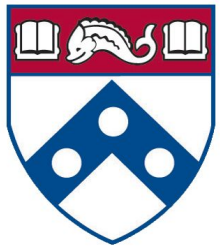
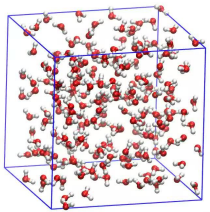
RECSEM REU 2017- Molecular Dynamics of Epoxy Resin Systems

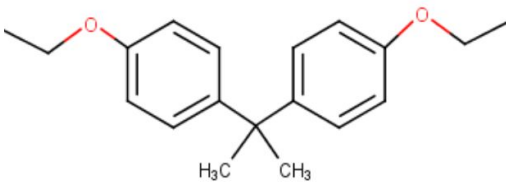
Stephen Wu and Lam Tran
Dr. Lonnie Crosby



Molecular Dynamics

- Molecular Dynamics
  - Simulations that numerically solve the equations of motion for a system of particles as a function of time given a force field describing particle interactions.
  - Microscopic length and time scales (nm/angstrom, ps/ns). Results “can be as accurate as needed”.
  - Relative to actual experiments, MD simulations can save time and money. Furthermore, they can oftentimes more easily reveal physical properties of a system (structure, microscopic interactions, etc.)

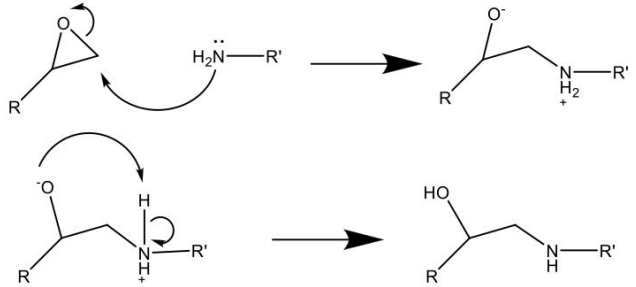




Epoxy Resins

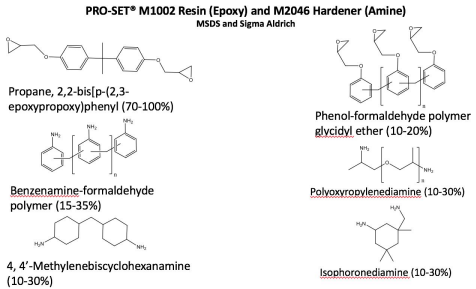
- Epoxy Resins
  - First developed in the 1930s and used today in a wide range of applications.
  - High strength/durability, low shrinkage and excellent adhesive and insulative properties.
  - Composed of a base resin (BADGE, cycloaliphatic, biobased, etc.) and a hardener/curative (amine type, alkali, catalytic) that confers additional properties.

Epoxy – Amine Crosslinking Reaction (ReaxFF N/C/O/H)



Project Purpose and Goals-Why?

- Use MD simulations to examine the physical properties of the ProSet M1002 base resin/M2046 amine hardener system as a function of the components and the extent of crosslinking.
  - Glass Transition Temperature Tg
  - ∂V terms- Thermal expansion coefficient α (~∂V/∂T), Isothermal compressibility κ (~∂V/∂P)
- How does the epoxy resin system adhere to aluminum surfaces?

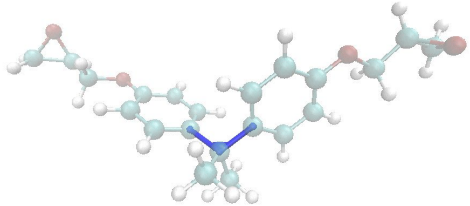


Overall Project Steps

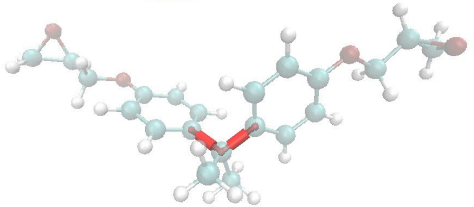
- Parameterization of BADGE and 4, 4’-Methylenebiscyclohexanamine under CHARMM36 forcefield
  - Individual parameterization of atomtype, atom, bond, angle and proper/improper dihedrals
  - Packed molecule; Lowdin partial charge population analysis; and energy minimization
- Crosslinking of epoxy resin system
  - Activation of molecular structures; iterative, stepwise bond formation under distance cutoff
- Tests to determine physical properties of system
  - Cooling down simulation to ascertain glass transition temperature and coefficient of thermal expansion

