MD Chemistry

Molecular Dynamics Simulations of Epoxy Resin Systems to Study Physical Properties

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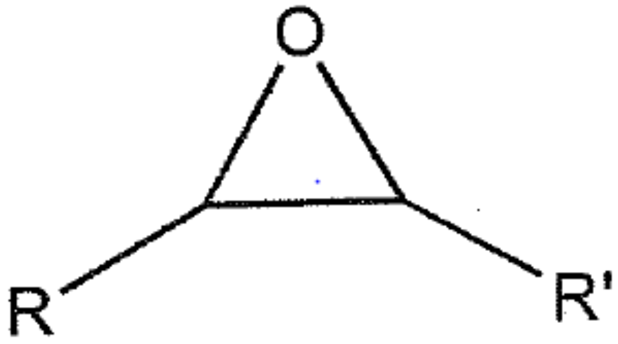
What is an epoxy resin?

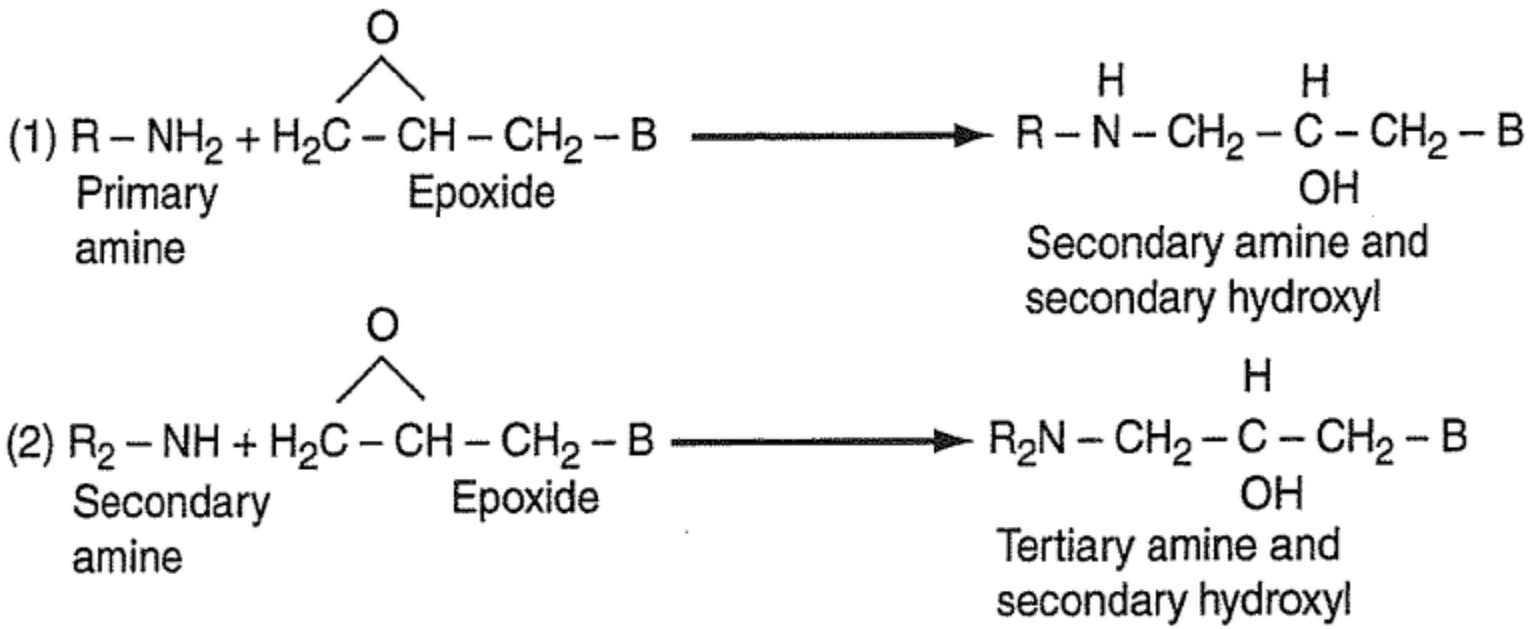
- Thermosetting polymer in which the primary cross-linking process involves the reaction of an epoxide group



Curing Process

- Base resin with epoxide functional group
- Amine hardener

Curing reaction



Molecular Dynamics Simulations

1. Divide time into discrete time steps
2. At each time step:

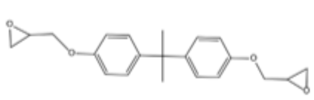
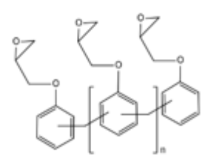
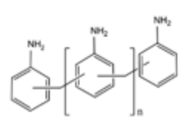
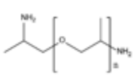
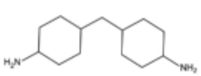
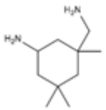
- Compute the force acting on each atoms, using molecular mechanics force fields.
- Update the position and velocity of each atom according to Newton's equation of motion

