

MOLECULAR SIMULATIONS OF CRYSTALLIZABLE POLYMERS UNDER FLOW

By

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TECHNICAL SUMMARY

Semicrystalline polymers are ubiquitous in packaging, consumer products, and textiles, with their properties fundamentally governed by crystallization kinetics during processing. Flow and thermal histories during manufacturing like extrusion, molding, and sealing, couple with crystallization to determine final material properties. This thesis develops computational models across multiple scales to understand and predict how flow influences crystallization and rheological behavior in semicrystalline polymers. The work progresses from molecular-level understanding of nucleation to process-scale modeling and addresses computational challenges encountered at each scale.

The first part of this work uses non-equilibrium molecular dynamics (NEMD) to examine flow-enhanced nucleation (FEN) of polyethylene under biaxial extensional flows which is a class of flows directly relevant to industrial processes but largely unexplored computationally. Simulations reveal that nucleation kinetics depend on Kuhn segment orientation rather than extra stress, with the stress-optical rule breaking down under biaxial flow conditions. Nucleation occurs preferentially in nematic-ordered domains, and a model based on the nematic order tensor successfully describes FEN across all flow types studied, including shear, uniaxial, and biaxial extensional flows.

However, these brute-force NEMD simulations are limited to deep supercooling and low molecular weights, restricting their direct applicability to industrially relevant conditions. To overcome these computational limitations, advanced sampling techniques are explored. Forward Flux Sampling (FFS) is implemented for polymer nucleation, with the goal of enabling access to rare nucleation events at shallower undercoolings. While FFS provides computational benefits and is internally self-consistent, systematic investigation reveals persistent discrepancies with brute-force rates that likely stem from the slow relaxation dynamics characteristic of polymers, informing future development of rare-event techniques for these systems.

The molecular insights from the nucleation studies motivate the need for models that connect molecular-level details to process-scale behavior. The second part of this thesis addresses this need through the coupled rheological-thermal response of crystallizable polymers during heat sealing, a process in which flow, heat transfer, and crystallization are tightly interdependent. A comprehensive thermo-rheological model is developed for the heat sealing process in multilayer films, integrating heat transfer, crystallization kinetics, and molecular-level rheology through the crystallizable discrete slip-link model (cDSM). By

incorporating molecular weight distribution and short-chain branching distribution as explicit inputs, the model reveals how resin selection impacts seal quality. Experimental validation on industrial multilayer polyethylene films demonstrates that fractional flow volume correlates with hermeticity, providing a predictive tool for resin design and selection.

While the cDSM enables molecular-level fidelity in process simulations, its stochastic nature makes it computationally expensive; particularly for the repeated evaluations required in process optimization or computational fluid dynamics. To address this bottleneck, machine learning is leveraged to augment constitutive equations. The Rheological Universal Differential Equations (RUDEs) framework is extended to entangled polymer melts, replacing the base Oldroyd-B model with the Rolie-Poly model and training tensor basis neural networks on discrete slip-link model data. The resulting surrogate model achieves three to four orders of magnitude speedup over the slip-link simulations while maintaining accuracy and transferability across molecular weights, compositions, and flow protocols.

Taken together, this thesis demonstrates that molecular-level details like chain conformation, molecular weight distribution, and short-chain branching, are essential inputs for predicting both the early stages of crystallization and the processing behavior of semicrystalline polymers. The computational approaches developed here, spanning molecular dynamics, stochastic rheological models, and machine learning surrogates, provide a framework for translating these molecular characteristics into predictions of process outcomes at industrially relevant scales.

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