Simple Model Polymer Nanocomposites and Effect of Interfacial Adsorption Strength

Lisa M. Hall

H.C. “Slip” Slider Assistant Professor
William G. Lowrie Department of Chemical and Biomolecular Engineering

THE OHIO STATE UNIVERSITY
Theory/Simulation with Coarse-Grained Molecular Models

• Coarse-grained polymers
  • Freely jointed bead-based chains, beads represent multiple atoms
  • Efficient, captures monomer scale packing, good for complex systems with nanoscale order

• Statistical mechanical theories
  • Fluids density functional theory, liquid state theory, SCFT
  • Fast, typically no dynamics

• Molecular dynamics simulations
  • Positions as a function of time
  • Can be slow to equilibrate

Fluids density functional theory, block copolymer double gyroid phase

Molecular dynamics simulations, ionic aggregates in an ionomer melt
Prior Work: Developing Simple Model using PRISM Theory

- Polymer Reference Interaction Site Model liquid state theory: molecular statistical mechanical approach
- Captures monomer-scale packing
- Equilibrium, no phase separation

$$\tilde{H}(k) = \sim(k)\tilde{C}(k)[\sim(k) + \tilde{H}(k)]$$

Closure for p-p and p-n (PY):

$$C_{ij}(r) = \left(1 - e^{\beta U_{ij}(r)}\right)g_{ij}(r)$$

Closure for n-n (HNC):

$$C_{ij}(r) = -\beta U_{ij}(r) - \ln(g_{ij}(r)) + g_{ij}(r) - 1$$

Inter/intramolecular potentials (chemistry)

Intramolecular pair correlation (polymer connectivity)

3 coupled nonlinear integral equations

use inexact Newton’s method

$$g_{ij}(r)$$ (pair correlation functions)

Scattering structure factor

Thermodynamic quantities: PMF, B_2
Single Adjustable Parameter Nanocomposite Model

- Chemistry

- Model: freely jointed chain polymer, exponential attraction with particle

- Polymer-particle attraction strength $\varepsilon_{pn}$ accounts for chemistry: more H-bonding, higher $\varepsilon_{pn}$

- Dilution changes effective $\varepsilon_{pn}$

- Very simple model describes all major features

Particle size 10 monomer diameters
Theory/Experimental $S(k)$ Comparison

- 44 nm silica in PEO of MW 400, 1000; unentangled (N~10, 25)
- Compare with theory: $\varepsilon_{pn}=0.55$ for PEO
- Lower $\varepsilon_{pn}=0.35$ compares to PTHF
- Changing one chemical parameter reproduces the qualitative experimental scattering trends!

fillers in PEO appear larger, more organized than pure hard spheres
Current Work: Nanoparticle-Constrained Random Walks

- Random walks reflect off nanoparticles, how does this affect conformation?
- End to end vector depends on direction and nanoparticle arrangement
- End to end vector length correlates with entanglements

Average end-to-end vector components from a random starting location

Simple cubic system starting between two NPs (polymer stretches out between NPs)

Particle packing fraction 1/3

Particle size 10 RW step lengths
Nanoparticle-Constrained Random Walks

- Random walk entanglements calculated using Z1 algorithm (for FCC systems)
- Relative entanglements match with MD simulation result
- Simple topology drives reduction in entanglements of NP systems?

![Graph showing entanglements relative to bulk system as a function of particle packing fraction]

- Blue: constrained random walks
- Red: MD simulations of Li et al. PRL 109, 11801
- Black: unconstrained random walks

Particle size 10 RW step lengths
Coarse-Grained Molecular Dynamics Simulations

- Obtain dynamics, detailed picture of molecular organization
- Goal: use simple models to give physical insight into experimentally relevant trends
- Kremer-Grest bead-spring chains
- Using repulsive-only part of LJ potential (efficient)

Decide on system, interatomic potentials; place in simulation box

Numerically integrate Newton’s laws (e.g. using LAMMPS)

All atomic coordinates, evolving in time (many saved snapshots)

Structural and dynamic analysis

Pair correlation functions, dynamic quantities, etc.
Molecular Dynamics Model

- Kremer-Grest bead-spring chains (no angle potentials)
- Using repulsive-only part of LJ potential (efficient)
- Single attractive interaction represents adsorption strength of monomers on particle

\[
u = kR_0^2 \ln \left( 1 + \left( \frac{r}{R_0} \right)^2 \right)\]

