

University of Tennessee at Chattanooga

UTC Scholar

ReSEARCH Dialogues Conference Proceedings ReSEARCH Dialogues Conference Proceedings
2020

Apr 15th, 1:00 PM - 3:00 PM

Molecular Dynamic Study of Polymer Chains to Viscoelastic Response

Evan Gildernew

University of Tennessee at Chattanooga

Eleni Panagiotou

University of Tennessee at Chattanooga

Follow this and additional works at: <https://scholar.utc.edu/research-dialogues>

Recommended Citation

Gildernew, Evan and Panagiotou, Eleni, "Molecular Dynamic Study of Polymer Chains to Viscoelastic Response". *ReSEARCH Dialogues Conference proceedings*. https://scholar.utc.edu/research-dialogues/2020/day2_posters/108.

This posters is brought to you for free and open access by the Conferences and Events at UTC Scholar. It has been accepted for inclusion in ReSEARCH Dialogues Conference Proceedings by an authorized administrator of UTC Scholar. For more information, please contact scholar@utc.edu.

Molecular Dynamic Study of Polymer Chains to Viscoelastic Response



UNIVERSITY OF TENNESSEE
CHATTANOOGA

Evan Gildernew* and Eleni Panagiotou**

*Department of Chemical Engineering and **Department of Mathematics and SimCenter

Abstract

We use molecular dynamics simulations of coarse grained models of polymer melts to study the viscoelasticity of polymeric material as a function of their molecular weight. These results will be used in future work to examine how the topology of the constituent chains correlates with viscoelasticity.

Introduction

The entanglement of polymers significantly affects their viscoelastic response. However, the notion of entanglement remains elusive. We propose to use topology¹ to define and measure entanglement in polymers rigorously. To examine how topological entanglement, correlates with mechanical response of materials, we study materials whose entanglement varies. In practice, the entanglement of polymer chains is expected to vary with molecular weight. In this poster we present the mechanical response of polymeric material as a function of their molecular weight, which will be used in our future work to correlate with topological entanglement.

Methods

Systems comprising polymers of 20, 100, 200, 300, and 400 multi-bead chains were modeled with periodic boundary conditions. The systems were equilibrated and then subjected to oscillatory shear flow. The simulations were developed utilizing the Large-scale Atomic/Massively Parallel Simulator (LAMMPS) executed on SimCenter clusters. The 100 chain system at .001 frequency ran for over 6 weeks utilizing 64 cpus in parallel.

Simulation parameters:

Lennard-Jones potential

Interactions between non-binding molecules was regulated by the Lennard-Jones potential.

$$E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad r < r_c$$

FENE Bonds

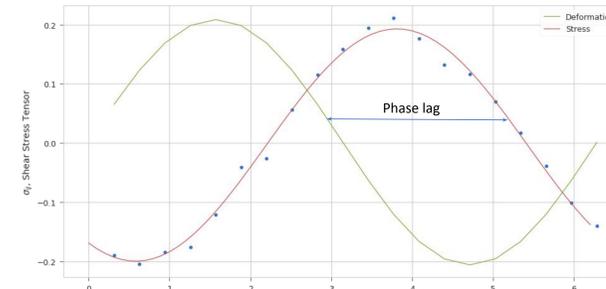
The finite extensible nonlinear elastic (FENE) potential simulated the individual bead-spring polymer binding molecule characteristics.

$$E = -0.5KR_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right] + 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon$$

Langevin thermostat

Interaction with implicit solvent was modeled using a Langevin in NVE.

$$m \frac{dV}{dt} = -\gamma V - \nabla \Phi(X) + \sqrt{2k_B T \gamma} \frac{dB_t}{dt}$$



Least Squares fit of Deformed and Stress, computes investigative properties

Lees-Edwards boundary conditions

Oscillatory shear was imposed on the bulk system using the Lees-Edwards Boundary condition which simulates simple shear for a periodic boundary condition volume. Velocities are modified according to a shear rate.



