Discovering Morphology Mapping with 3D printing at the NCD-SWEET Beamline at ALBA Synchrotron

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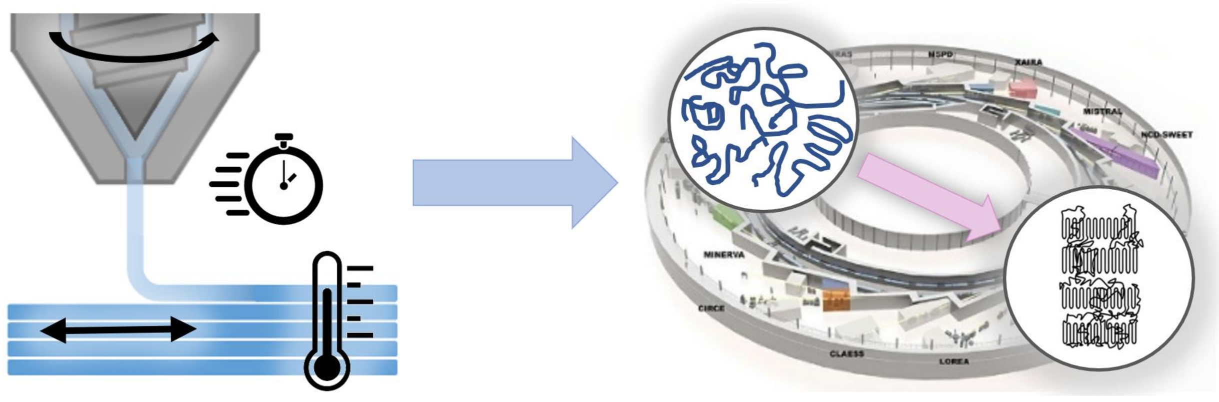
GRAPHICAL ABSTRACT



Experiment Design

The replicate the extrusion-based 3d printing operation at the NCD-SWEET Beamline, the designed equipment comprises three main parts: feeder, extruder, and a rotating collector. The model presented in Figure 1 simulates fabrication along a moving platform, with a theoretically infinite path (following the perimeter of the main collector roll). It makes use of a single extruder with a dual channel screw forcing the melt flow through a 300 µm inner diameter needle with a high length to diameter ratio (L/D ≈500).

The apparatus allows the control of the extrusion temperature, extrusion velocity, and write velocity (print speed). The extruder is fed with a melt from a pellet reservoir, and a compressed air source is required to feed the system.

Input instruments, such as the power supply, the heater-controlling modules, and the computer for remote control were placed separately of the beamline platform.