Finitely extensible bonding potential

\[
U_{LJ}(r) = 4 \delta i j \frac{12}{r} - \frac{6}{r}
\]

LJ, cut and shifted to 0 at minimum

\[
T = 1 \quad = 1 \quad pp = 1
\]

- Still difficult to equilibrate
  - Use Monte Carlo moves initially
  - Large NPs will not have time to explore box: start by comparing fixed particle configurations

\[
u = -kR_0^2 \ln \left( 1 - \frac{r}{R_0} \right)^2
\]

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

\[
U\% = \frac{U}{kT} \times 100
\]

\[
u = \frac{1}{3} \pi \sigma^2 u
\]

\[
u = \frac{1}{6} \pi \sigma^3 u
\]
Molecular Dynamics: Preliminary Investigations

- Goal: compare NP systems to bulk to see effect of particle arrangement, interactions
- Two types of systems:
  1. NPs in FCC or random arrangement
     - Study effect of NP arrangement; NPs fixed during simulation
     - Repulsive only
     - N=100 or 500
  2. Dilute NPs
     - Study effect of monomer-particle attraction
     - Analyze polymer dynamics as function of distance from particle
     - N=40
Effect of NPs on Polymer Conformation

- Nanoparticles stretch chain conformations versus bulk
- Seen in mean squared internal distance between monomers $n$ bonds apart on same chain, normalized by $n$ (flat for random walk)
- Effect not large at 25% NP

<table>
<thead>
<tr>
<th>N = 500</th>
<th>N = 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;R_g^2&gt;$</td>
<td>$&lt;R_{EE}^2&gt;$</td>
</tr>
<tr>
<td>FCC</td>
<td>138 ± 1</td>
</tr>
<tr>
<td>Pure Melt</td>
<td>128 ± 1</td>
</tr>
</tbody>
</table>
Little Change in Relaxation Times at 25% NP

- Analyze polymer end-to-end autocorrelation function; relaxation times fit with KWW stretched exponential
- N=500 systems require long simulations for accurate dynamics
- Effect of adding 25% NPs is small

<table>
<thead>
<tr>
<th></th>
<th>Pure Melt $N_{\text{chain}} = 100$</th>
<th>Pure Melt $N_{\text{chain}} = 500$</th>
<th>FCC $N_{\text{chain}} = 100$</th>
<th>FCC $N_{\text{chain}} = 500$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>0.69</td>
<td>0.51</td>
<td>0.66</td>
<td>0.51</td>
</tr>
<tr>
<td>$\tau$</td>
<td>9800</td>
<td>788000</td>
<td>9300</td>
<td>977000</td>
</tr>
</tbody>
</table>
Monomer Adsorption

- Pair correlation function shows strong local layering; even at $\varepsilon_{pn} = 5$ where $g(r)$ peaks near 5, we can get good statistics on relaxation times through this efficient model.
- Ongoing investigation: can we use copolymers with monomers of different adsorption strengths, varying sequence to tune relaxation behavior?
Acknowledgements

- Cooper Tire and Rubber Company
- Alex Trazkovich
- Jeffrey Ethier
- Jonathan Brown
- Daniel Sussman (UPenn)
- H.C. “Slip” Slider Professorship
- Ohio Supercomputer Center
- NSF CAREER 1454343
Simulation Method

- Goal: use simple models to give physical insight into experimentally relevant trends
- Molecular dynamics: place particles in box, find forces, numerically integrate to get new positions over time (LAMMPS)
- NVT ensemble, Langevin thermostat
  \[ f_i = -m_i \Gamma v_i + W_i(t) \]
  - \( \Gamma \) is the damping constant (= 1)
  - \( W \) is a random noise term coupled to the temperature thru the fluctuation-dissipation theorem
- System and potentials
  - The repulsive LJ potential; cutoff and shifted at \( r_c = 2^{1/6} \sigma \)
    \[ u = 4\frac{12}{r} - \frac{6}{r^6} \]
  - FENE bonds: have a maximum extent
    \[ u = k R_0^2 \ln \left( \frac{1}{(r / R_0)^2} \right) \]
  - Reduced temperature = 1