3D printing non-cylindrical strands: Morphological and structural implications

Yago Raymond, Emilie Thorel, Margaux Liversain, Antonio Riveiro, Juan Pou, Maria-Pau Ginebra

Keywords: Direct ink writing, Microextrusion, Robocasting, Ceramic, Calcium phosphate

Abstract

Conventional direct ink writing uses circular nozzles and, therefore, results in cylindrical strands. 3D printing with non-circular nozzles adds new degrees of freedom to this versatile technology, and allows obtaining structures with higher specific surface area or even introducing concave surfaces in the printed architecture. This is an enticing prospect for countless applications, including tissue engineering, chemical reaction catalysts, water evaporators and electrochemical energy storage devices. Despite this, it has been hardly explored by the 3D-printing community. Herein, we develop for the first time 3D printed structures with complex filament section morphologies using a custom-made modular nozzle and a self-setting ceramic ink. The fast elastic recovery of the ink allows obtaining good shape fidelity in the printed filaments, permitting the creation of intricate surfaces with up to 30% concavity and increasing up to 2.5 times the specific surface area compared to cylindrical strands. The use of non-circular nozzles introduces some specific constraints in the printing process. The geometry of the nozzle determines the stable printing directions, and nozzle orientation becomes a critical parameter to achieve a stable printing. Strand torsion, a phenomenon that remains unnoticed with circular nozzles, may result in relevant changes in the geometrical features of the printed structures.

1. Introduction

Filament-based direct ink writing (DIW) is one of the additive manufacturing technologies that has attracted most attention in recent years due to its great versatility and the possibility of using different types of materials, from hydrogels to ceramics or metals. It is based on the extrusion of an ink or paste through a nozzle to obtain a continuous filament. This allows from the control of the printing path to the manufacturing of dense parts with complex geometries, and porous architectures with 3D periodic structures [1]. Conventional DIW uses circular nozzles and, therefore, results in cylindrical strands. Tuning the strand geometry would enable to introduce an additional level of control to the printed structures, opening up a wide range of new unexplored possibilities.

The most straightforward application is related to the possibility to increase the specific surface area (SSA) of the printed structures. In recent years, DIW manufacturing processes have raised an interest in applications where a high interaction surface is needed, due to the high SSA that can be achieved in the porous periodic 3D strand structures. Among all the shapes in two-dimensional space with the same area, the circle is the one with the smallest perimeter, therefore, with the smallest SSA [2]. The use of deposition nozzles with a higher aspect ratio would allow obtaining strand geometries with more intricate cross-sections than the circle, increasing the structure’s SSA. Applications like chemical reaction catalysts [3,4], water evaporators [5], and electrochemical energy storage devices [6] would benefit from this increment of SSA,
resulting in higher efficiency of the respective processes.

Furthermore, DIW is a promising technology for the fabrication of textured ceramics [7,8], i.e., materials with anisotropic polycrystalline microstructure, which can enhance a wide variety of properties (e.g. magnetic, superconductive, ion conductive, thermoelectric, piezoelectric, optical, thermally conductive, and structural) [9]. The fabrication of these structures through DIW allows three-dimensional geometrical freedom and fine control of the texture orientation. It represents a suitable strategy in applications where a certain degree of control over crystallographic orientation is required (e.g. cylindrical sonar projectors [10]). Textured ceramics are commonly obtained by templated grain growth (TGG). Briefly, large anisotropic single crystals dispersed into a fine granular powder matrix are oriented epitaxially and sintered to trigger nucleation and crystal growth [11]. The epitaxial orientation of the single crystals can be achieved by shear processes, where tape casting is one of the most common approaches. The extrusion process of a paste through a nozzle occurring in DIW also leads to crystal orientation. However, with traditional circular nozzles, this orientation is concentric and proportional to the shear stress of each region of the cross-section [7,12]. By using nozzles with rectangular high aspect ratio profiles, more similar to the ones used in tape casting [13], it would be possible to orient the crystals in one single crystallographic direction, achieving properties closer to those of the monocrystal.