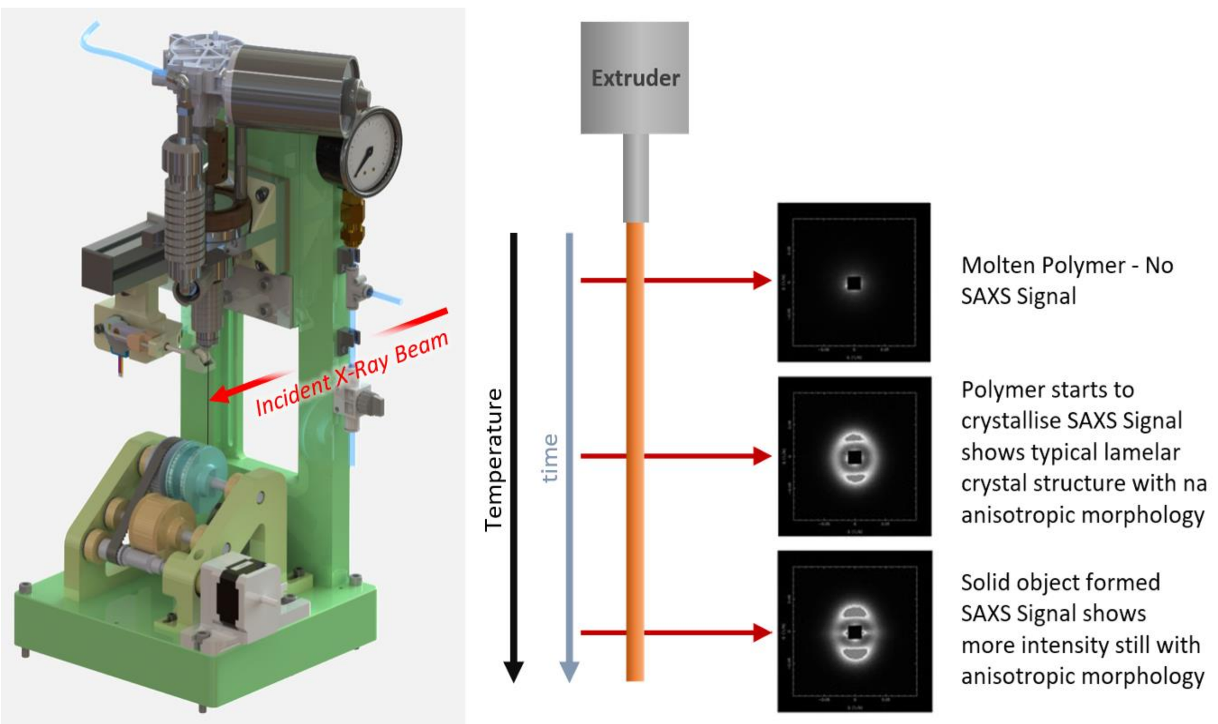


Figure 1 – Left: a CAD representation of the 3D printer developed for this work. Right: a schematic of the quasi-static state of the extrudate in a constant gradient of temperature. The evolution of the structure can be evaluated by moving the incident X-ray beam down the jet. Adapted from [6].

Conclusions and Future Work

The 3d printer worked successfully, and it was shown that is possible to control the processing parameters to produce deposited polymeric material with different morphologies that exhibit different physical properties.

Varying the input parameters in real-time during manufacturing provides a method of depositing the polymer with distinct properties in different zones of a printed part.

With the 3D printing in situ studies of time-resolved X-ray scattering, it was possible to establish some correlations between the printing conditions and the level of preferred orientation in the deposited material.

Future developments are expected, especially regarding the design exploration of products to take advantage of this new approach.

Introduction

Direct digital manufacture is a production technique that enables parts to be fabricated directly from their digital definition, allowing mass customization in several areas, including biomedical applications [1, 2].

In 3D Printing, the majority of developments have been focused on object shape reproduction. Some attention has been given to the process parameters in order to optimize polymer melt flow rate [3]. The influence of the manufacturing input variables on the mechanical properties of the prints, as with all polymer processing technologies, is also known [4]. An example of that is the shear and elongation of the polymer melt flow passing through a restricting die [5]. However, there is not a significant effort to design materials themselves during additive manufacturing.

This work is focused on this issue, envisioning the complete digital definition of produced part, from geometry to material properties. In this work, in situ time-resolving small-angle X-ray scattering measurements were performed at the ALBA Synchrotron Light Source, in Barcelona. Resorting to a customized 3D printer, the aim was to evaluate the possibility of morphology control of semi-crystalline polymers during extruder-based 3D printing. The ultimate goal of the project is to create a methodology to realise patterns of material properties, specifically the modulus of the polymer, along the printed parts.

Materials and Methods

Samples Material:

In this experiment, the team was able to print with polycaprolactone (PCL) and low-density polyethylene (LDPE). The work in this poster is focused on the PCL samples. The material was supplied in the form of small pellets (~3mm) with an M_w = 50,000 by Perstorp (Cheshire, UK).

Experimental Procedure:

Analysing the samples as they were being printed required a constant temperature profile of the extrudate filaments. Thus, the extrudates were observed in a quasi-steady state, in which the development of the structure and the morphology with time could be assessed by moving the platform up and down; repositioning the incident x-ray beam along the extrusion axis (as represented in Figure 1). Remotely controlled, each trial consisted of a scan of 20 steps of 0.1mm with a 1-second data collection period.

In Figure 2, it is possible to observe the equipment mounted on the beamline platform.

Results

The most expressive result can be observed in Figure 3, which shows 2 rows of SAXS patterns. The bottom patterns are related to extrudates produced at a higher write speed.

As it is possible to notice in the right-hand pattern, the solidified filaments produced at a low speed have a broadly isotropic crystal orientation; whereas the equivalent pattern in the bottom, row reveals a high level of orientation (as indicated by the two sharp maxima above and below the zero-angle point).

The pronounced level of orientation of the lamellar crystals shown in the bottom row of SAXS patterns is very typical of row-nucleated crystallisation, when the row nuclei generate a common and highly aligned templating mechanism. This behaviour is likely due to the fact that the higher write speed leads to faster cooling, once the extruded material is moved away from the hot end of the extruder more rapidly. This means that crystallisation should occur before the extended chains have totally or completely relaxed. This phenomenon, according to other studies [7], can be related to the increase of the elastic modulus by more than a factor of 2.

