Continuous 3D Printing of Hierarchically Structured Microfoamed Objects

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We report the design and results of a novel process combining 3D printing and foaming to produce microfoamed polymeric structures, from simple strands to more complex architectures, using physical blowing agents. Foaming processes are extensively operated in polymeric cellular materials industry to produce pores, yet without spatial control of their positioning. This intrinsic stochasticity may introduce imperfections, which reduce the mechanical properties of the material, thus regular (e.g., periodic) porous structures would be more desirable. 3D printing allows to fabricate polymeric cellular materials with empty spaces in a well-defined periodic structure. To this end, very expensive 3D printers are required to achieve micron-resolution pores. Correspondingly, the production time is dramatically large and becomes a bottleneck to the industrial scale-up. Herein, an innovative technique combining the simplicity of polymer foaming with the precision of 3D printing is presented. The resulting materials have the advantages of both the techniques: they have a micron-controlled cell structure and can be printed at reasonable costs and time. The proposed approach is validated using a bio-based and compostable polymer, namely, polylactic acid (PLA). The resulting foamed strands and hierarchical structures are novel in terms of morphology and show a controlled local porosity and superior mechanical properties.

1. Introduction

3D printing has been revolutionizing the way to transform materials into functional objects by virtue of 1) an incredible freedom of design compared with traditional techniques, 2) a high sustainability due to waste minimization, and 3) the possibility of mass customization because, for moderate quantities of items, it is more economical than traditional techniques.[1] The number of applications is quickly raising in a wide range of fields, for instance, in automotive for moquette and prototypes, in medicine for implants and scaffolds, and in construction industry for the fabrication of components or even buildings.[2–4] Among the numerous techniques for 3D printing, fused deposition modeling (FDM) uses a continuous filament of a thermoplastic polymer to 3D print layers of materials. The filament is heated at the nozzle of a printer and extruded through a small orifice on a platform or on top of previously printed layers. We present here an innovative version of FDM to print foams. Our novel technique, which could be defined “3D foam printing,” produces microfoamed strands and structures by inline impregnation of a physical blowing agent in the filament that will foam at the nozzle exit. In what follows, we refer to the polymer fed to the printer as “filament” and to the foamed polymer exiting the nozzle as “strand.”

Foams are widely applied in several technological fields, offering distinctive characteristics that derive from their porous internal morphology.[5–8] The characteristic size of the pores, their shape, and their hierarchical organization are important factors in determining the structure–property relationship in these materials.[9] Indeed, hierarchical porous structures outperform their nonhierarchical counterparts in regard to mechanical behavior and accessible active surface.[9] For example, honeycomb and lattice cellular structures show superior mechanical robustness and energy absorption performances. As a matter of fact, nature has often chosen optimized hierarchical structures to shape life on our planet.[6] 3D printing of foamed hierarchical structures, which is appealing in several industrial fields, is still challenging due to the difficulty of forming internal microporous structures with the existing printing techniques.[10,11] Efforts have been made to print polymers into cellular or mesh structures by piling up extruded strands, where macroscale pores are generated by the computer-designed spacing between the filamentary struts. Nevertheless, the extruded strands are still densely packed, and the porous structure is directly restricted by the printing resolution, which results in a low porosity limited to the external strand surface; moreover, the printing time increases as the cost to pay for high resolutions.[8] Many attempts have been made to
produce 3D printed foams with high porosity and intrastrand micropores.\cite{9,12,13} The current solutions are based on two-stage approaches that consist in a first step where structures with interstrand macroporosity are printed and a second step where the intrastrand microporosity is produced by freeze-drying\cite{13} or batch foaming.\cite{12} Recently, a solution has been proposed where the first step consists of preparing either an emulsion\cite{14} or a treated filament,\cite{15} which, in the second step, is heated up through a 3D printer to produce the final foamed strand. Such approaches suffer the complexity of multistage processes and are seldom capable of fine control of the foamed strand morphologies. Therefore, less expensive and less time-consuming alternative methods that could address these limitations and cover a wide range of controlled pore size and morphology are highly demanded to enable full exploitation of the rich design space offered by hierarchical structures.\cite{16,17,18}

