Molecular Dynamics Simulations of Polyvinyl Chloride for the Accurate Prediction of Novel Biobased Polymer Properties

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Fossil Energy Emissions Mitigation

https://youtu.be/jAqboGRMiT8

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Introduction

- **Motivation: create a sustainable polymer pipeline**
- Only 1% of the plastics produced come from renewable sources
- Plastic contribution to global CO2 emission is expected to grow from 5% to 15% of emission by 2050
- A circular plastics economy is needed to sustainably generate plastic and reduce waste

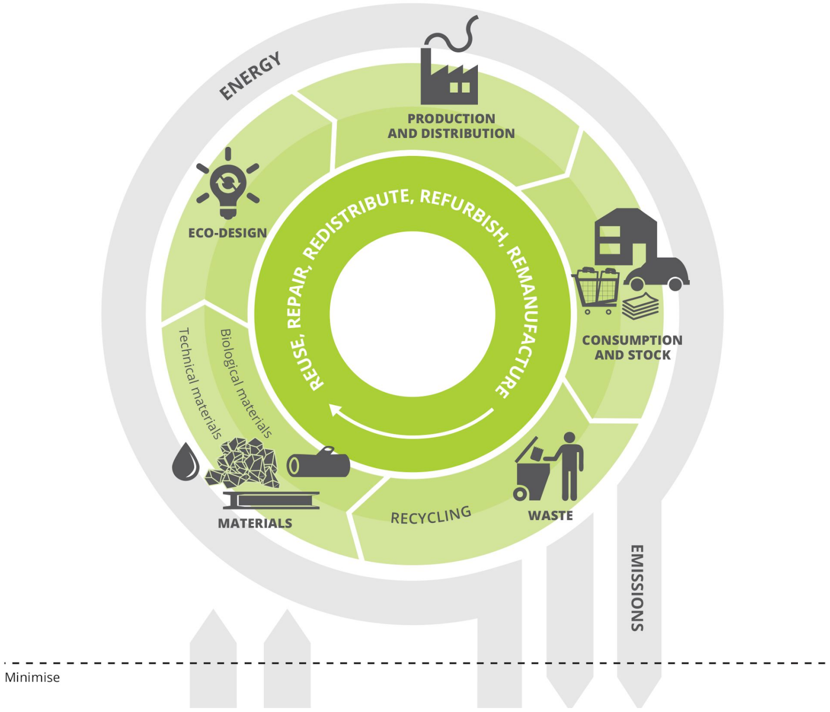

Fig.1 Schematic for a circular economy where raw materials are recycled from design, production, and consumption and derived from sustainable sources. At the same time, energy use and emissions are minimized. Reproduced from the European Environmental Agency Report 2015.

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Objective

★ **Evaluate MD force fields to determine their accuracy; implement best practices for simulation property testing**

ML training set: Literature data on polymer properties (e.g. Tg)

List of potential novel, renewable monomers

Machine Learning: Identifies what biobased polymers can be made from the novel monomers and predicts their properties

Large list of potential novel, renewable polymers and predicted properties

Molecular Dynamics Simulations: Evaluates candidate novel polymers for additional properties

Pruned list of potential polymers

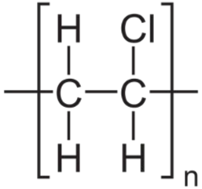
Experimental Fabrication: Determines how to make the polymer (e. g. catalysts) and tests actual properties

Polymers with desirable properties that can be synthesized

Technoeconomic Analysis (TEA) and Life- Cycle Assessment (LCA): Determines environmental and dollar cost of producing the polymer

Identification of environmentally and economically favorable novel polymers

Simulation Methods



CHARMM-GUI
Effective Simulation Input Generator and More

- PVC is a well-characterized, widely-used thermoplastic polymer
- Model: 86 x 86 x 86 Å box of linear, atactic PVC (48 x 103 atoms) packed and equilibrated (coarse-grained) using CHARMM-GUI.
- CHARMM General Force Field (CGenFF) parameters
- As a case study, techniques developed in this study will be expanded to other polymers

