

Molecular Dynamics Simulation of Epoxy Resin Systems

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I. Background

Epoxy resins are a group of molecules that contain an epoxy group, as displayed in Figure 1. After an exposure to heat, epoxides bond with hardeners in the crosslinking reaction. This creates polymer chains in a process called curing, and the system undergoes changes from liquid form to solid [1]. Furthermore, after curing, epoxy resins are energy intensive to revert them back to their original state [2]. For the above reasons, epoxies are often used as adhesives, coatings, encapsulates, casting materials or other applications [1]. Additional molecules can be introduced to change the behavior and structure of the system according to the chemist's specifications.

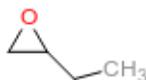


FIG. 1. A molecule containing a three-membered epoxy ring. Hydrogens are not shown.

Epoxy resins are prevalent in industrial application due to the ease of setting up and carrying out the curing reaction [1]. As a result, many experimental procedures have been carried out to study the material properties of epoxy systems, such as glass transition temperature, compression and tensile strength, and iso-thermal compressibility [2]. Due to the rise of computing power over recent years as well as advancement in materials science software, it has been possible to computationally study epoxy systems to model their physical behavior. Computational studies of epoxies aim to both mimic real life epoxy behavior and produce models that provide valid measurements of the system.

Molecular dynamics (MD) simulations were adopted in our experiments. They focus on solving Newton's equations of motion over a time scale of nanoseconds. In doing so, the position and momentum of the atoms in the simulation is updated every femtosecond. Supercomputers, in our case the Stampede2 in UC San Diego, were used to run the computationally expensive experiments within

several hours. The benefit of computationally studying these systems is that unknown experimental values can be found after the methodology of the experiment has been validated.

We investigated two epoxy systems. The first one was the Diglycidyl ether of bisphenol A and Isophoronediamine system, also known as BADGE and IPD respectively, shown in Figure 2. We also constructed the activated form of the molecules, shown in Figure 4. These activated monomers are not physically possible, rather they were used in the simulations to bond the activated monomers together. The second system was Diglycidyl ether of 1,4-butanediol and Isophoronediamine, also known as DGEBD and IPD, shown in Figure 3 as well as their activated forms (not shown). These systems were chosen for their simplicity as well as the availability of experimental reference materials which are allowed for verification of the modeling techniques [2].

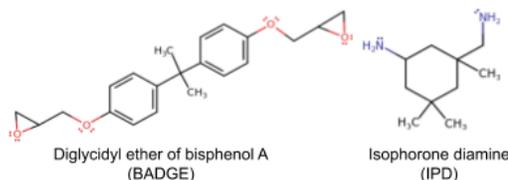


FIG. 2. Monomers composing the BADGE and IPD system.

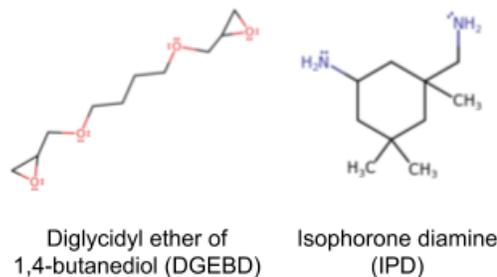


FIG. 3. Monomers composing the DGEBD and IPD system.

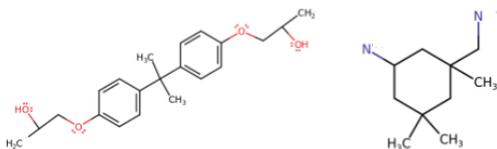


FIG. 4. Activated forms of BADGE and IPD. These molecules are used when simulating the crosslinking reaction and do not exist in real life.

A. The Crosslinking Reaction

Crosslinking is the term used to describe the reaction which takes place during curing. Figures 5 & 6 describe the reaction mechanism of an amine group crosslinks with an epoxy group [4]. The solvent in this case would be an organic substance which can receive protons from the amine group and also donate them to the hydroxide (OH) group. In real reaction, a carbon in the epoxy group is attacked by the nitrogen, which causes the breaking of a carbon-oxygen bond. When doing simulations, instead of following the real reaction mechanism, we used an activated system shown in Figure 4. The activated system is one in which the bonds in the epoxy rings have already been broken and the hydrogens which would be donated to the solvent are removed. By using the activated system, we could use the bond/create command in LAMMPS to only simulate the forming of the bond between nitrogen and carbon. This reaction is shown in Figure 7.



FIG. 5. The first step of the crosslinking mechanism.



FIG. 6. The second step of the crosslinking mechanism in solvent.