Past Progress

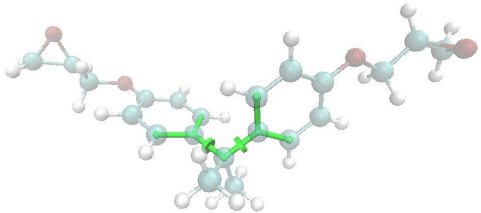
- Parameterization on each individual molecules
  - Construct topology files in OPLS-AA/CHARMM36
    - Bonded potential
    - Nonbonded potential
  - Structural optimization:
    - Spatial coordinates
    - Partial charge
- GROMACS sample test to calibrate and visualize the simulation system:
  - Water-solvated oxirane simulation
  - Methane-solvated oxirane simulation



$$\sum_{\text{bonds}} K_b(b - b_0)^2$$



$$\sum_{\text{angles}} K_\theta(\theta - \theta_0)^2$$



$$\sum_{\text{dihedrals}} K_\phi(1 + \cos(n\phi - \delta)) + \sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2$$

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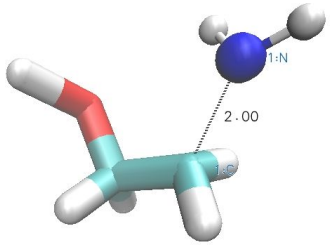
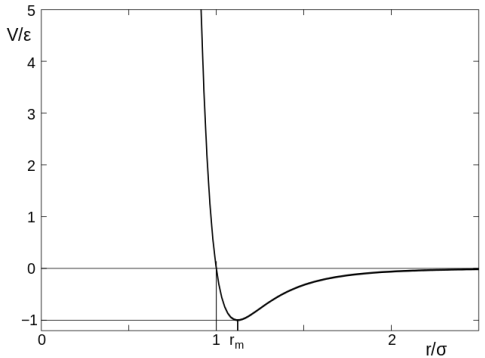


$$\sum_{\text{nonb,pair}} \frac{q_i q_j}{4\pi D r_{ij}}$$



$$\sum_{\text{nonb,pair}} \varepsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right]$$

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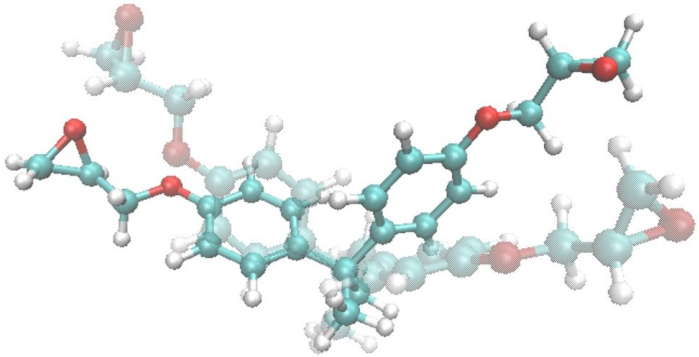

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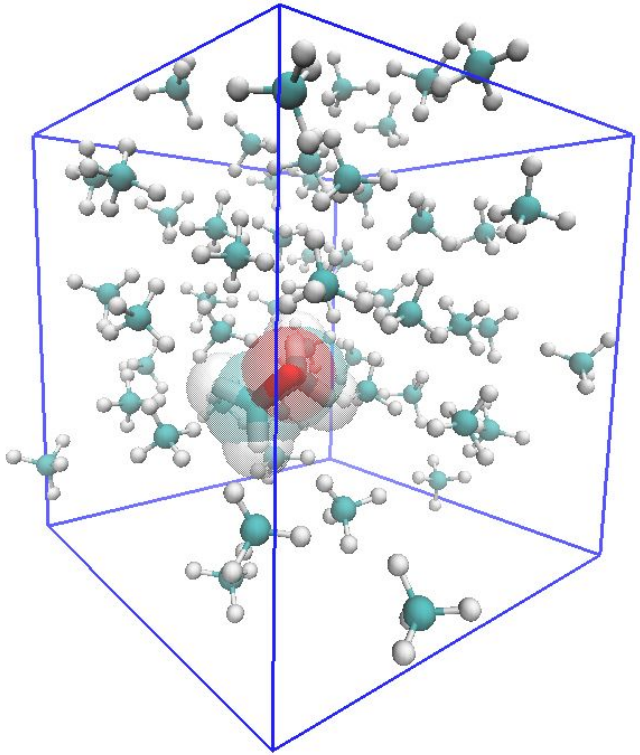
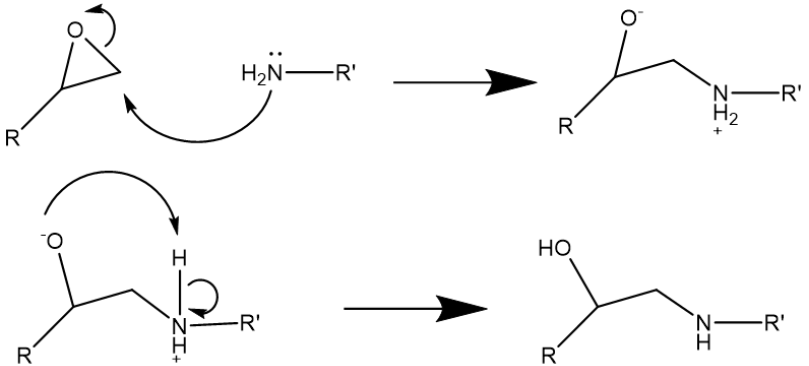


