Multi-Scale Simulation of Interfacial Phenomena and Nano-Particle Placement in Polymer Matrix Composites

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### Report Documentation Page

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Interfaces: Cradle of Materials Functionality


P. Podsiadlo et al. Biomacro. 6, 2914 (2005)

M. Shtein, pers. comm.

Battery Anode: dendrite growth
E. Garcia, Purdue U.

A. Tuteja, UM

MEMS
Sandia National Labs
Generate realistic structural models of interfacial regions by reproducing reactions and transport phenomena that underlie their formation.

Predict properties of these models.

Identify governing factors.

Simulation-Based Predictive Design

- Generate realistic structural models of interfacial regions by reproducing reactions and transport phenomena that underlie their formation.
- Predict properties of these models.
- Identify governing factors.

Simulation-Based Predictive Design Loop

Enhanced Design Cycle

- Synthesis & Fabrication
- Characterization & Property Measurement
- Interpretation of Experiments & Data Analysis
- Prediction of Structure and Properties
- Computation
- Feed-forward
Simulation Approach
- Accurate force field models

Generating Realistic Structures
- Types of Structure Formation Processes

Structural Ubiquities
- Surface Patterning
- Pronounced Layering
- Densification of Polymer Near Interface
- Formation of Gaps and Voids

Property Prediction & Analysis of Governing Principles
- Interfacial Strength Models
- Thermal Boundary Resistance

Summary and Outlook
Realistic structural models that account for nano-scale features are needed to predict interfacial properties.

Models generated using reactive molecular dynamics simulations.

Accurate description of atomic interaction models.

Simulation Framework:

- Reactive force field
  - variable coordination & coordination-dependent angular constraints
  - Covalent attractive
  - Repulsive
  - Charge transfer function
  - Coulomb
  - Total

Reactive Molecular Dynamics Simulations:
  - Local structure; Force field parameterization
  - Extended structure; Reaction Mechanisms; Predict Thermo-mechanical properties

Coarse-Grain Particle Dynamics Simulations:
  - Accelerated simulation of structural evolution

Validation, Verification and Interpretation.

HOMO
LUMO

Density Functional Theory Calculations

Adhesive forces can cause local density gradients and defects.

Pronounced layering of polymer near interfaces affects mechanical properties.

Polymer chains span layers in “staircase” pattern.

Vapor deposition  In situ polymerization

Generating Realistic Structural Models of Interfaces
Generating Realistic Interfacial Structures

Three methods proved successful:
1. Juxtaposition of truncated bulk structures followed by relaxation
2. Simulation of the deposition process of thin layers
3. Simulation of the polymerization process near a substrate.

Vapor deposition of CuPc on Ag. Molecules reorganize on the surface before the next one arrives.

Polymerization of polyethylene in the gap between two Cu surfaces at various degrees of cure. Simulation involves a heuristic bonding scheme.
Systematic exploration of the chemical nature and structural complexity of interface systems

- Force field optimization based on the results from first-principles quantum mechanical calculations
- Development and verification of the structure generation strategy
- Property prediction and validation with known experimental data
- Structural analysis and identification of structure property correlations
Alkane/Metal: Simulation Details

- Structure generated with random linear alkanes near fcc [100] surface
- Target thickness of 50 Å
- NPT phase required for structural stability
Surface Pattering – Chain Length

- Alkanes of length $n$
- Chain segments in direct surface contact are shown
- Pattern no longer change appearance beyond threshold $n$

Alkanes on Cu
2D Pair Correlation Functions

- Slice projected into 2 dimensions before pcf calculated
- Normalized according to overall average number density
- Upper: Nickel Lower: Lead Left to Right: n=10, n=20, n=50
Density Profiles Across Polymer Layer

Voids present in the structures are reflected in the density profiles. Average density of bulk alkanes shown by dotted orange line.
Surface Patterning – Substrate Lattice

No apparent trend in surface patterns depending on substrate lattice parameters and interaction strength.
Deposition of Polyimide on Si (100)

DFT optimized interaction potential for PMB molecule in bulk and with substrate

- Silicon bulk and surface
- (2x1) dimer-reconstruction of the surface
- Surface steps on reconstructed surface
Polyimide on Si (100): Contact/Non-Contact

Non-contact versus Contact Adhesion

a) Relaxation from a high-temperature state to a glassy state with under-critical interface coupling
b) Relaxation from a high-temperature state to a glassy state with interface coupling in excess of the critical

\[ \varepsilon_{Si} < \varepsilon_{Si}^c \]

\[ \varepsilon_{Si} > \varepsilon_{Si}^c \]

Simulated behavior (within the classical model of Si-PMB interfaces) is described well by the de Boer-Hamaker model with:

\[ U_{Si-PI}^R(z_0) = 4\pi \varepsilon \rho_{Si} \left\{ \frac{\sigma^{12}}{360} \left( \frac{1}{z_0^8} - \frac{1}{R_c^8} \right) \right\} \]

\[ U_{Si-PI}^A = 4\pi \varepsilon \rho_{Si} \left\{ \frac{\sigma^6}{12} \left( \frac{1}{z_0^2} - \frac{1}{R_c^2} \right) \right\} \]

- Homogeneous a-PMB layer on silicon
- No relaxation at the interface
- Provides reference states
Void Formation Near Free Surface

![Image of void formation near free surface]

![Graph showing the number density ratio vs. distance from the interface (Å)]
Energy Regimes of \textit{a-PMB-Si}(001) Interfaces: Adhesive Energy Transition

- A non-contact regime holds for small coupling strength.

- The transition from non-contact to contact regime is characterized by an abrupt change in $W_s$, with rapid increase with coupling strength.

