosity and diffusivity (D) of PLA have an Arrhenius-like temperature dependency, reading

$$\eta(T) = \eta_{ref} e^{-\frac{E_a}{R}(\frac{1}{T_{ref}} - \frac{1}{T})} \quad (3.5)$$

$$D(T) = D_{ref} e^{-\frac{E_b}{R}(\frac{1}{T_{ref}} - \frac{1}{T})} \quad (3.6)$$

with $\eta_{ref}=2000$ Pa s, $D_{ref} = 0.7 \times 10^{-9}$ m^2/s , $E_a=31984$ J/mol, $E_b=2341$ J/mol, $R=8.214$ J/(mol K) the universal gas constant, and $T_{ref}=473$ K. For simplicity, Equation 3.5 was used to describe the rheological behaviour of the material also below its melting temperature, namely, for simulation purposes, the solid PLA has been treated as a liquid with a very large viscosity. The values of PLA specific heat and thermal conductivity were set to 1800 J/(kg K) and 0.163 W/(m K)[34], respectively.

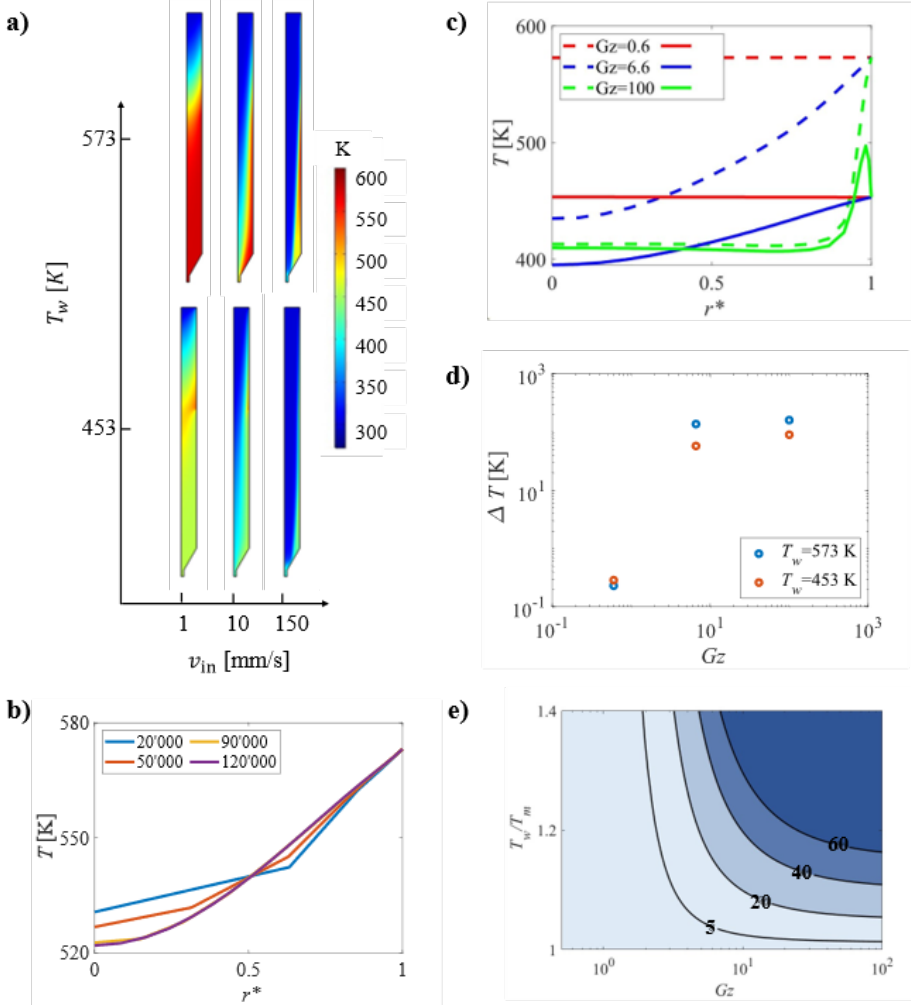


Figure 3.6. analysis on the filament temperature during the 3D printing process, via computational methods. a) Colour maps of the steady-state temperature field inside the nozzle of the 3D printer at different values of the printing velocity and temperature at the nozzle wall; b) temperature profile along the nozzle exit radius at $v_{in} = 150$ mm/s, $T_w = 573$ K, and four different mesh resolutions (the legend reports the number of triangular mesh elements); c) temperature of the polymer at the nozzle outlet as a function of the radial coordinate at different values of Gz and $T_w = 453$ and 573 K (solid and dashed lines, respectively); d) maximum difference between T_w and T at the nozzle outlet as a function of Gz at $T_w = 453$ and 573 K; e) contour plot of ΔT as a function of Gz and $T_w/T_{melting}$

The geometry of the computational domain mimics that of the actual printing nozzle and is shown in Figure 3.6a: by exploiting the axial symmetry of the nozzle of the printer, a 2D axisymmetric geometrical domain is implemented, where the symmetry axis is the vertical side on the left. Concerning the fluid dynamic boundary conditions, axial symmetry is imposed on the channel axis, an outflow condition at atmospheric pressure is imposed on the nozzle outlet (bottom horizontal boundary), no-slip/no-penetration conditions are imposed on the channel wall (right boundary), and a fully developed velocity profile is imposed at the channel inlet with flow rates equal to 0.13, 1.3, and 13 mm^3/s , corresponding to the printing velocities mentioned above. Regarding the thermal boundary conditions, the fluid enters the nozzle at 298K (top boundary), axial symmetry is imposed on the axis, a null conductive flux is imposed on the outlet section, and a piecewise temperature profile is imposed along the outer wall: in particular, the wall temperature linearly increases from 298K to T_w within 8 mm from the inlet, then it is fixed at T_w until the nozzle outlet. Such boundary condition accounts for the increase of temperature from room temperature to T_w that, in a standard FFF printer, happens in the thermal bridge (the parts that joins the cold- to the hot-end [35]). The model is solved at the steady-state by the finite element method on an unstructured grid made of 120'000 triangular elements, which proved to be sufficient to achieve the numerical convergence in the worst case, i.e., at the largest v_{in} - and T_w -values (see Figure 3.6b). The model was solved under operating conditions among those applied in the experiments: in particular, two wall temperatures ($T_w = 453$ and 573 K), and three printing velocities ($v_{in} = 1, 10$ and 150 mm/s) were considered. Figure 3.6a shows the temperature field at these six operating conditions. Only at the lowest v_{in} (1 mm/s, corresponding to $Gz = 0.6$), the temperature of the fluid is uniform at the nozzle exit. At $v_{in} = 10$ and 150 mm/s (corresponding to $Gz = 6.6$ and 100), a large portion of the filament remains at relatively low temperature up to the converging section. The radial profiles of the polymer temperature at the nozzle exit are shown in Figure 3.6c. At $Gz = 0.6$, the temperature is uniform both at $T_w = 453$ and 573 K (red solid and dashed lines, respectively), whereas, at $Gz = 6.6$, the temperature decreases monotonically from the periphery to the centre of the nozzle both at $T_w = 453$ and 573 K (blue solid and dashed lines, respectively); at

Gz = 100, the temperature decreases monotonically from the periphery to the centre of the nozzle at $T_w = 573\text{K}$ (green dashed line), whereas, at $T_w = 453\text{K}$, there is a slight maximum of the temperature close to the wall due to the viscous dissipation followed by a temperature decrease due to the convective heating when proceeding towards the centre of the strand (green solid line). The difference $\Delta T = T_w - T|_{r=0}$, is plotted as a function of Gz in Figure 3.6d. The simulation results confirm that, at low Gz, the temperature is uniform ($\Delta T \approx 0$), whereas, at high Gz, $\Delta T \approx 100\text{K}$. It can also be noted that, for the operating conditions under investigation, a larger T_w implies a larger ΔT . Finally, Figure 3.6e shows the contour plot containing the ΔT isolines as a function of Gz and T_w/T_m , where $T_m = 433\text{K}$ is the melting temperature of PLA based on the DSC results. The isolines at $\Delta T > 90\text{K}$ in Figure 3.6e correspond to the zone in which the DM was observed in the experiments (Figure 3.5f): these results confirm that the novel cellular morphology is attained in presence of strong temperature non-uniformities in the printed polymer strand and suggest that the DM can be achieved at high T_w/T_m and Gz.

3.4.3 Bubble growth modelling and simulation

In this section, a very crude model of the bubble growth in the strand coming out the nozzle is proposed to interpret the experimental evidence. In particular, our goal is to understand how the orientation of the bubbles depends on their position in the strand. For the sake of simplicity, we just consider initially spherical bubbles much larger than the nucleation seeds. In this way, their growth will qualitatively signal the anisotropy, if any, related to the different operating conditions modulated by the Graetz number. The three-dimensional computational domain for such simulation is shown in Figure 3.7: we consider one quarter of a cylindrical strand slice with a height, H , $\overline{AD} = \overline{BE} = \overline{CF} = 600\mu\text{m}$, and initial radius, R_s , $\overline{AB} = 500\mu\text{m}$. Five initially spherical gas bubbles (B1, B2, B3, B4, and B5 in Figure 3.7) with equal radius $R_{0b} = 50\mu\text{m}$ are distributed within the domain with the centers having coordinates x-y-z: B1) 0-0-H/2, B2) $R_s/3-R_s/3-H/2$, B3) $2R_s/3-2R_s/3-2H/3$, B4) $R_s/3-2R_s/3-2H/3$, B5) $2R_s/3-R_s/3-2H/3$. The bubbles are treated as ‘holes’ in the computational domain, so no balance equations are solved in the gas phase. The driving force for the bubble expansion is the difference between the gas pressure

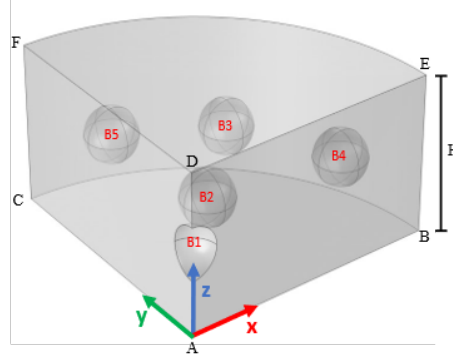


Figure 3.7. Schematic picture of the computational domain used in bubble growth simulations and the initial positions of five bubbles (B1, B2, B3, B4 and B5) inside the domain.

inside the bubble, $p_g(t)$, and the ambient pressure, p_a . Assuming the liquid phase to be incompressible and inertialess, its dynamics is governed by the mass, momentum, and energy balance equations in the Stokes formulation ($Re \ll 1$). As initial condition we impose zero velocity. The boundary on EBCF is:

$$[-p\mathbf{I} + 2\eta(T)\mathbf{D}] \cdot \mathbf{n} = -p_a \mathbf{n} \quad (3.7)$$

where $\mathbf{n}$ is the outwardly directed unit vector normal to the boundary. Symmetry on the other boundaries (ABED, ACFD, ABC, DEF) is imposed. Since the fluid is incompressible, any increase in bubble volume produces a corresponding expansion of the domain, working against the external pressure. At the bubble boundaries, the fluid traction is balanced by the gas pressure and the surface tension force:

$$[-p\mathbf{I} + 2\eta(T)\mathbf{D}] \cdot \mathbf{n} = -p_g \mathbf{n} + \sigma \mathbf{n} \nabla \cdot \mathbf{n} \quad (3.8)$$

where σ is the surface tension and $\mathbf{n}$ the outwardly directed unit vector normal to the boundary. The concentration of the gas in the liquid, c , is assumed to be governed by a simple Fickian diffusion equation:

$$\frac{\partial c}{\partial t} = D(T) \nabla^2 c \quad (3.9)$$

where D is a characteristic diffusivity of the blowing agent into the polymer (assumed to be temperature-dependent based on Eq. 3.6). The concentration of the gas at the bubble-liquid interface is given by the Henry's law $c = Hp_g$ where H is Henry's constant. As initial condition for the concentration, we impose $c = Hp_{sol}$, with $p_{sol} = 3\text{bar}$. The boundary condition on EBCF is $c=0$. Symmetry of the concentration field on the other boundaries of the computational domain (ABED, ACFD, DEF and ABC) is assumed. Mass conservation across the fluid-bubble interface implies[30]

$$\frac{d}{dt}\left(\frac{p_g V_b}{RT}\right) = D(T) \int \nabla \cdot \mathbf{n} dA \quad (3.10)$$

The values of the physical parameters of the PLA/ CO_2 system in the typical process conditions (i.e., at 555K) are $H=1 \text{ mol}/(\text{atm } m^3)$ and D as reported in Eq.3.6.