Past Progress

- Target reaction
  - Cross-linking bond between epoxide and amine
  - Crosslinked fragment parameterization
- LAMMPS ReaxFF simulation
  - CHONSSiNaAl.ff: (C/H/O/N/S/Si/Na/Al)
    - Non-activated system
    - Activated system
- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process



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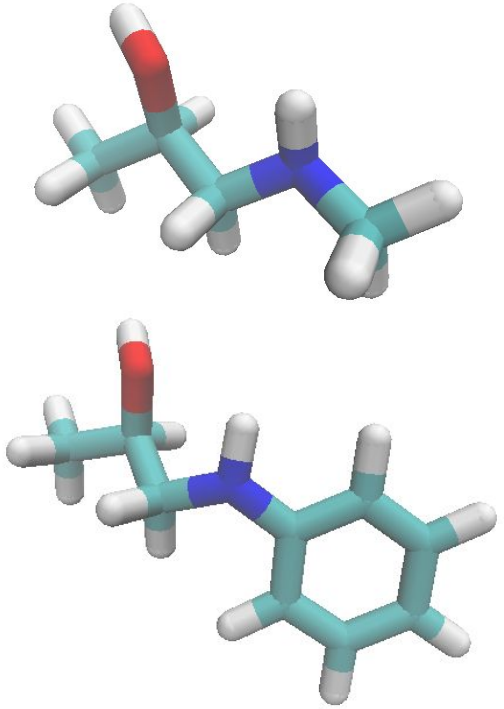

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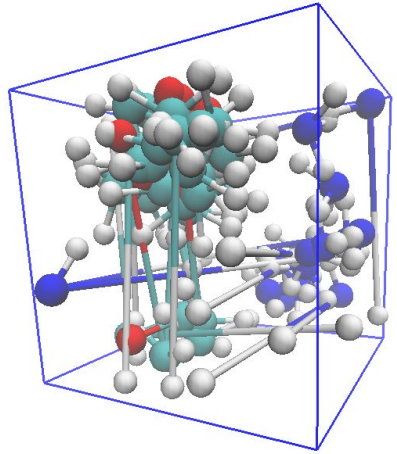

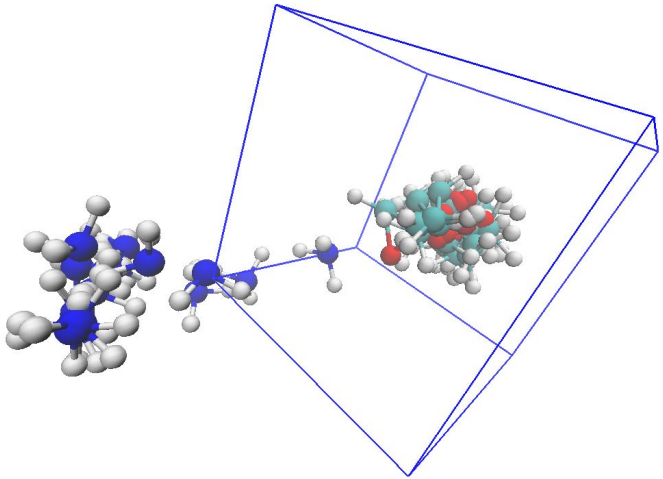

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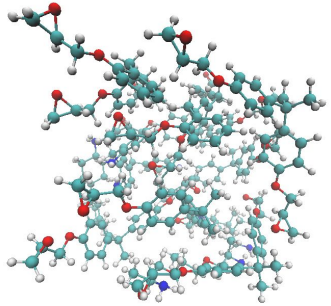