After the two stages of this reaction, the neutral nitrogen now has the potential to react with another epoxy group and again lose its hydrogen to the solvent which provides the hydrogen for the hydroxide group. After undergoing the crosslinking reaction for the second time, the nitrogen now has no hydrogens left to react with the solvent. Thus, in order to continue crosslinking, it must break one of the bonds that had just formed from previous crosslinking reaction. This is why the crosslinking stops after two iterations. Additionally, the carbon involved in crosslinking can only undergo such process

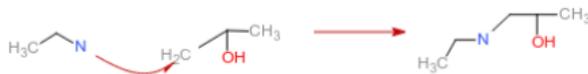


FIG. 7. Simulated crosslinking reaction using activated molecules.

once, as it can only have a maximum of four bonds. Thus, the stoichiometry of the reaction is 2 epoxies : 1 hardener. While there is extensive research regarding properly simulating the crosslinking reaction, our simulations were focused on measuring physical properties after the crosslinking reaction [10]. We accepted that our crosslinking model is not accurate, but the crosslinked system obtained afterwards is accurate.

B. Force Fields Used in the Simulation

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software was used to run the molecular dynamics simulations [8]. There are four main steps to run the simulations: provide an initial position and velocity for each of the atoms, calculate the forces (and thus acceleration) on each atom according to the CHARMM General Force Field (CGenFF), move the atoms according to the defined acceleration and velocity of each atom, and repeat the cycle. All movement of atoms within LAMMPS stems from solutions to equations that describe the potential energy of the interactions between each atom [3]. Figure 8 shows the particular potential energy summation used for CGenFF [3]. Through the relation $F = -\partial U / \partial r$, one can determine the forces acting on each atom. There are two primary types of interactions, intramolecular (atoms in the same molecule) and intermolecular (atoms from different molecules or far away from one another but within the same molecule). The bonds, angles, dihedrals, and Urey-Bradley term all describe intramolecular interactions, approximated as various types of harmonic springs. On the other hand, both “nonb, pair” terms describe the intermolecular interactions, modeled as a coulombic interaction and as a Lennard-Jones interaction. The Lennard-Jones interaction is used to describe interactions of neutral atoms that are not bonded to one another.

Each symbol corresponds to the following:

K refers to a force constant,

b_0 = Equilibrium bond distance,

θ_0 = Equilibrium angle

δ = Dihedral phase

$r_{1,3:0}$ = Equilibrium distance between first and third atom in an angle

q_i = Charge of atom i

q_j = Charge of atom j

r_{ij} = Distance between atoms i and j

ϵ_{ij} = Lennard-Jones well depth

In order to evaluate each term of the force field, each

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

FIG. 8. Additive potential energy describing the CHARMM General Force Field.

equilibrium value must be specified before being input to the model. In order to ensure all relevant parameters are input into the system, each atom must be typed according to the bonds and atoms that surround it. Additionally, each bond, angle and dihedral (torsion) is given a parameter based on the neighboring atoms. Nevertheless, for our systems, about half of all dihedrals, one-third of all angles, and a handful of bonds did not have explicit parameters listed. Thus, for these combinations we made educated guesses about the values of parameters based on similarities to other combinations that have known parameters.

II. Procedure

A. Building Monomers

We built the molecules of our epoxy systems with Visual Molecular Dynamics (VMD) software, utilizing the molefacture tool which creates molecules from scratch [5]. As shown in Figure 9, it is possible to select an atom (represented by the orange sphere on the hydrogen) and either change the atom's element or change the Hydrogen to a fragment of a functional group. This allowed for the creation of monomers such as DGEBD, which is shown in Figure 10.

Since we built the monomers with several fragments, the overall structure of the molecules may not be stable or have a minimized energy. Therefore, the structure of each molecule was optimized using NWChem, a tool developed for the purpose of using electron density functional theory to optimize the electron density of a system in such a way that it minimizes the energy of the entire molecule [7]. Additionally, the program defines the partial charge assigned to each atom through Lowdin Charge Analysis. Using this knowledge, we reassign the electron charge in order for the net charge of the molecule to remain neutral after altering the structure to the activated structure.

After the individual molecules were built, we created a

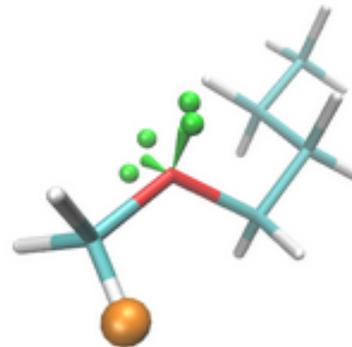


FIG. 9. Constructing DGEBD in Molefacture in VMD.