Printing non-cylindrical strands could also find an application in the field of bone regeneration. DIW has been proposed as a promising technology for the fabrication of patient-specific synthetic bone grafts [14] based on the possibility of printing gel-based pastes with a high concentration of ceramic charges. Moreover, the design of self-setting ceramic inks opens the door to associating them with biological molecules, or combining them with cell-containing bioinks. In this application, the 3D-printed structure acts as a scaffold for bone formation and ingrowth. Recent studies have shown that the geometrical features of the scaffold architecture play a key role in tissue regeneration. Rumpler et al. evidenced that the surface area and local curvature of the porosity...
has a strong influence on the tissue growth rate in vitro [15]. Moreover, Barba et al. proved that foam-like scaffolds with concave pores promoted bone formation and osteoinduction, contrary to 3D-printed scaffolds with convex surfaces. This was attributed to the microenvironment created in the confined cavities that acted as osteogenic niches, conducive to cellular differentiation and functionality, ultimately leading to the formation of new bone [16]. Nevertheless, traditional DIW structures result in cylindrical strands and, therefore, convex surfaces. Using nozzles with the appropriate non-circular orifice geometry would allow introducing concave surfaces in the 3D-printed structures while also increasing the bone-biomedical contact area, thus improving the potential of bone regeneration.

Even though the possibility of using square or hexagonal nozzles was put forward more than 15 years ago by Rao et al. [17], the use of non-circular nozzles has not been further explored by the 3D printing community, and the implications of the complex filament geometries in the printing process and the printed structures were not analysed in depth.

In the present work, we describe the fabrication of DIW ceramic structures with different strand morphologies by using a custom-made modular nozzle with interchangeable discs containing orifices with complex geometries. A self-setting calcium phosphate ink was used, which does not require any sintering step and does not exhibit shrinkage during the consolidation process [18]. One of the goals is to obtain strand cross-sections leading to a higher specific surface area of the filaments, and we describe for the first time the fabrication of strands with concave surfaces. Additionally, we describe the strand torsion occurring when changing the deposition direction, a phenomenon also occurring in the DIW of cylindrical strands that until the date went unnoticed due to the characteristic symmetry of this geometry. Furthermore, we discuss the implications of the strand geometry in the printing configuration and the restrictions and limitations that arise when using standard DIW positioning systems.

2. Materials and methods

2.1. Nozzle design

A custom modular nozzle that fits interchangeable thin discs with multiple orifice geometries was designed (SolidWorks, Dassault Systems, Velizy-Villacoublay, France) and machined in polyether ether ketone (PEEK) (Fig. 1A). The orifices were designed with similar dimensions while exploring different simple geometries. Discs of 3 mm in diameter and six different orifice geometries were micromachined from Teonex® polyethylene naphthalate (PEN) films (150 µm thick) using a diode end-pumped neodymium-doped yttrium orthovanadate (Nd: YVO4) laser (PowerLine E, Rofin-Sinar, MI, USA) emitting a TEM00 pulsed laser beam (M2 < 1.2) at 355 nm wavelength (Fig. 1B). The entire process was performed in an air atmosphere. The laser beam was focused on the surface of the PEN films using a F-theta lens with 235 mm focal length. In consequence, the laser spot diameter on the surface of the sample was approximately 11 µm. Galvanometric mirrors were used to scan the laser beam across the polymeric samples. The processing parameters used for micromachining were: average laser power P = 0.5 W, scanning speed v = 8 mm/s, and pulse frequency f = 20 kHz. After processing, micromachined films were cleaned by ultrasonication in an acetone bath for 10 min followed by rinsing with distilled water to remove any residue on the surface.