Purpose

- Implement the methods of Molecular Dynamics to a model epoxy resin system
- Measure the physical properties of the System
- See if the results are comparable to experimental data

Initial System Construction

- Composition based on Material Safety Data Sheet for PRO-SET M1002 Resin and M2046 Hardener
- Volume chosen to match listed typical density: 1065 kg/m^3

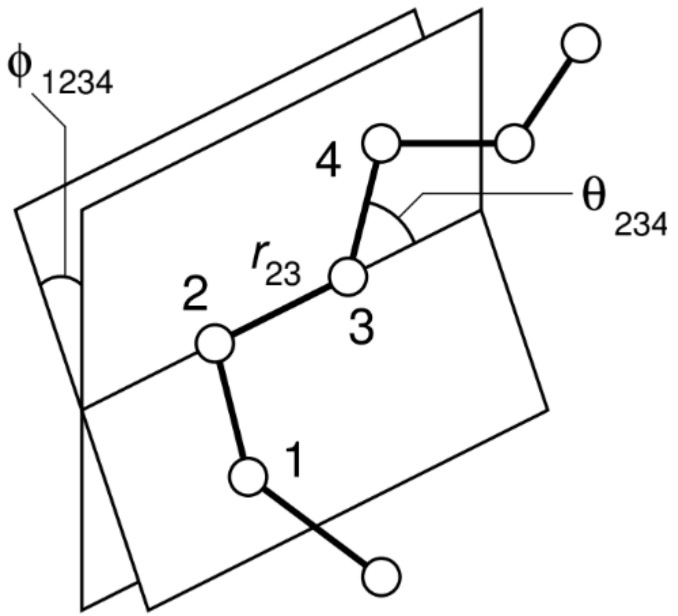
						
	Propane, 2,2-bis[p-(2,3-Epoxypropoxy)phenyl [BADGE]	Phenol-formaldehyde polymer glycidyl ether [PDGE formaldehyde]	Benzenamine-formaldehyde polymer [Aniline formaldehyde]	Polyoxyropylenediamine [POPDA]	4, 4'-Methylenebiscycl-ohexanamine [Methylene-BCHA]	Isophoronediamine [IPDA]
Mole fraction:	50%	16.7%	8.3%	8.3%	8.3%	8.3%

Initial System Construction

1. Construct individual monomers from fragments using Molefacture extension in Visual Molecular Dynamics (VMD)
2. Optimize geometry via Density Functional Theory in NWChem
3. Löwdin population analysis to determine partial charge on each atom
4. Create a periodic box system and put multiples of each monomer using Packmol
5. Use Tk console in VMD to create a LAMMPS data file for the system
6. Parameterize molecular forces under the CHARMM36 General Force Field by direct listing or analogy

CHARMM Force Field

$$
\begin{aligned}
U_{\text{CHARMM}} = &\sum_{\text{bonds}} K_b (b - b_0)^2 \\
&+ \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 \\
&+ \sum_{\text{dihedrals}} K_\phi (1 + \cos(n\phi - \delta)) \\
&+ \sum_{\text{improper}} K_\varphi (\varphi - \varphi_0)^2 \\
&+ \sum_{\text{Urey-Bradley}} K_{UB} (r_{1,3} - r_{1,3;0})^2 \\
&+ \sum_{\text{CMAP}} u_{\text{CMAP}}(\Phi, \Psi) \\
&+ \sum_{\text{nonb,pair}} \frac{q_i q_j}{4\pi D r_{ij}} \\
&+ \sum_{\text{nonb,pair}} \varepsilon_{ij} \left[\left(\frac{R_{\min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{\min,ij}}{r_{ij}} \right)^{6} \right]
\end{aligned}
$$