Lees-Edwards boundary conditions in 2D

Irving-Kirkwood method

Stress tensor calculated using Irving-Kirkwood method.

$$\sigma_{i,k} = \frac{1}{V} \sum_n \sum_{j=1}^{n-1} \langle f_j^{(i)} \cdot (x_{q_n}^{(k)} - x_{q_j}^{(k)}) \rangle$$

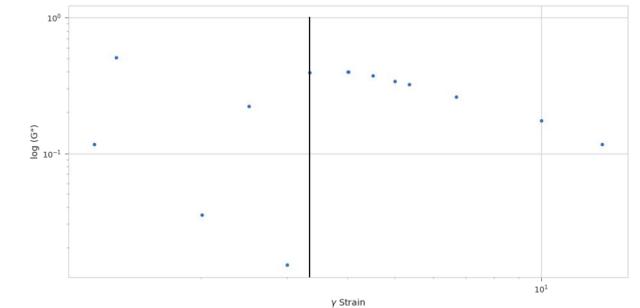
$$g(t) = G_2(\omega)\eta_0 \cos(\omega t) + G_1(\omega)\eta_0 \sin(\omega t)$$

Loss modulus (Liquid-like) Storage modulus (Solid-like)

Least squares fit to phase lag function fitting

Phase Lag Calculation

Phase lag between the deformed and stressed shear stress tensors across t describes solid like and liquid like behavior of polymer melts. Solid behaviors have phase lags close to 0. Phase lags close to pi/2 describe liquid behaviors.



Strain study graph: for determination of linear viscoelastic region, the horizontal line represents our suitable working strain amplitude.

Quantifying Linear viscoelastic properties

The focus of our research was to examine polymer melts under oscillatory shear flow. Two dynamic moduli were derived from the stress strain relationship.

$$G' - \text{solid-like descriptor Storage modulus} \quad G' = \frac{\sqrt{\text{Maxima } \sigma}}{\gamma} * \sin(\delta)$$

$$G'' - \text{liquid-like descriptor loss modulus} \quad G'' = \sqrt{\frac{2 * \text{Avg } \sigma}{\pi}} * \frac{\cos(\delta)}{\gamma}$$

Suitable Working Strain Amplitude

A working strain amplitude was investigated. The strain desired needed to be low enough to be linear region² but not in a noisy region. The line marked in the above figure represents the working strain used in future simulations.

Results

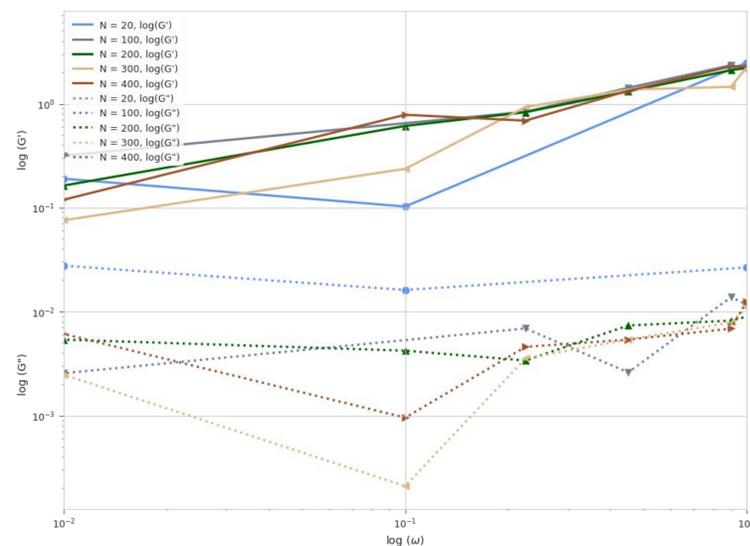
The frequency dependence of the storage modulus (G') is plotted in the solid lines representing the five polymer melt systems. Across all systems we see solid like behavior decrease as oscillatory shear flow is decreased. The loss modulus (G'') behaviors also depend on frequency and respond in an expected manner. As frequency is decreased fluid like behavior is observed trending up for the melt systems.

The higher frequency viscoelastic behavior is converged for both G' and G''. As the frequencies decrease there is separation between systems. This kind of characterization is expected and can be used to correlate with molecular weight and entanglement.