2.2. 3D printing

Three-dimensional structures composed of different strand geometries were obtained by microextrusion of a calcium phosphate self-setting paste [19]. Here, tricalcium phosphate (α-TCP) powder was mixed with a poloxamer-based hydrogel obtaining a ceramic suspension, which was introduced in a 3 mL cartridge (QuantX™ 8001001 Syringe Barrel, Fisnar, MN, USA) and extruded through a nozzle using a direct ink writing device (Heavy Duty Paste Extruder, CIM-UPC, Barcelona, Spain). The nozzle orifice was aligned to the nozzle displacement path so that the vertical and horizontal directions of Fig. 1B were lined up with the two orthogonal printing directions. Strands with the six different non-circular cross-sections (Fig. 1B) were extruded and compared to a control strand obtained with a tapered dispensing tip (Smooth Flow Tapered Dispensing Tip, Gauge 22, Fisnar, MN, USA) with an inner diameter of 410 µm. The printing pattern consisted of an arrangement of successive layers of parallel strands, each layer oriented orthogonally to adjacent layers. The strand-to-strand separation was 250 µm and the layer overlapping was 15% of the nozzle size. The plunger extrusion rate was adjusted individually for each condition according to its respective orifice area to guarantee that the ink extrusion speed matched the nozzle displacement speed. Moreover, the printing speed was optimised according to the requirements of the nozzle orifice geometries. Cylindrical constructs of 10 mm in diameter and 5 mm in height were printed. The green structures were subjected to a hydrothermal treatment as described elsewhere [19] resulting in the hydrolysis of α-TCP to calcium-deficient hydroxyapatite (CDHA), with the subsequent hardening of the 3D-printed structures.

2.3. Strand shape fidelity assessment

The shape fidelity of the extrusion process was assessed by comparing the geometries of the nozzles with the strand cross-sections. The printed structures were embedded in PMMA resin (Technovit 7200, Heraeus Kulzer GmbH, Hanau, Germany) inside moulds and stored under vacuum conditions in a dark environment for two days. Then, the embedded samples were photopolymerised (Exakt 520, EXAKT Advanced Technologies, GmbH, Norderstedt, Germany) for 12 h under UV light followed by 12 h under white light. The resulting blocks were cut with a precision diamond band saw (Exakt 300, EXAKT Advanced Technologies, GmbH, Norderstedt, Germany) in a plane perpendicular to the strands cross-sections and through the central axis of the cylinders, and water-sanded down to P4000 grit size (Micro grinder, Exakt 400 CS, EXAKT Advanced Technologies, GmbH, Norderstedt, Germany). The resulting cuts and the printing nozzles were coated with a thin carbon layer and observed by scanning electron microscopy (SEM, PhenomXL, Phenom World, Thermo Fisher Scientific MA, USA) with a beam intensity of 10 kV, using a backscattered electron detector (BSD).

The images were segmented and analysed with an image analysis software (Fiji, ImageJ [20]) to obtain the aspect ratio, perimeter and area of the different nozzles and filament sections. Moreover, the concavity of each geometry was quantified by determining the convex hull of each geometry, which is the minimum convex polygon that includes all the points [21,22]. Combining these data, two indexes that describe the concavity level were defined: i) the Perimeter Concavity Ratio (PCR), which is the ratio between the perimeter of the original shape and the perimeter of the convex hull, being 1 for a completely convex shape and increasing as the concavity of the original shape increases; ii) the Surface Concavity Percentage (SCP), which represents the percentage of area within the convex hull region that is occupied by a concave porosity. This index equals 0% for a completely convex shape and tends to 100% for shapes with higher concavity.