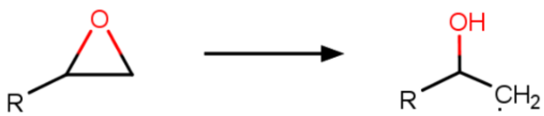


Cross-linking Procedure

stoichiometric ratio

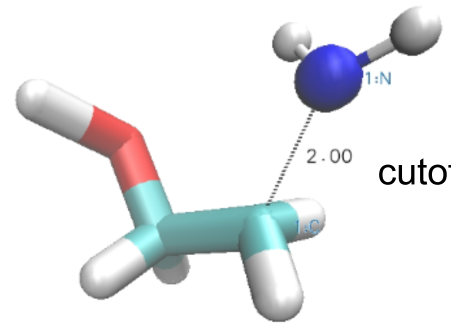
1

amine group



2

epoxy group

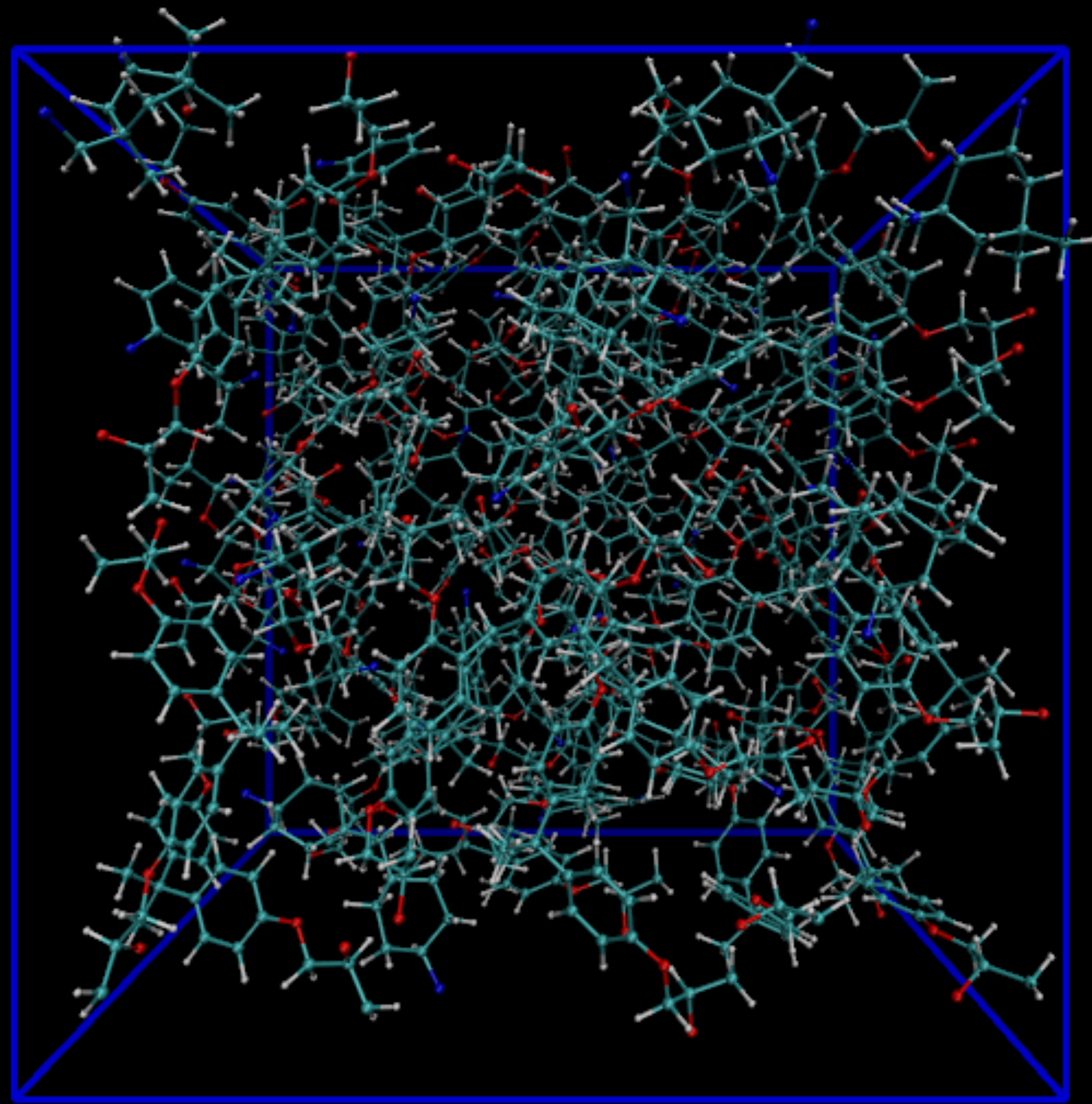


cutoff distance

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

(5% $\sim$ 80%)

Systems with different crosslinking percentages were generated by different time durations in canonical ensemble.

