Molecular Dynamics Simulations of Epoxy Resin Systems

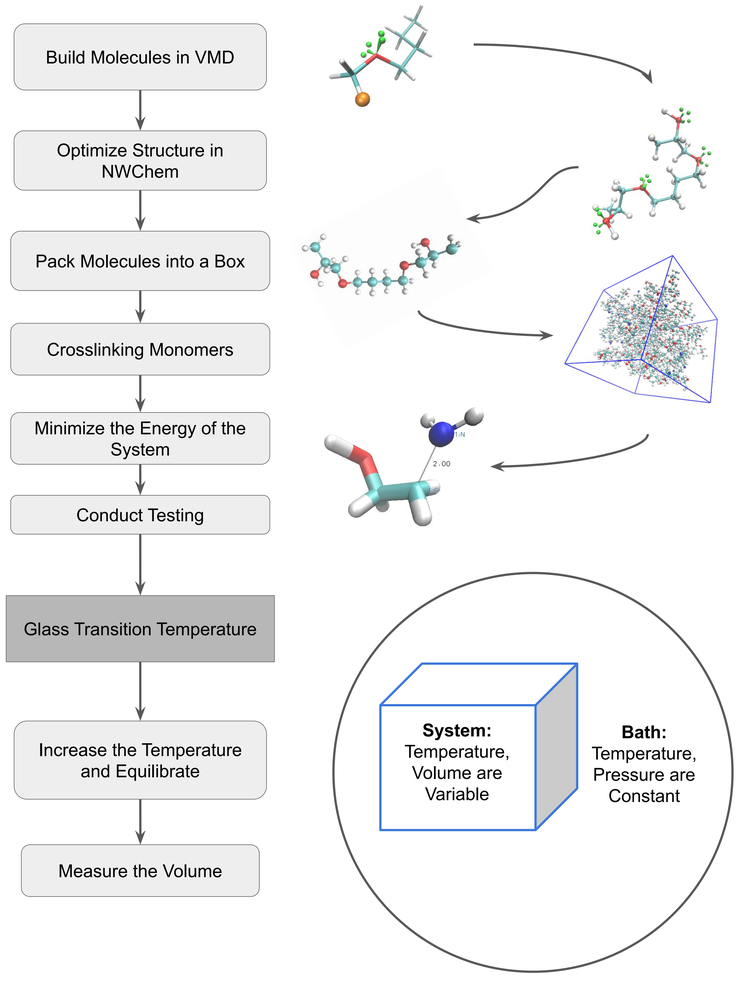
Aidan Glaser Schoff, Vassar College, Poughkeepsie NY
Tzu Hsien Tan, City University of Hong Kong
Mentors: Dr. Lonnie Crosby, JICS UTK
Dr. Kwai Wong, JICS UTK

Introduction

Epoxy resins are a class of thermoset polymers that have a wide range of applications in everyday lives, including adhesives, coatings, encapsulates, casting materials, etc. To fulfill different criteria in these applications, one can let the epoxy resins cross-link with anime hardeners, producing cured resin system. The number of cross-linked molecules can influence the physical properties of the system significantly. In this project, we investigate how cross-linking affects physical properties by using Molecular Dynamics (MD) simulation. The properties of interest include the glass transition temperature, thermal expansion coefficient, and isothermal compressibility.

The MD simulation consists of computer algorithms which is based on classical equations of motion. The forces and position of atoms are calculated over a very short timestep of 1 femtosecond. By equilibrating the system for a long time period, in the range of nanoseconds, the physical properties can be properly studied. Moreover, we can perform measurements that are difficult to conduct in real experiments as they are expensive in human-hours and in material costs.

Preparation of the System



Crosslinking Reaction

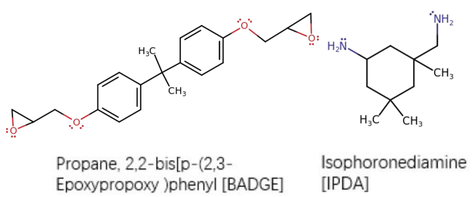


Figure 1. Monomers of epoxy resin (BADGE) and amine hardener (IPDA)

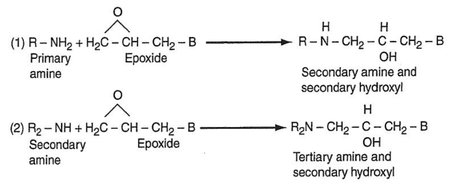


Figure 2. Crosslinking reaction in solvent

Underlying Mechanism to LAMMPS Simulation

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is the software which we used to run molecular dynamics simulations. All movement of atoms within LAMMPS stems from solutions to equations that describe forces on each atom. There are four distinct types of interactions: bonds, angles, dihedrals, and non-bonded interactions. Each atom has a specific type, which is based on its element as well as the atoms that surround it. Additionally, each bond, angle and dihedral is given a parameter based on the types of atoms which surround the central atom.

