Study of mechanical and thermal behavior of polymeric ablator using MD

Abhishek Kumar
PhD Student

Veera Sundararaghavan
Assistant Professor of Aerospace Engineering
University of Michigan, Ann Arbor
Outline

• Introduction and Prior Work on Ceramics Matrix Composites
• Molecular Modeling
• Mechanical and Thermal Analysis of Polymer
• Argon Theory
• Thermal Decomposition
• Conclusion and Future Work
Molecular changes in heat shield materials

Oxidative decomposition of fiber and matrix

Thermal decomposition of matrix

Microstructure: Carbon fiber oxidation

Ablation zone
Char zone
Pyrolysis zone

Orion Crew Module
Heatshield
Prior work: Multiscale oxidation modeling

Meso-scale

Nano-scale

Micro-scale
Linking with molecular dynamics

- Employing molecular dynamics for reaction rate: $O_2$ $CO_2$

Details: MD simulation of $CO_2$ formation on graphite surface (Reactive force field potentials, NVT, 1000 K, (cyan:Carbon atoms, red:Oxygen atoms)
A Multiscale Simulation – Macro-micro

Molecular modeling of cross-linked polymers

- Polymer matrix can be built using only the knowledge of chemistry of the building blocks (monomers)
- A variety of cross-linking densities, network defects, intramolecular loops can be generated automatically.
- Molecular dynamics simulations at a variety of temperatures, strain rates and loading modes (shear/tensile/hydrostatic strain states)
- Novel techniques to test mechanical properties, identify failure events, application to chemistry-by-design.
Modeling Epoxies (Bisphenol A-DDS)

Dendrimer building approach for computing the initial structure with a given cross-link density
Modeling PICA

Molecular structure of cured phenolic resins.
Minimum energy structure obtained through a series of annealing steps followed by a conjugate minimization procedure until correct density is achieved.
Energy minimization to compute the stable structure

Initial dendrimer
Lattice size (x-): 210 Å

Conjugate gradient minimization (80 Å)
Stage 1 annealing process to attain stable structure

NPT at 298K
Cell Length (81.29, 81.93, 82.14)
Density 0.5654

NPT at 500K
Cell Length (73.75, 74.32, 74.52)
Density 0.5758

Conjugate gradient minimization
Cell Length (71.64, 72.94, 72.89)
Density 0.6176
Stage 2 annealing process to attain stable structure

NPT at 298K
Cell Length
(66.97, 68.18, 68.13)
Density 0.7562

NPT at 500K
Cell Length
(65.71, 67.76, 67.24)
Density 0.8371

Conjugate gradient minimization
Cell Length
(64.33, 66.34, 65.84)
Density 0.8608
Final structure in MS after 5 anneals

Final Structure
Cell Length (57.82, 60.72, 59.19)
Density 1.1036
CVFF force field in LAMMPS

- System ported to LAMMPS for further tests using CVFF force field.
- Fine LJ/coul cut-off of 15.5 Å was chosen with no tail correction.
- Bond stretch energies and bending energies matched exactly with materials studio.
- Further 12 step annealing was performed in LAMMPS until convergence of density.
- Two different epoxy cells were tested. One with 4601 atoms and another with 19610 atoms: Both cells gave the same final density.
- Properties of both cells were compared to show convergence with respect to cell size.
Thermal Expansion Behavior

Linear coefficient of thermal expansion between 223K to 323K is measured to be $54.6 \times 10^{-6} /K$ from this figure which matches with experimental value available in literature.
Elastic properties: Test of isotropy

\[ E_{\text{avg}} = 4.83 \text{ Gpa} \]

\[ \nu = 0.33 \]
Computation of physical properties

Tensile test

P = 1 atm (lateral bc)

Strain enforced

Tensile or compressive tests

\[ y = -0.01156x + 8.555 \]
Compressive Stress-Strain Response

![Graph showing compressive stress-strain response at different temperatures (1K, 112K, 301K)].

The graphs illustrate the compressive stress-strain response at different temperatures, with a linear fit equation $y = -0.0009417x + 0.7127$ provided.
Double-Kink Formation

\[ \Delta G = \frac{3\pi\mu\omega^2 r^3}{16(1-\nu)} - \frac{9\pi\mu\omega^2 r^3}{8(1-\nu)} \left( \frac{r}{z} \right)^5 - \pi\mu\omega^2 r^3 \frac{\tau z}{\mu r} \]
Kink formation

Strain of 0%

Strain of 12%
Prediction of experimental yield stress

![Graph showing yield stress vs. temperature and strain]

- MD simulations (strain rate $10^{10}$/sec)
- Argon theory
- Prediction at quasi-static loading rate

- Experimental results (Hainz and Wiggins, 2010)
- Yield stress predicted by MD/Argon theory
Next step: Pyrolysis modeling

VALIDATION STEPS FOR MOLECULAR MODEL FOR A CROSS-LINKED POLYMER

1. Equilibrated polymer structures built using dendrimer approach
2. Annealing performed to achieve correct density
3. Validated molecular model with dilatometric curves, compared thermal expansion with experiments and tested for elastic isotropy
4. Yielding and large deformation behavior compares well with Argon theory prediction, ability to predict experimental yield stress.

NEXT STEP: Perform detailed analysis of thermal decomposition
REAX Force Fields

- ReaxFF is used to examine decomposition process
- It allows for accurate description of bond breaking and bond formation because it is based on bond order/bond distance relationship
- Bond Order are updated at every iteration, the connectivity of system can continuously change.
- It incorporates non-bonded interactions between every atom regardless of connectivity, and repulsion of atoms at close range are avoided by shielding.
- The EEM method, a geometry dependent charge calculation scheme, is employed to account for polarization effects.
Thermal Decomposition of Epoxy

At 1ps

Initial Structure
3 ps
4 ps
MULTI-SCALE STRUCTURAL SIMULATIONS LABORATORY

10 ps
15 ps
Thermal Decomposition of Pica

Initial Structure

1 ps
5ps
Conclusions and Future work

• Observed the thermal decomposition of Epoxy and PICA using MD simulation.
• Work to develop a multi-scale model to simulate in-depth pyrolysis process.
• Compute the parameters associated with chemical and transport process of pyrolysis and verify them with results obtained by Spectroscopy
• Study the interaction of O₂ with epoxy and PICA and observe the bond formation during the process.
THANK YOU FOR YOUR ATTENTION!

QUESTIONS ??????