Additionally, a rheological evaluation was performed to determine the viscoelastic properties of the ink. For this purpose, a rheometer (Discovery HR-2, TA Instruments, DE, USA) equipped with a rough parallel plate geometry (20 mm Ø) and a solvent trap to prevent ink drying was used. The analysis was performed at a controlled temperature of 18 °C and a geometry gap of 0.5 mm. A first strain sweep test was carried out under oscillatory mode at a frequency of 1 Hz from 0.01% to 1000%, to monitor the storage and loss modulus and to determine the linear viscoelastic region (LVR) and the flow point (FP). Those were used to determine the low and high shear strain levels used in the three interval thixotropy test (3ITT) performed under oscillatory mode (10 Hz)
to assess the elastic recovery of the paste [23]. This test simulates the shear rate profile of the extrusion process and allows to assess the transition kinetics of the ink from fluid-like flow (second interval) to elastic shape retention (third interval) [24]. The assay consisted of a first interval applying a small amplitude oscillatory shear, corresponding to low shear strain (LVR) of 0.02% for 50 s followed by a second interval at a large amplitude oscillatory shear, corresponding to high shear strain (FP) of 1000% for 50 s and a final interval applying the same conditions of the first interval, i.e., with low shear strain stage of 0.02%, for 100 s.

Fig. 2. (A) Comparison of the nozzle orifice (NZL) and the cross-section of the 3D-printed strands (STR) for the different tested geometries. Red arrows indicate sharp curvature regions of the nozzles, where the shape was less preserved. No strand is shown for “Shape 6” nozzle because it was not possible to print 3D structures with this nozzle geometry, as described in section 3.2. (B) Geometrical attributes measured both in the nozzles and strands (NZL and STR, respectively). (C) Scheme illustrating the measurement process for different geometrical indicators: Aspect Ratio (AR), Perimeter Concavity Ratio (PCR) and Surface Concavity Percentage (SCP). Examples of the control shape, with highly convex geometry, and shape 2, presenting some concave regions. (D) Results of the concavity indicators for the different geometries. Scale bars: 300 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. Structural characterisation

Prior to the resin embedding process, 3D reconstructions of the structures were acquired (one sample per condition) by micro-computed tomography (μ-CT). The machine (SkyScan 1172, Bruker Micro-CT, Kontich, Belgium) was operated with a source voltage of 100 kV and source current of 100 μA. Images were collected with a step size of 0.2°, over the 0–180° range, with an exposure time of 3100 ms. A resolution of 26.3 μm/voxel with isotropic voxel size was used. Subsequently, acquisitions were reconstructed to image stacks with a previous beam-
indicated on the diagram. (B) Three interval thixotropy test (3ITT) showing the elastic recovery of the ink.

The volume of material (MV) and surface of material (MS) in the total volume of the VOI (TV) were measured by: (1) CTAn, an image analysis plugin, Fiji, ImageJ). Afterwards, the binarised images were transformed to 3D triangle meshes, i.e., Standard Triangle Language format (STL), with an image analysis software (“3D viewer” plugin, Fiji, ImageJ). The volume of material (MV) and surface of material (MS) in the total volume of the VOI (TV) were measured by: (1) CTAn, an image analysis software dedicated to μ-CT analysis (“3D Analysis” tool, CTAn, Bruker Micro-CT, Kontich, Belgium); (2) Fiji, the polyvalent open-source image analysis software (“BoneJ” plugin [25], Fiji, ImageJ, NIH-LOCI, U.S.A.); (3) measurement on the 3D mesh using MeshLab, an open-source STL processing software (MeshLab, ISTI, Pisa, Italy [26]); and (4) a theoretical estimate based on the measurement of strand diameter and perimeter, VOI dimensions and the number of strands in the VOI. Different geometrical attributes of the 3D-printed structures were assessed. The percentage of porosity was measured based on the proportion of MV in the TV. The pore size distribution was calculated using a sphere fitting algorithm [27] (“3D analysis” tool, CTAn, Bruker Micro-CT, Kontich, Belgium). Finally, the specific surface area (SSA) normalised by volume of strand (mm$^2$/mm$^3$) and by length of strand (mm$^2$/strand mm) was calculated by dividing MS over MV and over the total length of the strands in each VOI respectively.