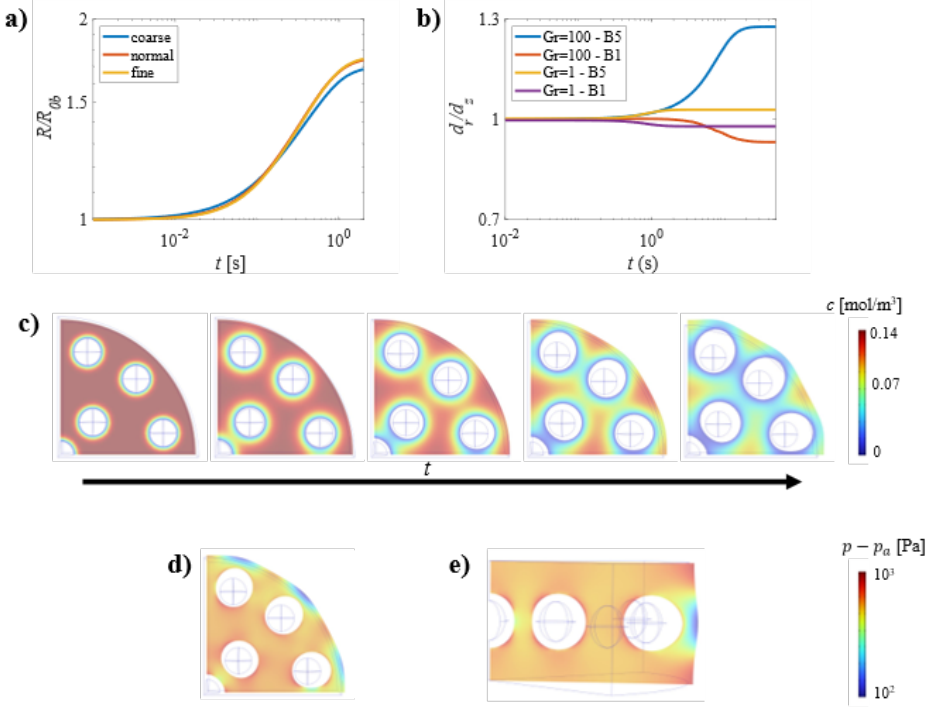


Figure 3.8. bubble growth simulations. a) Average radius of a bubble as a function of time at different numbers of elements of the mesh (see legend); b) time history of the ratio a_f with reference to two bubbles and two Gz -values (see legend); c) gas concentration field on the xy-plane at $z = H/2$ at five different time instants during bubble growth; d) pressure field on the xy-plane at $z = H/2$ and e) pressure field on the plane passing through the origin and the centres of the bubbles B1, B2, and B3. All the snapshots refer to a simulation at $T_w = 555\text{K}$ and $Gz = 100$.

The energy balance on the liquid phase reads:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p \mathbf{u} \cdot \nabla T = k \nabla^2 T + \boldsymbol{\tau} : \nabla \mathbf{u} \quad (3.11)$$

Viscous dissipation is accounted for in the thermal energy balance, where the velocity gradient in the fluid is generated by the bubble growth. To account for the cooling through the external surface, we impose room tem-

perature and free air convection on the external boundary (EBCF) with a convective heat transfer coefficient, $h = 3 \frac{W}{m^2 K}$ [36]. Symmetry of the temperature field on the other boundaries of the computational domain (ABED, ACFD, DEF and ABC) is assumed. Adiabatic conditions are set at the bubble surfaces; hence, we neglect the expected cooling of the polymer taking place during the fast expansion of the bubbles. The initial radial profile of the temperature in the strand (either uniform or nonuniform) is considered equal to the profile at the nozzle exit computed in the previous section. The viscosity and diffusivity of the PLA and their dependencies on the temperature are set as in Eqs. (3.5)-(3.6). We, thus, neglect the plasticization effect of the blowing agent on both transport properties. Due to the bubble expansion, the computational domain deforms during the simulation. The Yeoh method is used to smooth the deformation of the mesh elements [31, 3]. A mesh convergence study was performed on a test case with a temperature profile obtained at $T_w = 555$ K and $Gz = 100$, using three different meshes. Mesh convergence was evaluated in terms of $R/R_0 b$, where R is defined as the mean of the dimensions of the bubbles in the radial and axial directions, $R = (d_r + d_z)/2$ (see Figure 3.8a). The two finer meshes give very similar results, so the mesh with 140'000 tetrahedral elements was used. To deal with the large deformations of the bubbles when they get closer, mesh refinement is performed, when necessary, thus ensuring the presence of a minimum number of elements in the liquid film between the bubbles. It is worth remarking that, like all the sharp-interface methods, the technique used in this work does not allow to deal with bubble coalescence. On the other hand, it allows to give a very accurate description of the stress fields in the thin layers in between the bubbles, which are relevant for the prediction of the foam morphology. Figure 3.8b reports the time history of the ratio a_f of the bubble B1 (at the centre of the strand) and B5 (in the periphery of the strand) at $T_w = 555$ K and $Gz = 1$ and 100. At $Gz = 1$, the bubbles B1 and B5 (represented by the yellow and violet curve, respectively) are both almost spherical (i.e., $a_f \approx 1$) over the entire time of the simulation. At $Gz = 100$, the bubble B5 is strongly stretched in the radial direction, with $a_f \gg 1$, whereas the bubble B1 is stretched in the extrusion direction with $a_f < 1$. In this latter condition, the very large viscosity of the colder PLA close to the symmetry axis significantly slows down the growth of bubble B1 with respect to

bubble B5. The simulation results support the argument that the different orientations of the bubbles can be attributed to the combined effects of high temperature non-uniformity and radial strand expansion, yielding a preferential bubble growth in the extrusion direction at the strand axis and in the radial direction at the strand periphery. Figure 3.8c shows the gas concentration field on the xy-plane at $z = H/2$ at five successive time steps for $T_w = 555\text{K}$ and $Gz = 100$. Incidentally, it should be noted that the intersections between the plane and the bubbles show that the cross sections of the three bubbles on the periphery (B3, B4, and B5) are stretched radially, whereas those of the internal bubbles (B1 and B2) remain almost circular for the entire simulation time, confirming the presence of the DM. The colours represent the gas concentration in the polymer and show that the blowing agent is consumed faster in the periphery of the strand due to the transport towards the ambient and the faster growth of the bubbles in the region with a larger diffusivity and a lower viscosity. The viscosity field (arising from the temperature field) implies that the bubbles in the peripheral region of the strand grow faster than those in the centre and this, in turn, implies that they reach larger final volumes being able to expand in the radial direction free from obstacles. On the other hand, the external bubbles hinder the radial growth of the internal ones, even squeezing them in the extrusion direction, as it can be deduced from Figures 3.8d and 3.8e, which display the field of the relative pressure, $p - p_a$, on the planes at $z = H/2$ (both at $T_w = 555\text{ K}$, $Gz = 1$, and $t = 1\text{ s}$). A limitation of our very simple model for the anisotropic growth of the bubbles is the assumption of identical nucleation density and time in the strand. This assumption implies the complete negligibility of temperature and stress dependence of the nucleation. Needless to say, this assumption can result in a quantitative mismatch between experimental and numerical results in terms of bubble size. Nevertheless, the model provides a strong argument to explain the formation of the DM. Of course, a more detailed modelling will be needed to address the bubble growth quantitatively.

3.5 Conclusion

In this work, we report experiments and modelling of the production of microcellular foamed polylactic acid (PLA) strands with complex cell morphologies, obtained by a cost-effective additive manufacturing foam

technology. The results of an extensive experimental campaign show insightful maps of bubble morphology within microcellular foamed strands of PLA blown with CO_2 as a function of the design parameters, namely, the temperature of the printer hot-end and the printing velocity. It appears that, at large values of the Graetz number, the presence of temperature gradients in the cross-section of the strand at the exit of the nozzle is the main cause of the formation of the double morphology. Our results can be summarized in three key points: - the ability to produce microcellular foamed strands with cells having two orientations (radial in the periphery and longitudinal in the centre of the strand), named double morphology (DM), which resembles the macro/micro-morphology of the woodpecker's beak and cranial bone[29]; - the engineering of the process conditions for the formation of different DMs: in particular, the key parameter was found to be the Graetz number, Gz , i.e., the ratio of heat diffusion time and residence time inside the printer hot-end, which must be much larger than one to induce a temperature non-uniformity in the strand being foamed. The map of theoretical conditions (hot-end temperature and Gz) allowing the production of the desired DM has been validated by an extensive experimental campaign and, in view of its dimensionless formulation, can be potentially extended to other polymeric systems; - the understanding of the DM formation mechanism through a modelling of bubble growth in media having non-uniform temperature-dependent transport properties: this explains why, in the periphery of the strand, the bubbles preferentially grow in the radial direction. The results presented in this work give a better understanding of the foaming mechanism in the innovative additive foam manufacturing process and open the possibility of fine-tuning the orientation of cells inside printed strands, yielding sustainable-by-design printed lightweight structures with peculiar mechanical, thermal, and electrical properties. Graded foams, varying in density or morphology, often excel in balancing multiple properties compared to those with uniform structures. For instance, Bao et al.[37] demonstrated that polystyrene foams with cells oriented perpendicular to the impact direction exhibit enhanced mechanical properties. This improvement is attributed to several factors: increased solid material on the fracture surface, finer cell distribution, higher energy absorption during crack propagation, and potential molecular chain reinforcement induced by bubble-shearing. This work presents a new approach

to control and design ad-hoc anisotropic graded cell morphology for engineering applications in different fields.

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Chapter 4

Modelling and Validation of a Starch-Based Extrusion Die

This chapter is based on the original version of the scientific paper published in the AIP Conference Proceedings in May 2024. The paper is available at: <https://doi.org/10.1063/5.0204565>.

Validated Modelling of Complex Geometry Dies for Extrusion Foaming of Starch-Based Mixtures

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4.1 Abstract

Biobased materials offer a good alternative to the widespread use of fossil-based plastic. Foamed plastics used in various industries such as packaging, automotive, marine, and aerospace may result in sea, soil, and air pollution due to insufficient waste management systems. One of the most abundant biobased materials is starch derived from natural sources such as potatoes, tapioca, and corn. This class of materials can be handled as a thermoplastic material and employed in the foaming extrusion process by using plasticizers (such as water and glycerol) and other additives. Starch foams as a biobased and biodegradable product could be a promising alternative to expandable polystyrene (EPS) or expanded polypropylene (EPP). Their application remains, however, difficult due to issues related to moisture content and irregular swelling at the die exit, both of which affect the final product properties and well-defined shape of an extrudate. Typically, to obtain the required shape of the extrudate, a die with an approximate shape is created and iteratively adjusted based on the quality of the extrusion until the shape matches the desired one, which is still considered an art. This work aims to develop and validate a fluid dynamics model for starch-based mixtures flowing in a die and relate the

shape of the foamed extrudate cross-section with the predicted die geometry and estimated flow conditions to reduce trial and error iterations. The calculated pressure drop and velocity profile are compared to experimental data. Also, the die swell phenomenon (or Barrus effect) is investigated by numerical simulation to predict the final shape of the extrudate.

4.2 Introduction

Starch-based plastics can be an alternative to replace fossil-based materials. Pollution generated by the excessive consumption of fossil-based, not degradable is first destructive to the environment and then to living creatures. Plastic pollution impacts various terrestrial habitats, including the sea, soil, and air. [1]. Single-use plastics have a significant influence on pollution. For example, foamed packaging material can greatly impact the environment when it is not collected and recycled. Naturally occurring biodegradable plastics can contribute to the solution. Among all biobased products, starch plays a key part; although the usage of starch-based films is known, applications involving light thick foams are just starting. Starch may be used as a thermoplastic material for foaming extrusion as a green alternative to extruded polystyrene (EPS) or extruded polypropylene (EPP) [2, 3]. The most typical characterization methods used in the industrial world to evaluate foams are foam density, expansion index, recyclability, mechanical properties, pricing, and dimensional precision [4, 5, 6, 7, 8]. The dimensional precision of the final foamed product obtained by a die is one of the most challenging properties for the engineering of a stable foam extrusion process, and it seems entirely dependent on die design. In the past, the die design was considered an art and the optimization of the shape of the die was still based on trial-and-error methods. For example, it is known that to obtain flat profile surfaces when starting from a rectangular die, the introduction of an equal curvature on all the sides of the exit of the die is needed to compensate for the effect of the die swell [9], which is related to the release of the elastic energy held by the material when it is no longer constrained by the walls and is free to expand. In the case of a Newtonian fluid, the die swell can be explained by the reorganisation of the velocity profile, whereas elastic

recovery can be attributed to viscoelastic materials [4, 5, 10]. Understanding the flow behaviour, which is linked to all the viscoelastic properties of the fluids coupled with the die design, could be an essential element for governing the extrusion in terms of pressure control and in terms of controlling the final foamed shape. This is challenging in viscoelastic materials because, once the melted material approaches the converging zone of the die on the fluid, a considerable contraction deformation occurs, resulting in a flow field characterized by both shear and elongational components [11]. In addition to the natural swell of a polymer, foaming also affects the expansion at the die exit and makes it more difficult to achieve the desired final shape of the cross-section of the profile. Die swell simulations are always challenging and becoming increasingly complex year by year, improving the results by implementing accurate viscoelastic models [11], 3D geometries [12], and temperature fluctuation [13]. In the present work, we employ Computational Fluids Dynamics (CFD) simulations to reduce the trial-and-error approach in die design and to obtain a specified desired final shape of the cross-section of the foamed product.

