SANDIA REPORT
SAND2021-14887
Printed November 2021

Modeling the Nonlinear Rheology of Polymer Additive Manufacturing

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ABSTRACT

This report summarizes molecular and continuum simulation studies focused on developing physics-based predictive models for the evolution of polymer molecular order during the nonlinear processing flows of additive manufacturing. Our molecular simulations of polymer elongation flows identified novel mechanisms of fluid dissipation for various polymer architectures that might be harnessed to enhance material processability. In order to predict the complex thermal and flow history of polymer realistic additive manufacturing processes, we have developed and deployed a high-performance mesh-free hydrodynamics module in Sandia's LAMMPS software. This module called RHEO – short for Reproducing Hydrodynamics and Elastic Objects – hybridizes an updated-Lagrange reproducing-kernel method for complex fluids with a bonded particle method (BPM) to capture solidification and solid objects in multiphase flows. In combination, our two methods allow rapid, multiscale characterization of the hydrodynamics and molecular evolution of polymers in realistic processing geometries.

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ACRONYMS AND DEFINITIONS

Abbreviation	Definition
AM	Additive Manufacturing
FD	Filament Deposition
RHEO	Reproducing Hydrodynamics & Elastic Objects
LAMMPS	Large Atomic Molecular Massively Parallel Simulator
PPA	poly(phthalaldehyde)
cPPA	cyclic poly(phthalaldehyde)

1. OVERVIEW NANOSTRUCTURE EVOLUTION DURING POLYMER ADDITIVE MANUFACTURING

Additive manufacturing (AM) is a fabrication scheme where material is systematically added to a structure to build up a usable part. By layering new material, AM methods can build structures with complex and innovative geometries that provide energy savings through improved mechanics, more efficient use of material, and streamlined assembly.[1] A wide variety of AM techniques exist for most classes of materials; however, methods using polymer materials (plastics) have rapidly gained interest due to their low cost and versatility. Polymer feedstocks both weigh less and cost less than typical metals and become workable at much lower temperatures, making fabrication easier and more energy efficient. Once primarily used for rapid prototyping, polymer AM parts can now be found in an increasing number of end-use applications in transportation and defense.[1] This rapid growth of polymer AM highlights an exciting trend in American manufacturing; however, continued expansion of polymer AM applications requires meeting key material challenges in the fabrication process.

Polymer AM faces challenges caused by a poor understanding of how the material properties are altered during flow through AM fabricators. In common fabrication processes like fused-filament deposition (FD) (Figure 1), polymer filaments are heated to a molten state and then extruded through a nozzle onto the part surface. This extrusion produces extensional flows that stretch and reorganize the polymer material at the molecular scale.[2] This reorganization can dramatically alter the viscosity of the flowing polymer, which complicates fabrication process design and greatly limits useable feedstock materials. Most fabricators require careful tuning of temperature and flow rate so polymer viscosities stay within a narrow, workable range. Since little is understood about how extensional flows change polymer microstructure and viscosity, identifying optimal fabrication conditions and feedstock materials is difficult. This makes fabricator design an arduous task that requires hundreds of man-hours of experimentation to calibrate equipment and protocols. As a result, most fabricators can only work with 1 or 2 polymer feedstocks, and the majority of polymer AM applications are dominated by a handful of materials.[1]

Expanding the range of polymer feedstocks and designing fabricators to be interoperable with them are major R&D goals that must be met before polymer AM can be widely adopted. While these challenges can be met with sufficient hours of trial and error, more systematic and efficient methods are needed for continued expansion of polymer AM. Designers need predictive, physics-based models that allow them to rapidly identify feedstock materials and optimize fabrication settings for specific material feedstocks and part designs. Such models require understanding how polymer feedstock material flows through the fabricator and how the microstructure of deposited polymer evolves during welding to impact performance. A physics-based understanding of both these stages would not only allow fabricators to be optimized for specific materials and part designs but could also provide a rational approach for identifying new feedstock materials. Looking ahead, physical models connecting polymer architecture to flow processing could facilitate development of fabricators that adaptively control flow conditions to tailor material properties in real time.

