MIT Portugal Project Report

Additive Manufacturing of Semicrystalline Polymers: Flow and Morphology

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1. Research results and accomplishments

Additive manufacturing is a process for fabricating 3D parts from a digital model. For polymers, complex parts are fabricated by Fused Deposition Modeling (FDM) based on a digital specification of the desired form. However, material properties are poorly controlled, especially for semicrystalline polymers. To make printable parts truly useful, we must understand—and model—how molecular structure sets rheology and crystallization and how these processes interact during printing, so we can design conditions that deliver consistent, high-performance products.

In collaboration with the INOV-AM and Bioshoes4ALL programs, which provide in-situ measurements of morphology evolution, we started building a state-of-the-art multiscale model that couples rheology to crystallization along the print path and predicts semicrystalline morphology from material and process parameters. This model will enable tighter property control and speed up the development of new feedstocks and model-based control systems.

1.1 Multiscale model

The overarching goal of this project is the development, testing and validation of a model for processing and solidification of a semicrystalline polymer in an extruder-based 3D printing process. To accomplish this goal, we are implementing a multi-scale model of the FDM process, illustrated in Fig.1, comprising (1) a continuum level model of melt extrusion and deposition on a rotating collector; (2) a meso-scale constitutive model that accounts for the two-way coupling between crystallization kinetics and evolving rheology of a crystallizing melt; and (3) a description of the local morphology as a function of time and position in terms of metrics that correlate with material properties.

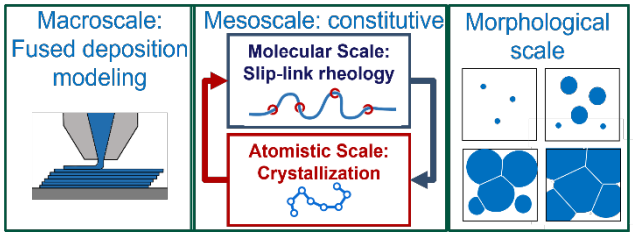

Figure 1: Diagram of the coupling between continuum level model of additive manufacturing process; mesoscale constitutive model that couples crystallization to flow; and morphological modeling of microstructure development.

1.2 Current state of the model and computational studies

We started by implementing our mesoscale model that couples melt rheology to crystallization kinetics. For this part of the project, we built upon a constitutive model introduced by Schieber et al in 2003 [1]. It's a single-chain model that follows the temporal evolution of a probe chain in the melt and uses slip-links to represent entanglements with other chains, hence its name: discrete slip-link model (DSM). The Rutledge group recently extended DSM to partially crystallized polymer melts and found good agreement with small amplitude oscillatory shear measurements (SAOS) [2]. The key feature of the model is the augmentation of the probe chain ensemble with "dangling" (anchored at one end) and "bridging" (anchored at both ends) chains that account for the slowing down and eventual formation of a crystallite network as crystallization in the polymer melt proceeds.

We couple the slip-link model to a crystallization kinetics model that yields the degree of crystallinity, χ. The DSM then uses χ to update two parameters governing crystallization, the volume fractions of bridging and dangling chains (ϕ_B, ϕ_D), and a vertical shift factor (G_{sh}) for the viscoelastic moduli. The χ-dependence of these parameters is obtained by parameterizing the model to match SAOS measurements as crystallization proceeds.

Since the DSM is now parameterized to track the resin's partial crystallinity, we need a kinetics model to compute $\chi(t)$. We use the Schneider equations [3] with the Avrami impingement correction. The Schneider system comprises four coupled ODEs for the crystallite extended volume fraction φ_0, total surface φ_1, total size φ_2, and number density φ_3, and it separates growth from nucleation kinetics. We determine the growth and nucleation rates from bulk crystallization data (FSC/DSC) across a wide temperature range, as well as literature data, and then we fit analytical forms. Growth follows the Hoffman–Lauritzen (HL) relation, while nucleation is enhanced by chain orientation/stretching quantified by the slip-link model's conformation tensor, **C**. Specifically, we use the second invariant of the nematic order tensor, $J_2(\mathbf{P}_2)$, where $\mathbf{P}_2 = (3\mathbf{S}–\mathbf{I})/2$ and $\mathbf{S} = \mathbf{C}/\lambda^2$. This orientation can accelerate nucleation by orders of magnitude. Using molecular dynamics simulations, our lab derived the enhancement factor and validated it against experiments for various flows [4]. The resulting relationship is:

$$I = I_q(T) \sum_{p=1}^{p} v_p \exp\left[\theta \sqrt{J_2\left(P_{2,p}\right)}\right],$$

where $I_q(T)$ is a temperature-dependent quiescent nucleation rate described by a Classical Nucleation Theory-inspired relation, θ is an adjustable parameter, and the exponential function is weighted over the molecular weight modes (p) of our resin.