4.3 Materials and Methods

Simulations and experimental trials through the simulated dies have been performed. In the experimental part, the starting point was a powdered starch mixture based on potato starch. Native potato starch contains around 18% moisture, by mixing with other ingredients, the moisture content (MC) was controlled. The natural water content present in the starch was used as a blowing agent. The moisture content varied between 13 – 17%. Potato starch is provided by KMC (Denmark). A 45 mm twin-screw extruder, with an L/D of 42, six gravimetric feeders, a blowing agent dosing station, and a Torpedo melt cooler were used at the SULZER plant (Switzerland). The powdered starch mixture was fed into the extruder. The pilot line extruder includes 11 heating sections. A temperature profile ranging from 50°C to 145°C, and a die temperature of 180°C were used to ensure a smooth surface of the foamed product. The rpm of the screws was set to 135. The temperatures in the melt cooler zone were changed to modify the intrinsic viscosity of the mixture and control the pressure drop in the die. The circular die was produced by stainless steel by ADM laser

(Italy). For the numerical simulations, COMSOL Multiphysics v6.0 was used.

4.4 Discussion and Results

The die geometry chosen for performing the experiments and simulations is reported in Figure 4.1. The inlet dimension is denoted by D_{in} , the outlet dimension is D_{out} , the convergence angle is θ , the length of the convergence section is L_{conv} , and the inlet length is denoted by L_{in} , respectively. The screw rpm, the machine temperature profile and flow rate were configured in the extruder software. In Table 4.1 the values of the geometrical parameters are listed.

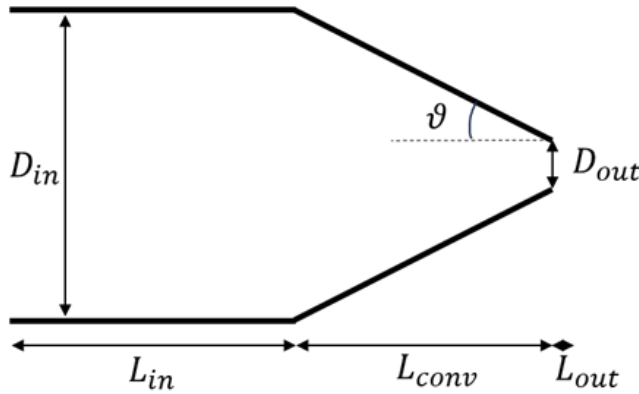


Figure 4.1. Geometry of die.

D_{in}	27 [mm]
D_{out}	4.5 [mm]
L_{in}	12 [mm]
L_{conv}	25.5 [mm]
θ	24°

Table 4.1. Geometrical parameters of the die.

Several factors influence the extrudate shape during die swell measurements; the most prominent ones are listed below:

- a) gravity's effects on the foamed extrudate's final shape.
- b) the transient zone of extrudate diameter from the nozzle exit to the steady state zone.
- c) the oscillation of the pressure drop.
- d) the oscillation of the flow rate and temperature in the die region.

4.4.1 Mathematical Model

The numerical simulations are carried out by solving the mass and momentum balance to estimate the pressure drop, velocity profile, and die swell prediction. An axis of symmetry can be identified based on the shape of the extrusion die, as shown in Figure 4.2, hence the problem was simulated in a 2D axisymmetric domain. Different die convergence angles were simulated. For brevity, only the results corresponding to the angle used in the experiments are shown in this paper. The length of the free boundaries has been chosen sufficiently long to avoid any influence of the inlet and outlet boundary conditions on the simulation results. The origin of the axes was set at the die exit on the symmetry axis. We utilised a time-dependent study with the addition of the COMSOL Polymer Flow module. The moving mesh technique was employed. The simulations were conducted by resolving the momentum balance equations governing the fluid dynamics of the melted polymer through the die and the surrounding environment. We assume a single-phase system, incompressible fluid, and laminar flow conditions due to the low Reynolds number. The effect of gravity was left out because the viscous forces are greater than the gravitational ones. The fluid was at the temperature imposed at the inlet, the temperature was supposed to be the melt cooler temperature, 130°C . The die walls are at 180°C , while the free surface was set to ambient temperature and surface tension was not included in the momentum calculation. Although the energy equation was not numerically solved, the thermal conditions of the system enabled the determination of the rheological parameters utilised in the simulations. With these assumptions, the mass

and momentum balance equation for starch material read as:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \boldsymbol{\sigma} + \mathbf{F} \quad (4.1)$$

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

Where $\mathbf{u}$ is the velocity, p is the pressure, ρ is the density, ∇ is the nabla operator, $\mathbf{F}$ is an external body force, and sigma is the total stress tensor and is defined as

$$\boldsymbol{\sigma} = -p\mathbf{I} + 2\mu_p\mathbf{K} + \mathbf{T} \quad (4.3)$$

where $\mathbf{I}$ is the identity matrix, $\mathbf{T}$ is the extra stress contribution of the polymer and $\mathbf{K}$ is the rate of strain tensor which is defined as

$$\mathbf{K} = \mu_s(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (4.4)$$

The rheological model used was the Oldroyd-B accounting for elasticity. This is at variance with the power law model used by Della Valle et al. [14] which includes shear-thinning but no elasticity. The model parameters (relaxation time λ , solvent viscosity μ_s , and polymer viscosity μ_p) were obtained by fitting the rheological data at 130°C. The Oldroyd-B constitutive equation describes the transport of polymer stress in the flow:

$$\overset{\nabla}{\mathbf{T}}_{em} + \mathbf{T} = 2\mu_s\mathbf{K} \quad (4.5)$$

where $\overset{\nabla}{\mathbf{T}}_{em}$ is the upper convected time derivative of the extra stress tensor.

4.4.2 Initial and Boundary Conditions

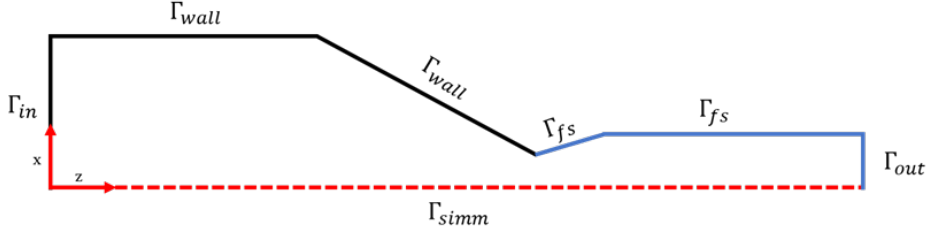


Figure 4.2. Simulation domain.

Concerning Figure 4.2, in inflow Γ_{in} a mass flow rate of 15 [kg/h] was set, no-slip condition on the wall Γ_{wall} , in the outlet Γ_{out} a constant pressure is applied. The dimension of Γ_{in} is chosen according to the exit section of the pilot line in order to have no material losses or recirculating regions, the length of Γ_{wall} is chosen in order to have a fully developed velocity profile in the section thanks the evaluation of the hydrodynamic entrance length in case of laminar flow ($0.0575 \times Re \times D_{in}$), instead the length of the free surface walls, Γ_{fs} , were obtained thanks to a mesh convergence analysis, and also testing the increase of the length that has no effect on the outcomes; instead, it increases the computing function. In addition, a small divergent region was considered in the free surface domain, it emerged that if the created geometry was basically a rectangle of height H , the software would not converge since it could not manage large mesh deformations. To prevent such a situation, the height of the jet must be chosen to be slightly more than the height of the die to make the beginning geometry closer to the desired final geometry, this option of beginning geometry has no effect on the outcomes. Finally, a symmetry condition is set at the boundary Γ_{simm} . Regarding the moving mesh, at the outlet Γ_{out} a mesh slip condition was applied whereby the mesh can only move in the tangential direction. A free mesh movement is set on the interface, and, on the remaining boundaries, the mesh is fixed. Finally, a boundary condition for the extra stressor T is required at the inlet Γ_{in} and we set it to 0. The initial values of this problem were set to zero in the entire domain, with velocity, pressure, and stress, and the starch material

filling the entire domain. The characteristic length was determined as the D_{out} . The characteristic velocity was the average velocity at the inlet D_{in} and was referred to as u_{in} . Figure 4.3 a) shows the initial mesh of the domain and the b) show the final mesh of the domain after the reaching of stationary region for the swelling and after the remeshing. The mesh was built as a user-controlled with finer mesh dimensions as reference. The number of initial elements of the mesh was 849 while after the deformation and remeshing and after 1s the number of elements became 901.

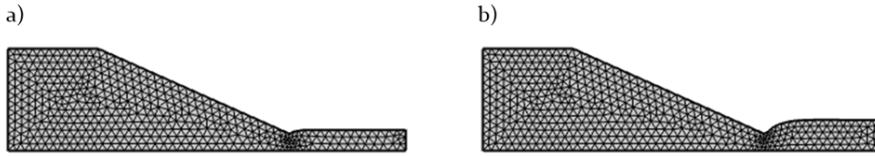


Figure 4.3. a) Fluid geometry with mesh at time 0 s b) Fluid geometry with mesh at time 1 s.

4.5 Results

Experiments were performed using the same starch mixture and moisture content to validate the pressure drop and die swell. By controlling the pressure drop, by changing the melt cooler temperature, we change the intrinsic viscosity of the material, and we can control the final shape of the foamed product. Figure 4.4 shows the pressure drop history with a 3D revolution of the 2D simulation domain. The maximum pressure in the simulation was 5.5 bar instead during the experiments the pressure at the die inlet of the extruder machine reached 10 bar. This discrepancy can be explained by the simplification assumptions discussed in the mathematical model section.

Figure 4.5 shows the velocity magnitude profile in a 3D revolution of the 2D domain. This allows us to check that we have a homogeneous flow at the exit of the die to avoid possible shape deformations. Our key hypothesis is to assume a single-phase system without considering the foaming process. The die swell phenomenon and, consequently, the diameter of the final extrudate (D_{Final}) is influenced by two contributions, i.e., the die swell

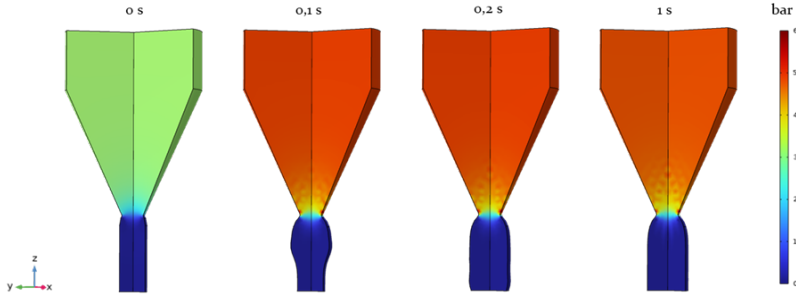


Figure 4.4. Pressure drop and die swell evolution in time.

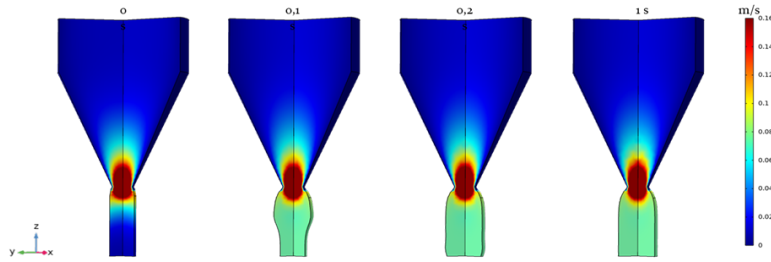


Figure 4.5. 3D velocity profile and die swell evolution in time.

of the polymer due to fluid elasticity [5], and the swelling induced by the foaming process. Assuming an isotropic foaming, the swelling related to the foaming process can be calculated as the $\sqrt[3]{\frac{\rho}{\rho_F}}$, where ρ is the density of the powder material and ρ_F is the density of the final foamed tube. The simulations only account for the first contribution and the evolution of the extrudate diameter D_{sim} is reported in Figure 4.6. To compare the predictions of the model with the final profile dimension, we assumed that the predicted diameter can be rescaled by the density ratio factor previously discussed, i.e.:

$$D_{Final} = D_{sim} \cdot \sqrt[3]{\frac{\rho}{\rho_F}} \quad (4.6)$$

Figure 4.7 shows the cross-section of one experiment for the validation of the model, where the diameter of the foamed product is 12.7 mm. The diameter calculated through Eq. 4.6 is 17.7 mm. The difference is likely due to the simplification hypothesis, and to the fact that the Oldroyd-B model does not perfectly describe the extensional rheological properties of the material.