Most common physical models of polymer dynamics fail when applied to strong extensional flows.[3] These models do not accurately describe how extensional flow reorganizes polymer microstructure and thus they fail to accurately predict the flow of feedstock in many processing conditions. Improving current models is challenging because it requires detailed information about polymer microstructure during flow that is inaccessible to typical experiments. Without microscopic data, modelers have been forced to guess how flow changes polymer microstructure. A variety of such model frameworks have been proposed in attempts to better predict experimental data, but they make conflicting predictions.[4,5]

The project combined Sandia's high-performance computing capabilities with state-of-the-art molecular simulation techniques to develop a systematic understanding of the nonlinear flow of entangled polymer liquids during nonlinear extensional flows. Insights from our molecular scale simulations have identified new physical mechanisms governing the processability of polymers with a variety of chain architectures. These insights have in turn enabled the development of better physics-based models for polymer dynamics in nonlinear processing flows.

To facilitate the use of new models for polymer hydrodynamics, this project has also developed and deployed a new mesh-free modeling framework for viscoelastic material processing. This new software package RHEO – Reproducing Hydrodynamics & Elastic Objects – combines reproducing kernel smooth particle hydrodynamics for viscoelastic fluids with a bonded-particle method for material solidification. RHEO can model the extrusion, cooling, and solidification of polymer materials in realistic additive manufacturing geometries, allowing us to apply our new physics-based models to predict polymer nanostructure evolution during additive manufacturing.

This report summarizes the research output of this project. All scientific results have been published as scientific journal articles which can be accessed for further details.

2. SUMMARY OF RESEARCH RESULTS

2.1. MD of Polymer Dynamics Undergoing Extensional Deformation

2.1.1. Stress Relaxation of Highly Oriented Linear Polymer Melts

This study used molecular dynamics simulations to understand the relaxation of entangled linear polymer melts deformed far from equilibrium by uniaxial extensional flow. In an early study,[6] melts were elongated to large strains for Rouse Weissenberg numbers (flow strengths) ranging from 0.16 to 25. This produced states with a wide range of chain alignment. In this study, we ceased the flow, and the systems were allowed to relax until twice the equilibrium disentanglement time. We correlated the relaxation of the stress with changes in the conformation of chains and the geometry of the tube confining them.

Notably, we observed that chains rapidly relax to conformations consistent with their *equilibrium* entanglement structure, regardless of how much flow organized and disentangled them. These results are counter to recent work that suggests orientation causes a large, stretch-dependent reduction in the entanglement density that can only be recovered slowly by reptation on the equilibrium disentanglement time. Our results not only raised fundamental questions about the nature of entanglement in aligned polymer melts. They also have major implications for the dynamics of polymers during thermal welding in fused-filament additive manufacturing. The full results were published in *Macromolecules*.[7]

2.1.2. Discovery of Topological Linking in Elongated Ring Polymer Melts

Inspired by recent experiments that showed that ring polymer melts exhibit exotic and unexplainable behavior during extensional flow,[8] we performed molecular simulations of ring polymer melts to identify what this nonlinear flow mechanism was. Our MD investigation was successful, and we were able to identify a new nonlinear-mechanism of polymer entanglement that drives ring polymers to link together into long, supramolecular daisy-chains. The flow-driven self-assembly of ring polymers produces a massive rise in extensional viscosity in ring melts during extensional flows but does not occur in shear flows. This high selectivity in nonlinear response is a new phenomenon in polymer physics and could be harnessed to create flow-responsive polymer formulations. The complete study was published in *Physical Review Letters*.[9]

The results of this project were selected by the DOE Office of Science as a web highlight in Basic Energy Sciences. The article "Elongated Ring Polymers Get Tied Up in Knots" can be found here: https://www.energy.gov/science/bes/articles/elongated-ring-polymers-get-tied-knots.