After parameterizing the crystallization kinetics model, we couple it to the slip-link model to track the temporal evolution of the crystallizing polymer in terms of rheology and morphology. Figure 2 illustrates the coupling for an isothermal shear flow at a shear rate $\dot{\gamma} = 2.3\ s^{-1}$ and temperature T = 84 °C, and also reports the morphological outputs from the Schneider rate equations. In Fig. 2a, the slip-link model predicts the time evolution of the shear viscosity, which increases and ultimately diverges as the crystallinity approaches its maximum. The slip-link model provides the conformation tensor **C** to the crystallization kinetics model, which estimates the relative crystallinity χ (Fig. 2b). Based on χ, we update the chain composition by adjusting ϕ_B, ϕ_D, and G_{sh}, thereby converting free chains into dangling and bridging chains. At any time, the coupled framework can output morphological information for the crystallizing polymer (green box in Fig. 2).

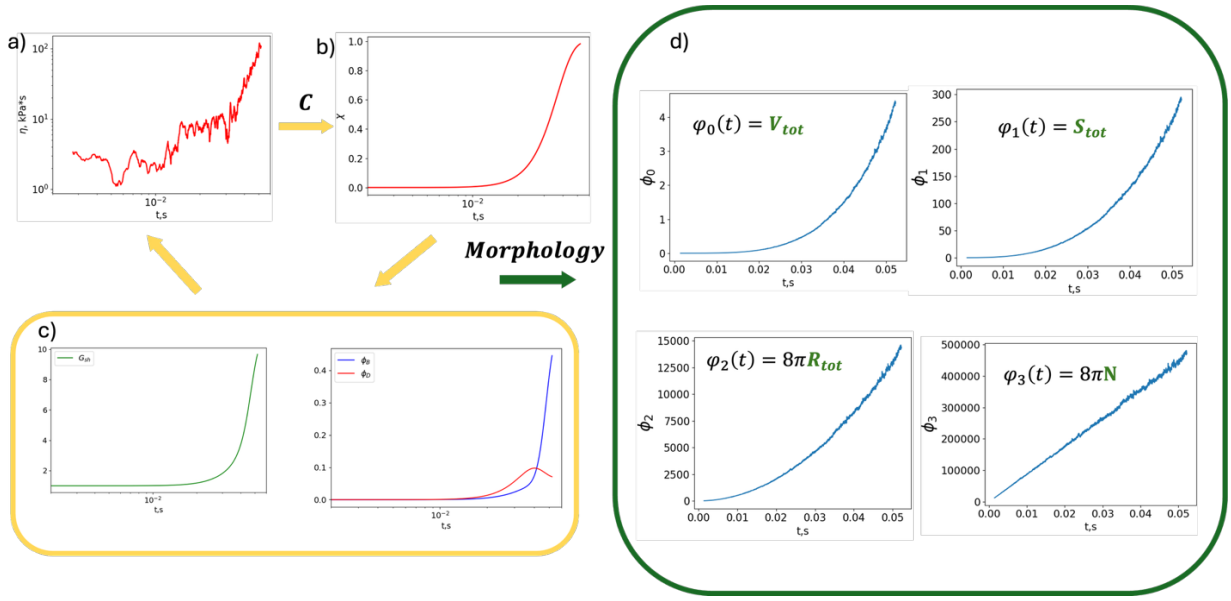

Figure 2: a) Shear viscosity plot as a function of time, b) Relative crystallinity over time, c) Slip-link adjustable parameters over time, d) Schneider morphology outputs

These morphological outputs from our simulations must ultimately be compared with experimental scattering data. To enable this, we use a scattering intensity model that converts morphology into two-dimensional (2D) scattering patterns or 1D intensity profiles along selected directions, which can then be juxtaposed with experiments. The model distinguishes two crystallite populations based on flow history. Under flow-induced crystallization—i.e., when the applied flow stretches and orients chains and they have not relaxed before nucleation—extended chains act as row nuclei ("shish") that template chain-folded lamellae ("kebabs") growing normal to the flow direction, yielding anisotropic structures. By contrast, when crystallization occurs from fully relaxed chains, nucleation is driven by other heterogeneities and an isotropic spherulitic morphology results.