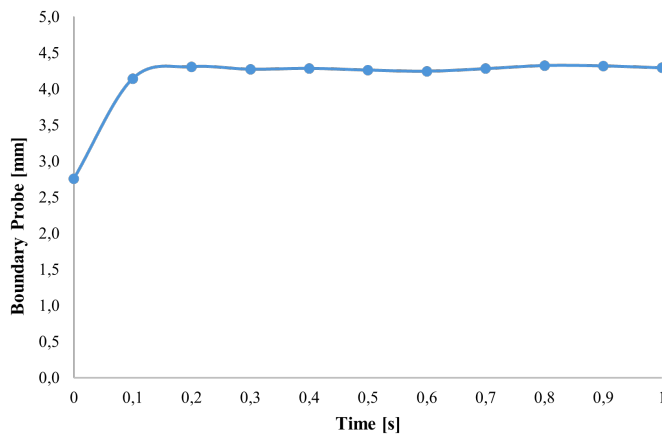


Figure 4.6. Die swell probe plot over time.

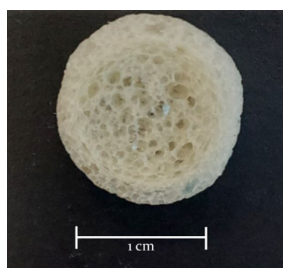


Figure 4.7. Cross-section of the foamed samples.

4.6 Conclusions and Outlook

In this work, the design of extrusion dies was made by using Computational Fluids Dynamics (CFD) to reduce the trial-and-error process. The shape precision goal was achieved and can be controlled by acting on the formulation (additives) but above all on the die design: convergence angle and die exit dimensions. In Figure 4.8 are reported three different experiments with three different flow rates but the same MC; which in this typology of system is the driving force for the process; versus the isotropic expansion conditions. The red dots mark the simulation output (D_{Final}) while in blue are marked the obtained experimental results (D_E). The difference in terms of percentage is 28,2% for sample 1, 13% for sample 2 and 19% for sample 3.

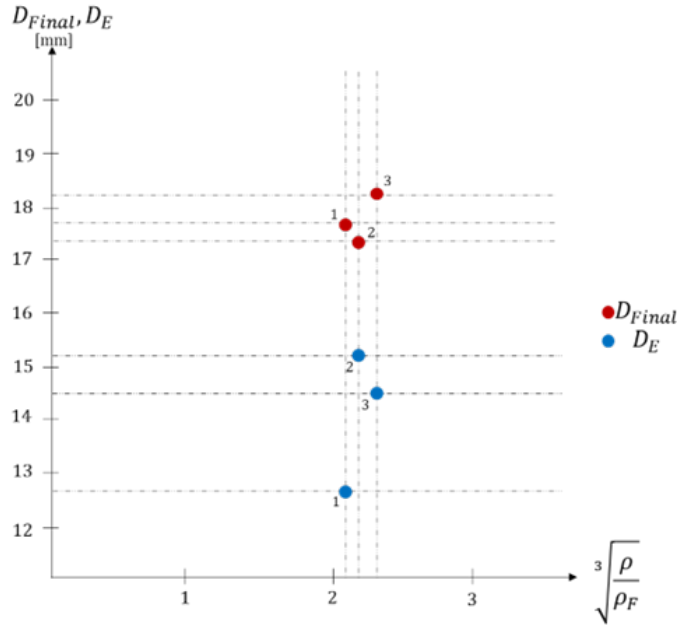


Figure 4.8. Comparison between simulations results and experimental results

These discrepancies between the measured and simulated data can be attributed to the hypothesis we used in the modelling: the no-slip con-

dition at the die wall, a single-phase system without a foaming process, the neglect of surface tension and gravity, and the last one, an isotropic swelling of the material. Furthermore, temperature inhomogeneities that arise in the trials could represent obstacles to our prediction, as simulations are not able to detect such inhomogeneities. Another cause for the data discrepancy is that the model employed to fit the rheological data (Oldroyd-B) did not adequately describe the extensional rheology of the starch material. Qualitatively, the Oldroyd-B model captures the interplay of the physical phenomena involved in the process. However, there are significant quantitative discrepancies. Although the Weissenberg (Wi) and Deborah (De) numbers are considerably lower than 1, foam extrusion induces strong extensional flows, especially at the die exit. Due to its mathematical formulation, the Oldroyd-B model predicts an infinite increase in extensional viscosity at high deformation rates, leading to potentially unrealistic predictions and often numerical instability.

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Chapter 5

Shape Instabilities

This chapter is based on the original version of the scientific paper under submission.

Using CFD Simulations to Predict and Control Shape Instabilities in Slit Die for Foam Extrusion

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5.1 Abstract

This manuscript presents a comprehensive comparison between computational fluid dynamics (CFD) finite element simulations and experimental results obtained from a twin-screw extruder for foaming extrusion processes. Both simulations and experiments were conducted using slit dies to investigate the prevention and control of shape instabilities in the extruded foam. The experimental apparatus permits the variation of processing variables, with a consequent assessment of their influence on the foaming behaviour and morphology of the extrudate. The results demonstrate the effectiveness of CFD in predicting flow behaviour and instability formation, with a high degree of accuracy in alignment with simulation data. The findings contribute to a deeper understanding of foam extrusion dynamics, offering a framework for optimising extruder die design and significantly enhance product quality in industrial applications.

5.2 Introduction

Solid foams are a class of versatile cellular materials with a wide range of applications, from packaging and tissue engineering [1] to food [2] and 3D printing [3, 4]. They are known for their lightweight, enhanced mechanical properties (e.g., high specific mechanical strength [5], tensile elasticity [6], and energy absorption [7]), and insulation/shielding capabilities against sound, heat, and electromagnetic fields [8].

In recent years, as growing environmental awareness has encouraged the adoption of more sustainable materials and the development of a circular economy, researchers have been exploring the use of renewable feedstocks and green additives to produce solid foams with improved reusability and recyclability. Some examples include geopolymers [9], bio-based polyurethane foams [10], vegetable fillers [10], and waste by-product fillers [11, 12] such as fly ash.

One of the manufacturing technologies employed to produce foamed materials is foaming extrusion, i.e., a process in which bubbles are formed in a polymer matrix during extrusion. This technique significantly improves mechanical properties through lightweight structuring, resulting in high specific strength, toughness, and impact resistance. The key application fields of foaming extrusion are: packaging (e.g., for food, electronic devices, medical equipment, and automotive components) [13], thermal insulation [14], noise reduction [15], filtration and adsorption [16], cushioning and padding [17], energy harvesting [18], and drug-loaded scaffolds for tissue engineering [19].

Of all the mechanical components of the extrusion line, the die is the most critical in determining the shape and properties of the final product. The die is a metal conduit that gives the material a specific cross-sectional shape and is responsible for regulating the flow of the melt and controlling the expansion of the foam to achieve the desired density and morphology. The presence of a die improves extrusion efficiency and ensures that the foam is precisely molded while maintaining the integrity of the material. The die design affects the temperature, pressure, and velocity field experienced by the polymer, thus influencing the final properties of the product. The most important aspects to consider when designing a die for foam extrusion are: dimensional accuracy of the final foamed product [20, 21], pressure profile (which is crucial for the bubble growth) [22], material properties (rheological and thermal) [17], and the cross-sectional shape [23].

Different die cross-sections are used depending on the final application of the foamed material. The main products of foam extrusion, i.e., boards, sheets, and films, differ from each other mainly in terms of thickness and flexibility, as defined by ASTM D883-23 [24]. Boards are generally thicker than 6 mm and have good rigidity; sheets are between 0.25 mm and 6 mm thick and have good flexibility; films are less than 0.25 mm thick and are

extremely flexible.

The types of dies commonly used to produce these specific forms of foamed products are the strand die and the slit die. The former consists of several parallel channels (typically with a circular cross-section), while the latter has a single slit-like opening. Although both have pros and cons, slit dies are usually preferred since: i) slit dies provide a more uniform thickness and surface quality, which are important requirements for applications where consistent mechanical properties and appearance are important; ii) slit dies allow higher production rates compared to strand dies; iii) in strand dies adhesion problems between the individual strands or the unfoamed areas between them may occur.

The main drawback of using a slit die is the occurrence of flow instabilities at the outlet if the die is not properly designed. This results in shape irregularities with the formation of a wavy or ridged pattern on the surface of the extruded polymer foam. Such material folds, also named corrugations [25], affect mechanical properties, appearance, and functional performance. The origin of this phenomenon has not yet been clearly defined in the literature. It can be traced back to a number of factors, such as premature foaming inside the die, non-uniform distribution of temperature and velocity, pressure drop irregularities, loss of foam expansion control, and inadequate cooling of the product at the exit.

Computational Fluid Dynamics (CFD) has significantly expanded its application in extrusion processes, particularly in the optimisation of die design [26]. Indeed, by simulating the flow and heat transfer throughout the extrusion line for different materials and operating conditions, it is possible to identify and prevent potential problems such as shape and surface instabilities. Thus, a comprehensive simulation study not only helps to improve product quality and increase process efficiency, but it also reduces the time and costs associated with a purely experimental trial-and-error approach. Despite the extensive use of numerical simulations for extrusion, the scientific literature still lacks a work that combines die-swell expansion and foaming swelling in a single simulation. At most, the foaming has been taken into account as a multiplicative term to scale the deformation in the final results [27].

In this work, experiments and numerical simulations are performed on the extrusion of a foamed board from a slit die and the results are

compared. Two die geometries and two pulling velocities are considered, characterising the foamed product and highlighting the occurrence of shape instabilities. The numerical simulations are carried out with a commercial code that includes the foaming in the extrusion modelling and are able to reproduce the experimental behaviour.

5.3 Materials and Methods

5.3.1 Experiments

Materials

The polymer used for the experiments is a low-density polyethylene (LDPE) type 2602 from Sabic (The Netherlands) used as received. The blowing agent is isobutane with a purity of 99.9% purchased from Linde Group (Naples, Italy).

Extrusion Line

Figure 5.1 represents a schematic diagram of the extrusion line used to prepare the foam samples. It contains a dosing devices, an intermeshing co-rotating twin-screw extruder (where the foaming agent is injected), a melt conditioning section, the die, and a pulling system. Each extruder screw has a diameter of 45 mm and a length to diameter ratio of 24. The conditioning section consists of a melt cooler (Spiral cooler 450 by Strasser&Partners, Switzerland) to cool the polymer melt to the desired foaming temperature, and a static mixer (SMX50 by Sulzer, Switzerland) to homogenise the radial temperature profile within the melt.

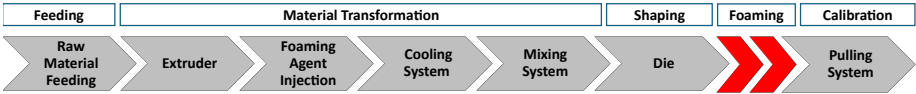


Figure 5.1. Extrusion line sketch.

The slit die considered in this work is shown in Figure 5.2, with two axonometric views (panels a and b) and two orthogonal views (panels c and d). While the outer geometry and dimensions are determined by the pilot line used for the experimental campaign, the design of the exit face has been redesigned following the work of Spanjaards *et al.* [26] and based on the findings of an earlier experimental campaign conducted prior to this study. It is important to note, however, that the data from this earlier campaign remain confidential. This die has been successfully applied, in another work, to the foam extrusion of starch-based mixtures as reported in the work of Tammaro *et al.* [28]. The values of the geometric parameters

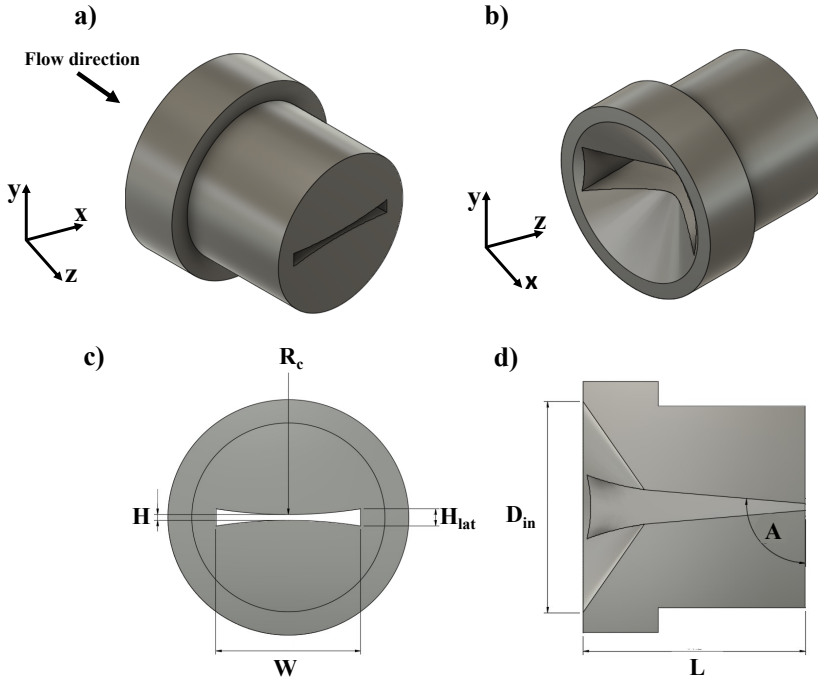


Figure 5.2. Different views of the slit die. a) Axonometric view of the outlet, b) Axonometric view of the inlet, c) Front view, d) Lateral section.

indicated in Figures 5.2c and 5.2d, which characterise the die, are reported in Table 5.1. Two similar dies were designed, differing only in the radius of

curvature R_c and thus in the central height H . The corresponding values are indicated in Table 5.1 as H_1 and H_2 .