We here propose a simple and cost/time-effective 3D printing technique to produce microfoamed strands in only one step. We achieve a fine tuning of cell morphology in the printed strands by designing the operating conditions through the modeling of transport phenomena. We report the results of an extensive experimental campaign for the production of microfoamed strands with a controlled density and morphology. Model-based design of the operating conditions results in the formation of structures with a wide range of densities and pore sizes (from 10 to 500 μm). The proposed approach opens up a broad scenario of opportunities to optimize mechanical, thermal, and electrical properties of 3D printed structures. Noteworthy, our approach is here applied with use of a biodegradable and bio-based polymer, i.e., polyactic acid (PLA), thus allowing for a sustainable production.

2. Experimental Section

PLA, grade NW4043D from NatureWorksLLC, was used in this study and its physical properties are resumed in Table 1.\cite{19}

PLA pellets were dried overnight at 60 °C in oven under vacuum conditions before any manipulation. A PLA filament with diameter of 1.75 mm was produced using a Composer350 extruder (from 3DEVO company, The Netherlands), whose process parameters are shown in Table 2. A Prusa Research I3 Mk3s 3D printer was then used to foam the filament. The blowing agent, acetone, was supplied by Sigma-Aldrich (Germany).

Table 1. Physical properties of PLA used to produce the filament.

| Physical properties          | Value | ASTM method |
|-----------------------------|-------|--------------|
| Specific gravity [g cc⁻¹]   | 1.24  | D792         |
| MFR (g/10 min) @ 210 °C/2.16 kg | 6     | D1238        |
| Relative viscosity @ 1.0 g DL⁻¹ in chloroform at 30 °C | 4.0 | D5225        |
| Clarity                     | Transparent |         |
| Peak melt temperature [°C]  | 145–160 | D3418        |
| Glass transition temperature [°C] | 55–60 | D3418        |
| Tensile yield strength [MPa] | 60    | D882         |
| Tensile modulus [MPa]       | 3.6   | D882         |
| Tensile strength at break [MPa] | 60    | D882         |

The foams were characterized to determine their bulk density (ρ) and cell density (N). ρ was measured according to ASTM D7710 using an analytical balance (Mettler Toledo, Columbus, OH). 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 (Hitachi TM 3000 SEM). The SEM images reported in the manuscript were taken from a cross section that was chosen randomly from the foamed samples. Each foaming experiment was repeated at least three times for calculating the cell size distribution. N was calculated as

\[
N = \frac{\rho_p}{\rho} \left( \frac{H}{A} \right)^{\frac{1}{3}}
\]

where \(\rho_p\) is the density of the solid sample and \(n\) is the number of cells in the area \(A\) of the SEM micrograph. The cell size was measured according to ASTM D3576. The expansion ratio was calculated as \(\rho_p/\rho\). A custom-made MATLAB algorithm was used to measure the cell size distribution in the cross section of the samples. The microfoamed strands were 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 maximum tensile stress, \(\sigma_{\text{max}}\), 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 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⁻¹. To calculate the crystallinity degree, the foamed strands were heated at 10 °C min⁻¹ 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

\[
w_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{cc}} \times 100
\]

where \(\Delta H_m\), \(\Delta H_{cc}\), and \(\Delta H_c^0\) 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 g⁻¹\cite{20}. Three replications were made for each sample to obtain an average value. For measuring the local crystallinity content (as detailed in Section 4), the strands were peeled off by cutting them in liquid nitrogen with razor blades.