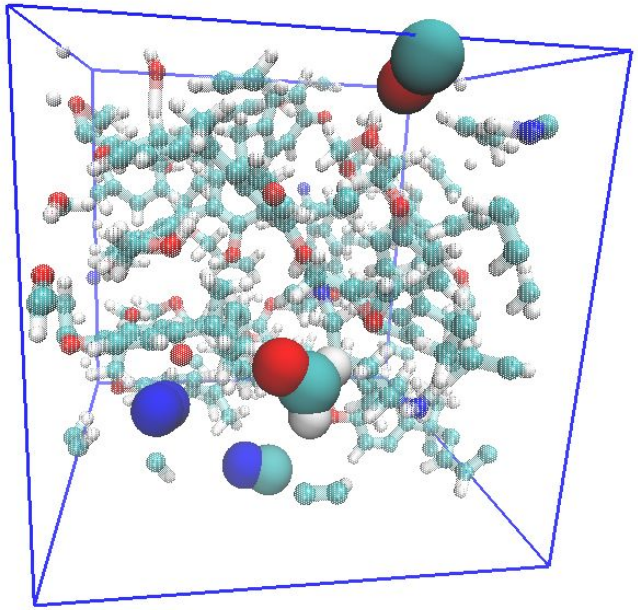

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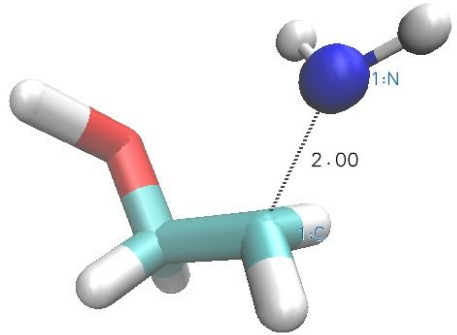

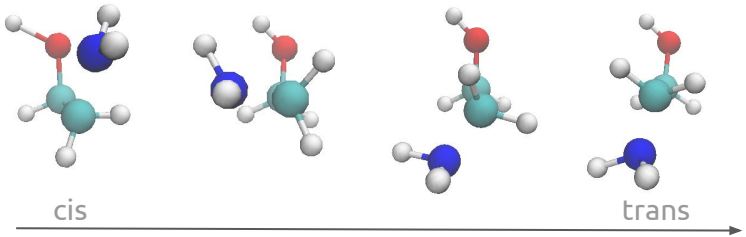

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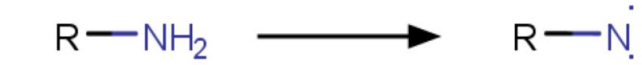
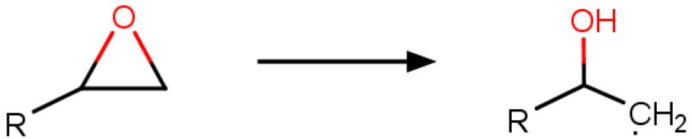
Target radical





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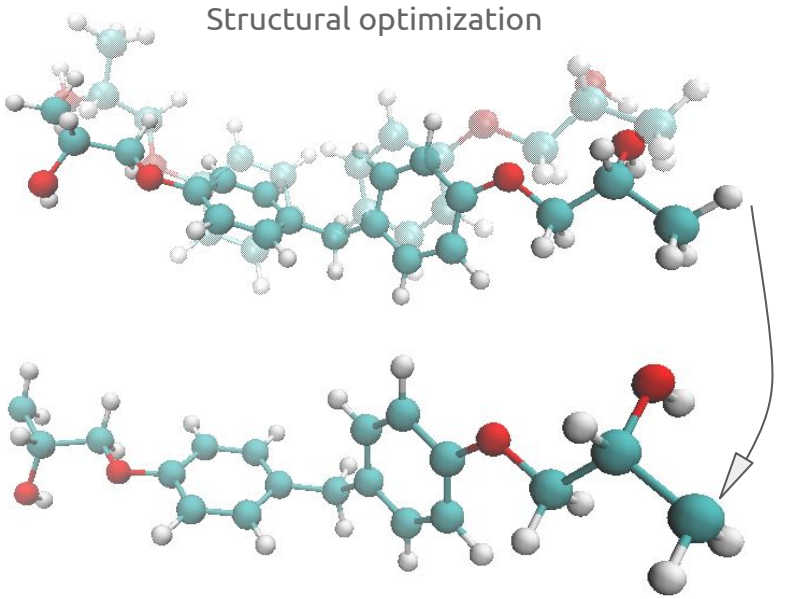

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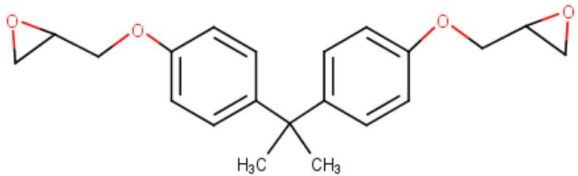

