Atomic Scale Deformation Mechanisms of Amorphous Polyethylene under Tensile Loading

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Outline

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• Evolution of Internal Structure Variables
  • Chain Dihedral Angle, Chain Orientation, Chain Entanglement
• Conclusions
Introduction

Polymers play an increasing role in materials science for new industrial materials

- Flexibility of tuning properties through a number of degrees of freedom:
  - monomers, branching, tacticity, co-polymers, blends, composites, etc.
- For example, the “Car of tomorrow” is made of Lexan polycarbonate and BASF has produced a thermoplastic truck engine sump

[Image: Car of tomorrow, The c,m,n open source concept car [1]]
[Image: First thermoplastic truck engine sump, 1/3 less weight than an aluminum sump]

How do we begin to quantify the uncertainty that exists in nanoscale simulations of polymer deformation? How does this propagate or influence multiscale models?
Introduction

Multiscale models for polymer material response: How does this nanoscale information and its uncertainty enter into multiscale models of polymer response?

Multiscale Polymer Modeling [1]

[1] Bouvard et al., JEMT, 2009
Simulation Methodology

Amorphous Polyethylene Potential

- United atom method potential
- Dreiding potential [1]

\[ E_{total} = E_b(r) + E_\theta(\theta) + E_\phi(\phi) + E_{nb}(r) \]

- **Bond stretching**
  \[ E_b(r) = \frac{1}{2} K_b (r - r_0)^2 \]

- **Bond angle**
  \[ E_\theta(\theta) = \frac{1}{2} K_\theta (\theta - \theta_0)^2 \]

- **Bond torsion**
  \[ E_\phi(\phi) = \sum_{i=0}^{3} C_i (\cos \phi)^i \]

- **Van der Waals**
  \[ E_{nb}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_b )</td>
<td>350 kcal/mol</td>
</tr>
<tr>
<td>( r_0 )</td>
<td>1.53 Ångstroms</td>
</tr>
<tr>
<td>( K_\theta )</td>
<td>60 kcal/mol/Ångstrom²</td>
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<tr>
<td>( \theta_0 )</td>
<td>1.911 rad</td>
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<tr>
<td>( C_0 )</td>
<td>1.736 kcal/mol</td>
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<tr>
<td>( C_1 )</td>
<td>-4.490 kcal/mol</td>
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<tr>
<td>( C_2 )</td>
<td>0.776 kcal/mol</td>
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<tr>
<td>( C_3 )</td>
<td>6.990 kcal/mol</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>4.01 Ångstroms</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>0.112 kcal/mol</td>
</tr>
</tbody>
</table>

Simulation Methodology

Simulation Cell Conditions [1,2]
- Parallel MD code, LAMMPS [3]
- 3 Chain Lengths – 100, 1000, 2000-mers
- 3 Chain Numbers – 20, 200, 2000
- 3 Temperatures – 100K, 250K, 400K
- 3 Strain Rates – 10^8 s^{-1}, 10^9 s^{-1}, 10^{10} s^{-1}
- 4 Lateral Boundary Conditions
- Multiple Instantiations

Initialization/Equilibration
- Monte Carlo self-avoiding random walk to generate amorphous cell with 4 step equilibration:
  1. Relax in NVT @ 500K,
  2. Relax in NPT @ 500K,
  3. Cool to deformation temperature,
  4. Relax in NPT at temperature

\[ \bar{r} = 1.529 \text{ Angstroms} \]
\[ \bar{\theta} = 109.27^\circ \]
\[ \% \text{ Trans} = 68.3\% \text{ (250 K)} \]
\[ \rho = 0.87 - 0.91 \text{ g/cm}^3 \]

Simulation Methodology

Deformation

- Uniaxial strain of $10^{10}$ s$^{-1}$ in the loading direction (e.g., perpendicular to GB)
- NPT equations of motion are used for zero stress condition on the lateral boundaries (except for simulations exploring lateral boundary conditions)
- Periodic output of atomic coordinates for postprocessing along with macroscopic stress, energy, and strain components

Simulation Results
Stress-Strain Response

[Image of stress-strain curves showing characteristic response at strain rates and temperatures.]

