Changing the Paradigm in Design for 3D printing – Morphology Mapping

Daniel P da Silva[1, a], Paula Pascoal Faria[1,b], Artur Mateus[1,c] ,
Ruben Silva[1d], Tiago Ruivo[2] and Geoffrey R Mitchell[1,e*]
[1]Centre for Rapid and Sustainable Product Development, Polytechnic of Leiria, 2430-080 Marinha Grande, Portugal

[2] Erofio Atlantico SA Rua do Pinhal n.° 200, Jardoeira
2440-373 Batahla, Leiria, Portugal
[a]Daniel.P.Silva@ipleiria.pt, [b]Paula.Faria@ipleiria.pt, [c]Artur.mateus@ipleiria.pt,
[c] ruben.j.silva@ipleiria.pt and [e]Geoffrey.mitchell@ipleiria.pt

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Abstract. 3D printing is one of a number of emerging technologies within the additive manufacturing umbrella, which allows us to manufacture any self-supporting structure. In recent years considerable effort has been dedicated to the hi-fidelity reproduction of complex shapes as 3D printing has morphed from prototyping to manufacturing. However, scant attention has been paid to the other many advantages of 3D printing. This contribution is part of a project which is focused on addressing that matter. We focus on the use of semi-crystalline thermoplastic polymers and on extruder based 3d printing. In such technology, the molten plastic is extruded through a fine needle and emerges as a filament which is deposited on to the build platform. For a semi-crystalline polymer, the extrusion process coupled to the cooling process determines to a large extent the morphology of the deposited material and therefore the physical properties, such as the modulus which may vary by as much as three times. Several of the print parameters, such as the extrusion temperature, the extrusion rate and the write speed during the print process, can be varied during the print process and therefore it is possible to deposit material in different parts of the build process with different morphologies and consequently different properties. We describe this as morphology mapping and it opens up the possibility of using 3D printing to print variable properties in the same part from the same material. The variation of properties will be strongly dependent on the type of material. This approach could offer an alternative to multi-material printing. This presentation starts with this proposition which is supported by in-situ small-angle x-ray scattering experiments of 3D printing and details how this can be used in practical manner. Although this is a deceptively simple concept, there are a number of hurdles to overcome. For example, the change in properties is very directional, which may require new printer technology and design. Design for 3D printing appears to be very conservative, whereas this concept will enable the prospect of design by function, rather than design by shape or form, which itself could transform the process of design, allowing optimization of the design and material use. We highlight the possibilities through specific designs and the possibilities for new design concepts.

1 Introduction

3D printing is an emerging technology, which allows us to manufacture any self-supporting structure [1]. Considerable effort has been dedicated to the hi-fidelity reproduction of complex shapes however, little attention has been paid to the other many advantages of 3D printing. This contribution is focused on addressing this matter. Here we focus on the use of thermoplastics and on extruder based 3d printing. In this technology, the molten plastic is extruded through a fine needle and emerges as a filament which is deposited on to the build platform. For a semi-crystalline polymer, the extrusion process coupled to the cooling process determines to a large extent the morphology of the deposited material and therefore the physical properties, such as the modulus which may vary by as much as three times [2,3]. As we can vary the print parameters, such as the extrusion temperature, the extrusion rate and the write speed during the print process, it is therefore possible to deposit material in different parts of the build process with different morphologies and consequently different properties. This opens up the possibility of 3D printing to print variable properties in the same part, with the same material. The variation of properties will be strongly dependent on the type of material. We term this process “morphology mapping”. This approach could offer an alternative to multi-material printing, without the attendant issue of adhesion at the boundaries between materials. This paper starts with this proposition which is supported by in-situ small-angle x-ray scattering (SAXS) experiments of 3D printing [3,4] and details how this can be used in practical manner. Although this is a deceptively simple concept, there are a number of hurdles to overcome. For example, the change in properties is very directional, which may require new printer technology and design. Design for 3D printing appears to be very conservative, whereas this concept will enable the prospect of design by function, rather than design by shape or form, which itself could transform the process of design, allowing optimization of the design and material use. We highlight the possibilities through specific test designs and the possibilities for new design concepts.

2 Controlling the morphology of a single extruded strand

The extrusion of a molten polymer through a restricting die may lead to some flow alignment processes which will be dependent on the extrusion parameters, the die geometry and the molecular weight characteristics of the polymer. In order to study this in a quantitative manner, we have designed, and fabricated a pellet fed extruder-based 3D printer which can be mounted on the NCD-SWEET Small-angle X-ray Scattering Beam line at the ALBA Synchrotron Light Source in Barcelona [3]. Figure 1 shows this 3-D printer mounted on the beam line.