3. Results and discussion

2.5. Finite element analysis

Linear static finite element simulation under elastic behaviour was performed on the different μ-CT-based STL reconstructions to assess the influence of the strand geometry on the stress distribution in the structure. The models used were first discretised using 4-node linear tetrahedral elements (C3D4). A uniaxial compression test under displacement-controlled loading along the Z printing axis was simulated.

The boundary conditions were defined on the nodes of the top and bottom faces of the mesh. Whereas the displacement of the bottom nodes was fixed in the Z direction, a vertical displacement of 0.0439 mm that corresponded to a compression strain of 0.1% was imposed for the top nodes. The Young modulus of the material after hydrothermal consolidation was experimentally determined by testing in compression massive cylinders (6 mm in diameter and 12 mm in height), under the same conditions applied in the simulation (quasi-static uniaxial compression loading, displacement control mode at 1 mm/s). The value obtained, 2.8 ± 0.9 GPa is congruent with the high porosity and microstructure of this type of self-setting ceramic materials, which consist of an entangled network of precipitated crystals [28-29]. A Poisson’s ratio of 0.27 was selected for this analysis, as commonly reported for hydroxyapatite (HA) in the literature [30]. An elastic and isotropic model was used for this purpose. The finite element analysis (FEA) was performed on ABAQUS (Dassault Systèmes, France).

3.1. Strand morphology and shape fidelity of the microextrusion process

The morphology of the nozzles and the corresponding strands are shown in Fig. 2A. It is important to point out that a self-setting ink, which does not shrink during the hardening process [18], was chosen for this study in order to eliminate any dimensional change of the filament after extrusion. The strands retained to a large extent the shape of the extrusion nozzle, although some morphological deviations were observed at the regions where the orifice presented sharper curvatures (Fig. 2A, red arrows). As a consequence, the strand section area was larger than the nozzle area for the nozzles exhibiting more intricate shapes (Fig. 2B), and a decreasing trend of the concavity indicators was observed when comparing nozzles to strands (Fig. 2C-D). The two concavity indicators used were able to quantify the geometries’ concavity, showing the same trends, coherent with the morphology observations (Fig. 2A). Nevertheless, the SCP resulted to be more sensitive and, therefore, a better indicator than the PCR. The discrepancies between the shape of the nozzle and the strand morphology can be attributed to two main possible causes, namely: i) the slow elastic recovery of the ink; or ii) the deformation of the nozzle during the extrusion process. The rheological tests showed that the ink exhibited a shear thinning behaviour, with an elastic modulus G’ in the viscoelastic region above 2 × 10$^6$ Pa, and a crossover of the G’ and G” (known as the flow point) at a shear strain around 40% (Fig. 3A). Regarding the elastic recovery of the ink, the three interval thixotropy test (3ITT) (Fig. 3B) evidenced that, upon the release of a high shear strain simulating the extrusion process, the transition from viscous prevalence (G”>G’) to elastic prevalence (G’>G”) was quasi-instantaneous. These findings entail an optimum retention of the...
Fig. 4. 3D reconstruction and XZ and YZ cross-sections of the μ-CT images of the 3D structures printed with the different nozzle geometries. Scale bar: 2 mm.
extruded strand shape, guaranteeing a high shape fidelity.

Having an ink with a fast viscosity recovery upon extrusion is of paramount importance to guarantee the strand shape fidelity when using nozzles with orifices other than circular, as the regions of the geometry with higher gradients of curvature will suffer the effects of surface tension, smoothing the edges and tending to the minimal-energy circular-cross-section geometry [31]. This phenomenon is accentuated in geometries with smaller curvature radii.

After ruling out the rheological behaviour of the ink as a cause of the strand shape deviations, the most likely explanation is the deformation...
of the polymeric disc that makes up the nozzle as a result of the high pressure during the extrusion process [32]. This deformation must be elastic, as no evidence of plastic deformation was found after inspecting used extrusion discs. The fact that greater deviations on the shape fidelity occur at overhanging features of the thin plastic discs is a further evidence that points towards this hypothesis. A solution to this problem would be to use more rigid materials (e.g. metallic) or thicker discs in the nozzles.