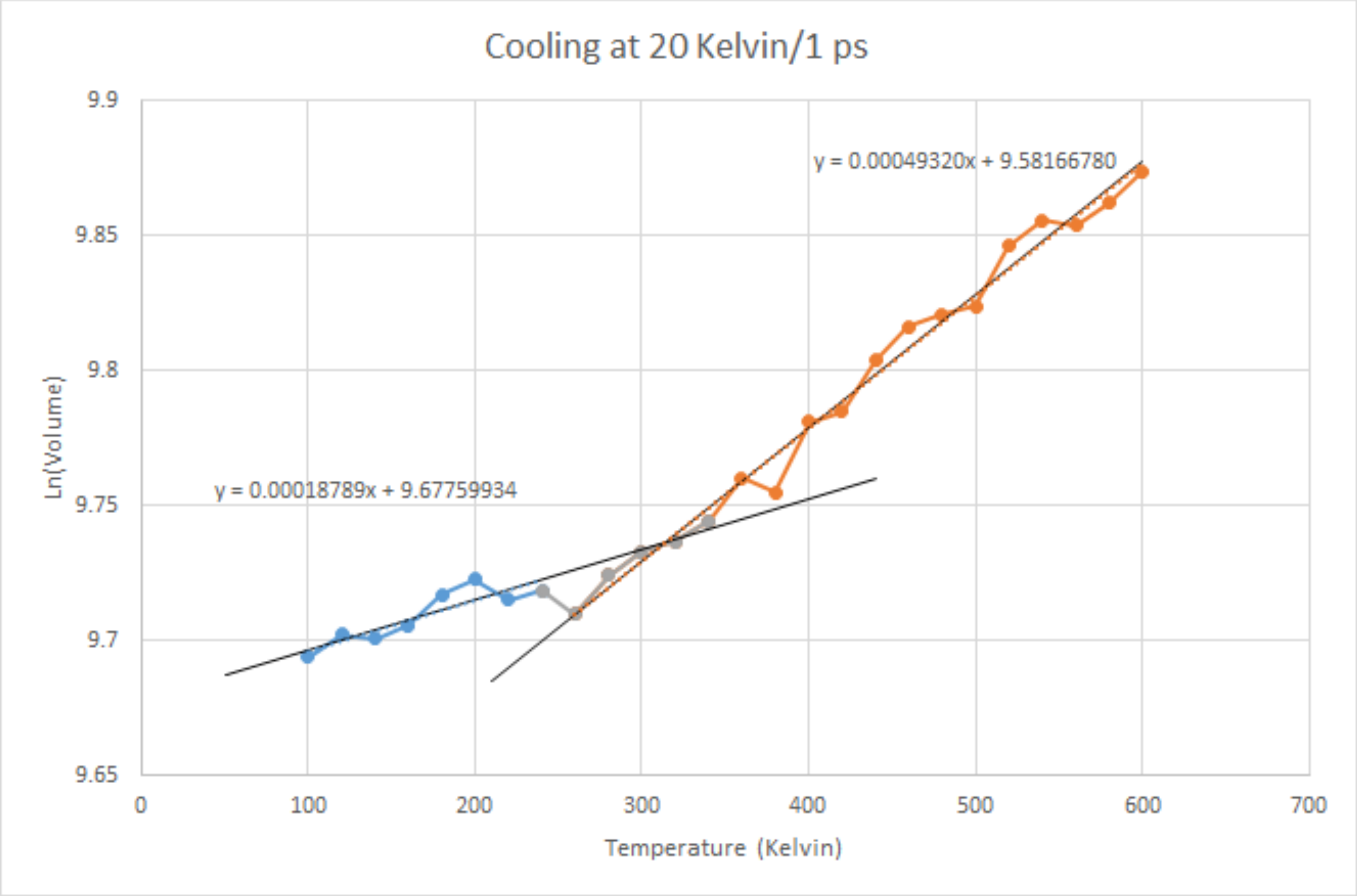


Method

- We use the canonical ensemble (NVT) to keep the volume and constant and set a constant temperature
- We use the isothermal-isobaric ensemble (NPT) to allow the volume to fluctuate in response to a constant externally applied pressure

Results - Thermal Expansion & Glass Transition Temperature

- Minimize the energy of the system
- Equilibrate the system to 600 K and 1 atm using NVT and then NPT ensembles
- Cool the system at a rate of 20 K/ps
- At each 20 K interval, run energy minimization, 1 ps of NVT and then 1 ps of NPT
- Average the volume over the last 0.5 ps of NPT