Characteristic stress-strain curve at strain rate of $10^{10}$ s$^{-1}$

Simulation Results

Effect of Chain Length / Chain Number

- Increase in total united atoms => reduces stress variability
- Increase in polymer chain length => increase in stress

Simulation Results

Effect of Temperature

- Higher temperature => more viscous response
- Lower temperature => more pronounced peak

Simulation Results

Effect of Strain Rate

• Lower strain rate => lower stress required
• Higher strain rate => more pronounced yield peak

Simulation Results
Effect of Lateral Boundary Condition

- Lack of pressure dissipation leads to triaxial stress state
- Heat dissipation important at higher strains
Simulation Results
Effect of Lateral Boundary Condition

Amorphous Polyethylene
100 chains of 1000 monomers each
$10^{10}$ s$^{-1}$ true strain rate
100 K initial temperature

Stress (MPa)

Tensile direction
Non-loading direction

NPT
NPH
NVE
NVT

True Strain

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Simulation Results
Effect of Lateral Boundary Condition

NPT Lateral Boundary Conditions  NVT Lateral Boundary Conditions

0% Strain

25% Strain

50% Strain

100% Strain
Simulation Results
Energy Partitioning Evolution

Characteristic stress-strain curve and corresponding energy partitioning at strain rate of $10^{10}$ s$^{-1}$

Simulation Results
Stress Partitioning Evolution

Characteristic stress-strain curve and corresponding energy partitioning at strain rate of $10^{10}$ s$^{-1}$
Simulation Results
Chain Dihedral (torsion) Evolution

- Lower strain rate => % trans transformations occurs at lower strains
  - Transformation rate appears independent of strain rate
  - Smaller chain length => higher initial % trans, same trend

Simulation Results
Chain Orientation Evolution

- Increasing strain => increasing chain orientation parallel to loading direction (decreasing perpendicular to loading)

Simulation Results
Chain Entanglement Evolution

- Increasing strain $\Rightarrow$ decreasing chain entanglement
- Decreasing strain rate $\Rightarrow$ faster disentanglement rate
- Smaller chain length $\Rightarrow$ lower initial entanglement, similar trend

Chain entanglement is fairly similar for both conditions, but chain dihedral angle evolution changes with boundary condition.
Running a Polymer Deformation Example

LAMMPS Input Script

Here is an example LAMMPS input script. The ‘name’ variable is the name of the LAMMPS data file which contains the atom positions. The ‘PE’ is attached below after the input script.

```bash
# DEFORM DREIDING LAMMPS INPUT SCRIPT
#
# Filename: in.deform_dreiding.txt
# Author: Mark Jachopp, 2010
#
# The methodology outlined here follows that from
# Hossain, Jachopp, et al. 2010, Polymer. Please
# cite accordingly. The following script requires
# a LAMMPS data file containing the coordinates and
# appropriate bond/angle/dihedral lists for each
# united atom.
# Execute the script through:
# lmp_exe < in.deform_dreiding.txt
#
# VARIABLES
variable name index PE_no10_c11000.dat
variable simname index PE_no10_c11000

# Initialization
unit real
boundary p p p
atom_style molecular
log log.$(simname).txt
read_data $(name)

# Dreiding potential information
neighbor 9.4 bin
```

https://ccg.hpc.msstate.edu
⇒ Nanoscale
⇒ Atomistic Deformation of Amorphous Polyethylene
Main Points:

• Developing a generalized framework for investigating amorphous polymer deformation response at the nanoscale
• Investigating sources of uncertainty in these deformation simulations
• Quantitatively studying the evolution in structure for informing internal state variable models at higher length scales.
Thank you!

Thank you for your time!
Questions?

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