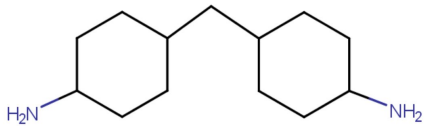

BADGE - 4,4’-Methylenebiscyclohexanamine system

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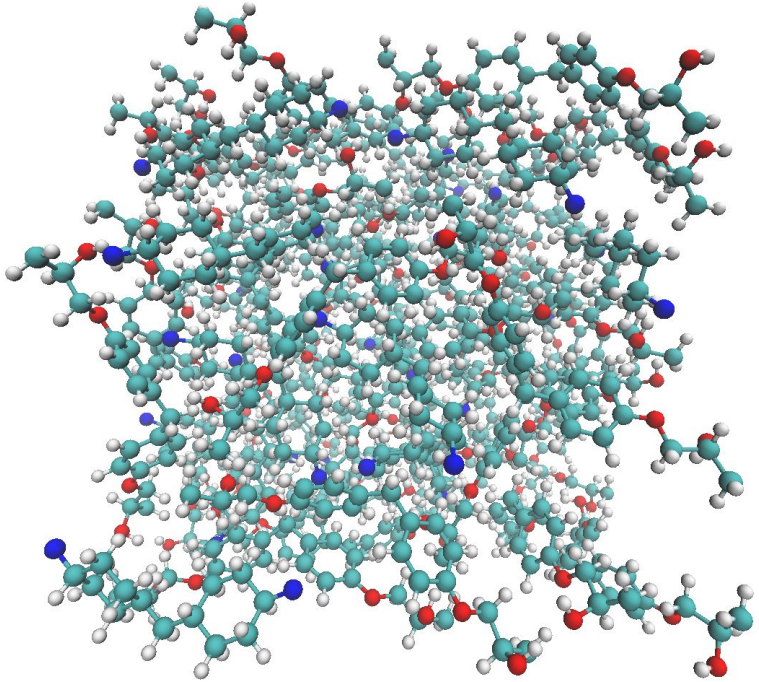

(40,20) system

Past Progress

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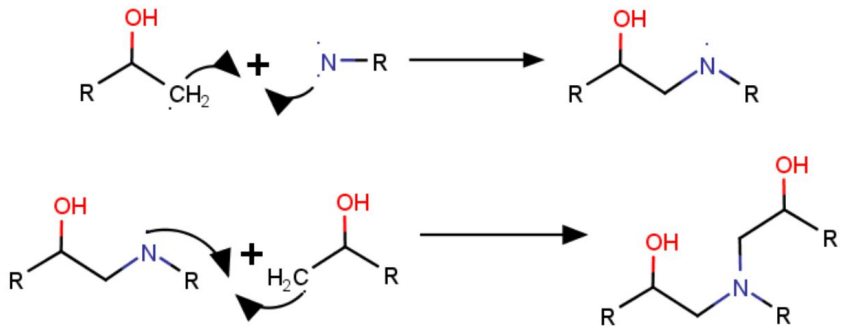
  - Crosslinked fragment parameterization
- LAMMPS ReaxFF simulation
  - CHONSSiNaAl.ff: (C/H/O/N/S/Si/Na/Al)
    - Non-activated system
    - Activated system
- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process - assumptions
    - Reactivity of primary and secondary amine
    - Hydrogen saturation

Target reaction



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    - Activated system
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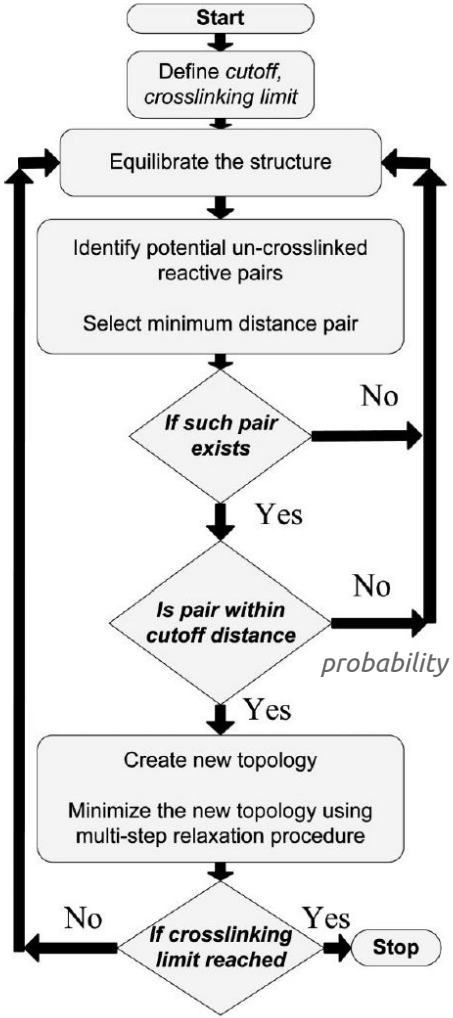
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process - bond/create
    - Cut-off distance
    - Bond-forming probability