Table 5.1. Geometric parameters

Name	Symbol	Value
Width	W	20 [mm]
Inlet Diameter	D_{in}	42 [mm]
Lateral Height	H_{lat}	3.6 [mm]
Die Length	L	30 [mm]
Taper Angle	A	10° [°]
Die 1 Height	H_1	0.83 [mm]
Die 2 Height	H_2	1.69 [mm]

Characterization of the Foamed Board

A Sony Leica camera with a 50 mm lens is used to photograph the produced samples and evaluate their shape and surface roughness. The foam bulk density is measured according to ASTM D792 using an analytical balance (Mettler Toledo, Columbus, OH, USA). The cellular morphology is assessed from Scanning Electron Microscope (Hitachi TM 3000 SEM, Japan) images of random internal cross-sections. In preparation for SEM analysis, the samples are cooled in liquid nitrogen, cut with a razor blade, and then covered with gold using a sputter coater. A MATLAB script is used to compute the cell density ρ_b , the average bubble area and aspect ratio.

5.3.2 Simulations

Governing Equations

Assuming creeping flow, isothermal conditions, and negligible effect of gravity, the fluid dynamics is governed by the mass and momentum balance equations:

$$\nabla \cdot \rho \mathbf{u} = 0 \quad (5.1)$$

$$-\nabla p + \nabla \cdot \mathbf{T} = \mathbf{0} \quad (5.2)$$

where ρ is the density, $\mathbf{u}$ is the velocity, p is the pressure, and $\mathbf{T}$ is the stress tensor. The stress tensor for a generalised Newtonian fluid is given by:

$$\mathbf{T} = 2\eta(\dot{\gamma})\mathbf{D} \quad (5.3)$$

where $\mathbf{D}$ is the rate of deformation tensor:

$$\mathbf{D} = \frac{1}{2} (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \quad (5.4)$$

and $\dot{\gamma} = \sqrt{2\mathbf{D} : \mathbf{D}}$ is the shear rate.

The fluid viscosity is modelled through the power-law constitutive equation:

$$\eta = K \dot{\gamma}^{n-1} \quad (5.5)$$

where K is the consistency index and n is the power law index. The constitutive parameters are calculated from rotational rheological measurements.

Bubble Growth Model

Bubble growth is included in the simulations through the model proposed by Arefmanesh *et al.* [29]. Such model assumes that gas diffusion is much faster than bubble expansion and that the matrix behaves as a viscous material. The bubble does not grow indefinitely, since only a finite amount of gas can be used for growth, and these bubbles will reach a steady state when the gas is exhausted. Another parameter that can affect bubble growth is the surface tension. This is especially true for small bubbles. One effect of the surface tension gradient established in the interstitial space can inhibit the coalescence of tiny gas bubbles [30] and this can lead to a retard in the bubble growth by providing additional resistance to the motion of the bubble boundary [31, 32].

In foaming extrusion, the swelling of the material at the exit of the die, is controlled more by bubble growth than the rheology of the material due to bubble stability (collapsing or coalescence phenomenon), bubble shape and resistance to deformation [33]. As an outcome, the spotlight is on a single transport equation that is driven by the bubble growth in the computational framework. The approach has been developed from seven assumptions. [34], 1) nucleation is not taken into account, consequently an initial diameter of bubbles is provided; 2) the bubbles are spherical for the entire

duration of growth; 3) neglect the inertia term, in this way the pressure in the bubble is constant; 4) thermal effects are negligible during bubble growth; 5) The flow is considered incompressible creeping (in our case, Re is the order of 10^{-6}); 6) there is no gas available in the surrounding environment.; 7) while growing, the bubbles have no interaction with each other. The model starts from a single elemental unit cell, shown in Figure 5.3, where the polymer matrix surrounds a bubble. The elemental cell has a mass m_{cell} , the bubble has a radius of R . The total volume of the cell is given by the volume of the polymer matrix V and the bubble volume V_B . Having the total volume of the cell and the mass of the cell is possible to compute the density of the cell:

$$\rho = \frac{m_{cell}}{V + V_B} = \frac{m_{cell}}{V + \frac{4}{3}\pi R^3} \quad (5.6)$$

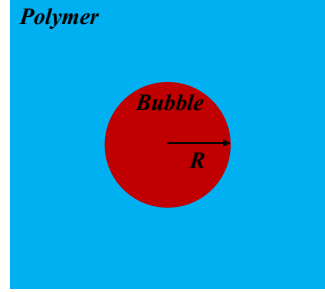


Figure 5.3. Elemental unit cell of the model.

In the absence of a blowing agent, the density of the polymer matrix can be derived using 5.6, $\rho_p = \frac{m_{cell}}{V}$. To extend the definition to a system consisting of more than one elemental cell, we define N as the number of cells per volume unit of gas or polymer mixture $N = \frac{1}{V}$. When the blowing agent is present, this indicates the presence of a bubble with a radius R , the density of the mixture of polymer and blowing agent is:

$$\rho = \frac{\rho_p}{1 + \frac{4}{3}\pi R^3} \quad (5.7)$$

While foaming advances, viscosity changes, with macroscopic viscosity decreasing as volume increases. The model assumed that the zero-shear viscosity behaves in the same way as the density:

$$\eta_0 = \frac{\eta_{p0}}{\frac{4}{3}\pi R^3} \quad (5.8)$$

The common variable in all the equations is the radius R , hence, to solve

the equation system, a constitutive equation for R is required. As mentioned at the beginning of the paragraph, this constitutive equation is derived from Arefmanesh model:

$$\frac{dR}{dt} = bR^{\frac{a-1}{a}} \left\{ \frac{(p_g - p)R - 2\Gamma}{4\mu} \right\}^{\frac{1}{a}} \quad (5.9)$$

Where p_g is the gas pressure inside the bubble, Γ is the surface tension, p pressure of the polymer matrix, μ is the macroscopic viscosity of the foam, b is an adjustable parameter, known as a booster to control the foaming, and a is an index which can introduce non-linearities in the model. This foaming model in Ansys Polyflow, actually, is implemented only with a generalised Newtonian fluid.

Simulation Geometry

In order to reduce the computational effort, a simplified version of the dies was considered while preserving the main geometrical features. The features of the domain are shown in Figure 5.4, where grey is the portion of the fluid inside the die and the light blue part is the free surface part of the fluid without boundary constriction, free to expand and deform. The geometrical dimensions are listed in Table 5.1. In Figure 5.4, the only new elements are R_{C1} (Figure 5.4a), and R_{C2} (Figure 5.4b) which refers to the two different curvature radius correlated to the difference in the height of the die exit.

Initial and Boundary Conditions

The necessary physical parameters for the simulation can be divided into material properties and foaming properties. Among the material properties are the density, ρ , and viscosity law, which in this case follows a power law requiring the input of parameters the consistency index, k , and the power law index, n . For the foaming properties, the simulation software requires the initial pressure of the bubbles, ρ_b , the number of bubbles per unit volume, $\#N$, the initial bubbles radius, R , the viscosity of the gas/polymer mix, η_{mix} , and the booster parameter, b , as described in Equation 3. The initial conditions applied at the inlet, D_{in} , is the volumetric flow rate $\dot{V}$, as conditions for fluid flow, and for foaming the

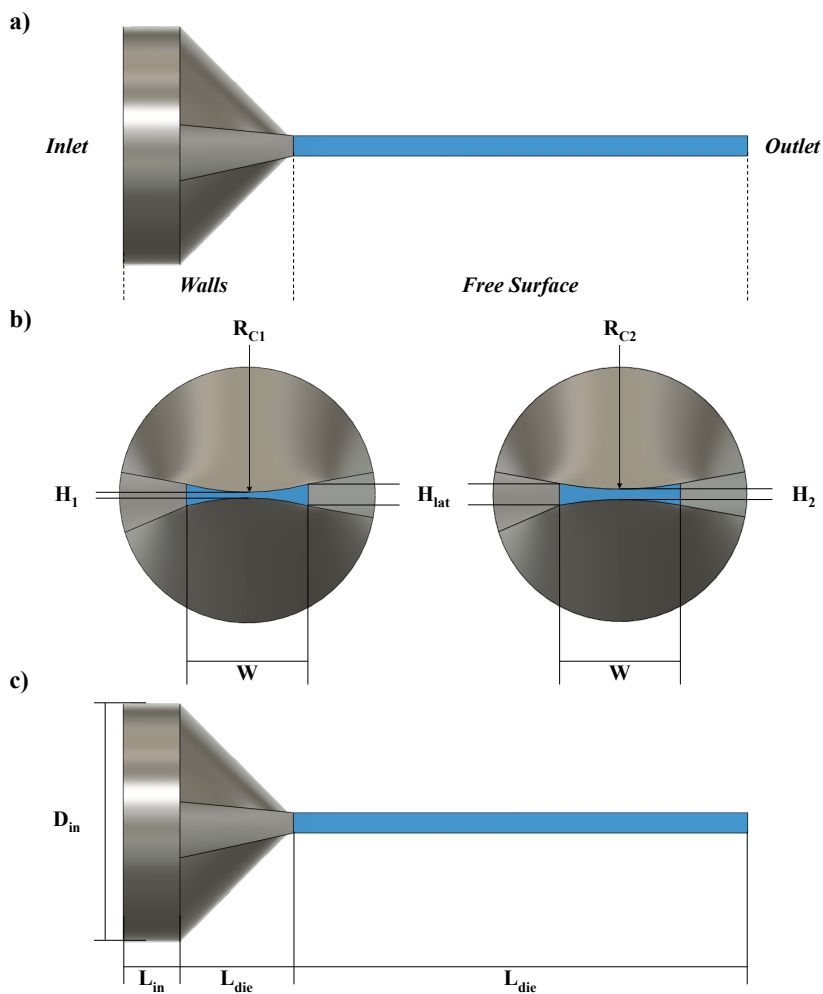


Figure 5.4. Simulations domain. a) The name of the boundaries of the domain, b) Front view of the die with the small central height and front view of the die with a big central height and c) the lateral view of domain.

Physical Property	Conditions
Material	Material density, ρ
Material	Viscosity consistency index, k Power law index, n
Foaming	Initial bubble pressure, p_b
Foaming	Number of bubbles per unit volume, #N
Foaming	Viscosity of polymer/gas mixture, η_{mix}
Foaming	Booster parameter, b

Table 5.2. Geometrical parameters of the simulation domain

conditions set is the initial dimension of the bubbles of the blowing agent (R), no-slip condition on the die walls (L_{in} and L_{die}) is set, by setting the normal and tangential velocities to zero. The subscripts n and t indicate the normal and tangential components of the force and velocity. The simulation domain and the boundaries are reported in Figure 5.4. The length of L_{in} was chosen to have a fully developed velocity profile, parabolic profile, in the section by evaluating the hydrodynamic entrance length ($L_e = 0.057 \times Re \times D_{in}$) in the case of a laminar flow ($Re < 2000$, $Re = (\frac{\rho v d}{\eta})$). The length of L_{fs} was obtained thanks to testing the different lengths of the free surface domain and noticing that it has no effect on the result of the computations except for computational time. At the outlet, due to the sufficient length of the L_{fs} , all the normal and tangential forces, including the pressure, have been set to zero. The physical, initial and boundary conditions applied to the 3D flow domain are summarised in Table 5.2 and Table 5.3. The number of iterations was 30 to get an acceptable result from simulations, Powr-law was used for shear rate dependence on viscosity. In Polyflow the Picard iteration of viscosity was chosen.