3. The Novel 3D Foam Printing

To end up with a single-stage strand foaming during printing, one needs the following processes to be completed in series: 1) solubilization of the blowing agent in the filament to be foamed, 2) evolution 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, and 5) deposition of the foamed filament. Therefore, the proposed technology can be schematized with the following units (see Figure 1): a) solubilization of the blowing agent into the filament, b) desorption of the blowing agent, c) melting, d) foaming, and e) adhesion of the strands. Mass transport phenomena in the first two units are modeled to achieve specific foam morphologies in the foamed strand. We go into details of the single units below (except for e, which is discussed in the Section 4).

3.1. Solubilization

The thermoplastic polymeric filament is impregnated inline with a liquid bath containing a mixture of a blowing and a nonblowing agent (Figure 2a). In this work, we used acetone as the blowing agent for the inline impregnation of PLA filaments. Acetone was chosen because it is a good solvent for PLA,[21] thus it can be used for a fast inline impregnation of the filament. The level of the bath and the concentration of the blowing agent in the liquid can be fixed at will. Inline impregnation allows to tune the concentration of the blowing agent while the object is printed. Indeed, the residence time of the filament in the bath (t_{sol}) can be changed by varying the level of the liquid without the need of changing the printing speed. Furthermore, both homogeneous and inhomogeneous concentration profiles of the blowing agent in the polymer can be achieved by tuning the residence time and liquid bath concentration. We remark that, for the sake of simplicity, the solubilization here presented is based on a liquid bath; nonetheless, a solubilization stage with a gas can be implemented with a closed autoclave.

3.2. Desorption

When the filament exits the bath, it enters the desorption zone. Here, one can promote desorption so as to generate a nonuniform blowing agent profile within the filament that, in turn, allows to obtain custom cellular morphologies in the foaming zone.[22–25] If this is not wanted, a negligible desorption might be also achieved. Desorption can be effectively controlled by modulating the residence time (t_{des}) of the polymer in this zone.[25,26]

3.3. Melting

As for the standard 3D printing, the impregnated filament is melted before accessing the nozzle.[27–29] Herein, the gas solubilized into the filament may affect the melting kinetics and form bubbles if the pressure is not sufficiently high.

3.4. Printing and Foaming

The rapid pressure drop in the nozzle triggers bubble nucleation followed by bubble growth. Consequently, the printed strand reaches the desired density and morphology. According to the units shown in Figure 1, we modified the 3D printer as reported in Figure 2b, where it is possible to notice the beaker filled with the liquid bath containing the blowing agent assembled on the printer structure before the extruder inlet.

The accessible ranges of the operating conditions are shown in Table 3. The nozzle temperature can be changed arbitrarily through the 3D printer software. Conceptually, the lower limit is given by the melting temperature of the polymer (i.e., about 170 °C for PLA) and the upper limit is the temperature at which the polymer starts to degrade (about 280 °C for PLA); thus, a temperature operating range in between these two limits is considered. The software fixes the wall temperature of the brass nozzle in the 3D printer, which affects the melting kinetics of the filament and, therefore, the instant at which the gas foaming starts.

Figure 1. Sketch of the 3D foam printing with continuous solubilization. The color of the filament represents schematically the blowing agent profile: gray corresponds to the absence of blowing agent and blue to the presence of solubilized blowing agent.
The foaming temperature, $T_{\text{foam}}$, is defined equal to the nozzle temperature. Also, the printing speed can be changed at will by the 3D printer software, which sets the polymer flow rate through the nozzle; thus, the pressure drop that, in turn, can trigger the gas foaming. The largest speed is limited by slip at gears.[30] Finally, $t_{\text{sol}}$ and $t_{\text{des}}$ can be chosen based on the desired concentration profile of the blowing agent in the filament (as it is reported in the next section). $t_{\text{sol}}$ can be tuned by changing the printing speed and/or the liquid height in the beaker, whereas $t_{\text{des}}$ can be tuned by changing the printing speed and/or the distance between the beaker and the melting zone. In this work, both $t_{\text{sol}}$ and $t_{\text{des}}$ range from 0.1 to 5 min, which are values comparable with the characteristic diffusion time of acetone in PLA at room pressure and temperature for the problem at hand.