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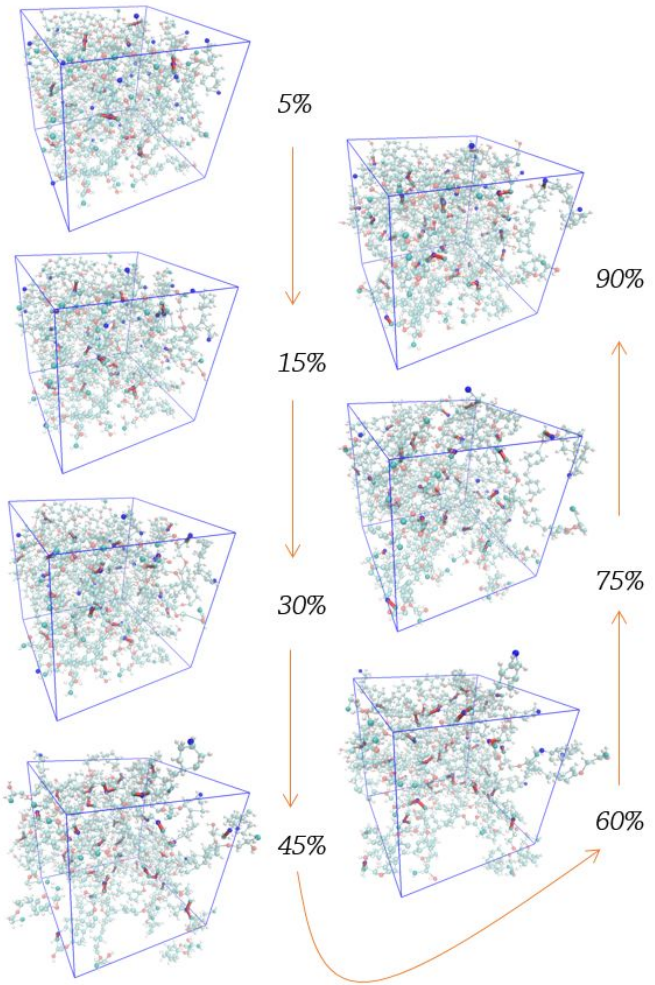
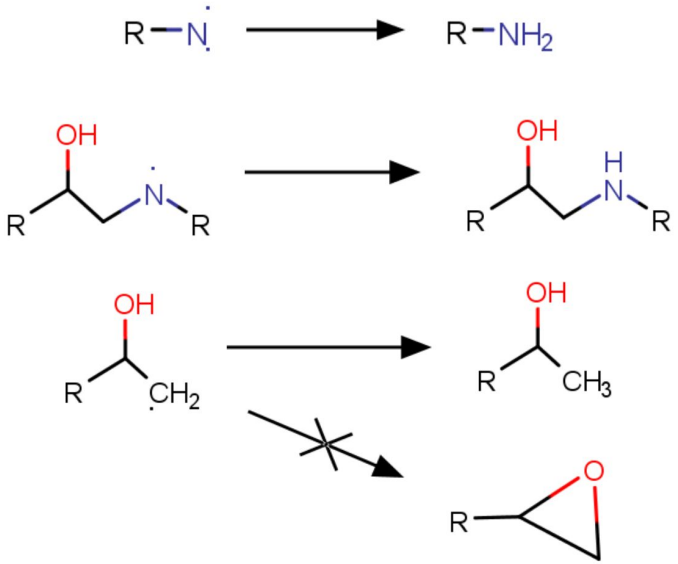
    - Activated system
- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process - reaction coordinates

$$\text{crosslinking percentage} = 1 - \frac{\text{noncrosslinked carbon radicals}}{\text{total potential crosslinks}}$$



Past Progress

- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process
  - Cross-linked structure - deactivation
- Thermal and volumetric properties
  - Isobaric cooling simulation
    - Glass transition temperature Tg
    - Thermal expansion coefficient α
  - Isothermal depressurization simulation
    - Isothermal compressibility κ