Mesh

Figures 5.5a and 5.5c show the mesh used for the simulation of the two dies with curvature radius R_{C1} and R_{C2} , respectively. As previously mentioned, mesh deformation is applied only on the free-surface domain whereas the mesh remains fixed for the domain inside the nozzle. Since

Boundary	Conditions
Inlet	Fully developed flow, $\dot{V}$ Initial bubble radius, R
Outlet	Zero Force $f_n = f_t = 0$
Free Surface	Mesh deformation
Walls	No-slip $v_n = v_t = 0$

Table 5.3. Initial and Boundaries conditions

the numerical procedure moves the mesh nodes until the final equilibrium state is reached, the number of mesh nodes and elements do not change during the simulation. The streamwise deformation method is used to adapt the computational mesh to the deformation of the polymer flow, orienting the mesh motion to the direction of the flow. This approach is effective in the polymer swelling and bubble growth simulations where the material undergoes significant expansion or deformation. By moving the mesh along the flow direction, this method minimises mesh distortion, preserves element quality, and improves numerical stability. In particular, it helps to track the free surface as it expands after exiting the die, avoiding excessive mesh skewness or stretching that could otherwise lead to inaccurate results. It also ensures that the bubble growth process, driven by changes in fluid density, is captured with high fidelity as the mesh smoothly adapts to the expanding fluid domain without introducing numerical instabilities. Combined with mesh smoothing techniques, the streamwise deformation approach maintains a well-conditioned computational domain throughout the simulation, supporting accurate and stable predictions of polymer behaviour under different flow conditions. Regarding the type of mesh elements, hex dominant on the die wall, these elements are primarily hexahedral with tetrahedral elements in regions where the hexahedral features are not feasible and some prismatic elements near boundary layers to ensure smooth transitions, and the sweep method; with this method, the elements of the mesh are hexahedral on the free surface. The mesh skewness was set to 0.3, to have low distortion of the elements. The number of mesh elements is around 90000 for the die 1 and about 80000 for the die 2.

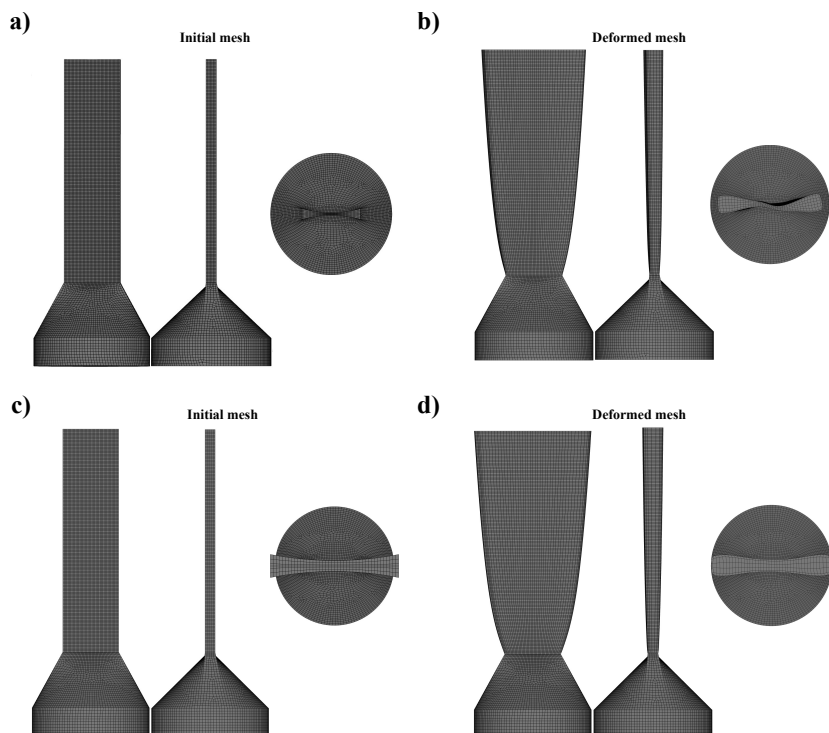


Figure 5.5. a) Initial mesh of the Die 1 domain, b) final mesh at the end of the Die 1 domain, c) initial mesh of the Die 2 domain and d) final mesh of the Die 2 domain.

Dies	Nodes	Elements
Die 1	90493	88328
Die 2	81025	78482

Table 5.4. Mesh nodes and elements.

5.4 Results

5.4.1 Experiments

In this section, the foamed boards obtained from different dies are shown. The two dies were designed with a different H . These dies during the extrusion experiments in the specific process conditions lead to particular shape instabilities and we focused on controlling it, thanks to the use of simulations. This instability was expected at a low-density goal with a high aspect ratio. These instabilities were controlled in two ways: by increasing the haul-off velocity (pulling velocity) and reducing the aspect ratio by increasing the height of the die exit in the central part. Among the

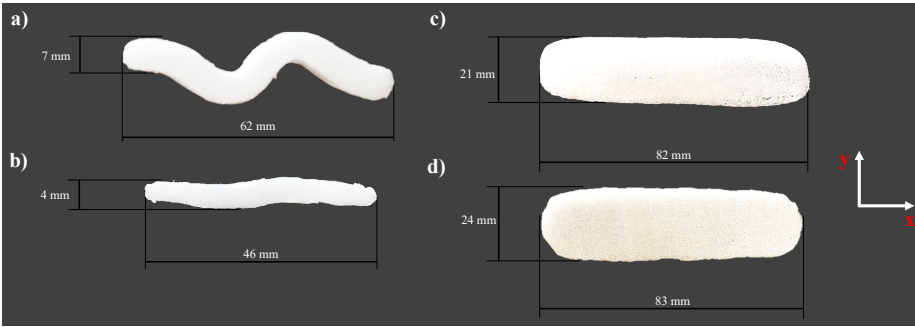


Figure 5.6. Experimental results a) S-shape obtained from the die with the high aspect ratio, b) foam from the same die of a) but with a high haul-off, and c) foam obtained with a lower aspect ratio, d) foam from the same die of c) but with a lower haul-off.

exhaustive experimental campaign, we focus on the experiment shown in Figure 5.6. To simplify the notation experiment with the letter a), which will be known as the s-shape, experiment with letter b) as pulling, and the last one with the letter c) known as the lower aspect ratio, d) same as c) but with a slower pulling rate.

The sample in Figure 5.6, marked with the letter a has a density of 57 kg m^{-3} , a length of 62 mm and a height of 7 mm, in this case, it is also possible to compute a linearized length of 67.6 mm. The expansion ratio, i.e. the ratio between the size of the extrudate and the size of the die,

is 3 in the x-direction and 2.8 in the y-direction. The sample in Figure 5.6 with the letter b has a density of 75 kg m^{-3} , a length of 46 mm and a height of 4 mm, also, in this case, we can compute the linearized length of 46.2. Expansion ratio in the x-direction of 2.1 and y-direction of 1.5. In this test, a high haul-off was used, 0.42 m/s. The sample in Figure 8, with letter c, showed a density of 45 kg m^{-3} , a length of 82 mm and a height of 21 mm. The Expansion ratio in the x-direction is 3.6 and an expansion ratio in the y-direction of 8.7. The haul-off in this experiment is 0.22 m/s. The last sample in Figure 5.6, with the letter d, presents a density of 46.7 kg m^{-3} , a length of 83 mm and a height of 24 mm. The expansion ratio in the x-direction is 3.7 while the expansion ratio in the y-direction is 8.6. In this case, the pulling is 0.13 m/s.

Figure 5.7 illustrates two different views of the four boards just discussed. Specifically, Fig. 5.7 a reports the lateral view of the samples and the Fig. 5.7 b shows the bottom view of the foamed board samples. In the industrial sector, all extruded foams undergo a post-production treatment standard, which is necessary to remove the external layer known as the "skin" [35]. This process is essential for improving mechanical properties, creating a more homogeneous surface, adhesion to other materials, and inspecting the internal structure of the foam, known as the "core". Core inspection is critical in identifying potential problems such as poor material blending or inadequate control of operating parameters to ensure the foam meets the required quality standards. These two regions exhibit distinct bubble morphologies: in the skin, bubbles adopt an elongated shape due to shear stress and rapid cooling, whereas in the core, they grow without a preferential direction, leading to a more uniform distribution. This phenomenon can be observed experimentally, as shown in the SEM images in figure 8. The morphologies produced during the extrusion process vary significantly depending on the die geometry and pulling velocity. Foams extruded with a high aspect ratio die exhibit a pronounced S-shaped instability (Fig. 5.7 a.1 and b.1) that deviates strongly from the desired shape, making them unsuitable for most applications. Increasing the pulling velocity reduces this instability and produces a less pronounced S-shape (Fig. 5.7 a.3 and b.3) with improved linearity. However, this morphology still presents significant challenges, as the deformed regions must be removed during post-production. This results in significant material loss, making

the final foam excessively thin and mechanically fragile. As a result, these foams have limited applications and are generally unsuitable for structural applications or load-bearing components. In comparison, foams extruded with a high aspect ratio die do not develop S-instability. At low pulling velocities, they exhibit surface corrugation (Fig. 5.7 a.2 and b.2) which diminishes with increasing velocity, resulting in a straighter morphology with minor residual surface irregularities (Fig. 5.7 a.4 and b.4). These foams are more versatile and suitable for a wider range of applications, provided the surface finish meets the specific requirements. The pronounced and attenuated S-shaped foams have significant limitations due to their inherent material loss and resulting fragility, whereas foams produced with the high aspect ratio die offer greater practical utility

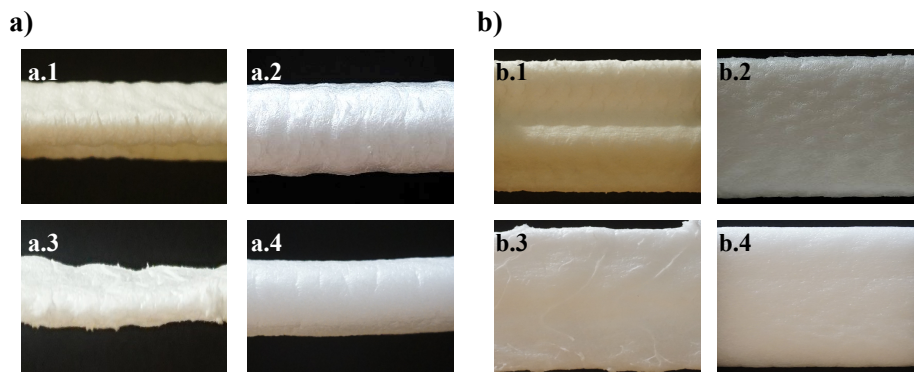
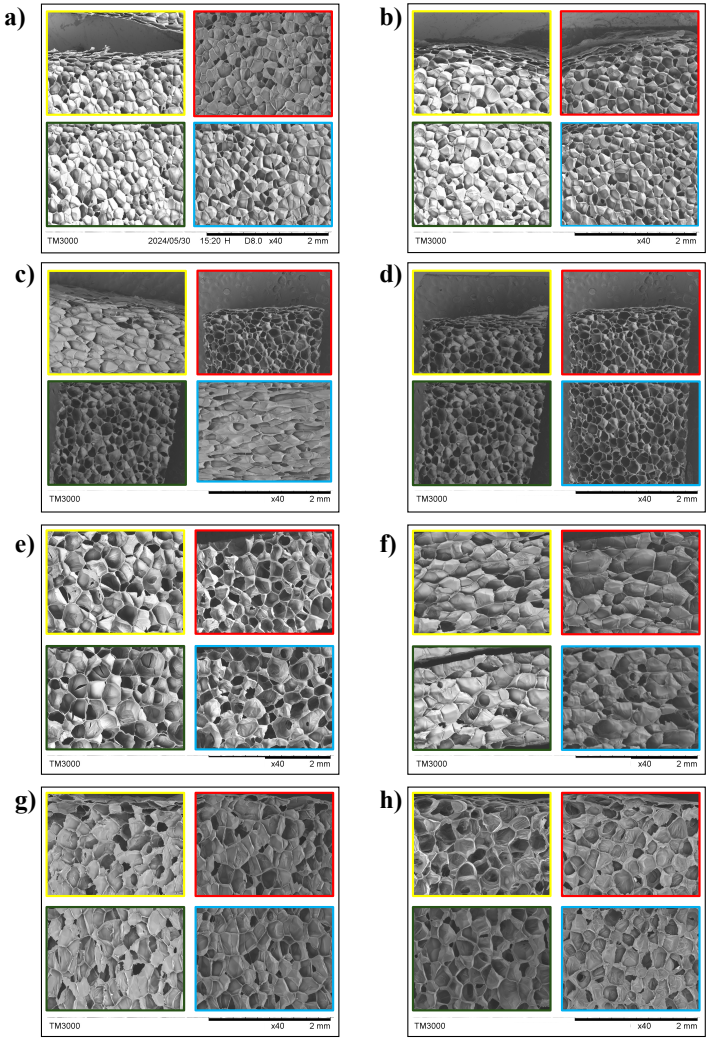
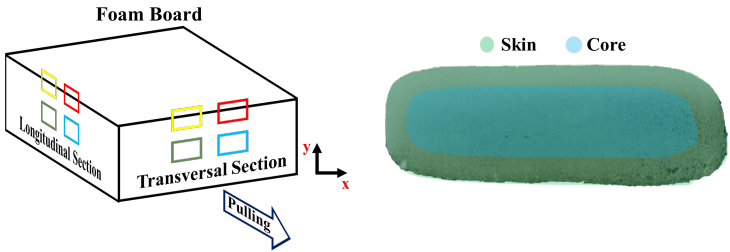


Figure 5.7. a) Shows a side view of the foams board, highlighting their height, while group b) displays a top view of the foams, emphasising their thickness.