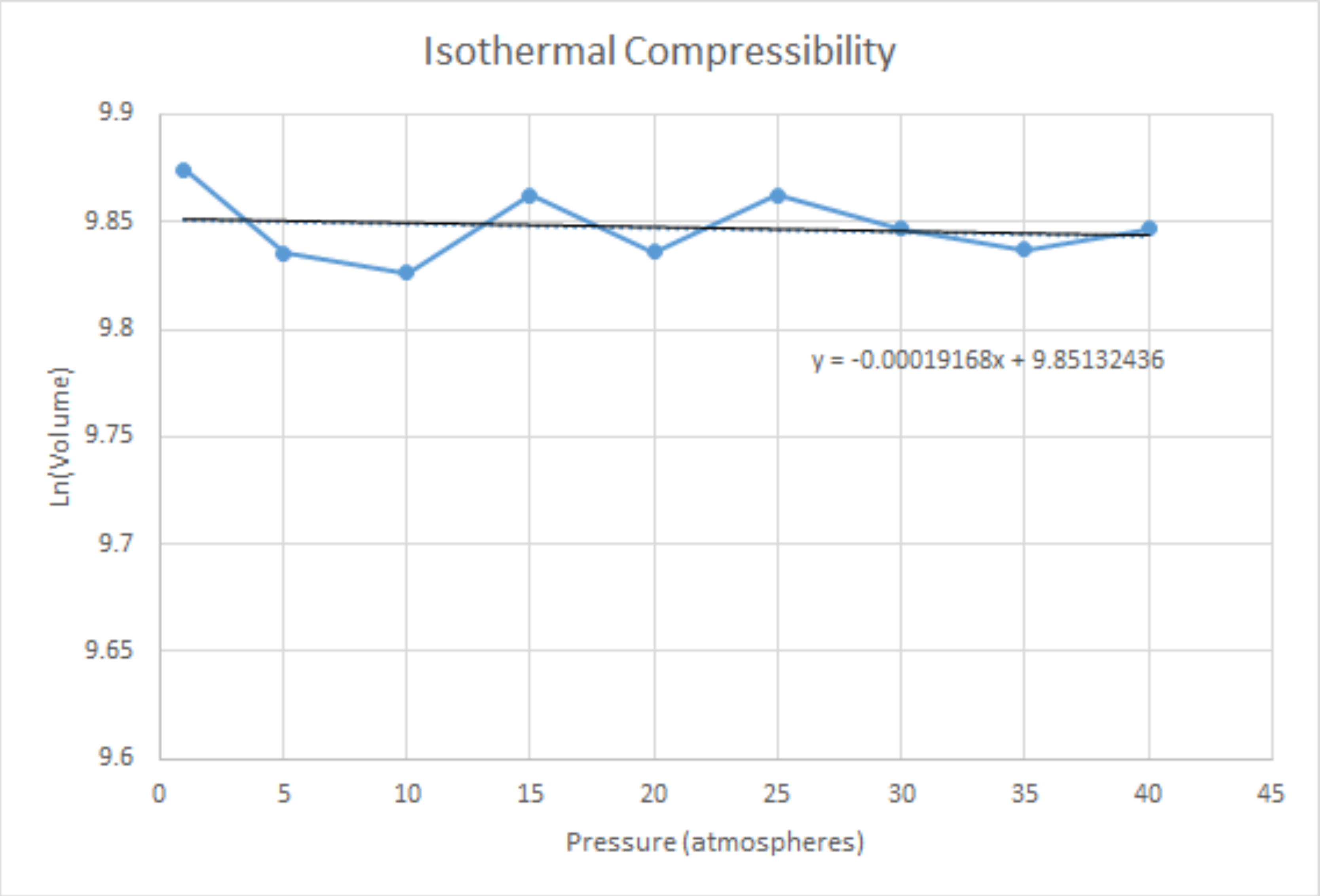


$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial ln(V)}{\partial T}\right)_P$$