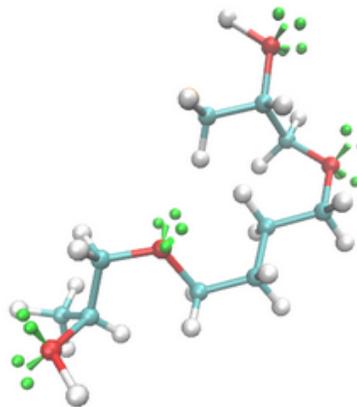


FIG. 10. Activated DGEBD monomer made with Molefacture in VMD.

simulation box of each epoxy system using the program Packmol [6]. This program allows individual molecules to be confined to a cube of specified dimensions, which is later used as the periodic simulation box in LAMMPS. In order to pack each molecule in Packmol, we had to determine the desired density of the system according to experimental values and subsequently determine the mass and volume of the box which achieves this density. Additionally, the molar ratio of epoxy groups to amine groups must be 2:1 to maintain the stoichiometry of the reaction.

In the case of the BADGE-IPD system, the desired density of the system was $1.13g/cm^3$ and the desired mass of 40 BADGE molecules and 20 IPD molecules was 17000 atomic mass units and thus the initial volume of the box was 24,990 Angstroms cubed at a side length of 29.2 Angstroms [2]. Although the simulation box is 29.2 Angstroms in length, a much larger volume was simulated due to the periodic boundary conditions of the box. The periodic boundary conditions simulate an exact copy of the central box on each of its surrounding sides. Figures 11 & 12 show periodic boundary conditions for a single box and also for all images of the box that surrounds the central box. Due to the period boundary conditions, the

system essentially becomes a very large basis set for a crystal. If the initial box is too small, then the overall structure of the entire copied system is unphysical in that it resembles a crystal structure rather than an amorphous structure.

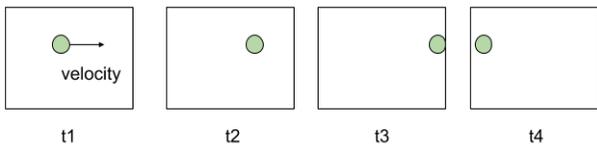


FIG. 11. Green atom moving as time progresses to the right and returning on the left due to periodic boundary conditions.

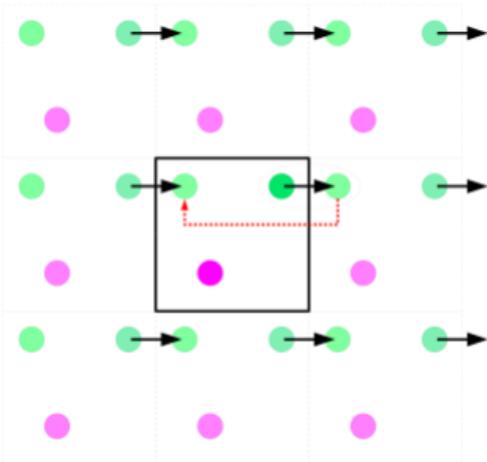


FIG. 12. Description of atom moving according to periodic bounding conditions while surrounded by images of central box.

B. Bonding the Epoxy System

Unlike the actual reaction mechanism described in the Crosslinking section, our simulation does not take into account the breaking of bonds. Instead, we utilized the bond/create command of LAMMPS, which allows us to form bonds between specified atoms if they are within a certain bonding radius [8]. This is why the activated form of the monomers are used rather than the normal form of the monomers. We let the epoxy system crosslink in the NVT ensemble while at 1600K for 0.5ns. As the simulation progresses, we can obtain systems with increasing crosslinking percentage (i.e. more bonds are created). The crosslinking percentage can be calculated as

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

C. Measuring the Properties of the System

Glass transition temperature (T_g) is an important parameter that describes the state transition behavior of the resin system. When the temperature is below T_g , the resin is in rigid “glassy state”, whereas above T_g , the resin is in soft “rubbery state” [1]. Since the volume of resin in rubbery state expands more than that in glassy state as temperature goes up, we can find out the glass transition temperature by calculating the thermal expansion coefficients of resin system in glassy state and rubbery state, respectively.

Thermal expansion coefficient (α) is a quantity that describes the volume expansion of a material when its temperature rises. At constant pressure, the thermal expansion coefficient is defined as

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

Therefore, the value of α can be obtained by computing the slope of natural logarithm of volume v.s. temperature curve. Since α is distinct in glassy and rubbery states, we can locate T_g where α experiences a rapid change.