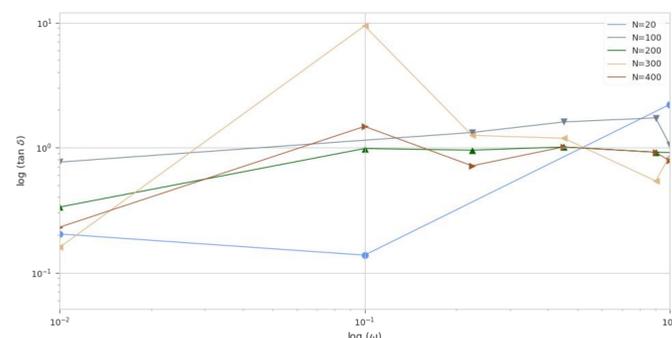
The longer chain polymer systems would have greater molecular weight and a higher degree of entanglement. There is a critical chain length of 100, above which systems should begin ordering based on entanglement in lower frequencies. This can be glimpsed in the 300 and 400 bead systems at frequency .001. Future work might be able to extend these simulations to greater resolve ordering based on entanglement.

Loss factor, tangent delta is plotted. It is used to describe the ability of material to absorb and disperse energy. In situ, it represents the ability to adsorb oscillatory shear force, across systems of increasing weight and entanglement. A loss factor of 0 represents no energy is lost to heat. As the polymer melts move to lower frequencies, and more fluid like behavior is characterized, we see loss factors decrease.

Both sets of calculations are in agreement describing the behavior of the polymers.



Simulated viscoelastic spectrum, Systems (N = 200,300,400) closely track with the typical viscoelastic spectrum for an entangled polymer system in the rubbery plateau region. Systems below N=100 do not have necessary chain length to express entanglement characteristics.

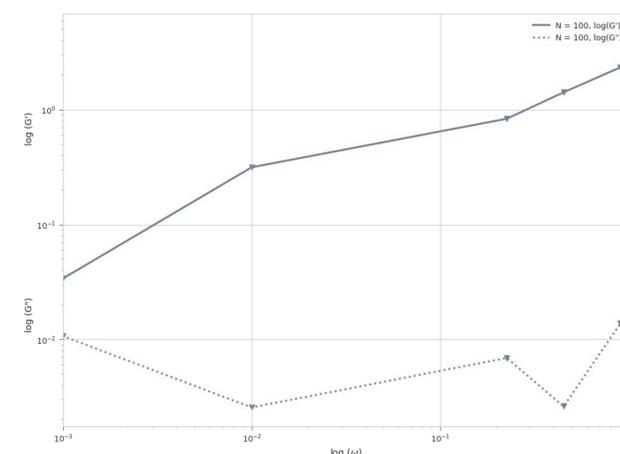


Loss factor (tangent delta)

The effect of entanglement is not obvious in this range of frequencies, but exist in lower frequencies.

The 100 bead polymer system had extended simulation times at lower frequencies allowing characterization to .001 frequency. The storage and loss modulus were beginning to converge. If that trend continued the 100 bead melt was approaching the terminal region of the viscoelastic spectrum.

By extrapolation of these results we will obtain approximate estimates of the characteristic times of each system.



System N=100, frequency .001, approaching transition region.

Conclusion and Future Work

A linear viscoelastic region to study was determined. Our coarse grained polymer model (FENE) successfully characterized viscoelastic behavior as it is widely understood under oscillatory shear flow. The five systems studied responded as expected across a frequency spectrum. In the future, characterization of polymer beads by topology will be included to quantify the relationship between entanglement and viscoelastic behavior.

References

- Panagiotou, E., Millett, K. C., & Atzberger, P. J. (2019). Topological Methods for Polymeric Materials: Characterizing the Relationship Between Polymer Entanglement and Viscoelasticity. *Polymers*, 11(3), 437. <https://doi.org/10.3390/polym11030437>
- Cifre, J.G.H., Hess, S. and Kröger, M. (2004). Linear Viscoelastic Behavior of Unentangled Polymer Melts via Non-Equilibrium Molecular Dynamics. *Macromol. Theory Simul.*, 13: 748-753. doi:10.1002/mats.200400021

Acknowledgements

Evan Gildernew and EP were supported by CEACSE 2020 "A study on the local and global effects of polymer entanglement in material properties and biological functions."

Eleni Panagiotou was also supported by NSF DMS-1913180