The CHARMM (Chemistry at HARvard Macromolecular Mechanics) General Force Field was used to describe the forces on each atom given the atom-type and specified parameters.

$$
\begin{aligned}
U_{\mathrm{CHARMM}} = & \sum_{\text{bonds}} K_b(b-b_0)^2 \\
& + \sum_{\text{angles}} K_\theta(\theta-\theta_0)^2 \\
& + \sum_{\text{dihedrals}} K_\phi(1+\cos(n\phi-\delta)) \\
& + \sum_{\text{nonb,pair}} \frac{q_i q_j}{4\pi D r_{ij}} \\
& + \sum_{\text{nonb,pair}} \varepsilon_{ij}\left[\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{\min,ij}}{r_{ij}}\right)^{6}\right]
\end{aligned}
$$

Figure 3. The CHARMM force field used in our simulations

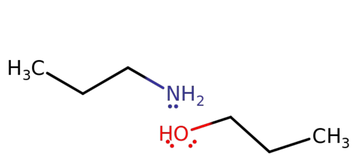


Figure 4. Nitrogen and Oxygen act as a Non-Bonded Pair

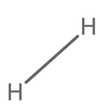


Figure 5. Bond

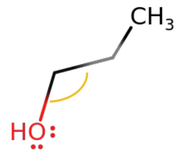


Figure 6. Angle

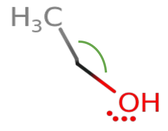


Figure 7. Dihedral / Torsion

Experimental Procedure

1. Assign suitable parameters for simulation: the length of a timestep in our case was 0.5fs, and apply periodic boundary condition to the system.
2. Perform energy minimization on the simulation box.
3. Equilibrate the system at 600 Kelvin, 1 atm, for 50 ps in NVT ensemble followed by 150ps NPT ensemble.
4. Decrease the temperature from 600K to 200K by an interval of 20K. At each temperature, run 0.5 ps of NVT ensemble followed by 10ps of NPT ensemble. This results in an equilibrated system. The volume is averaged over the last 0.25ps every 1ps of the NPT simulation.
5. The data is then plotted, as shown in Figure 8. The point of intersection indicates the glass transition temperature.

Preliminary Results

The following chart illustrates the relation between volume of the 85% cross-linked BADGE-IPDA resin system and temperature. As the temperature rises, we can observe there is a sudden increase in slope of the fitting curve at around 433K, which is the glass transition temperature. This value is close to the experimental measured 436K [Sindt]. From the slope of the curve, we can further determine the thermal expansion coefficient.

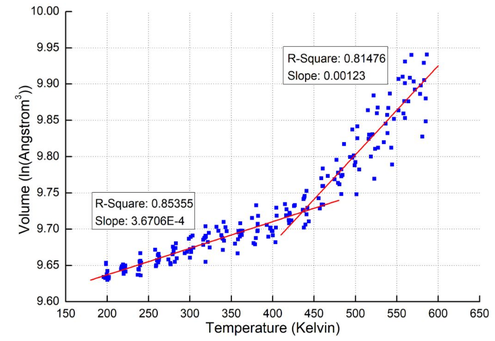


Figure 8. The volume-temperature relation of 85% crosslinked BADGE-IPDA resin system

Conclusions and Future Steps

Successes:
- Construct epoxy resin systems and optimize structure.
- Cross-link systems and measure glass transition temperature.
- Preliminary results are close to experimental values.

Struggles:
- Implementation of measurement of systems in LAMMPS.
- Type matching each atom within our system.

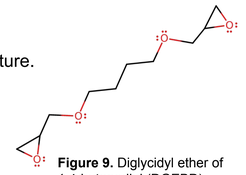


Figure 9. Diglycidyl ether of 1,4-butanediol (DGEBD)

Future Steps:
- Measure the thermal expansion coefficient and and isothermal compressibility.
- Measure the glass transition temperature of DGEBD-IPDA system and compare with experimentally obtained values.

Acknowledgements

This project was sponsored by the National Science Foundation through Research Experience for Undergraduates (REU) award, with additional support from the Joint Institute of Computational Sciences at University of Tennessee, Knoxville. This project used allocations from the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation. In addition, the computing work was also performed on technical workstations donated by the BP High Performance Computing Team.

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