Changing the design paradigm – 3D Printing on molecular texture in plastics



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Introduction

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Additive manufacturing is now more than a prototyping set of technologies, it is a viable manufacturing methodology that allows mass customization and the achievement of complex shapes [1]. The focus of the developments in **3D printing** is often on geometric and dimensional reproduction of the digital form of the product.

In polymer processing technologies, the manufacturing parameters affect the mechanical properties of the final products, and this is also well established in 3D printing **[2]**. It is known that, when polymers with high molecular weight are extruded through a die with an appropriate length-to-diameter ratio, a preferred orientation in the melt can be induced. When the temperature decreases, a highly anisotropic crystalline morphology is formed. Consequently, this morphology unravels different mechanical properties in comparison with the morphology formed from a quiescent melt. In accordance with **[3]**, this can result in a significant increase in the elastic modulus.

The present work shows some results of **morphology analysis** with in situ X-ray scattering, employing a customized 3d printer adapted to an X-ray scattering beamline at the ALBA Synchrotron, correlating the processing parameters with the preferred molecular orientation.

The focus of this project is to explore the scope for depositing materials with different properties by controlling the structure and morphology of the polymers, more than replicating shapes. With new degrees of freedom, the team is working in order to apply this methodology, in non-planar layers of deposited material, in order to obtain new designs of material along a given designed model.



Figure 1 – Left: Schematic of the ALBA Synchrotron and the domain of the analysis. Middle: Photograph of the customized 3D Printer at the NCD-SWEET Beamline. 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 **[4]**.

- Morphology Analysis

As previously mentioned, the team used a customized 3D printer to evaluate the morphology control of semi-crystalline polymers during extrusion. This model, mounted on the NCD- SWEET beamline platform, as observed in **Figure 1**, allows the deposition of material onto a rotating platform, resorting to a single extruder with a dual channel screw. Plastic pellets are heated and the melt flows through a 300 µm inner diameter needle with a considerable length-to-diameter ratio (L/D \approx 36).

With the configurable heat zones and the remote control of extrusion velocity, and collector velocity (write speed), the team performed printing trials with polycaprolactone (PCL) and low-density polyethylene (LDPE). The extrudates were observed in a quasi-steady state with a constant temperature profile (as represented on the right side of Figure 1). repositioning the incident x-ray beam along the extrusion axis, and moving the platform on the z-axis, scans of 20 steps of 0.1mm with a 1-second data collection period were captured. In **Figure 2**, an example of the resultant small-angle X-ray scattering (SAXS) patterns, is presented for each material. As it is possible to conclude in these measurements, the filaments (solidified extrudates) produced at a low speed have a broadly isotropic crystal orientation; whereas a higher level of orientation is revealed for a higher write speed (as indicated by the two sharp maxima above and below the zero-angle point). This might be associated with the crystallization occurring before the extended chains have totally or completely relaxed.



Figure 2 – LDPE (left) and PCL (right) SAXS patterns obtained at different writing speeds.

-Conclusions and Future Work

So far, the morphology analysis in 3D printing has been successful, and it was proven that it is possible to produce extrudates of a polymeric material with different morphologies, by controlling the processing parameters. Some correlations between the printing conditions and the level of preferred orientation in the deposited material have been established. As an output, this strategy of polymer deposition results in a mapping of properties along a printed part.

Future developments are expected, regarding the application of the analysis outputs in a non-planar extrusion-based 3D printer in order to obtain new geometries with distinct layer sections reinforced along the extrusion direction, as represented in **Figure 3**. Moreover, new results are expected in regard to temperature variation and slicing strategies, and the overall mechanical behavior of the manufactured parts; employing the information retrieved by the multiscale modeling of polymer processing, to be developed in partnership with MIT.



Figure 3 – Solution proposal of non-planar 3D Printing with different properties along the whole part, and with a single material.

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Acknowledgements:

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