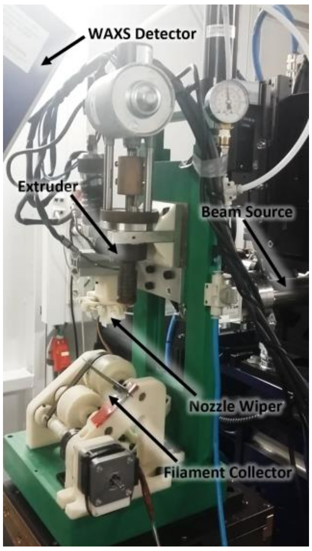

Figure 1 The 3D printer mounted on the NCD-SWEET Beamline at the ALBA Synchrotron Light Source in Barcelona

In this work the standard translation build platform of the 3D printer is replaced by a rotational platform which enables the possibility of higher write speeds and ensures that a clean build platform is presented to the extrudate on a continuous basis. The incident x-ray beam passes through the extruded strand at a particular distance from the extrusion die. In the polymer melt there is no contrast for x-ray scattering to provide information on the extension and alignment of the polymer chains. To obtain such information, we would need to use a mixture of per-deuterated and per-hydrogenated chains with small-angle neutron scattering techniques to reveal such information [5]. In this work, we will use the system to quantify the preferred orientation of the crystals which form on cooling templated by the anisotropic nature of the extruded melt [6-8]. In this work we focus on the extrusion of poly(ε-caprolactone) (PCL), a semi-crystalline biocompatible and biodegradable polymer [9]. It was supplied in the form of small pellets (~3mm) with a Mw =50,000 by Perstorp (Cheshire, UK). This polymer exhibits a polydisperse distribution of molecular weight and it is the longest chains which become extended and aligned with the extrusion axis as shown schematically in Figure 2. As a particular volume of the extrudate moves away from the hot extruder zone, the polymer cools and eventually reaches the temperature at which the maximum rate of crystallisation occurs. If at that point, the extended chains are still present and have not relaxed back to isotropic random coils, then the extended chains act as row nuclei and template the formation of chain folded lamellar crystals which grow in a direction normal to the extend chain nuclei as shown schematically in Figure 2.

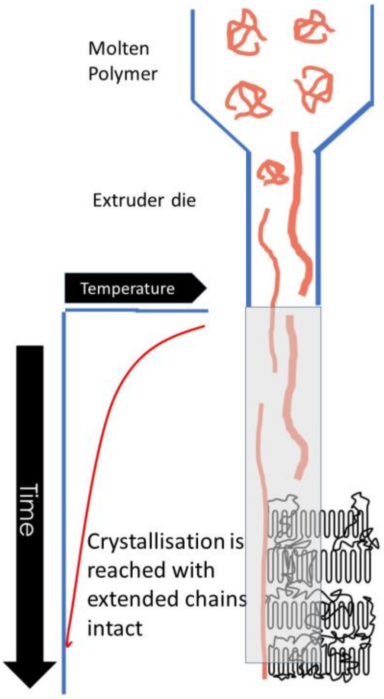

Figure 2 A schematic of the extrusion process, illustrating the generation of extended chains in the restricting extruder die which leads to the templated crystallisation of the chain folded lamellar crystals.

A single row nuclei will template the crystallisation within a cylinder of radius, at least 1μm [7]. As all the row nuclei in the extruded strand volume element will have the same orientation, then we will observe a high level of common preferred orientation of the chain folded lamellae. The level of preferred orientation will be related to the density of row nuclei, as the alternative is the formation of an isotropic distribution of lamellar crystals. In the simplest case, that of a single relaxation time relevant to a monodisperse molecular weight distribution, we can expect the number of row nuclei to follow an exponential decay dependent on the time which has elapsed since the extrudate emerged from the die and the ambient temperature. The relaxation time, τ, for the extended chains has been given by the reptation theory of de Gennes [10,11] which gives the time for a chain of length L made up on N statistical segments to diffuse out of the constraints of the tube as $\sim N^3\mu$ where $\mu$is the coefficient of friction of the chain creeping along the tube.

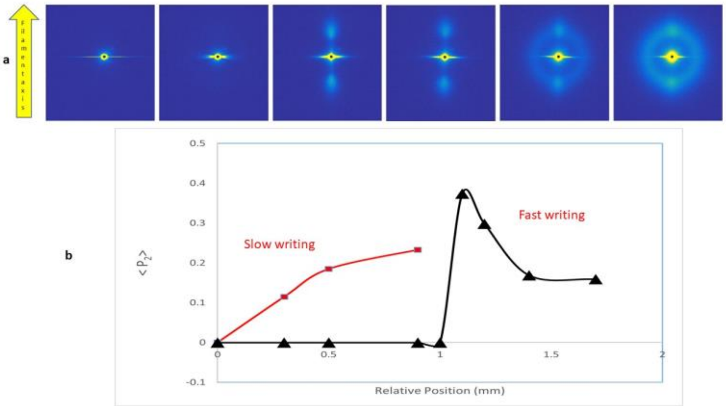

Figure 3 SAXS data obtained using the 3D printer shown in Figure 1, a) SAXS patterns taken at various positions relative to the extruder nozzle exit, moving from near to far left to right b) Plots of the global orientation parameter $<P_2>$ as a function of the position of the extrudate relative to the extruder nozzle exit for two different write speeds. The data presented are based on data in ref [3].