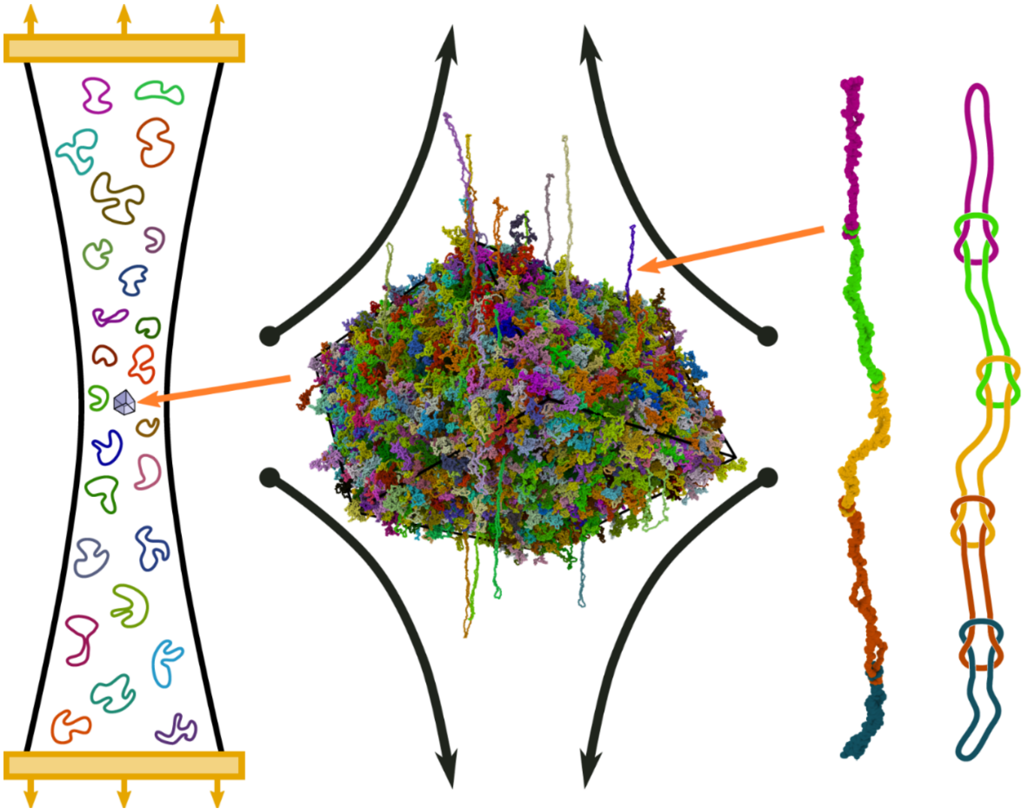


Figure 2-1. Illustration from the DOE Office of Science web highlight on our ring polymer elongation study.[9] The image illustrated how our molecular simulations (center) reproduce the flow conditions of filament stretch experiments (left) and identify the ring-linking mechanism (right) that controls the fluids viscosity.

2.1.3. Threading-Unthreading Transition of Elongated Ring-Linear Polymer Blends

Our successful use of simulations to interpret the experimental rheology of elongated ring polymers produced a collaboration with this experimental group to study a more complex system – blends of ring and linear polymers. Ring-Linear blends are much more complicated because the two-different polymer species entangle in new ways when mixed, as illustrated in the figure below. The resulting nanostructured blends produce polymer fluids with exotic nonlinear behaviors during strong extensional flows. A particular prominent feature of these fluids is that they show a maximum in flow stress during extensional flow – called a stress overshoot. Our experimental collaborators asked us if we could help verify the molecular origin of this overshoot.

Through a multi-team collaboration, we combined filament stretching rheology, small angle neutron scattering, and our molecular dynamics simulations to characterize this stress overshoot and verify that it was caused by the flow-driven unthreading of ring polymers entangled with linear polymers. By identifying the molecular mechanism of the stress overshoot, we have also learned how we can tune it to control polymer processability by modifying blend formulations. The details of this joint study have been published in *ACS Macro Letters*.[10]

