Molecular Dynamics Simulations of Epoxy Resin Systems

Stephen Wu[1], Lam Tran[2]
[1]City University of Hong Kong, [2]University of Pennsylvania

Abstract

Epoxy resins are applied in a wide range of applications due to their use-dependent mutability and their high strength, excellent adhesion and low shrinkage. Given that epoxy resins are used in important fields like high-performance aeronautics, it is important to understand their chemistry at a microscopic level to prevent larger-scale failures. In our project, we use molecular dynamics (MD) simulations to replicate the epoxy-amine crosslinking reaction that confers upon a epoxy resin system its desired properties using both nonreactive and reactive force field. Varying over a manufacturer-given range of molecular components and the coordinate of the crosslinking reaction, we hope to quantify physical properties of the epoxy resin system such as its isothermal compressibility, thermal expansion coefficient and chemical partition. In finding these values, we can understand and determine the suitability of using the resin in different environments.

Introduction

Epoxy resins are molecular systems that include an epoxide-group **(Figure 1)** containing base resin and a curative, with additional modifiers sometimes included for other properties. Specifically, the M1002/M2046 Pro-Set System we are working with consists of a BADGE (diglycidyl ether of bisphenol A) type base resin and an amine-type curative and is intended for usage as an adhesive. Curing an epoxy resin confers the system its hardness and resistant properties and involves the crosslinking between the epoxy group of the base resin and the amine of the curative. Curing can occur over a wide range of temperatures and rates, and the physical properties of the system change depending on the extent of the crosslinking, which forms large, relatively immobile molecular complexes.

We would like to explore the evolution of our epoxy resin system over the reaction coordinate of the cross-linking reaction using MD simulations. MD simulations solving Newton's equation for individual atoms, given a set of potential functions and parameters given by quantum mechanics, over very short (1fs) time steps. Integrating the steps together, we can model the trajectories of the atoms over a longer time, visualizing the initial bond breakage and later polymerization that characterizes the crosslinking. From our MD simulations, we can calculate physical properties such as the change in free energy over the reaction coordinate and the extent to which shifts in temperature or pressure affect the overall volume of the cured system.

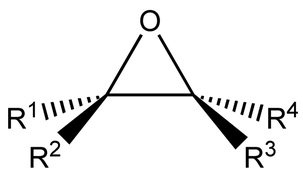


Figure 1. Epoxide group

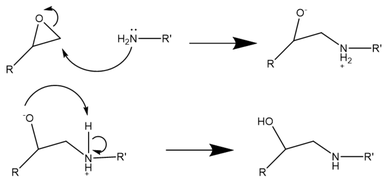


Figure 2. Epoxy-amine crosslinking

Methods and Materials

We used the GROMACS and LAMMPS MD simulation with both the CHARMM36 nonreactive force field and the ReaxFF reactive force field in our project. VMD was used for visualization of individual molecules and the output trajectories of the MD simulations. The steps we were took as follows:

- Parameterization of atom types, bond (stretch), angle (bend), dihedral (torsion) and improper dihedral types under CHARMM36[5,6] **(Figure 3)** ;
- Structural optimization **(Figure 4)** and partial charge distribution analysis[1,2];
- Packing of molecules into initial simulation box **(Figure 5)** and energy minimization[3,4,11];
- Equilibration of molecules under NVE, NVT, and NPT ensembles with temperature rescale every 100 steps[9];
- Reacted group activation **(Figure 6)** and partial charge rearrangement[10];
- Crosslinking formation **(Figure 7)** and protonation;
- Re-parameterize local crosslinking structure under CHARMM36[7];

Steps we are about to take:

- Re-equilibration and MD simulation of volume change[8];
- Data analysis: free energy calculation with umbrella sampling, etc.

This general procedure was used to gauge the stability of the cross-linked product, to set up an umbrella sampling simulation with minor input changes to measure changes in free energy along the reaction coordinate, and to quantify fluctuation properties of the system.