The cooling rate will be defined by the extrusion temperature and the ambient temperature and any other temperature controls.

The data shown in Figure 3 confirms these basic ideas. Figure 3b shows a plot of orientation obtained with a fast write speed. The first crystals which appear are highly aligned (Figure 3a), typical of a row nucleated system, but subsequent crystallisation is more isotropic as the extended chains relax prior to crystalllisation. The other curve shown in Figure 3b shows the results for a slow writing speed in which more isotropic crystallisation occurs as there has been more time for the extended chains to relax. By simply switching between different write speeds or other print parameters we can switch between different morphologies with different properties as shown in Figure 4 and hence we have morphology mapping. In 3D printing, adhesion between successive layers and between strands is important for the overall properties of the built part. Switching between the morphologies of Figure 4 may require optimisation of the process parameters to ensure good adhesion.

We can extend the value of the relaxation rate of the row nuclei, by replacing the long chains with acicular nanoparticles as nuclei which can include carbon nanotubes [6], graphene nanoplatelets [6] and self organising nanofibrils [12,13]. The low molar mass nucleating agent dibenzylidene sorbitol forms highly extended networks of nanofibrils, which can be aligned using modest shear rates and then acts as row nuclei to yield high levels of preferred orientation of the chain folded lamellar crystals [12,13]. The advantage of these types of row nuclei, is that the size of the particles increases the stability of the preferred orientation of the particles, providing a longer period for the cooling of the extrudate to the crystallisation point [14] and still maintain the templating process. Mitchell and Olley (2018) have demonstrated a variation on this methodology which can be used enable a templating orthogonal to the flow direction [15]. In this they use PCL with dibenzylidene sorbitol (DBS) together with small quantities of a terpolymer, based on polyvinyl butyral (PVB), which the authors deduce limits the axial ratio of the dibenzylidene sorbitol particles so that they appear to align normal to the flow direction as predicted by Jeffreys for low aspect ratio particles [16] and as a consequence the growth direction of the chain folded lamellar crystals lies parallel to the flow direction. These unambiguous results were obtained from experiments which employed a parallel plate shear cell [15] and were not performed using an extruder system, but we anticipate that with the correct selection of operational parameters, similar results would be obtained.

Now we need to bear in mind that the anisotropy in properties is directly related to the extrusion direction and therefore the path of the print head.

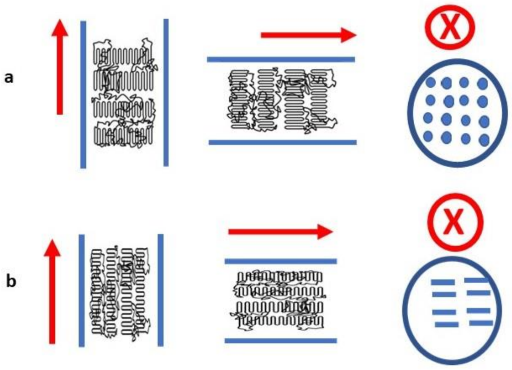

Figure 4 A schematic of the relationships between morphology in the extruded strand and the extrusion direction (a) with PCL, (b) using PCL, DBS and PVB as described in the text. The red symbols show the write direction, the blue lines are the boundaries of the extrudate.

Figure 4 shows the possibilities available with a printer working in a cartesian coordinate system. We emphasise that the write directions are not restricted to the orthogonal axes as shown. The orientation of the chain folded lamellar crystals not only has a strong influence on the mechanical properties but also on cell adhesion and degradation rates for an absorbable scaffold for tissue engineering.

3 Exploiting the control of morphology in a single 3D printed strand to fabricate 3D objects with enhanced properties

The processes described in the previous section allow the morphology to be controlled during the 3D printing process using the standard printing parameters. The range of the mechanical properties which it is possible to produce in this manner has been reported to be at least 3 times [2,3]. The challenge now is to develop methodologies for creating 3d objects with this variation in the mechanical and other properties. We can see this morphology mapping as a method for directional strengthening. This is a widely used technique in the case of composites where strengthening fillers are added in a uni-direction or as 0/90 cross ply.