3.2. Implications of the strand geometry in the printing process

The μ-CT reconstruction of the VOI of the different 3D-printed structures evidenced that some strand shapes resulted in more regular structures than others (Fig. 4). The structures printed with the control nozzle and the shapes 2, 3 and 5 were the most regular ones. On the contrary, shapes 1 and 4 resulted in more irregular architectures, unevenly spaced and randomly oriented strands.

This variable outcome emphasises the fact that using non-circular nozzles imposes some restrictions regarding the printing trajectories.

Fig. 6. Structural characterisation of the samples printed with different strand cross-sectional geometries: (A) Specific surface area (SSA) of the strands, calculated by normalising material surface (MS) per strand length; (B) SSA of the 3D-printed structures, calculated by normalising material surface (MS) per unit volume of strand (MV); (C) percentage of porosity, and (D) pore size distribution of the 3D-printed structures. (A–C) include four different quantification methods: Two of them based on the analysis of the μ-CT reconstruction using two alternative software (i.e., CTAn and Fiji); one third using the mesh obtained from the segmentation and meshing (STL) of the same μ-CT reconstruction (i.e., MeshLab); and one fourth using a theoretical estimation based on the SEM images of the strand cross-sections. The measurements of (D) are based on μ-CT analysis with CTAn software.
Unlike the cylindrical strands, which are rotation-invariant and allow a stable deposition regardless of the direction, the alternative geometries tested in this work give rise to a more complex scenario. The geometry of the nozzle dictates the printing directions leading to the deposition of a stable strand. One can determine the planes of stable deposits and the associated normal vectors (represented in Fig. 5A with dashed lines and arrows, respectively). To achieve a stable filament deposit, it is required that the direction of the normal vectors matches the deposition directions of the printing pattern. In the present work, the nozzle orientation was aligned to the printing directions of the orthogonal pattern (0 and 90°). Shapes 1, 2, 3, 5, and 6 present a suitable geometry for the orthogonal printing pattern used in this work. In contrast, shape 4 has the normal vectors in the 0–120–240° directions and, therefore, the strand deposition is unstable in the orthogonal (0–90°) deposition pattern (Fig. 5A), although it would be appropriate for another printing pattern matching the deposition orientations (e.g., honeycomb pattern, where the printing directions are 0–120–240°).

Another relevant parameter that has to be considered, which again highlights the relationship between nozzle geometry and the printing path, is the aspect ratio of the nozzle. If the layer height is fixed, as is the case in most currently available commercial devices, an aspect ratio close to one is required when printing structures that alternate different deposition directions in the successive layers. Otherwise, and especially if the aspect ratio of the orifice is high, it may become impossible to find a layer height that is suitable for all the printing directions. This may result in either wiggling of the strands, if the layer height is too large for one of the printing directions, or in flattened strands and damage on the previous layer if the layer height is set too low for the other printing direction. An example of this situation is shape 6 (Fig. 2B), with an aspect ratio of 1.28, that did not allow printing stable structures. This limitation could be overcome by adjusting the layer height for each deposition direction, which is not possible in the current commercially available slicing software.

Another relevant phenomenon that is brought to light when printing non-cylindrical strands and goes unnoticed when using the conventional circular nozzles is strand torsion. It occurs when there is a change in direction of the deposition path, and is associated with the fixed orientation of the extrusion nozzle (Fig. 5B and F). Although this happens independently of the shape of the filament, when the strand is cylindrical it is overlooked due to the rotation-invariant characteristic of the circular cross-section. Probably for this reason, to our knowledge it has never been pointed out before. As illustrated in Fig. 5B, for 3 different strand cross-sections, when the nozzle changes its trajectory by 180 degrees, the region of the strand that was first in the bottom is twisted, ending up in the top of the filament, which is a 180° torsion. If the nozzle changes its trajectory by making a 90-degree turn, the filament experiences a torsion of 90°, which depending on the nozzle symmetry, it can lead to a change in the orientation of the filament geometry in successive printing layers (Fig. 5C). This is clearly visible in the μ-CT reconstruction of the scaffolds printed with shape 1 nozzle (Fig. 4), where alternated strand orientations are found in successive layers. Here, the orientation of the strands in the XZ cross-section is in “I” shape and in the YZ section is in “H” shape, i.e., the deposition of the strand occurs in alternated sides depending on the layer deposition direction.