Past Progress

- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process
  - Cross-linked structure
- Thermal and volumetric properties
  - Isobaric cooling simulation
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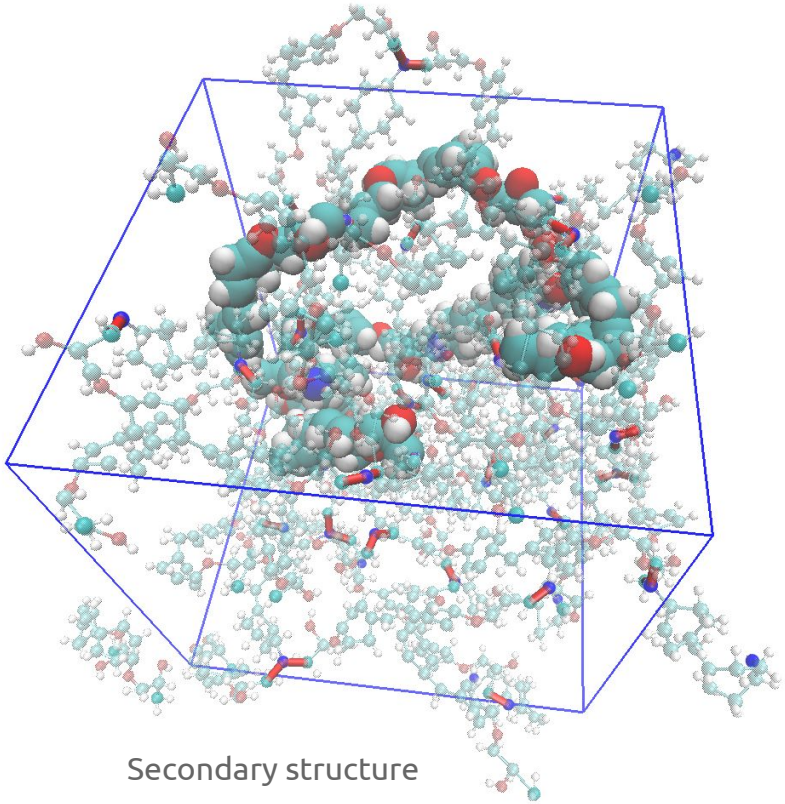
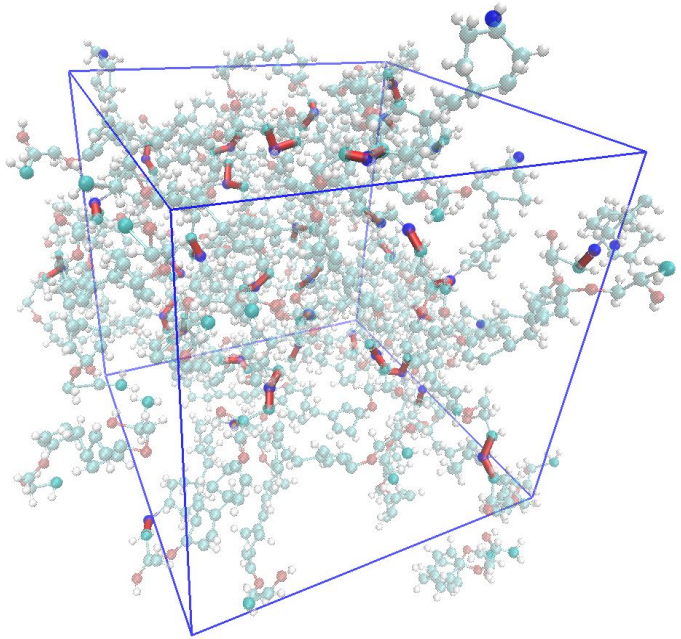


Secondary structure

Past Progress

- LAMMPS nonreactive FF MD simulation
  - Activation of potential chemical reactive sites
  - Reconstruction of simulation box
  - Cross-linking process
  - Cross-linked structure
- Thermal and volumetric properties
  - Isobaric cooling simulation
    - Glass transition temperature Tg
    - Thermal expansion coefficient α
  - Isothermal depressurization simulation
    - Isothermal compressibility κ



(40,20) system with 98.75% cross-linking percentage

$$\alpha(P,\varepsilon) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\varepsilon}$$