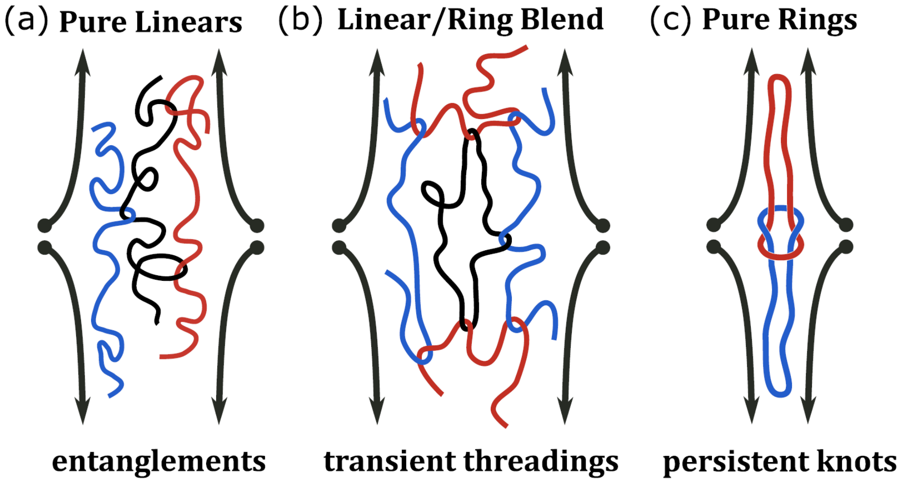


Figure 2-2. Illustration of polymer entanglement mechanisms that influence flow behavior for linear (a) ring (c) and blended linear/ring (b) chain architectures.

2.1.4. Systematic Characterization of Ring-Linear Blend Networks

As a follow up to our collaborative study on blends, we then applied molecular simulations to systematically study how ring/linear blend entanglement structure depends on the blending ratio of ring and linear chains. Molecular simulations were used to characterize the equilibrium dynamics, entanglement topology, and nonlinear extensional rheology of symmetric ring-linear polymer blends with systematically varied ring fraction ϕ_R. Our analysis identified a nonmonotonic tradeoff in network stability with changing ϕ_R with a maximum constraint density at $\phi_R \approx 0.4$. We were able to develop a simple argument to explain this maximum stability point in terms of the trade-off in entanglements produced by ring and linear polymers.

We also performed simulations of startup uniaxial elongation flows to relate the nonlinear response of the blends to their equilibrium network structure. We observed an extensional stress overshoot driven by an overstretching and recoil of ring polymers due to the convective unthreading of rings from linear chains. The size of this overshoot also shows a non-monotonic dependence on ϕ_R with an overshoot near the peak constraint density of the equilibrium network.

At the time of this report, this study has been accepted for publication in the Journal of Rheology but has not been published yet. A preprint version of this study is available.[11]