In order to further assess the effect of nozzle alignment on the orientation of the printed strands, we printed 3D structures with the shape 1 nozzle aligning the nozzle at 45° with respect to the 0–90° deposition directions of the tested orthogonal pattern. In this setup, we observed an alternated deposition of in H-like and in T-like orientations in adjacent strands (Fig. 5E). We hypothesise that in this case the strands tend to lay down to a more stable position, and the preferred conformation is the one that minimises torsional forces when there is a change of deposition direction, as illustrated in Fig. 5D.

3.3. Morphological analysis

The specific surface of the printed structures (Fig. 6A-B) was assessed using four methods. CTAn and MeshLab approaches gave similar results although they were based on very different principles, whereas the Fiji software, which uses the same approach as CTAn presented a shift up bias, even though preserving the same trends. Finally, the theoretical approximation was also shifted up but with considerably higher variability.

As expected, the surface area normalised per strand length (Fig. 6A) was directly correlated to the perimeter of the printed strands (Fig. 2B), and there were clear differences between the different nozzles. The not only value depended on the surface concavity percentage, as observed when comparing strands with the same section like the control and shape 2, but also on the size of the nozzle orifice, with larger orifices resulting in strands with larger surface per unit length, as in the case of shape 1 or 3. To better assess the contribution of shape changes rather than size changes, the surface area was normalised by strand volume
This allowed to isolate the morphological effect from the size effect and revealed clear differences between the different filament profiles. The control showed the smallest value, as expected, whereas the nozzle with shape 2 achieved the highest surface area per strand volume, doubling the value of the control.

Regarding porosity quantification, there was a good agreement between the different methods, being the theoretical approximation the one with higher discrepancies, which can be explained by the fact that it was based on ideal structures rather than the real printed ones. Despite all the 3D structures being printed with a constant inter-strand separation of 250 µm in the XY plane, considerable differences in the porosity percentage were observed, which can be explained by (1) the different strand dimensions; (2) the morphological diversity of the nozzle designs. The influence of these two parameters into the percentage of porosity is illustrated in Fig. 7, which shows that with a fixed inter-strand separation, bigger strand dimensions lead to smaller porosities (e.g., percentage of porosity in shape 5 > control, shape 2 > shape 3). Moreover, when comparing strands with similar dimensions, a strand design with smaller cross-section area leads to higher porosities.

As expected, due to the nature of the DIW process and the rectilinear fill pattern used, which results in an interconnected pore network, most porosity was open. A residual amount of closed porosity (less than 0.2% in all the cases) was observed with CTAn software, which can be attributed to small air bubbles trapped in the ink during the mixing process, as observed, for instance, in the SEM image of the cross-section of the control sample (Fig. 2A). Although all pores are interconnected and technically they can be considered as one single pore, the sphere-fitting algorithm allowed calculating the pore size distribution in the different 3D structures, which presented very dissimilar pore size distributions (Fig. 6D). The maximum frequency was not centred in 250 µm but in 300 µm in most cases. This shift to larger dimensions when compared to the imposed 250 µm inter-strand separation can be attributed to the fact that this technique measures the pores volumetrically, and in some regions and orientations the pore dimensions can be larger than the defined inter-strand separation. Apart from that, a correlation was observed between the sharpness of the distribution and the regularity of the printed structures, with the more regular structures like control and shape 2 nozzles (Fig. 4), presenting a sharper peak and a

![Image](image_url)
narrower pore size distribution.