To measure these values, we set up the simulation as follows. We applied periodic boundary condition to “enlarge” our system, making the system more realistic. Suitable parameters for simulation were assigned; for instance, we set the length of a timestep to be 0.5fs. To make the simulation box stable, we performed energy minimization to remove the energy produced in the crosslinking stage. Then, we ran 100ps of simulation in the canonical (NVT) ensemble to let the resin system reach thermal equilibrium at 800K, followed by 400ps of simulation in the isothermal-isobaric (NPT) ensemble to gradually change the volume of the system under standard atmospheric pressure (1 atm). Next, we cooled down the system from 800K to 10K by an interval of 10K. At each temperature, we performed 10ps of NVT followed by 40ps of NPT simulation, and the volume of the system was averaged over the last 2.5ps of the NPT simulation.

III. Results

The relation between the temperature and volume of the 90% crosslinked BADGE-IPD system is shown in Figure 13. The glass transition temperature was found to be 524.06K, where the two fitting curves intersect. However, the experimental measurement is 436K [2].

The thermal expansion coefficient we calculated in glassy state is $2.72 \times 10^{-4} \text{ K}^{-1}$, while in rubbery state is $2.06 \times 10^{-3} \text{ K}^{-1}$. The adjusted R-square values in both fitting curves are larger than 0.9, which indicates the distribution of data points is highly linear.

As for the 90% crosslinked DGEBD-IPD system, the result is shown in Figure 14. The experimental glass

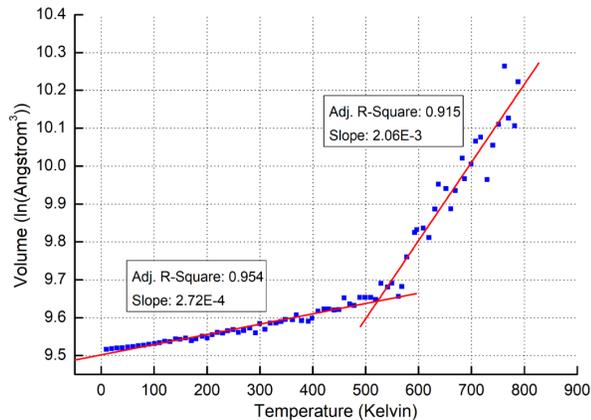


FIG. 13. Glass transition temperature and thermal expansion coefficient of the 90% crosslinked BADGE-IPD system.

transition temperature is 326K [2] while 439K is the value obtained from simulation, revealing that there was an error in our procedure.

The thermal expansion coefficient we measured is $2.72\text{e-}4 \text{ K}^{-1}$ in glassy state, and $2.06\text{e-}3 \text{ K}^{-1}$ in rubbery state, respectively.

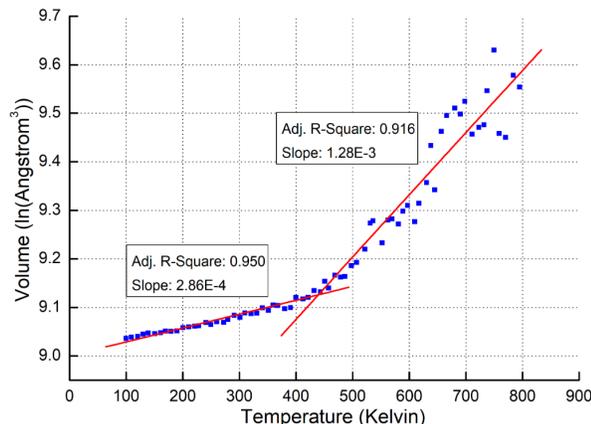


FIG. 14. Glass transition temperature and thermal expansion coefficient of the 90% crosslinked DGEBD-IPD system.

We also analyzed how changing the crosslinking percentage would affect the properties of the system. Figure 15 illustrates the relation between T_g and crosslinking percentage of the BADGE-IPD system. If we exclude the two data points with especially low T_g at 36.25% and 80%, we can notice the T_g approximately increases as the crosslinking percentage goes up.

Figures 16 & 17 shows how the thermal expansion coefficients of BADGE-IPD system at glassy and rubbery states change with respect to crosslinking percentage. We can notice the fluctuation of data points is significant. Hence, it's difficult to discover the relation between the crosslinking percentage and thermal expansion coefficient.