$$T_g = 314.21K$$

Results - Isothermal Compressibility

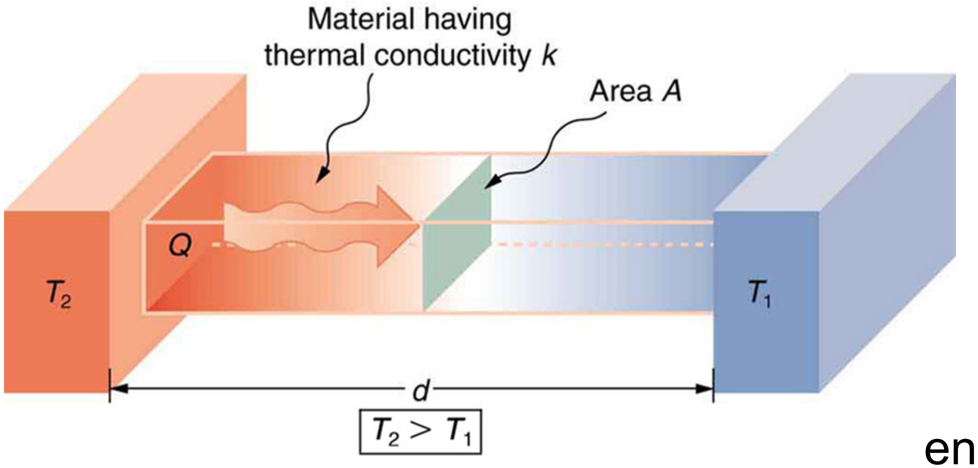
- Take cross-linked system that was already equilibrated to 1 atm and 600 K
- Increase isotropic exerted pressure at a rate of 5 atm/ps with constant temperature
- Run 1 ps of NPT ensemble at each 5 atm interval
- Average the volume over the last .5 ps



$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{\partial ln(V)}{\partial P}\right)_T = 1.92 \times 10^{-4}\ atm^{-1}$$

Thermal conductivity

(property of a material to conduct heat)



general expression

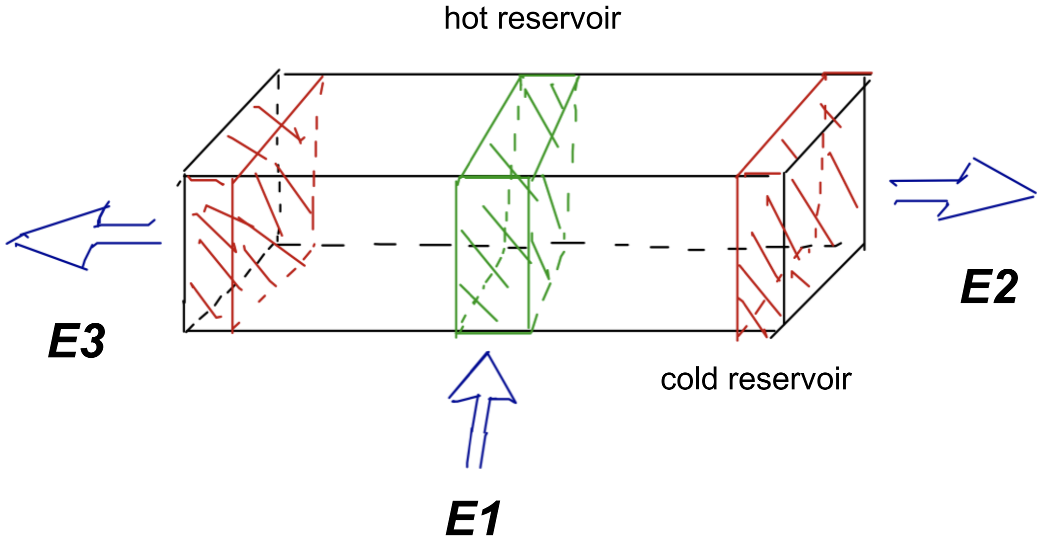
$$\vec{q} = -k\vec{\nabla}T$$

energy flux

(the rate of transfer of energy through a surface)