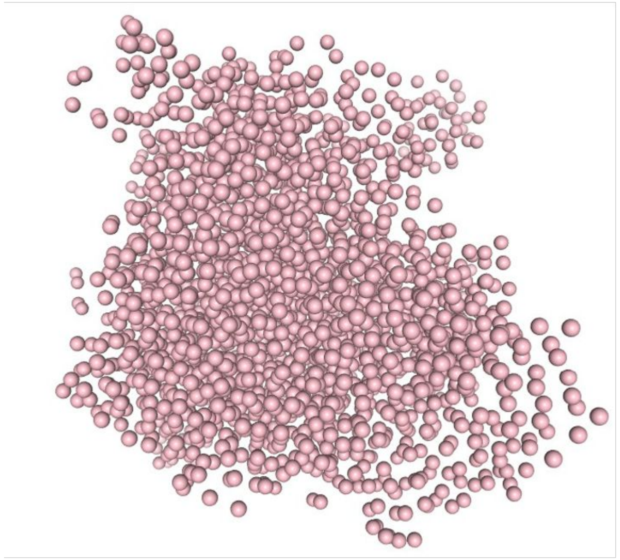


Fig. 3 Coarse-grained Kuhn-bead model of PVC system as equilibrated by CHARMM-GUI.

Property Calculation Methods

- Glass transition temperature: temperature at which the rate of change of the diffusion coefficient with respect to temperature of an inert gas within the polymer changes noticeably.
- Density: specific volumes at different degrees of polymerization
- Stress: system deformed along the x-axis to incrementally higher strain values, tensile stress calculated using pressure tensor. Tensile strength and elastic modulus calculated using stress-strain curve

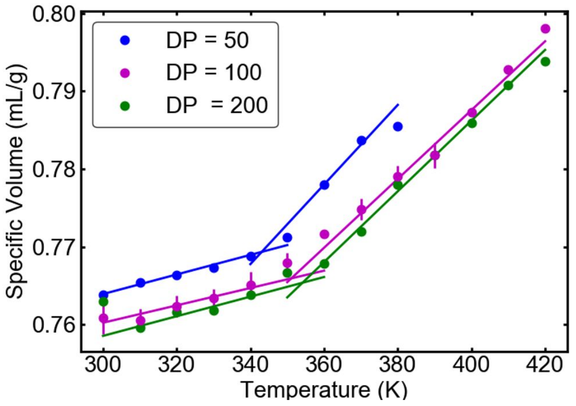


Fig. 4 Specific volume as a function of temperature

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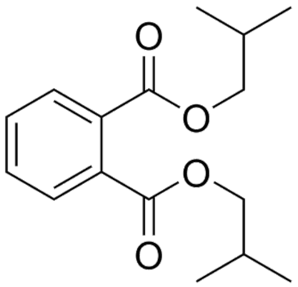
Results and Conclusions

- Mechanic properties from simulated models of PVC using the CGenFF forcefield align very well with experimental measurements of pure PVC.

	Experiment Rigid PVC	50 DP	100 DP	200 DP
Density (@300 K) (g/mL)	1.30-1.48	1.31	1.31	1.31
Glass Transition Temperature (K)	355	342	350	354
Tensile Strength (MPa)	38-55	38	40	42
Elastic Modulus (GPa)	2.5-4.7	0.76	0.45	0.37

Future work

- Optimize force fields for different classes of polymers.
- Implement an automated process to generate configurations (with added plasticizers), equilibrate, assign optimized forcefield parameters, and perform mechanical property tests for polymers.
- Perform high-throughput screening of potential renewable polymers to save experimentalists time in the lab.



Diisobutyl phthalate, a low-cost plasticizer that has high stability.

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