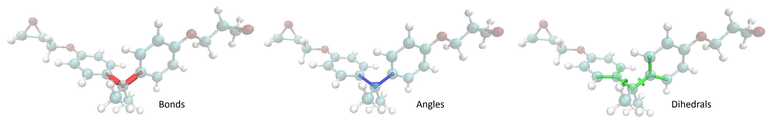


Figure 3. Parameterization – stretch, bend, torsion

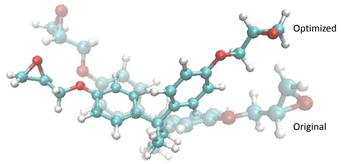


Figure 4. Structural optimization

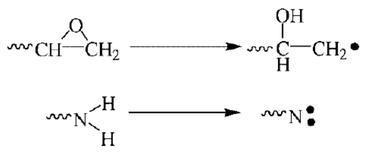


Figure 6. Epoxide and amine group activation

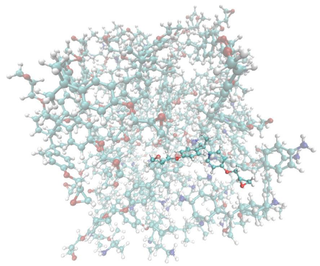


Figure 5. Simulation box

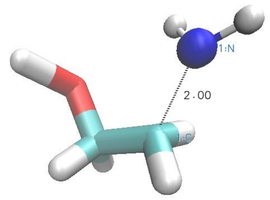
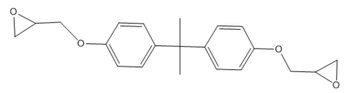


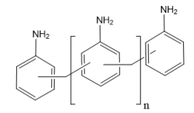
Figure 7. Sample crosslinking C-N bond

M1002-M2046 Pro-set Epoxy Resin System[12]

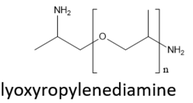


Propane, 2,2-bis[p-(2,3-epoxypropoxy)phenyl (70-100%)

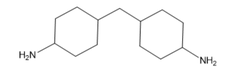
Phenol-formaldehyde polymer glycidyl ether (10-20%)



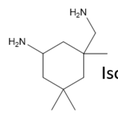
Benzenamine-formaldehyde polymer (15-35%)



Polyoxypropylenediamine (10-30%)



4, 4'-Methylenebiscyclohexanamine (10-30%)



Isophoronediamine (10-30%)

Current Results

We are still in the intermediate stages of our project, but we have already made some good progress. Several systems were constructed, parameterized and optimized in terms of each molecules and tested both nonreactive force field in GORMACS and Reactive force field in LAMMMPS. Apart from these, we've constructed activated molecules as shown in **(Figure 6)**,and reparametrized them into CHARMM36 force field. We've also wrote energy-minimized crosslinking bond topological file including atom positions and partial charges for the parameterization after crosslinking process.
From the activated structures in we've generated an initial small-scale (<10 molecule) crosslinking reaction stable under the microcanonical NVE ensemble and an approximation of the canonical NVT ensemble by fixing and rescaling temperature every 100 steps. We are currently working on scaling crosslinking formation under same condition to construct polymer structure.

Conclusions and Future Steps

Commercial epoxy resins are complicated systems involving precise mixtures of different types of base resins, curatives and additional modifiers. In our project, we've only modeled the major BADGE-type base resin and amine curative of the M1002/M2046 Pro-Set Epoxy Resin System. Nonetheless, we were able to simulate the basic crosslinking of the base resin and the curative, gaining a better understanding of how an epoxy resin cures. We show that molecular dynamics simulations are an appropriate means to visualize the crosslinking reaction integral to resin curing, see how the chemistry of the system changes dependent on the extent of the crosslinking, and determine the value of fluctuation properties that can affect applications of the resin. By the end of our project, we hope to quantify these values to determine suitability for its industrial application as an aluminum plate adhesive.

Mentor:
Dr. Lonnie Crosby
Joint Institute for Computational Sciences
lcrosby1@utk.edu

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