To check that the PLA strand reaches temperature conditions above its melting point before exiting the nozzle of the 3D printer, we performed a finite-element numerical simulation of the mass, momentum, and thermal energy transport phenomena occurring in it. A conservative verification of the achievement of the melting conditions was done by simulating the process in the “worst” case, namely, at the largest experimental printing speed and the lowest printing temperature. The details on the numerical simulation are given in the Supporting Information, where the color map of the temperature field inside the nozzle is also shown in Figure S2, Supporting Information.

### 4. Results

We now present the foams obtained using the novel 3D foam printing technology at varying concentration of the blowing agent and temperature. In addition, we show a tuning of the foam morphology by controlling the mass transport. A proof-of-concept of the feasibility of 3D foam structures will be also presented based on the results obtained with a single foamed strand.

#### 4.1. Microfoamed Strands by 3D Foam Printing

With the proposed setup, we investigated the effects of the two most important process variables, i.e., the blowing agent concentration and the foaming temperature, $T_{\text{foam}}$, on the density and the foam morphology of the strands. The average blowing agent concentration in the filament was varied by adjusting the solubilization time. In particular, a proper saturation is achieved when the acetone has diffused in the entire filament section. To quantify solubilization and desorption, two dimensionless times are defined: $t_{\text{sol}} = \frac{R^2}{2D}$ and $t_{\text{des}} = \frac{R^2}{D}$, where $R$ and $D$ are the radius of the filament and the diffusivity of the blowing agent (equal to about $5.5 \times 10^{-5}$ cm$^2$ s$^{-1}$, as detailed in the Supporting Information). So, for $t_{\text{sol}} < 1$, we expect a concentration gradient across the filament section, and the larger $t_{\text{sol}}$ the larger the average concentration of the blowing agent in the filament, whereas the blowing agent impregnates the entire filament section when $t_{\text{sol}} > 1$. On the contrary, $T_{\text{foam}}$ is a very important process variable to define the final foam structure both in terms of density and morphology. A bell-shaped curve typically describes the effect of $T_{\text{foam}}$ on the foam density, with a maximum of the expansion ratio at an optimal temperature, $T_{\text{foam}}^\text{optimal}$. Below $T_{\text{foam}}^\text{optimal}$, the viscosity of the polymer increases and crystallization or vitrification may occur. Above $T_{\text{foam}}^\text{optimal}$, the reduction of the polymer viscosity induces bubble coalescence and the increased diffusivity of the blowing agent is responsible for its loss through the external surface of the strand, followed by a corresponding reduction of foaming efficiency. All these phenomena hinder bubble growth.

**Figure 3** shows the cross sections of foamed strands obtained at $t_{\text{sol}} = 1$ (panel a), 2 (panel b), and 4 (panel c) at $t_{\text{sol}} \ll 1$ (namely, no desorption) and $T_{\text{foam}} = 210^\circ \text{C}$. As expected, we found bubbles distributed on the entire cross section of the strand. The cell density and the expansion ratio increase with the blowing agent concentration; going from left to right, we have $N = 550, 1200$, and $7000 \text{ # cm}^{-3}$ and the expansion ratio $R_p/\rho = 1.1$, 1.5, and 2.1. For filaments fully saturated with acetone,
our results on microfoamed strands are in good agreement with what was found by Kiran et al.\[32\] on batch-foamed PLA/acetone samples, confirming that the scale-down of the sample does not represent a limitation for our model system.

