Designing the Topological Structure of Next-Gen Thermoplastic Elastomers

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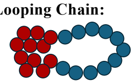
INTRODUCTION

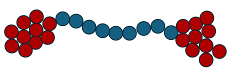
- Thermoplastic elastomers (TPEs)
  - Under researched topologically to maximize their durability, and thus sustainability, in modern manufacturing
  - Hard glassy tail regions with soft rubbery connecting regions
  - Glassy regions bunch together
    - Chains that terminate in the glassy sphere in which they began are "loops"
    - Chains that connect two glassy spheres are "bridges"
  - Chains can entangle themselves with other chains, providing strength to the polymer.
  - This research aims to uncover the effects of entangled loops on polymer strength

Model Chain:

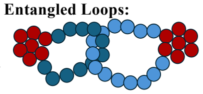
Looping Chain:



Bridging Chain:



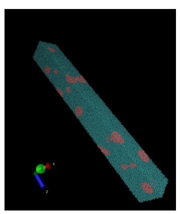
Entangled Loops:



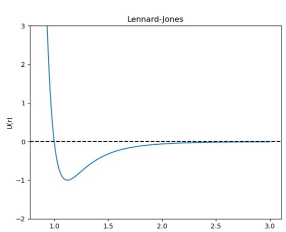
BACKGROUND

Thermoplastic elastomers are highly versatile materials with unique properties and uses.

- Found in rubber bands, tubing, etc.
- Glassy to rubbery connection triblock chains
  - (AA-BBBBB-AA)
- Changing properties under stress and strain that are not very well documented

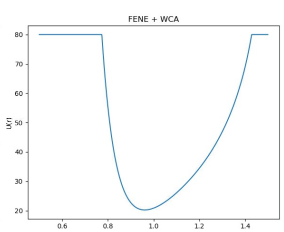


VMD visualization of a low looping starting configuration for a polymer simulation (pink glassy chain end regions)



Graph made using Matplotlib of Lennard-Jones forces that act between unbonded beads between chains using:

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



Graph made using Matplotlib of FENEWCA forces that act between bonded beads using:

$$U(r) = -\frac{1}{2}kr_0^2\ln\left(1 - \frac{r^2}{r_0^2}\right)$$

METHODOLOGY

HOOMD molecular dynamics simulations are the backbone of this research and take in many different parameters to control how bonded chains interact in a simulation. The goal of this research is to investigate TPE strength by simulating their relaxation and reconfiguration at low and high levels of looping and then analyzing the resulting simulated polymer.

Relaxation:

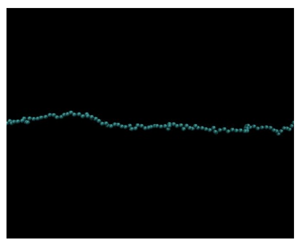
- Utilizes FENEWCA bonds to relax simulations and allow chains to disentangle
- Increase r_0 and allow the chains to freely disentangle before reconfiguring the system

FENEWCA given by:

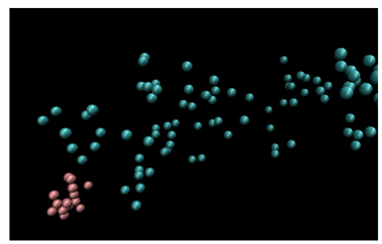
$$U(r) = -\frac{1}{2}kr_0^2\ln\left(1 - \frac{(r-\Delta)^2}{r_0^2}\right)$$

Table detailing the parameters of FENEWCA bonding between beads

Parameter	Symbol	Description
Spring constant	k	Stiffness of the bonding
Maximum bond extension	r_0	Maximum stretching point between two bonded beads
LJ energy	ϵ	Strength of WCA
WCA	$U_{WCA}(r)$	Lennard-Jones aspect of the simulation
Bead diameter	σ	Sets the size of each bead
Shift parameter	Δ	Sets equilibrium bond length



Single TPE chain in its initial state



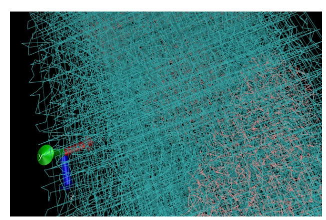
The single TPE chain pictured to the left after being relaxed by altering r_0

Reconfiguration:

- The product of the relaxation simulation is used as the starting configuration in a simulation that uses harmonic bonds to pull the bonds back together

Unwrapping:

- Simulations are contained in a finite box, but chains exist in an infinitely large space
  - Periodic boundary conditions fix this by looping chains that are exiting the simulation's box/boundary to the opposite side respective to where they were leaving
  - Needs to be undone before visualization and analysis



Wrapped starting configuration visualized via VMD

ANALYSIS

Radial Gyration in z:

- Measures how extended a chain is about the z axis using the chain's center of mass (COM)

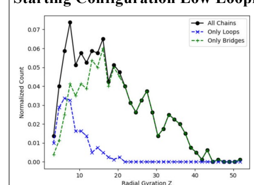
Rgz given by:

$$R_{gz} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(z_i - z_{COM})^2}$$

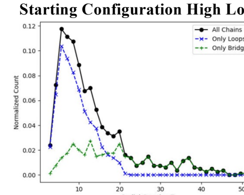
RESULTS

Tracking the radius of gyration about the z axis at each simulation step (Starting configuration, relaxation, reconfiguration) can indicate topological changes that affect polymer durability.

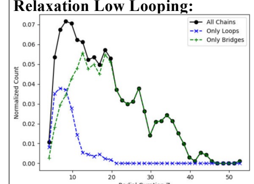
Starting Configuration Low Looping:



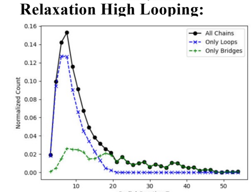
Starting Configuration High Looping:



Relaxation Low Looping:



Relaxation High Looping:



- It can be reasonably predicted that entangled loops play a significant role in TPE strength
  - Entangled loops may resist changes in topological strength more than entangled chains
  - Conclusive results for reconfigured high and low r_0 simulations are pending, and thus are not present on this poster

REFERENCES

[1] Anderson, J. A., Glaser, J., & Glotzer, S. C. (2020). HOOMD-blue: A Python package for high-performance molecular dynamics and hard particle Monte Carlo simulations. *Computational Materials Science*, *173*, 109363. 10.1016/j.commatsci.2019.109363

[2] Humphrey, W., Dalke, A., & Schulten, K. (1996). VMD - Visual Molecular Dynamics. *Journal of Molecular Graphics*, *14*, 33–38. http://www.ks.uiuc.edu/Research/vmd/

[3] Parker, A. J., & Rottler, J. (2015). Molecular Mechanisms of Plastic Deformation in Sphere-Forming Thermoplastic Elastomers. *Macromolecules.*, *48*(22), 8253–8261. https://doi.org/10.1021/acs.macromol.5b01339