3.4. Load distribution: finite element analysis

The maximal principal stress contours obtained from the simulation of a compressive strain of 0.1% in the elastic range are presented in Fig. 8. The structures cross-sections revealed a general trend in which the compression stresses were concentrated in the strand intersections, which act as structural pillars, whereas the regions of the strands linking these pillars are subjected to tensile stresses. This is coherent with the behaviour found in the literature for similar materials with brittle behaviour [33–36]. Miranda et al. reported a similar stress field distribution calculated by finite elements method (FEM), which was correlated with the fracture mode assessed experimentally, observing initial cracking of the unsupported strand segments unifying the pillars propagating parallel to the load axis due to tensile stress accumulation in this region [33]. Additionally, as expected, the structures with larger strands (e.g., shape 1) presented fewer and wider pillars with attenuated compressive stress gradients. These observations were also in agreement with other studies comparing structures with different inter-layer contact areas [19,37]. It was also evidenced that the smaller curvature radius found at the strand unions acted as stress concentrators. The use of strand geometries with concavities and abrupt curvatures introduced additional stress concentrators. Finally, the regularity of the printing pattern also played a key role in the homogeneity of the stress distribution, with higher values of tensile stresses registered in structures with more irregular deposition patterns (e.g. shape 4). The Von Mises equivalent stress distribution, which may be of interest for understanding the behaviour of the structures when ductile materials are used is provided in the supplementary information.

4. Conclusions

In summary, this study analyses the potential and the drawbacks of using non-circular nozzles in DIW, which can be exploited in a wide range of applications that already use this technique, like tissue engineering, chemical reaction catalysts, water evaporators and electrochemical energy storage devices. Amongst the benefits are the possibility to increase the specific surface area of the filaments and the 3D structures, or the introduction of concave surfaces, that can be beneficial for certain applications based on interfacial reactions or to create confined environments. Although modifying the geometry of the nozzle may seem of little relevance, it has enormous implications in the printing process and introduces an additional level of complexity in the 3D-printed structures. Printing with non-circular nozzles imposes some restrictions regarding the printing patterns since the stable deposition paths are limited and determined by the geometry of the printing nozzle. The alignment of the nozzle with the printing path and the aspect ratio of the nozzle become very important parameters to ensure the printing of stable and reproducible structures. Another relevant phenomenon that is brought to light when printing non-cylindrical strands while going unnoticed when using the conventional circular nozzles, is the stress anisotropy development, J. Am. Ceram. Soc. 94 (2011) 2053–2060.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Y. R. E.T. and M. L. are employees of Memetis Biomaterials S.L. and M.P.G. has an equity interest in this company, which may potentially benefit from the research results displayed in the present work.

Acknowledgements

This work was supported by the Spanish Ministry of Science, Innovation and Universities through the project PID2019-103892RB-I00/AEI/10.13039/501100011035 and the Generalitat de Catalunya under Grants 2017SGR-1165 and BASEED 001-P-001646, co-funded by European Regional Development Funds. YR acknowledges the Spanish Government for the Ph.D. grant DI-15-08184. MPG acknowledges the Generalitat de Catalunya for the ICREA Academia Award. The authors are grateful to Dr Araceli Aznar for her technical assistance with the μ-CT, Laura del Mazo for her aid with the rheological study, Antonia Molina for his support with the morphological analysis, and Mar Bonany and Christian Guirola for their assistance in the grammatical revision of the manuscript.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.addma.2021.102129.

References


CRediT authorship contribution statement

Yago Raymond: Conceptualisation, Investigation, Formal analysis, Data curation, Writing - original draft. Emilie Thorel: Investigation, Formal analysis, Writing - original draft. Juan Pou: Investigation. Maria-Pau Ginebra: Conceptualisation, Writing - review & editing, Supervision, Funding acquisition.