Past Progress

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  - Activation of potential chemical reactive sites
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  - Cross-linking process
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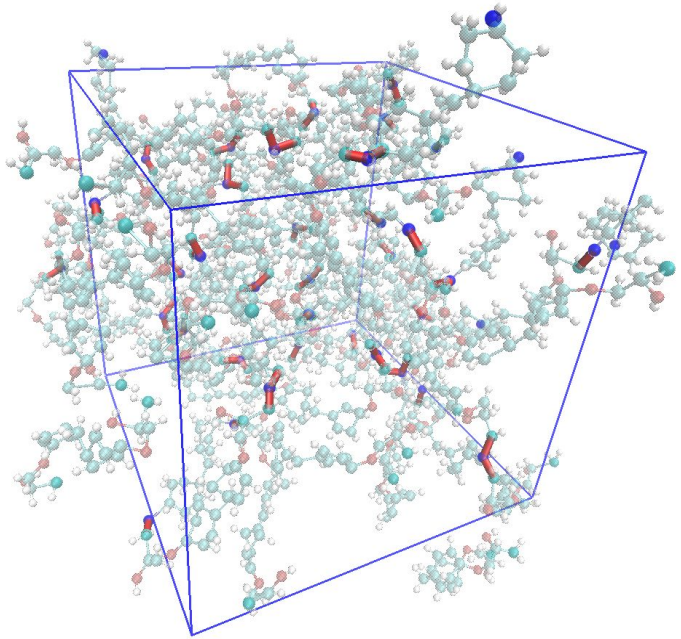


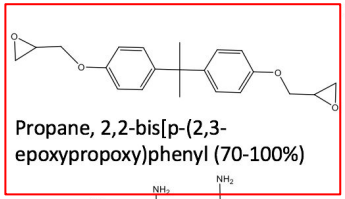
(40,20) system with 98.75% cross-linking percentage

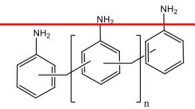
$$\kappa(T,\varepsilon) = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\varepsilon}$$

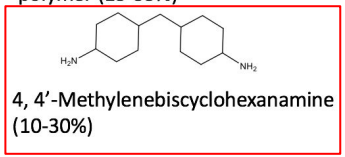
Research Implications

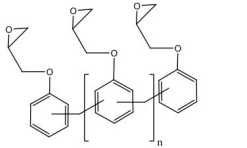
- In what ways does our project contribute to the study of epoxy resins using MD simulations?
  - Simulation of resin component molecules not previously studied and more molecules considered

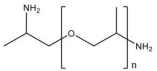
PRO-SET® M1002 Resin (Epoxy) and M2046 Hardener (Amine)
MSDS and Sigma Aldrich

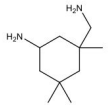












Research Implications

- In what ways does our project contribute to the study of epoxy resins using MD simulations?
  - Simulation of resin component molecules not previously studied and more molecules considered
  - Creation of epoxy resin system with higher crosslinking percentage at a still-reasonable bond creation cutoff

Authors	System	Cutoff Distance	Crosslinking Percentage
Us	BADGE/1761-71-3	12A	98.75%
Wang et al.	BADGE/isophorone diamine	10A	90.2%
Wu & Xu	BADGE/isophorone diamine	10A	93.7%
Choi et al.	EPON 862/TETA	9A	61%

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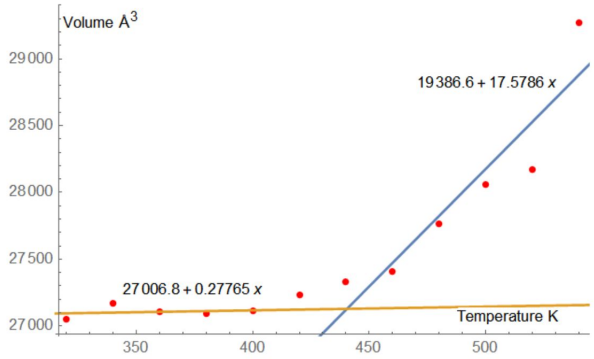

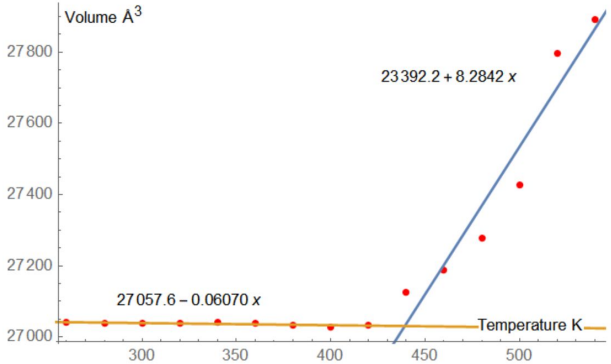

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References and Acknowledgements

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We would like to thank Dr. Crosby for his mentorship on the project and Dr. Wong for the REU experience. We hope future student groups will use and build upon our results to further the study of epoxy resins.