The analysis of the board shape clearly evidences the emergence of instabilities, which can be controlled in two ways: increasing the pulling velocity and/or reducing the aspect ratio of the die by increasing the height in the central part. After the external comparison of the different samples, we examined the inner morphology through the SEM images reported in Fig. 5.8. On the upper part of the figure, a graphical visualization of the analyzed regions in the sample is shown. The SEM image analysis is carried out with an in-house MATLAB script that measures the cell

density, the average diameter of bubbles, and the average area of bubbles, as illustrated in Fig. 5.9. The data obtained from the script are listed in Table 5.5. For each sample, denoted with the same letter as in Fig. 5.6, morphological information for the transversal and longitudinal regions of the sample are reported for both the core and skin. In extruded polymer foams, the morphology of the bubbles varies significantly between the skin and the core of the sample due to the thermal gradient and pressure conditions during the manufacturing process. In the skin region, the bubbles are smaller and have a higher cell density (number of bubbles per unit volume). This is primarily due to the rapid cooling of the material at the surface, which limits bubble expansion and confines a greater number of bubbles in a smaller volume. The resulting structure in this region is more compact. In contrast, in the core region, the bubbles are usually larger and the cell density is lower. This difference is due to the higher internal temperatures, which allow greater bubble expansion, and the larger available volume, which allows the bubbles to be more dispersed. As a result, the core structure is more homogeneous but less compact than the skin. Also, the distribution of bubble diameter is plotted in histograms in Figure 5.10. In particular, the histograms show the distribution of bubbles in the transversal section and longitudinal section of the foamed board in two different crops, the top part also known as “skin” and the core of the foamed board. The data obtained from the software, cell density ρ_p given by the number of bubble $\#N$ over the area of the crop, the Aver-

Figure 5.8. In the upper part, a schematic representation of a generic sample is shown, highlighting the two considered sections: longitudinal and transversal. The schematic also indicates the four sampling points taken from each face of the specimen. The image on the right illustrates the classification of the surface region as “skin” and the inner region as “core”. (a) SEM image of the longitudinal section of the S-shaped sample; (b) SEM image of the transversal section of the S-shaped sample. (c) Longitudinal section from the pulling experiment; (d) transversal section from the pulling experiment. (e) Longitudinal section of the experiment with a larger central height; (f) transversal section of the experiment with a larger central height. (g) Longitudinal section as in (e) but with a lower pulling velocity; (h) transversal section as in (f) but with a lower pulling velocity.



age Bubble Diameter d_{avg} and the Average Bubble Area A_{avg} are listed in Table below, Table 5.5. Where each experiment reported the data in the transversal and longitudinal sections, each section listed the data in two positions of the section: skin and the core of the sample, the centre.

As demonstrated in table 5.5 and the histograms in Figure 5.10, when the die exit is excessively diminutive, there is a substantial impediment to foam expansion, resulting in deformation and an effect on the internal morphology of the bubbles. This restricted expansion gives rise to smaller bubbles, as evidenced by the transverse and longitudinal sections of foam produced with die 1, which exhibits significantly diminished average bubble areas in comparison to foam produced with die 2. This is due to the smaller die exit, which prevents the bubbles from growing freely, resulting in a higher cell density as the nucleated cells are unable to expand or coalesce properly. The limited expansion also causes faster cooling of the foam, which further restricts bubble growth. Conversely, foam produced with die 2, which has a larger exit, experiences less restriction and allows for greater expansion, leading to larger bubbles with lower cell density. Despite this, a temperature gradient persists within the foam, with the centre maintaining a higher temperature than the periphery. This temperature disparity fosters enhanced bubble growth and coalescence within the core, consequently leading to a diminished cell density in that region when compared to the skin region. Furthermore, disparities in pulling speed exert a discernible influence on the morphology of the foam. Higher pulling

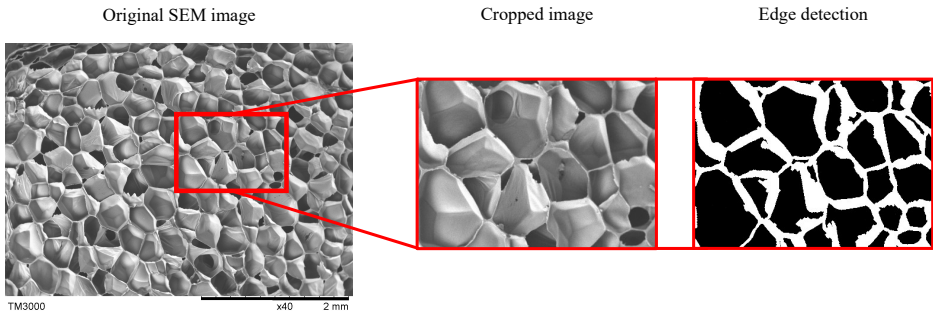


Figure 5.9. Procedure to obtain bubble dimension distribution in the SEM image.

Sample	Position	Cell Density ρ_b ($\#N/mm^2$)	Avg Bubble Diameter d_{avg} (mm)	Avg Bubble Area A_{avg} (mm^2)
a) Transversal	Core	23.3	0.19	0.03
	Skin	28.6	0.15	0.02
a) Longitudinal	Core	19.6	0.21	0.04
	Skin	24.4	0.19	0.03
b) Transversal	Core	31.3	0.13	0.01
	Skin	37.1	0.12	0.01
b) Longitudinal	Core	19.1	0.22	0.04
	Skin	23.8	0.20	0.03
c) Transversal	Core	9.1	0.32	0.08
	Skin	13.1	0.26	0.05
c) Longitudinal	Core	11.3	0.29	0.06
	Skin	19.7	0.20	0.03
d) Transversal	Core	12.1	0.29	0.07
	Skin	10.8	0.29	0.07
d) Longitudinal	Core	10.6	0.30	0.07
	Skin	13.4	0.26	0.05

Table 5.5. Foam characteristics from MATLAB, letters a), b), c) and d) refer to samples shown in Figure 5.6.

speeds, as observed in pairs (c-d), result in reduced cell density compared to pairs (a-b) due to accelerated foam expansion and more pronounced shear forces, which promote larger bubbles and reduce the number of nucleated cells. These disparities can be attributed to the variation in die geometry, which enables the foam to expand in a distinct manner and distributes stresses in different ways. Consequently, it can be concluded that die geometry, pulling speed, and thermal conditions during foam formation significantly influence the foam's internal morphology, including bubble size, cell density, and overall foam structure. It is therefore vital to understand these factors if optimising foam properties in various applications is to be achieved, as they determine the strength of the material, insulation, and other critical characteristics.

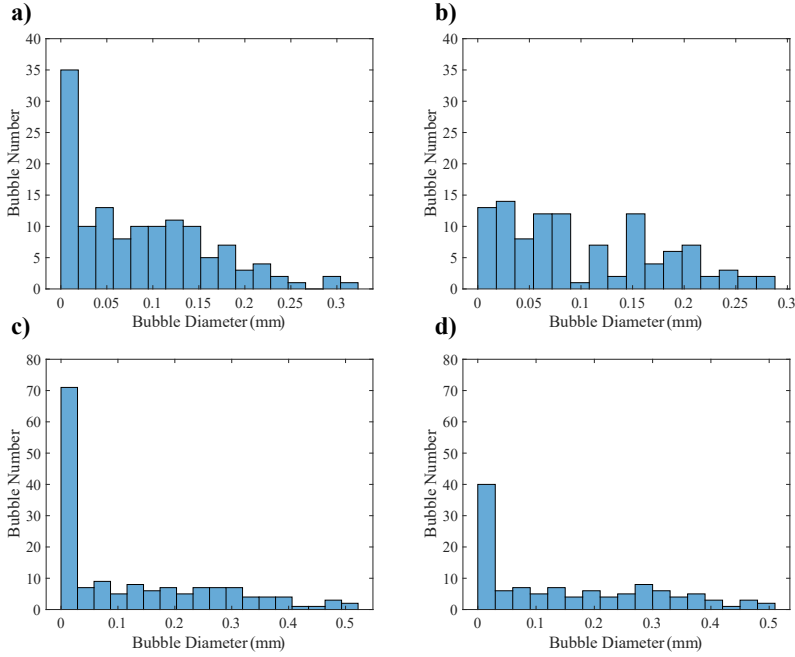


Figure 5.10. Example of histogram of the bubble dimension distribution of the experiments, SEM images shown in Figure 8. a) near the sample edge “skin” transversal view, b) central part of the transversal view, c) skin in the longitudinal view; and d) central part of the longitudinal view.

5.4.2 Simulations

One limitation in using CFD simulations for foaming extrusion dies, particularly in predicting die swell, is the complexity and computational intensity of accurately modelling the dynamic behaviour of the foaming process. The intricate interplay of factors such as material properties, foaming agents, die geometry, and process conditions can present challenges in developing precise CFD models that account for die swell accurately. Several works are present in the literature on approaches to predict the shape of the final product and the prediction of the swell of the die [27, 26, 33, 36, 37, 38]. The utilisation of Ansys Polyflow software with the tool material processing in foaming extrusion is distinguished by its

advanced capabilities for predicting extrudate shapes with precision and efficiency. Table 5.6 reports the process parameters used in the simulations. The reported rheological parameters have been evaluated from a comprehensive rheological study on LDPE by Agrawal et al. [39] at the shear rate evaluated in the die (70 1/s).

These simulations are conducted under steady-state conditions. The dies analysed have similar dimensions, as reported in Figure 5.4b and 5.4c, except for one dimension that change, the central height of the die exit H_2 bigger than the H_1 . To investigate how the instabilities observed during the experimental campaign arose, the pressure drop inside the die is reported in Figure 5.11a and the velocity profile over the width of the die, the exit face is reported in Figure 5.11b. The light blue dots and the green triangles represent the same die, with the only difference being a pulling velocity and a take-up velocity of the die exit surface; instead, the squares represent the die with the lower aspect ratio. The pressure drop result is not affected by the pulling but depends on the die dimension. Figure 5.11b reports the velocity magnitude distribution at the die exit. One of the main goals during die design is to guarantee that the velocity distribution is homogeneous, in accordance with the shape fidelity of the foamed board. This is evident in Figure 5.11b, where the velocity in the experiment with the lower aspect ratio results in a more homogeneous distribution in the section.

Parameters	Value
Polymer matrix consistency index, $\mathbf{k}$	500 $Pa \cdot s$
Polymer matrix power law index, $\mathbf{n}$	0.828
Polymer relaxation time, λ	1 s
Polymer/gas mixture viscosity	100 $Pa \cdot s$
Initial bubble radius	$5 \times 10^{-6} \text{ m}$
Initial gas pressure	$1 \times 10^7 \text{ Pa}$
Volumetric flow rate	$4.63 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$
Pulling velocity	0.3 m s^{-1}

Table 5.6. Simulation parameters

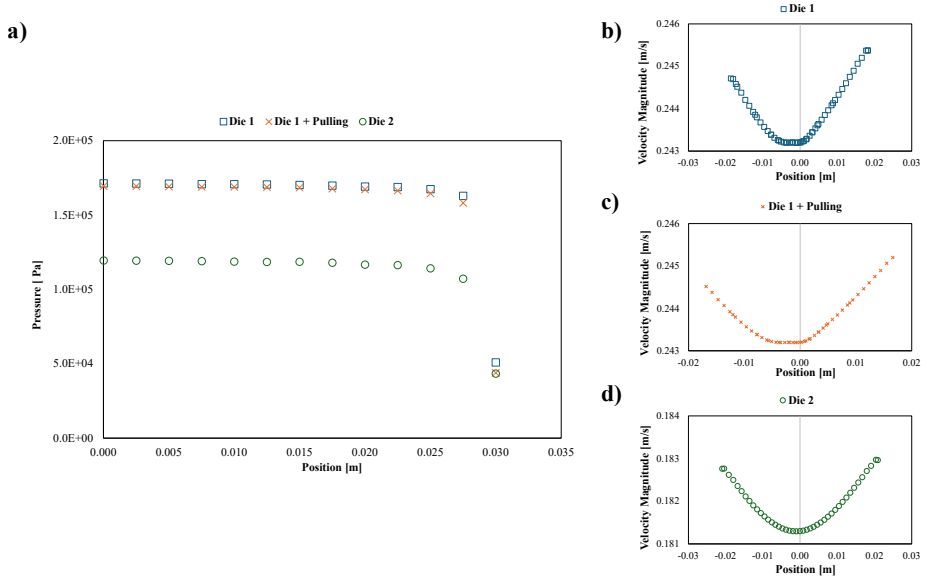


Figure 5.11. a) pressure drop in the die domain only; b) velocity profile in the width of the die exit of die 1, c) velocity profile in the width of the die exit of die 1 with the pulling of the exit surface and d) velocity profile in the width of the die exit of die 2.