**Figure 4a** shows the effect of $T_{\text{foam}}$ on the expansion ratio of the microfoamed strands at $t_{\text{sol}} = 1, 2, 4$. For the three cases under investigation, we found that the expansion ratio curves have the classical bell shape, and the maximum expansion ratio attains a larger value and shifts to lower $T_{\text{foam}}$ as $t_{\text{sol}}$ increases. Regarding the observed vertical shift of the bell-shaped curve, it corresponds to the expected larger amount of blowing agent contained in the filament when arriving at the nozzle. Regarding the horizontal shift, we speculate that it is a consequence of the plasticization effect.\[17\] The largest expansion ratio (i.e., about 2.8) is achieved at the largest $t_{\text{sol}} = 4$ and it is comparable with the largest expansion ratio achievable in industrial foam extrusion processes.\[17\] **Figure 4b** shows the dimensions of microfoamed strands obtained at $t_{\text{sol}} = 4$ and $T_{\text{foam}} = 200, 210, 220, 230, 240$, and 260 °C (from bottom to top).

With such proposed setup, a fast and gram-size analysis of the so-called foamability map\[23–25\] for a specific polymer can be conducted in a very efficient way. The 3D foam printer is, indeed, a fast and economical tool for characterizing new formulations, blowing agents, and processing conditions, as also shown in Figure 4. Our 3D foam printing technology has two important advantages: 1) very small amount of polymer/additives (in the order of grams) is needed to explore a wide range of process conditions without almost any operational cost, and 2) the efficacy of the continuous solubilization process for small-sized filaments minimizes the problems related to the mixing of blowing agents that are usually encountered in typical foam extrusion.

The foamed strands were characterized mechanically by means of microtensile tests over the entire range of densities: $\sigma_{\text{max}}$ (squares) and the specific maximum stress, $\sigma_{\text{max}}/\rho$ (circles), are shown in **Figure 5**. To perform the measurements, the foamed filaments were glued onto removable jaws as shown in the inset of Figure 5a, whereas a video of an entire test on a sample with $\rho = 350$ kg m$^{-3}$ is given in the Supporting Information (see Video 1, Supporting Information). As expected, $\sigma_{\text{max}}$ monotonically increases with the density and the $\sigma_{\text{max}}$ value of the “less foamed” sample, i.e., at the highest $\rho$, is in good agreement with the ultimate tensile strength of PLA reported in the literature.\[33\] Interestingly, the specific mechanical properties of the foamed strands are almost constant in the density range from 350 to 700 kg m$^{-3}$. The improvement of the specific mechanical properties of the PLA at low density can be ascribed to the increase in crystallinity due to 1) the larger plasticization effect at larger concentration of the blowing agent\[34\] and 2) the larger deformation rate due to the larger foam expansion.\[21,35\] Indeed, the DSC analysis revealed that the crystallinity content increases as the density of the foamed strands decreases. In **Figure 5b**, the DSC scan of a sample at $t_{\text{sol}} = 0$ (gray curve) and $t_{\text{sol}} = 4$ (black curve) is shown. During the first heating ramp, a cold crystallization, i.e., the exothermic peak at $\approx 110$ °C, happens only in the nonfoamed printed strand (gray circles). The foamed printed strand (black circles) has no cold

**Figure 3.** Sections of PLA strands foamed at $t_{\text{sol}} = 1$ (a), 2 (b), 4 (c) and $t_{\text{sol}} \ll 1$.

**Figure 4.** a) Expansion ratio of foamed strands as function of printing temperature at three different $t_{\text{sol}}$ (the lines are guide for eyes); b) optical images of expanded PLA strands at $t_{\text{sol}} = 4$ and different printing temperatures.
crystallization\textsuperscript{36,37} due to the high level of crystallinity reached during the foam printing process. In Table 4, the degree of crystallinity is reported for \( t_{\text{sol}} \) from 0 to 4 at \( T_{\text{foam}} = 210 \text{ °C} \).

We close this section by remarking the effective capability of the proposed continuous microfoaming technique to achieve substantial low density with uniform bubble distribution. The next two sections present how to achieve nontrivial foam morphologies and how to obtain efficient adhesion among the deposited strands in 3D printed structures.

