Molecular Dynamics Simulations of Epoxy Resin Systems to Study Physical Properties

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Introduction

Molecular dynamics (MD) is a computer simulation method for studying the physical movement of atoms and molecules. This project focuses on modeling thermoset epoxy resin systems, which are widely used in engineering applications, and studying their physical properties using molecular dynamics simulations. Epoxy resins are molecular systems that include an epoxide-group containing base resin as well as a an amine bonding curative, with additional modifiers sometimes included for other properties. PRO-SET M1002 resin and M2046 hardener **(Figure 1)** were used as raw materials to prepare the systems. They were mixed at a high temperature and were crosslinked (**Figure 2)** in what is known as a curing process to form epoxy resin systems at various crosslinking degrees under different time steps. We applied the CHARMM36 force field (**Figure 3)** to the MD simulation of the reaction and future measurement, where the parameterization of these coefficients affects how realistic our systems are. There are limitations to the accuracy of our model when compared with real experiment, but it saves experimental resources and time. This helps us to study the relationships among physical properties and chemical structures by an alternative method.

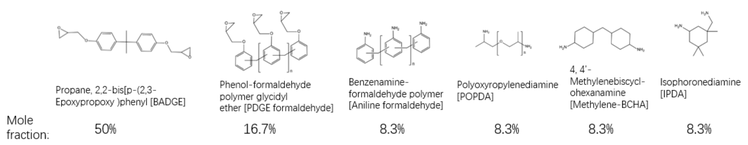

Figure 1. M1002-M2046 pro-set epoxy resin system

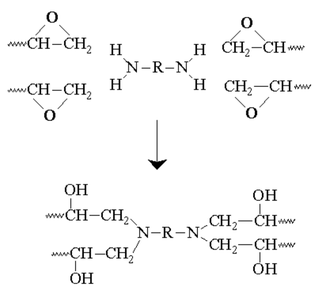

Figure 2. Curing reaction

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

Figure 3. CHARMM36 force field potential

Preparation of themoset epoxy resin systems

The epoxy resin systems were modeled by the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package, NWChem, Visual Molecular Dynamics (VMD), and Packmol. Here are the steps in detail.

- Creating molecules individually and supplementing with topological information in VMD;
- Structural optimization (**Figure 4)** and analysis of partial charge distribution using quantum mechanics simulation in NWChem;
- Parameterization of atom types, bond (stretch), angle (bend), dihedral (torsion) and improper dihedral types under the CHARMM36 Force Field;
- Packing of molecules into initial simulation box **(Figure 5)** using Packmol and energy minimization in LAMMPS;
- Reacted group activation **(Figure 6)** and partial charge rearrangement;
- Equilibration of molecules under NVE, NVT, and NPT ensembles;
- Crosslinking formation **(Figure 7)** based on cut-off distance using the LAMMPS fix bond/create command

The epoxy resin systems at various crosslinking percentages were created by the repetition of energy minimization and bond formation with different time steps under LAMMPS package. Periodic boundary conditions were applied to save computational cost while satisfying the requirements of bulk phase.

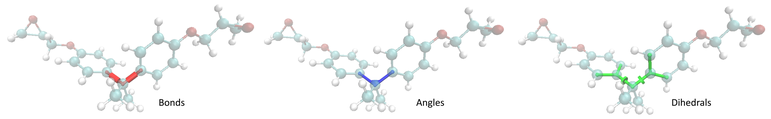

Figure 3. Parameterization – stretch, bend, torsion

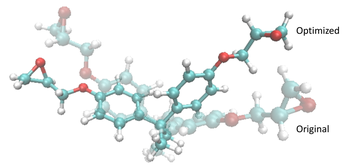

Figure 4. Structural optimization

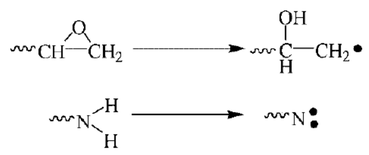

Figure 6. Epoxide and amine group activation

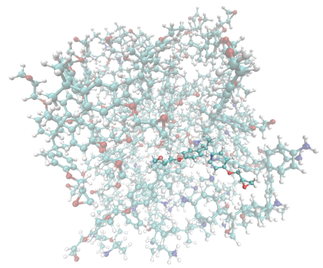

Figure 5. Simulation box

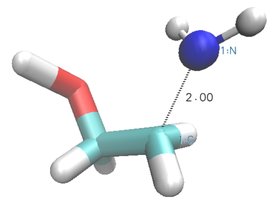

Figure 7. Sample crosslinking C-N bond

Measuring physical properties

We have prepared multiple epoxy resin systems at various crosslinking percentages. Our goal now is to run simultaneous simulations on each of these systems to measure physical properties that are significant to engineering applications and determine to what degree these quantities vary based on crosslinking percentage. The physical properties we want to measure include:

- Thermal expansion coefficient—a measure of how the volume of the system changes in response to a change in temperature
- Glass transition temperature—the temperature at which the system changes from a hard, "glassy" state to a viscous, rubbery state.
- Isothermal compressibility—how volume changes with respect to a change in the applied external pressure
- Thermal conductivity—a measure of how well heat flows through the system

Thermodynamic quantities (e.g. temperature, pressure, volume) of our system are measured by calculating ensemble averages in equilibrium. For the above physical properties, we need to apply different ensembles with different quantities fixed by external constraints. The LAMMPS package allows us to apply external fixes on our system so we can study the canonical, microcanonical, and isothermal-isobaric ensembles—NVT, NVE, and NPT respectively.

Conclusions and future steps

Thus far we have been able to successfully construct the six molecules needed for our model epoxy resin systems, optimized their geometries, and created several systems under similar conditions but at various stages of crosslinking. We have begun measuring several physical properties of our systems, and hope to determine how these properties vary for different crosslinking percentages.

To further our research we would like to study methods of making our model systems more realistic. One strategy we would like to employ to make our simulation more accurate is to increase the size of our system and crosslink a greater number of molecules. Our belief is that by making the system larger the quantities we are measuring at the microscopic level will more closely resemble a macroscopic, real world application.

Acknowldegements

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