temperature gradient

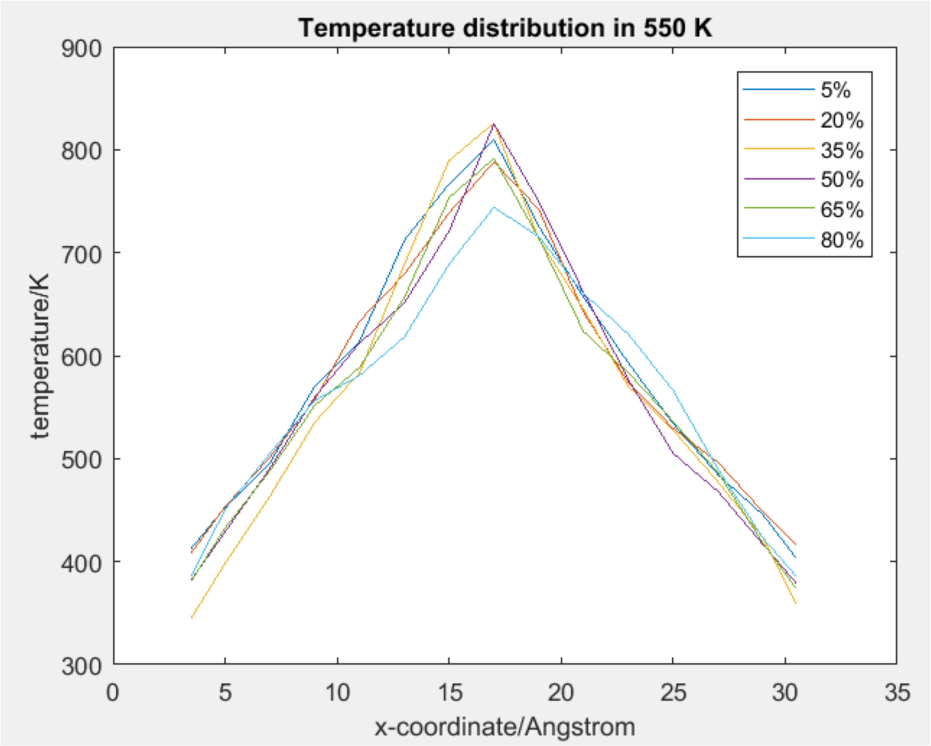
Thermal conductivity

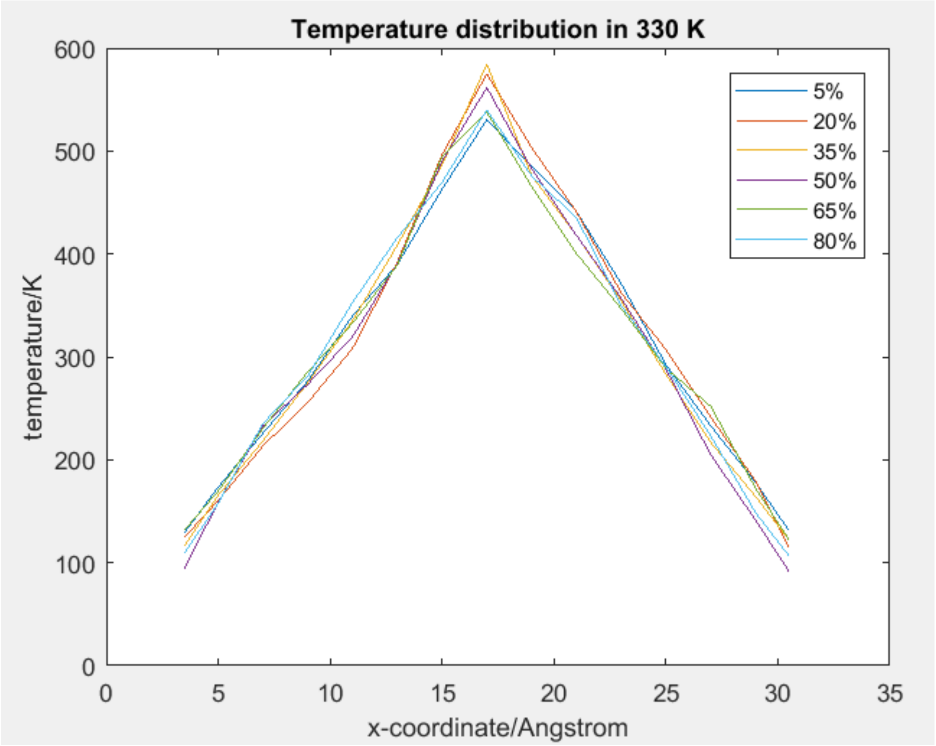


$E1 = E2 + E3$

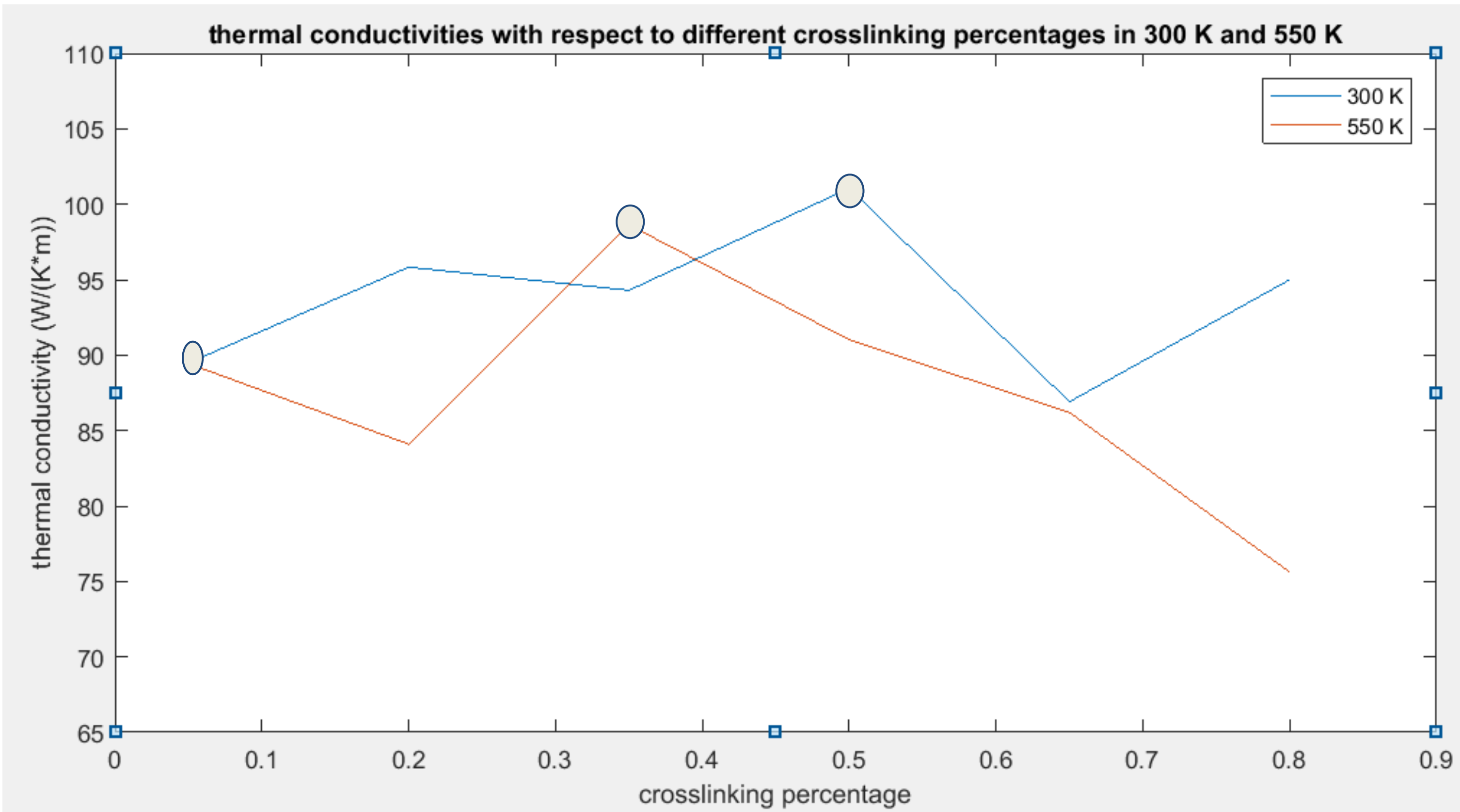
1. Relaxation in canonical and isothermal-isobaric ensemble for 5 ps before measurement
2. generating temperature gradient across the hole system
3. reaching equilibrium state in microcanonical ensemble after 130 ps
4. acquire the averaged temperature distribution

Thermal conductivity





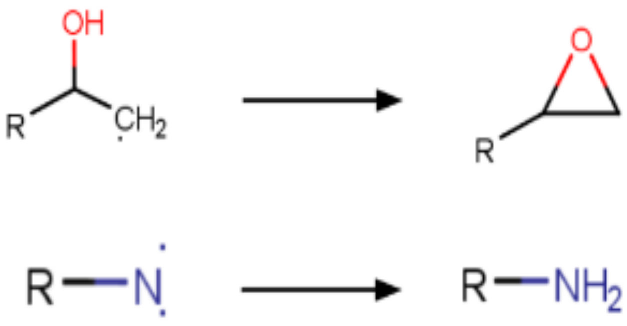
Thermal conductivity



Results - thermal conductivity

1. Thermal conductivity of cured epoxy resin at rubbery state is generally smaller than that at glassy state.
2. Thermal conductivity reach local minimum at 35% crosslinking at rubbery state and at 50% crosslinking at glassy state. Further experiment will be taken between 35% and 50% in terms of crosslinking percentage.
3. Thermal conductivity is around 90 W/(K*m), which is 500 times bigger than that in reality. Further series tests on this model were conducted to analyze related limitation and improve the accuracy.

Regeneration of functional groups



1. regenerate epoxy groups
2. create random hydrogen atoms rebonded into hydroxyl and amine groups
3. remove the remaining hydrogen atoms
4. update the partial charge in atoms

To improve the accuracy of our system

Conclusion

- We were able to effectively initialize and cross-link our epoxy resin systems
- We were successful in using molecular dynamics to measure the physical properties of our systems, with results comparable to previous similar studies
- In the future, we plan to apply new methods to improve the accuracy of our systems

References

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