An example of an object with considerable directional stiffening is a barrel which is widely used for the storage and transport of wine and beer. The earliest records of barrels dates to 2600 B.C [17]. The classic wooden barrel with metal hoops is durable and easy to handle. It is a most effective design. Figure 5, shows a replica of wooden barrel fabricated using a 3D printer with PLA and a FlashForge Creator 3 Series printer with heated build platform, which was held at 50°C and the extruder temperature was 210°C. The build orientation of the left hand barrel which is labelled as BV, is as shown in the photograph. Clearly we can replicate the shape of the barrel and much of the detail, but this has been built layer by layer and so the parts which were in the original made of wood and and are curved to give the barrel its shape, have none of the natural fibrous anisotropy of wood [18]. In the original barrel this was partly required in order to be able bend the wood to the shape required. It is a huge advantage to be able to fabricate the barrel in a single print without further assembly or processing. However, there is a major disadvantage in the 3D printing approach in that the properties are isotropic and constant.

Figure 5 Replicas of a classic wooden barrel with iron iron reinforcing hoops, fabricated using just PLA. The height of the barrel is 61mm. (a)The barrel (BV) was built with barrel height vertical on the build platform (b) the barrel (BH) was built with barrel length horizontal on the build platform. The barrels were compressed between parallel plates in the vertical direction. The images show the barrel after failure, in both cases the initial failure occurred at the interface between the layers. The right hand graph show the stress-strain curve recorded each deformation to failure.

Commented [DPdS1]: Measured value instead of hight of the digital defined object (STL).

We can approach this challenge in two ways, we can build each part separately, optimising the printing parameters to yield the best properties which will then require assembly. An alternative is to organise the design to allow the print path to follow directions where reinforcements are required.

As illustrated above in the barrel example, there are two specific directions for strengthening, the circular hoops and along the length of the “Staves” in terms of the original wood-based barrel structure. In the horizontal build option BH in Figure 5 we can almost achieve the latter. For a full implementation we will need to be able to print in cylindrical coordinates to achieve maximum enhancement. One advantage of direction reinforcement is that the remaining materials may be thinner and hence reduce the carbon footprint of the part.

The two barrels BV an BH were tested in compression between parallel plates with the barrel vertically mounted using an Instron 4505 tensile tester with a 100kN loadcell and a strain rate of $0.0014s^{-1}$. As shown in Figure 5, primary failure occurred at the interface between layers underlining the importance of the anisotropy of the wooden staves and the reinforcing hoops in the design.

An alternative approach is available for objects which can be printed with a continuous spiral-like print path. In such cases we can identify rules which define the morphology which will be deposited. In one example, we have printed an hexagonal lattice-like structure. The print path follows a continuous spiral-like path in which the print velocity V, is given by Vmin + (Vmax-Vmin) r/R where r is the distance from the centre and R is the radius of the object and Vmin and Vmax are the limits of the print velocity to be used. This type of structure is widely used as an absorbable scaffold for tissue engineering [19]. By changing the morphology continuously, it is possible to design a scaffold which degrades faster in the centre of the scaffold, leaving the peripheral parts to maintain the integrity of the scaffold.

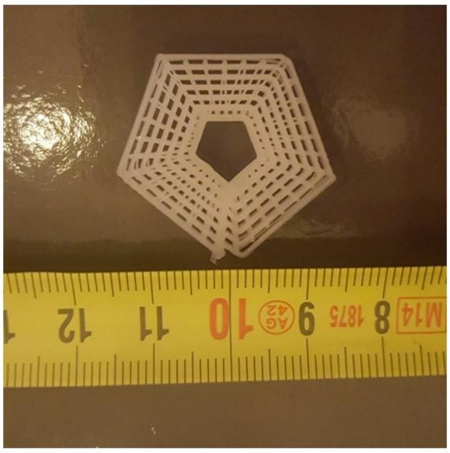

Figure 6 A photograph of a 3D printed hexagonal open scaffold-like object in which the modulus of the individual strands along the print direction is proportional to the distance from the centre of the object. The height of the object is ~ 2cm.

A question we have not referred to so far, what is the resolution of the morphology mapping? Experiments performed using the system shown in Figure 1, show the new morphology is full adopted within a distance equivalent to the diameter of a strand.

4 Summary

We have shown how we can use the process parameters, such as temperature, extrusion speed and write velocity of an extrusion based 3D printer to control the morphology of a semi-crystalline polymer which is deposited. We give alternative methods to control the morphology with respect to the extrusion axis and emphasise that these enhancements are only in the direction defined by the printer path. We highlight the design of a traditional wooden barrel to illustrate how directional reinforcement is used in a critical manner in the design of a wooden barrel with metal hoops and how this can be achieve with morphology mapping. We give a second practical example of a hexagonal shaped lattice of the type favoured as scaffolds for tissue engineering in which the object is printed so the centre of the scaffold is softer, while the peripheral part is stiff which is expected to impact on the differential degradation rate of the object. Morphology mapping is a very interesting concept and that the challenge is how to incorporate this in the design of parts.

5 Acknowledgements

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