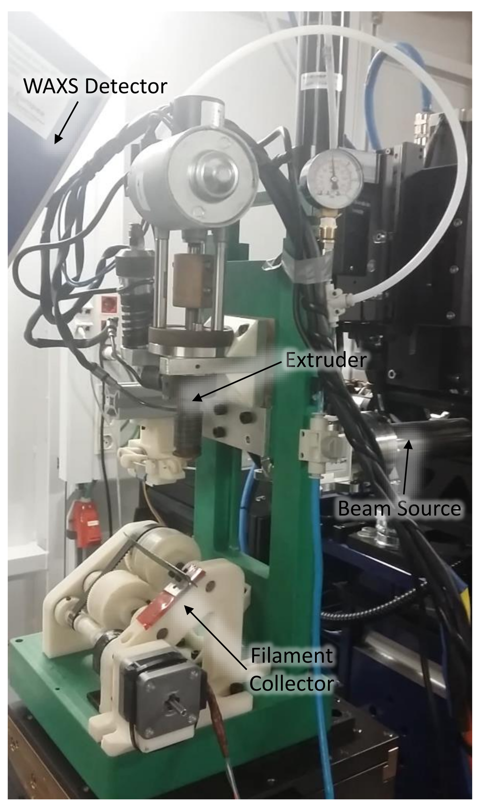


Figure 2 – Customized 3D Printer at the NCD-SWEET Beamline of ALBA Synchrotron.

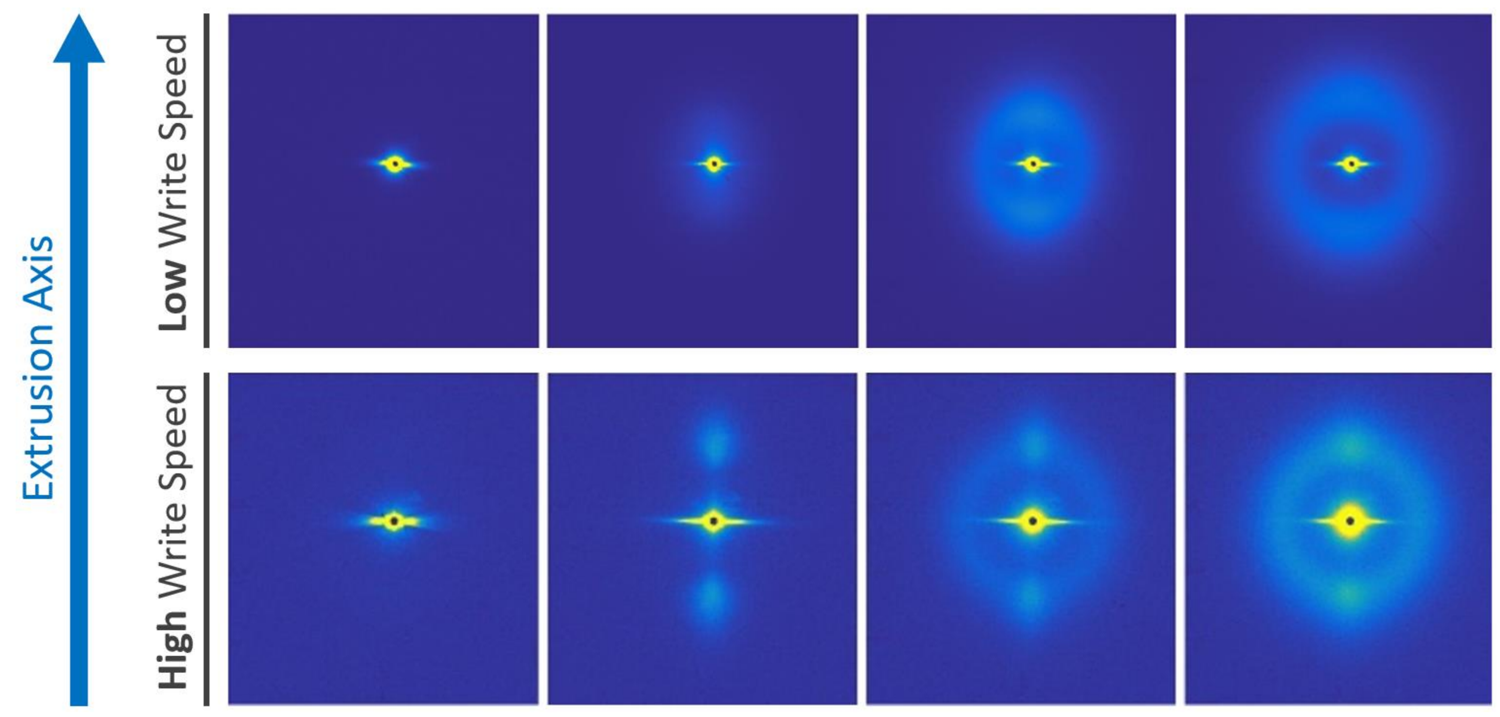


Figure 3 – SAXS patterns of the PCL extrudate measured with the incident X-ray beam positioned at increasing distances from the exit of the extruder die (x = 0 mm). The left-hand scans are the closest to the extruder die, and those to the right are positioned further away. For all of these images, the 3D printer parameters were fixed for extrusion temperature, extrusion speed, and ambient temperature. The scans from the top line correspond to a low write speed, and the bottom scans to a high write speed. Adapted from [6].

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