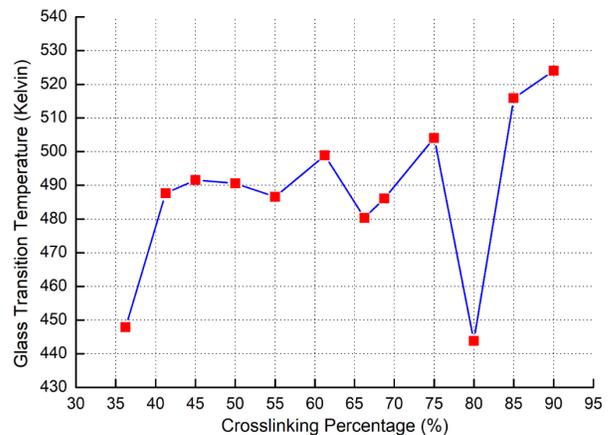


FIG. 15. Relation between crosslinking percentage and T_g of the BADGE-IPD system.

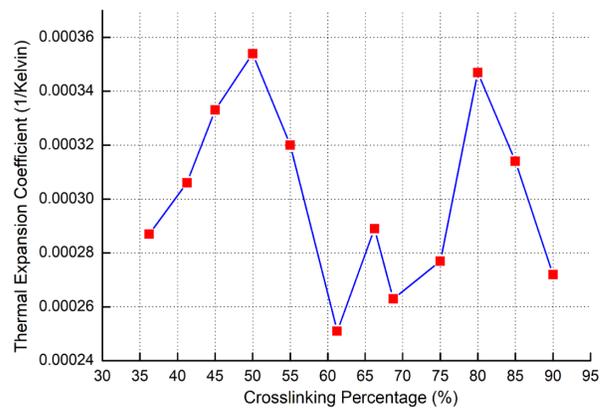


FIG. 16. The crosslinking percentage and corresponding α of the BADGE-IPD system in glassy state.

IV. Discussion and Future Work

In this project, we performed MD simulations on the BADGE-IPD and DGEBD-IPD systems to measure the glass transition temperature and thermal expansion coefficient. Nevertheless, reflecting on the results of the investigation, we did not come to a definitive conclusion that our model mirrored experimental values.

We consider there are several possible reasons that affects the accuracy of our results. Firstly, as mentioned previously, we couldn't find the parameters for some of the bonds, angles, and dihedrals. The guesses we made on these parameters may not good enough to reflect the real interactions. To boost the working efficiency on finding parameters, future groups can also investigate the CGenFF program which automatically types the atoms rather than manually typing the atoms. Secondly, for systems at some of the crosslinking percentages, the thermal expansion coefficient changes smoothly around the glass transition temperature, instead of undergoing a sharp change shown in Figure 13 & 14. Also, in the rub-

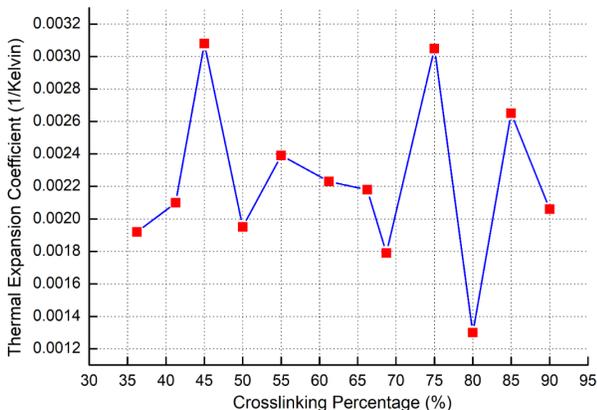


FIG. 17. The crosslinking percentage and corresponding α of the BADGE-IPD system in rubbery state.

bery state, the volume of these systems fluctuates more such that values of the adjusted R-square of linear fitting range from 0.77 to 0.85. Therefore, the inaccuracy in the thermal expansion coefficient will affect the determination on the glass transition temperature.

In addition, the effect of the size of the box was tested by doubling and quadrupling the number of molecules to see the effects on the glass transition temperature. The doubled and original size were compared, but there was not enough time to properly run the test on the quadruple mass system.

The next steps for the project are to determine why these values are not experimentally valid. The issue is likely related to either the force field that was used or the experimental methodology. To investigate if it is an issue with the force field, one could carry out the same experiment but using a different CHARMM force field or even a force field from a different classification. On the other hand, the experiment could be reproduced from start to finish with a different molecular system with known glass transition temperatures and see if those values are valid. We also noticed that density of each system was about double what the density should be (1.89 g/cm^3 v.s. actual values of 1.13 g/cm^3 at 300K). However, the previous year’s program had similarly non-experimental densities but with experimentally valid glass transition temperatures.

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VI. Citations

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