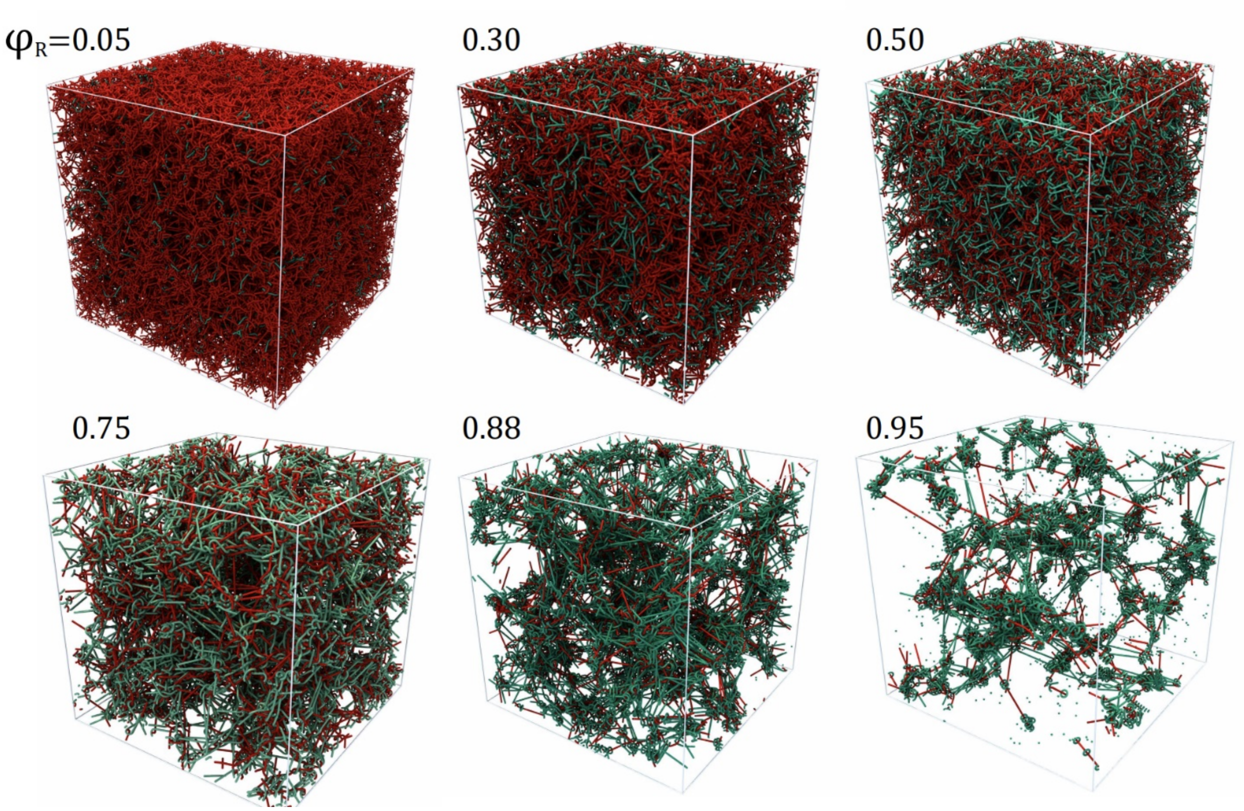


Figure 2-3. Entanglement network structures generated by primitive path analysis of ring-linear polymer blends for the indicated fraction of ring polymer ϕ_R. Linear polymers are colored red and ring polymers are teal. The structure formed by chain entanglement varies dramatically with varying blend composition.

2.1.5. A Microscopic Theory for Thermally Activated Creep in PE Fibers

In earlier work, O'Connor and Robbins developed a microscopic theory for the failure mechanism of high-performance polyethylene fibers.[12] This study fully developed that mechanism into a theory for the thermally activated creep of polyethylene fibers under constant tensile loads. This work shows how the tensile creep of a PE crystal maps onto the 1-Dimensional Frenkel-Kontorova model for 1D dislocation nucleation.[13] The analytic solutions of the Frenkel-Kontorova model are then developed to predict the Eyring energy for thermally activated tensile creep. This Eyring barrier can be expressed in terms of the basic properties of an orthorhombic polyethylene crystal, which we calculate from molecular dynamics simulations.

We show that the cheap and simple molecular simulations of an ordered state can accurately predict bounds for both the strength and plastic creep of polyethylene fibers. Similar approaches may work for other fibers. The full details of this study are published in a special issue of the *Journal of Chemical Physics*.[14]

2.1.6. Academic Alliance collaboration with Prof. Charles Schroeder

This collaboration with University of Illinois aimed to study the development of recyclable polymer materials that could serve as recoverable feedstocks for polymer manufacturing. This project combined experimental synthesis and rheology of poly(phthalaldehyde) (PPA) and its cyclic form cPPA, with molecular dynamics simulations of cyclic ring polymer melts in equilibrium and flow.

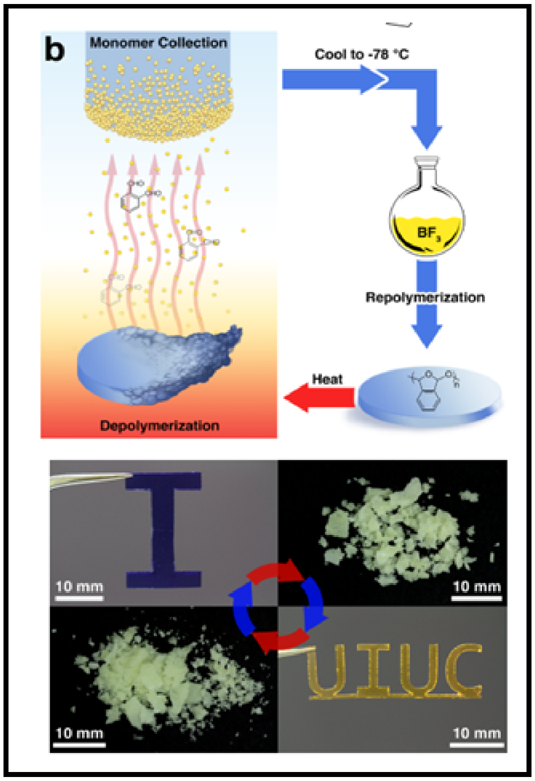


Figure 2-4. Illustration of the cPPA unsealing and recovery process provided by Prof. Charles Schroeder at University of Illinois.