\subsection*{4.2. Microfoamed Strands with Controlled Bubble Morphology by 3D Foam Printing}

The nucleation and growth of bubbles is strictly linked to the concentration of the gas in the polymer and it is expected that, by designing the gas concentration profile through a proper choice of the solubilization time, \( t_{\text{sol}} \), and the desorption time, \( t_{\text{des}} \), it is possible to control the final morphology of the printed strand. In the previous section, we presented the case of \( t_{\text{sol}} \geq 1 \) and \( t_{\text{des}} \ll 1 \), where a uniform final morphology derives from a uniform concentration of the blowing agent within the filament. By playing with these two characteristic times, different concentration profiles in the filament can be achieved. Figure 6 shows how the blowing agent profile changes depending on \( t_{\text{sol}} \) and \( t_{\text{des}} \). At \( t_{\text{sol}} \geq 1 \), the blowing agent has penetrated in the entire filament section at the end of solubilization, so, by progressively increasing \( t_{\text{des}} \), one can achieve the different situations depicted on the first row in Figure 6. Needless to say, by reducing \( t_{\text{sol}} \) and, correspondingly, modulating \( t_{\text{des}} \), a variety of different morphologies can be produced (see lower rows in Figure 6). We limited these considerations to axisymmetric morphologies, but more general situations are conceivable if, for example, the filament surface is appropriately treated. For the sake of simplicity, Figure 6 shows sharp interfaces between blowing-agent-rich and blowing-agent-poor regions. The real situation is, in general, blurred. The design of the blowing agent profile is achieved by solving a simple mass diffusion problem in the radial direction (neglecting axial diffusion)\textsuperscript{26} once the diffusion coefficient is known. Thus, by fixing the appropriate impregnation and desorption times, one can obtain the desired profile.

In Table 5, we present microfoamed strands with different blowing agent profiles produced at 210 °C. With \( t_{\text{sol}} < 1 \) and \( t_{\text{des}} \ll 1 \), the blowing agent penetrates only a small peripheral zone of the filament, thus the bubbles are expected to form only in such area. Indeed, a “ring” of bubbles is observed in the strand periphery, as shown on row 1 in Table 4. On the contrary, starting from a completely impregnated filament, i.e., \( t_{\text{sol}} \approx 6 \), \( t_{\text{des}} \) can be varied to obtain microfoamed strands with a denser skin with respect to the bulk. On row 2 of Table 4, the cross section of the filament is shown for three values of \( t_{\text{des}} \). It is apparent that, as \( t_{\text{des}} \) is increased, the bubbles are localized in a progressively

\begin{table}
\centering
\begin{tabular}{ll}
\hline
\textbf{\( t_{\text{sol}} \)} & \textbf{\( w_c \)}  \\
\hline
0 & 2 \pm 0.5  \\
1 & 20 \pm 1  \\
2 & 25 \pm 1  \\
4 & 34 \pm 3  \\
\hline
\end{tabular}
\caption{Crystallinity content of PLA strands at different \( t_{\text{sol}} \).}
\end{table}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6}
\caption{Sketch of the inline batch impregnation process and corresponding concentration profiles during the blowing agent solubilization and desorption. The blowing-agent-rich areas are shown in blue, whereas gray represents blowing-agent-poor areas.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{\textbf{a)} \( \sigma_{\text{max}} \) (squares, vertical axis on the left) and \( \sigma_{\text{max}}/\rho \) (circles, vertical axis on the right) as function of \( \rho \) for the foamed strands; \textbf{b)} first heating ramp for a non-foamed (gray circles) and a foamed printed strand (black circles).}
\end{figure}
Table 5. Different foam morphologies controlled by mass transport.

| Conditions | Expected foam morphology | Observed foam morphology |
|------------|--------------------------|--------------------------|
| $t_{sol} < 1$ | $t_{des}/C_{25}$ | $0.1$ $t_{des}/C_{25}$ |
| $t_{des}/C_{25} < 1$ | $t_{des}/C_{25}$ | $0.5$ $t_{des}/C_{25}$ |
| $t_{sol} = 6$ | $t_{des} \approx 0.1$ | $t_{des} \approx 0.5$ |
| $t_{des} \approx 1$ | | }

200\mu m
thinner core of the strand, whose expansion ratio correspondingly decreases.