The higher pressure drop along the whole die and the not homogeneous distribution of the velocity at the die exit can be closely related to the formation of the instability. Data of the die with the lower aspect ratio show these two quantities can be controlled by acting on the design of the die by reducing the pressure drop inside the die and having a more homogeneous distribution of the velocities in the section. This demonstrates how the simulations can be helpful in the field of die design avoid the trial-and-error method, which is time-consuming and economically expensive. Figure 5.12 reports the plot of the pressure drop in the whole domain, and it is possible to see also the different swelling of the free surface. Figure 5.13 shows the outlet region of the simulation to compare the shape of the simulated final product with the shape of the experimental product reported in figure 5.6. Figures 5.13 a, b, and c show the simulation result comparable with the experiment shown in Figures 8 a, b and c. Figure

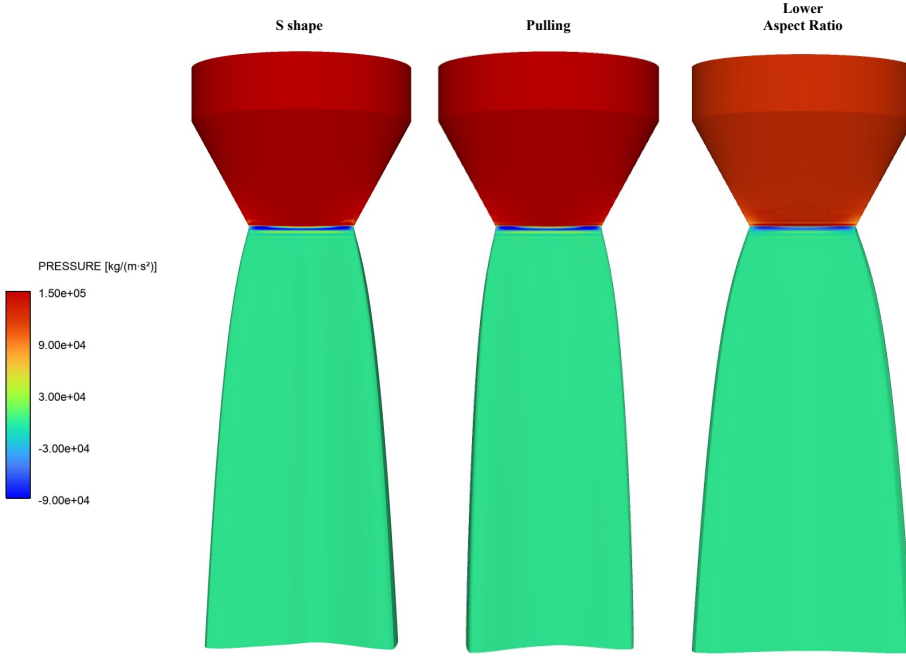


Figure 5.12. Top view of the pressure drop.

5.13 shows the result of the simulation with a slit die with the aspect ratio $\frac{W}{H} = 24$. Figure 5.13 b shows the result of the simulation with the same slit die as in Figure 5.13 b; the only difference is in the application of a take-up force on the outlet section parallel to the extrusion direction. Figure 5.13 c shows the result of the simulation with a different aspect ratio. As shown in Figure 5.13 b, the difference between these two dies is related to a different curvature radius, which results in a different height of the opening in the centre of the die. In the experiments and simulations, the S-shape also disappears.

Simulations with dies with different aspect ratios, meaning different curvature radii, have shown that the appearance of this instability, the S-shaped extrudate, stronger or weaker, has a threshold at a $\frac{W}{H} = 16$. Thus, for $\frac{W}{H} \geq 16$ we have the phenomenon of the S; for $\frac{W}{H} < 16$ the S vanishes.

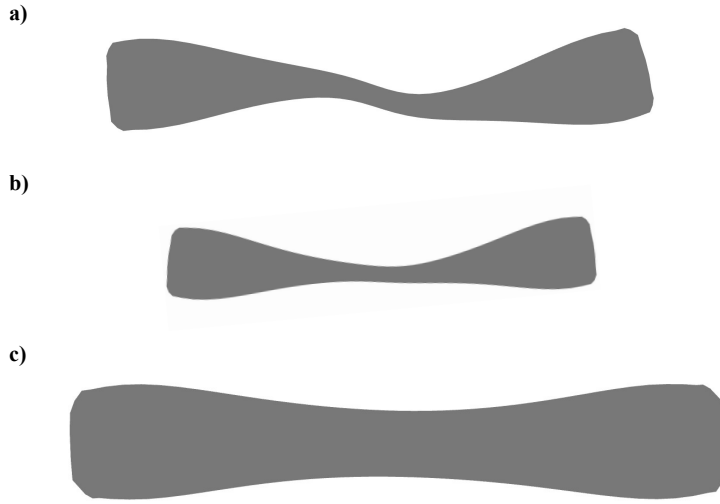


Figure 5.13. Shape prediction of the simulations is reported the bubble radius, a) prediction of slit die with bigger aspect ratio, b) prediction of die with a take-up force applied on the exit surface, and c) prediction of the slit die with a small aspect ratio.

5.5 Conclusions

In this work, we have demonstrated the ability of numerical simulations to predict the shape instabilities that occur in foam extrusion, thus providing a useful tool for designing extrusion dies to reduce such instabilities.

The presence of these instabilities in the shape causes the industry to produce excessive waste material in cases where it is possible to recover material for use. Not only does this cause significant additional economic costs due to the need for post-processing, but it is also an environmental problem due to the large amount of waste material. Therefore, controlling or predicting these instabilities can help reduce these two factors. By employing this method, it is also possible to reduce the trial-and-error method, commonly used in the die design, and this also leads to a reduction of the production of waste material and a reduction of the operative costs of tests.

The motivation behind the formation of these instabilities are closely related to the distribution of the velocity in the exit section of the die, and on the pressure drop along the die, we demonstrate how acting on the shape of the die, in particular in the exit shape, this affect the distribution of velocities and the pressure drop.

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Chapter 6

Conclusions

In conclusion, this thesis has explored the intricate dynamics of die design for the foam extrusion of starch materials, providing a comprehensive understanding of the underlying principles and practical implications of the processes involved. The research presented in this thesis is divided into five key chapters, each contributing to the overall objective of optimising die design and improving the quality of extruded starch products. The results of this work not only advance the academic discussions on foam extrusion but also have significant potential for industrial applications in food technology and materials science.

The first chapter provided a comprehensive review of the state of the art, highlighting the fundamental concepts of die design and foam extrusion and 3D printing and underlining the critical role of rheological properties in these processes.

The second chapter focused on a different but equally innovative area, the application of 3D printing techniques to starch- and protein-based inks. This work provided a comparative analysis of the porous structures obtained by cold and hot extrusion methods, revealing significant differences in morphology and mechanical properties. By examining the behaviour of starch and protein inks under these conditions, the chapter highlighted the potential for achieving tailored morphologies with controlled bubble sizes, suitable for applications such as meat analogues. This study highlighted the importance of processing parameters in determining the structural and mechanical properties of printed materials, providing new ways to develop

advanced food products with improved textural and nutritional qualities. The use of 3D printing to create specific morphologies represents a significant step forward in food design and processing, with implications for both customisation and scalability.

In Chapter three, a novel approach to simultaneous 3D printing and foaming was presented, resulting in unique morphological features within the extruded filaments. The observed dual orientation of bubbles (aligned both in the extrusion direction and radially) was attributed to the inhomogeneous temperature profile within the die. This finding has significant implications for the design of extrusion dies, as it suggests that thermal management is a critical factor influencing the structure of the final product. The ability to manipulate bubble orientation through die design could lead to improved textural properties in extruded starch products, thereby enhancing their appeal and functionality in food applications.

The fourth chapter examined computational simulations using COMSOL to predict die swell in a 2D axisymmetric domain. These simulations, based on the Oldroyd-B model, revealed the limitations of the model, in particular its inability to accurately predict die swell under varying flow conditions due to the inability to account for the extensional contributions associated with the process. This led to a critical evaluation of the model assumptions and highlighted the need for further refinement and adaptation of existing models to better reflect the complexities of starch-based materials. The insights provided by this combined investigation were invaluable in shaping subsequent research directions, in particular the exploration of alternative modelling approaches and experimental validations.

The final chapter discussed the industrial challenges associated with foaming extrusion, focusing in particular on the shape instabilities associated with the die geometry. These instabilities were studied using CFD simulations carried out in ANSYS Fluent with the Polyflow tool, which allows foaming to be activated during the simulation, even if limited to simpler inelastic models such as the power law model. This chapter has stressed the importance of geometric optimisation in die design, as even small changes in die exit face dimensions can have a significant impact on the stability and quality of the extruded product.

In summary, this thesis has made important contributions to the design of foam extrusion in general and starch foaming in particular, with

significant relevance to the packaging sector in particular and also to food applications of starches and proteins ink. The integration of computational modelling, experimental investigations, and theoretical analysis has provided a comprehensive view of the challenges and opportunities in this field. The results highlight the need for further research into the rheological behaviour of starch materials, the optimisation of die geometries, and the exploration of innovative processing techniques such as 3D printing. The main overall conclusions of this work are the ability to consistently foam starch to a specific product shape and with specific properties, the reduction of trial-and-error in die design through the use of CFD simulations, the discovery of a new morphology in 3D foam printing with multiple applications, the investigation of shape foam instability with industrial relevance, and the successful printing of starch and protein inks with specific morphology and bubble dimensions for use as meat analogues. By filling the gap between theory and practice, this work lays the foundation for future research efforts aiming to further refine die design and optimise foam extrusion processes for starch-based materials and the prevention of instability.

Author's Career

7.1 Author's Publications

1. **Claudio Esposito** et al., “*Validated Modelling of Complex Geometry Dies for Extrusion Foaming of Starch-Based Mixtures*”, AIP conference proceedings, 2024. DOI: <https://doi.org/10.1063/5.0204565>
2. Lorenzo Lombardi, Sara Consalvo, **Claudio Esposito**, Daniele Tamaro, “*Tailoring Texture and Functionality of Vegetable Protein Meat Analogues through 3D Printed Porous Structures*”, Food Hydrocolloids, 2025. DOI: <https://doi.org/10.1016/j.foodhyd.2024.110611>
3. **Claudio Esposito** et al., “*Orientation-graded morphologies in microcellular foams through additive manufacturing*”, Industrial & Engineering Chemistry Research, 2024. DOI: <https://doi.org/10.1021/acs.iecr.4c02307>.
4. **Claudio Esposito** et al., “*Using CFD Simulations to Predict and Control Shape Instabilities in Slit Die for Foam Extrusion*”, under submission.

7.2 Author's Patents

1. Lorenzo Lombardi^a, Daniele Tammaro^a, **Claudio Esposito**^a, Pier Luca Maffettone^a, Alessandro Manzo^b, Filippo Defina^b, Francesco Maria Sacerdoti^b, Massimiliano di Martino^b, *"Processo di manifattura additiva per la produzione di schiume di polimeri semicristallini senza l'uso di additivi"*, English Version: *"Additive manufacturing process for the production of semicrystalline polymer foams without the use of additives"*. Deposited October 10, 2024.

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(b) 3DnA s.r.l.

7.3 Author's Conference Participations

Oral Communications

1. The 38th International Conference Polymer Processing Society (PPS38), held in St.Gallen (Switzerland) on May 22-26, 2023.

Entitled: *"Validated Modelling of Complex Geometry Dies for Extrusion Foaming of Starch-Based Mixtures"*

2. The 19th International Congress of Rheology (ICR 19) held in Athens (Greece) from July 29 – August 4, 2023.

Entitled: *"Rheological characterisation and modelling of starch-based mixtures aiming at the optimisation of the extrusion foam process"*

Poster Communications

1. Tissue Engineering and Regenerative Medicine International Society (TERMIS) European chapter held in Manchester (United Kingdom) on March 28-31, 2023.

Entitled: *"3D printed foamed scaffolds for tissue engineering"*

2. XVIII Italian Society of Rheology Conference (SIR18) held in Capri (Italy) on September 12-14, 2024.
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Entitled: *"Shape instabilities control in slit dies design for foaming extrusion process"*

Invited Speaker

1. The Additive Manufacturing Symposium (online) organized by The University of Bath (United Kingdom) on June 21st, 2023.

Entitled: *"Starch and protein gel foams by 3D printing"*

7.4 Author's PhD Schools

1. **Summer school on Soft Matter System: From Fundamentals to Foods.** Cargese, Corsica, France, 23 Jul – 3 Aug, 2024. (50 hours).
2. **Trieste Next International Academy at Trieste Next:** Festival of Scientific Research. Trieste, Italy, 27-29 Sept, 2024. (24 hours).