The cPPA chemistry is of particular interest because it can be thermally depolymerized and recovered – enabling complete recovery and recycling of feedstock.

Key experimental results from this project have been:

1. Synthesis and characterization of high molecular-weight anionically-synthesized linear poly(phthalaldehyde) (PPA), amenable for comparisons to cationically-synthesized cyclic poly(phthalaldehyde) (cPPA)
2. Development of a processing protocol for poly(phthalaldehyde) where very little (~5%) depolymerization occurs during polymer processing, from the synthesis product to post-rheometry testing
3. Linear viscoelasticity via shear rheometry of 58.8 wt% high-MW cPPA (Mw > 400 kDa) in di-butyl phthalate systems showing somewhat-similar rheological signatures compared to lower-MW PPA (Mw ~180 kDa) at matched concentrations

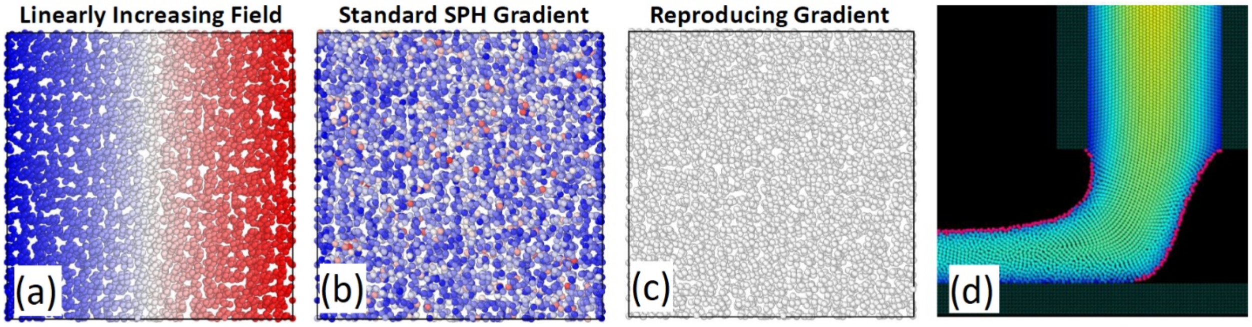
This synthesis protocol has enabled us to generate unprecedently pure melts of ultrahigh molecular weight ring polymers. This new class of polymer materials have many interesting and unexpected rheological and mechanical behaviors that we are currently exploring. Since this project began in the last year of this 3-year LDRD project, our results are still incomplete at the time of writing this report. However, we anticipate several journal publications within the next year.

2.2. RHEO LAMMPS Package for Modeling Additive Manufacturing

A final output of this project is the RHEO package for Sandia's LAMMPS software. RHEO is an opensource software for mesh-free modeling of viscoelastic fluids and solids. It is based on a reproducing-kernel formulation of smooth particle hydrodynamics that allows disordered collections of material points to consistently reproduce continuum material fields, as illustrated in the figure below.[15–17] This reconstruction allows RHEO to accurately model the evolution of material properties in the large-deformation conditions of material extrusion.

RHEO can also model mixed flows of fluids and deformable and breakable solids, and can model the solidification and melting of fluids and solids. This multiphase capability is accomplished by hybridizing an SPH fluid with the bonded-particle method module of LAMMPS. RHEO is not read for publication at the time of this publication, but we anticipate its details to be published in a journal article within the next year. It will also be released as an opensource module of Sandia's LAMMPS software with a complete documentation.

Eventually, RHEO will also be accelerated for graphic processing units (GPUs) through the kokkos package of LAMMPS.[18]



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