The localization of bubbles in the core or the periphery of the strands allows to change locally the properties of the polymer, which may be affected by the rapid expansion of the bubbles. Indeed, the crystallinity content measured in the core, \( w_c^2 \), for the morphologies in Table 4 is different from the crystallinity content in the periphery, \( w_p^2 \). In particular, we measured \( w_c^2 < w_p^2 \) for \( T_{\text{co}} < 1 \) and \( T_{\text{des}} < 1 \), while \( w_c^2 > w_p^2 \) for \( T_{\text{co}} \approx 6 \) and \( T_{\text{des}} > 0.1 \). This aspect affects the mechanical properties of the foamed strands, as seen in the previous section, and it adds a degree of freedom in the design of complex structures.

At \( T_{\text{co}} \approx 6 \), the total number of cells decreases from 440 at \( T_{\text{des}} = 0.1 \) to 273 at \( T_{\text{des}} = 1 \). Also, the average cell size decreases because the gas concentration in the filament decreases at increasing the desorption time. The cell size distribution for the foamed strands at \( T_{\text{co}} \approx 6 \) and different \( T_{\text{des}} \) is shown in Figure 7, where it can be observed that the peak cell size shifts to the left when \( T_{\text{des}} \) goes from 0.1 to 1.

Having demonstrated that it is possible to control foam density and morphology in the printed strands, we show in the next section that the novel technology is suitable also for printing foams with 3D hierarchical structures.

4.3. 3D Structures

3D hierarchical structures can be obtained by coupling strand morphologies and ad hoc printing design. A composite object with a simple geometry, shown in Figure 8, was designed for foam printing tests. Filaments having different solubilization and desorption conditions were printed with the same geometry and printing parameters, as shown in Table 6. As it is apparent from Figure 8a, the nonfoamed object is almost transparent, whereas the foamed object (shown in Figure 8b) is white due to the formation of small bubbles inside the strands.

The cross sections of the printed manufacts highlighted by the red-dashed lines were analyzed by SEM. Figure 9a shows the cross section of the manufact formed by nonfoamed strands, showing no bubbles (see also the zoom in Figure 9b), whereas Figure 9c shows that of the manufact composed by foamed strands, showing bubbles uniformly distributed in the cross section of each strand with a broad distribution of bubble sizes, going from 5 to 100 \( \mu \text{m} \). The zoom shown in Figure 9d allows to see that the strand surface is rough due to the "craters" left by bursting of superficial bubbles, which, in turn, enhances the adhesion among the strands as they compenetrate each other. On the contrary, in the nonfoamed sample, the strands are clearly separated and have less contact area (see Figure 9b).

The improved adhesion among the strands observed in the foamed manufact is expected to give it better mechanical properties. Using a filament conditioned with \( T_{\text{co}} \approx 2 \) and \( T_{\text{des}} \approx 1 \), strands foamed only in the core and with a dense skin layer were produced and piled up, as shown in Figure 9e (cross section) and 9f (longitudinal section). On the contrary, using a filament conditioned with \( T_{\text{co}} < 1 \) and \( T_{\text{des}} < 1 \), strands foamed only in the periphery and with a dense core were produced and piled up, as shown in Figure 9g (cross section) and 9h (longitudinal section). The presence of inter- and intra-strand porosity with controllable characteristic size confirms the possibility to produce second-order hierarchical structures with our modification of the 3D foam printing process. Interestingly, in the printed structures with skin layers, a process of secondary foaming can be noted at the welding lines, where localized bigger bubbles are present. This might be linked to the coupled mass and thermal transport phenomena occurring during foaming and will be modeled in an upcoming work.