- The rapid increase is due to density and order variations.

- For large values of the coupling strength, a slow increase is observed due to density saturation, with $W_s \sim \varepsilon_{Si}^\alpha$, where $\alpha \approx 0.5$. 
Density profiles of a-PMB-Si(001) Interfaces

- Density profiles dynamically evolve during relaxation with non-zero coupling between adherent and substrate.
- Interface relaxation (both density and ordering) largely define the adhesive behavior.

Peak density grows with coupling strength (1 vs. 2) but saturates at larger couplings (3 vs. 4).
Structural Order at a-PMB-Si(001) Interfaces

- Parallel ordering of PMB molecules with respect to the interface plane is preferred for large coupling strengths.
- At the interface, the ordering along grooves formed by 2x1 surface reconstruction is favored.
- Free surface acts as a repulsive wall.

Order Parameter

\[ S_{ua} = \frac{3}{2} \left\langle \cos^2(\theta) \right\rangle - \frac{1}{2} \]
Polymerization Method

- Variation of method proposed by Varshney\(^1\)
- More efficient than one-by-one reaction\(^2\)
- Less stress than static/all-at-once algorithm\(^2\)
- Depending on cutoff, should not reach 100% cure, which is realistic

1. V. Varshney et. al., *Macromolecules*, 41 (18), 2008
Reaction probability has minimal effect on the final structure of polyethylene

- Agrees with experimental study of chain growth polymers like PE and DCPD

Maximum chain length uncorrelated with reaction probability:

- 50%: 692; 75%: 811; 100%: 591

Reaction process does not prevent layering effects
Epoxy Reaction Paths

- DGEBF & DETA/TETA for hardeners
- 3 reaction pathways
  - Assumed equally reactive for a given cutoff radius
  - Assumes epoxide ring activated by presence of amine group

1° first reaction

2° reaction

1° second reaction
Epoxy Cure Simulations

Total RDFs as a function of the degree of cure

Total $g(r)$

Radius (Å)

Degree of Cure

5%

26%

59.4%

75%
Growth Behavior of CuPc

- Growth behavior before force field optimization

CuPc on Au (100)

CuPc on Au (111)

- Monolayer deposition of CuPc forms crystalline patterns on both (100) and (111) surfaces

- This growth behavior was only observed after force field optimization

Z.H. Cheng et al., JPC (2007)
CuPc molecule is deposited on Au(111)

TBR is smaller at the amorphous-CuPc/Au than the crystalline-CuPc/Au interface

<table>
<thead>
<tr>
<th>TBR ($10^{-8}$ m²K/W)</th>
<th>Amorphous-CuPc/Au</th>
<th>Crystalline-CuPc/Au</th>
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<td>1.96 ± 0.24</td>
<td>2.36 ± 0.20</td>
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<th>Thermal conductivity</th>
<th>MD (W/mK)</th>
<th>Exp (W/mK)</th>
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<tr>
<td>Amorphous CuPc</td>
<td>0.323 ± 0.005</td>
<td>0.32</td>
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<tr>
<td>crystalline-CuPc</td>
<td>0.388 ± 0.004</td>
<td>0.39</td>
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Adhesion Strength vs. Acoustic Mismatch Model

Acoustic Mismatch Model:

\[ TBR \propto \frac{1}{\tau_b} = \frac{(Z_1 + Z_2)^2}{4Z_1Z_2} \]

\[ Z = \rho \cdot u_p = \sqrt{\rho \cdot E} \]

For two substrates with the bulk moduli of Ag and Au respectively, the atomic weight of the substrate is changed while keeping interactions the same.

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<th>Ag</th>
<th>Au</th>
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<tr>
<td>Bulk Modulus (GPa)</td>
<td>100</td>
<td>180</td>
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<tr>
<td>Lattice Constant (Å)</td>
<td>4.09</td>
<td>4.08</td>
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<tr>
<td>Atomic Weight (g/mol)</td>
<td>107.8682</td>
<td>196.97</td>
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<tr>
<td>TBR^4 (10^{-8} m²K/W)</td>
<td>7.8 ± 1.6</td>
<td>5.4 ± 1.4</td>
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Ag has a larger TBR than Au in experiments. Adhesion strength dominates!

4 Y. Jin, et al. APL 98 093305 2011
Interface in Properties Only

\[ \rho_1, E_1 \]

\[ \rho_2, E_2 \]
Free surface energy for CuPc from Exp$^3$: 0.035 J/m$^2$ and Work of adhesion for CuPc is 0.07 J/m$^2$

Work of adhesion: CuPc/Al > CuPc/Au > CuPc/Ag

The adhesion between CuPc/Au or CuPc/Ag is weaker than CuPc/CuPc$^2$

Agrees with the peel off test results from experiment$^2$

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$^2$ Y. Jin, et al. MRS Spring Meeting 2011

$^3$ H. X. Wei, et al. APL 97, 083302 2010
Phonon Coupling at CuPc/Au Interface

- For CuPc/Au system, 1 layer of Au atoms are perturbed.
- Atomic velocity differences between perturbed and unperturbed systems are recorded to calculate phonon frequency spectrum.
Summary & Outlook

- Reproduce process to generate realistic structures for property predictions and interpretation of experiments

- Findings thus far reveal:
  - Predominance of polymer layering near interfaces (staircase patterns, surface-bulk separation, surface domains, void formation)
  - Transition between contact and non-contact adhesion
  - Thermal boundary resistance (phonon velocity, mechanical impedance, structural impedance)

- Ongoing work:
  - Quantify structural signatures in materials responses
  - Thermosets
  - Interfacial modulus
  - Controlling interfacial properties

Functional molecular layers, for monitoring, sensing, or energy harvesting