Our scattering model follows standard small-angle theory, $I = I_0\, P(q)\, S(q)$, where $P(q)$ is the single-crystallite form factor (shape/size/orientation), $S(q)$ is the structure factor capturing inter-particle spatial correlations, and I_0 is an overall scale. We consider two populations. (i) Isotropic spherulites are modeled as spheres with a size distribution, and the corresponding spherical form factor; inter-domain spatial correlations are described with the hard-sphere Percus–Yevick structure factor. (ii) Flow-induced anisotropic "shish–kebab" crystallites are approximated as cylinders. Their intensity uses the cylinder form factor averaged over a non-uniform orientation distribution (reflecting alignment by flow). The 2D patterns are computed by evaluating $P(q)$ and averaging over the size and orientation distributions.

The Schneider outputs supply the size distribution parameters for the scattering model: a mean spherulite radius and variance, and for cylinders a mean diameter with an

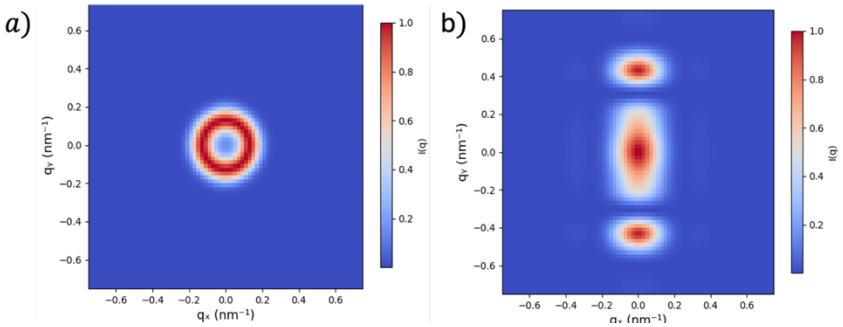

Figure 3: 2D scattering patterns for a) spherulites and b) shish-kebabs

analogous variance. The orientation distribution is inferred from the chain orientation encoded in the simulation conformation tensor **C**. Combining these inputs, we synthesize scattering intensities and generate 2D patterns for both spherulitic and shish-kebab morphologies as illustrated in Fig. 3.

1.3 Further implementations/ future developments

The continuum module of our multiscale model is in development. We split the printing process into two stages: (i) pressure-driven nozzle flow and (ii) uniaxial extension of the extruded filament to the collector. Phase 1 is complete and supplies nozzle-exit velocity and stress as boundary conditions for Phase 2, which is ongoing. Next, we will incorporate non-isothermal effects and then fully couple the continuum, mesoscopic (slip-link), and crystallization kinetics modules. Finally, we will validate the simulated scattering patterns against experimental data.

2. Interactions with our collaborators in Portugal

Our collaborators in Portugal are designing the experimental FDM module for collecting Small- and Wide-Angle X-ray Scattering data (SAXS/WAXS) on the NCD-SWEET beam line at the Alba facility in Barcelona. Monthly online meetings are conducted to review model developments and plan the experimental campaign. Beyond analyzing the 3D-printer process, we focus on material selection and key variables to measure (e.g., temperature, extrusion rate, film thickness). The team in Portugal is expert in performing in-situ SAXS/WAXS measurements [5]. Together, we have applied for beam time on the FDM in Spring 2026. A visit by Dr. Kolezakis and Prof. Rutledge is planned for Fall 2025 to meet the team in Portugal and finalize experimental details.

3. Publications and presentations

We plan to present our results at the APS March Meeting 2026.

References

[1] Schieber, J. D., J. Neergaard, and S. Gupta. “A Full-Chain, Temporary Network Model with Sliplinks, Chain- Length Fluctuations, Chain Connectivity and Chain Stretching.” J. Rheol. (N. Y. N. Y). 47, 213–233 (2003).
[2] Andreev, M., D. A. Nicholson, A. Kotula, J. D. Moore, J. den Doelder, and G. C. Rutledge. “Rheology of Crystallizing LLDPE.” J. Rheol. (N. Y. N. Y). 64, 1379–1389 (2020)
[3] Schneider, W., Köppl, A., Berger, J., “Non-Isothermal Crystallization: Crystallization of Polymers”, Intern. Polym. Process. II 1988, 151
[4] Nicholson, D. A., M. Andreev, K. L. Kearns, M. Chyasnavichyus, D. Monaenkova, J. Moore, J. den Doelder, and G. C. Rutledge. “Experiments and Modeling of Flow-Enhanced Nucleation in LLDPE.” J. Phys. Chem. B 126, 6529–6535 (2022).
[5] Da Silva, D.P., Pinheiro, J., Abdulghani, S., Lorger, C.K., Martinez, J.C., Solano, E., Mateus, A., Pascoal-Faria, P., and Mitchell, G.R., “Changing the Paradigm – Contolling Polymer Morphology during 3D Printing Defines Properties”, Polymers, 14, 1638 (2022).