The novel versatile 3D foam printing technique can be used to produce a broad window of hierarchically structured porous materials, taking advantages of all the deriving properties. The developed technology was tested to produce a scaffold with a complex geometrical shape. A downsized femur was designed and foam printed, as shown in Figure 10a. The overall density of the foamed femur is 400 kg m\(^{-3}\) and its cross section is shown in Figure 10b. The quality of the foamed cross section confirms that our technique is also suitable for printing complex geometries. The large deformation of the foamed strand can influence the
printing accuracy and resolution. The printing accuracy was adjusted by tuning the layer width and height based on the expansion ratio previously measured (in Figure 4). The printing resolution was recovered by means of a smaller nozzle diameter.

The presented 3D foam printing technique has been tested successfully with other blowing agents (i.e., ethanol, water) and polymers (i.e., polycaprolactone and polyvinyl alcohol).

Table 6. Printing conditions for the filaments composing the structure in Figure 8.

| Nozzle temperature | Printing speed | Fan speed | Bed temperature | Filament diameter | Nozzle diameter |
|--------------------|----------------|-----------|----------------|-------------------|----------------|
| 210 °C             | 20 mm s⁻¹      | 20%       | 60 °C          | 1.75 mm           | 0.4 mm         |

![Figure 9](image-url) 3D printed structures with filaments having different combinations of $t_{sol}$ and $t_{des}$. a) Cross section of nonfoamed strands; b) magnification of (a) highlighting strand adhesion; c) cross-section of foamed strands; d) magnification of (c) highlighting strand adhesion; e) cross-section and f) longitudinal section of foamed strands with skin layer; g) cross-section and h) longitudinal section of foamed strands with dense core.

Figure 10. a) 3D foam printed complex geometry mimicking a femur; b) cross-section of the femur corresponding to the red dashed line in panel (a).

The results show that the foaming can be controlled as efficiently as for PLA, and the morphologies will be presented in greater details in the future work.

5. Conclusion

We reported the design of a novel continuous 3D printing process to produce thermoplastic polymeric foams with physical blowing agents solubilized inline. As compared with the methods to produce 3D printed foams already reported in the literature, which involve two steps, our approach allows to perform printing and foaming in parallel in one step, with the advantages of a better geometrical resolution, a higher flexibility, and a lower process cost. The resulting 3D printed foams were analyzed morphologically by SEM, mechanically by tensile tests, and thermally by DSC. The modeling of the process by mass and heat balance supplies a tool to control the bubble morphology and position within the printed strands that, in turn, are connected to the mechanical properties. The maximum expansion ratio of the printed stands is around 3 and a bell-shape curve of the
expansion ratio versus foaming temperature has been reported and explained. The specific elastic modulus is constant (i.e., around 0.02 MPa m⁻³ kg⁻¹) in the density range from 400 to 650 kg m⁻³, and the reason has been addressed to the higher crystallinity content at lower density, also confirmed by the DSC measurements. This allows to build lighter structures without any worsening of the specific mechanical properties. The developed 3D foam printing technique allows to fabricate polymeric cellular materials that can be used to produce porous hierarchical structures in an economical and simple way. Needing only a few grams of materials and a few minutes for printing, our technique allows to save 40% of printed material and to quickly scan broad ranges of foaming conditions, e.g., foaming our technique allows to save 40% of printed material and to only a few grams of materials and a few minutes for printing, the possibility to form materials with the desired density through foaming combined to 3D printing will enable to design new products with ad hoc hierarchical structures, as the downsized femur shown in Figure 10.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
P.L.M. and D.T. conceived the work; D.T. made the experiments; P.L.M., M.M.V., and D.T. performed the modeling, R.D.G. made the SEM; M.M.V. made the simulations; and all wrote the manuscript.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
3D printing, biomedical scaffolds, bioprinting, energy storage, hierarchical structures, microfoams, polylactic acid

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