

Molecular Dynamics Simulations of Epoxy Resin Systems to Study Physical Properties

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Abstract

A commercial epoxy resin was modeled at the microscopic, molecular scale. The functional groups of individual monomers were activated, mixed at an elevated curing temperature, and then cross-linked at individual time steps when within a specified cutoff distance. Molecular dynamics simulations were then ran on the cross-linked system, making use of both canonical (NVT) and isothermal-isobaric (NPT) ensemble averages. The glass transition temperature, the thermal expansion coefficient for both the rubbery and glassy states, the isothermal compressibility, and the thermal conductivity were measured for the model system with numerical results given.

Purpose

The broad set of thermosetting polymers classified as epoxy resins are defined as such because the primary cross-linking process involves the reaction of an epoxide group—a three member ring that consists of two carbon atoms and one oxygen atom (See Figure 1). This epoxide functional group can react and bond with a wide variety of molecular bases known as hardeners or curatives. When an epoxide base resin is reacted with a bonding hardener in what is called the curing process, large numbers of these thermosetting reactions take place to form highly linked polymerized chains that are very strongly bonded. This cross-linking reaction between base resin and curative is what gives epoxy resins their distinct structure and physical properties.

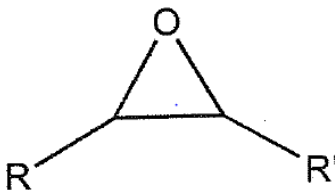


Figure 1: Epoxide Group.

Epoxy resins are used in a wide variety of commercial and industrial applications. They are extensively used in composite structures, particularly in the aerospace industry as adhesives, coatings, and casting materials [1]. The characteristics of epoxy resins that make them so desirable as a material for these applications is their excellent physical and thermal properties. In addition to their excellent adhesiveness, epoxy resins have high strength, low shrinkage, effective electrical insulation, high thermal resistance, as well as low cost and toxicity when compared to other thermoset resins. The properties considered in this study include the glass transition temperature (T_g), the thermal expansion coefficient (α) above and below that temperature, the isothermal compressibility (β), and the thermal conductivity of the epoxy resin system. The purpose in modeling an epoxy resin with computer simulations is to try and predict these physical properties to compare to experimental systems and to study ways of improving them.

Molecular Dynamics (MD) are a class of computer simulations used to study the physical movement of atoms and molecules that are subjected to given forces. The basic procedure in an MD simulation is to divide time into small, discrete time steps (on the order of femtoseconds), calculate the net force acting on each atom for a given time step, and use the calculated force to update the positions and velocities of each atom for the next time step via Newton’s Equation of Motion. The goal of these simulations is to use empirically determined force fields to examine the microscopic interactions between atoms and use the results of these measurements to extrapolate bulk properties that would otherwise need to be measured in a macroscopic laboratory [2].

There are many benefits to using MD to model an epoxy resin system. The greatest benefit is conserving experimental time and resources. Measuring physical properties for many resins with widely varying compositions in a laboratory can be very expensive and time consuming, but rerunning a simulation with different percent compositions is fairly easy. If it can be shown that the model system is an accurate representation of the macroscopic world and can give comparable results do those measured in a laboratory, then it is quite straightforward to make adjustments to the model and explore how to improve the desired physical properties of the resin. Our goal in this study is to do just that: we would like to implement the methods of MD to an epoxy resin, measure its physical properties, and see if the results are directly comparable to experimental data.

Initial System Construction

The epoxy base resins and amine hardeners regarded in this study are based on the composition of typical commercial epoxy resins used for modern applications. Specifically, we modeled the resins and hardeners based on their approximate percent compositions listed in the published Material Safety Data Sheets for the PRO-SET M1002 Resin and PRO-SET M2046 Hardener respectively [3][4]. Figure 2 shows the composition of our model system with the specific mole percentage we chose for each molecule.

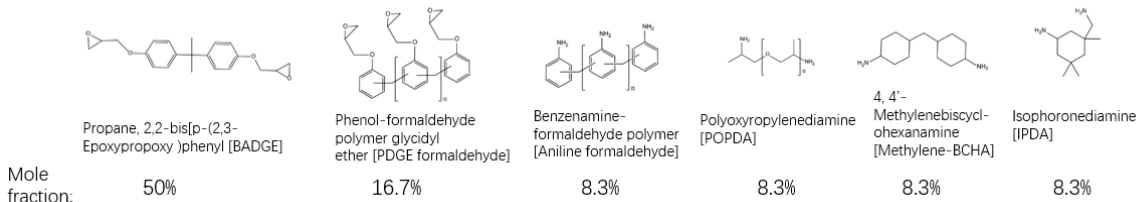


Figure 2: Composition of Model Epoxy Resin System

We constructed individual monomers from organic molecular fragments using the Molefactory extension in the Visual Molecular Dynamics (VMD) program [5]. After the monomers were constructed, we wrote the coordinate positions of the atoms in each monomer to an .xyz file. The atom coordinates were given as input in an NWChem script that used Density Functional Theory to optimize the structural geometry of each molecule with the 6-31G* basis set and B3LYP functional [6]. This NWChem script ran quantum mechanical simulations for the electron orbital densities of the atoms in each molecule to find the lowest energy configuration for the structure of the molecule. Additionally, we implemented a Löwdin population analysis after geometry optimization to determine the partial charge on each atom.

To combine the molecules into a single system, we wrote the optimized coordinates for each one into new .xyz files and then used the Packmol initial configuration software to insert multiples of each according to the above percentages into an initial box system [7]. We applied periodic boundary conditions to this system to remove an external constraint on our system, ensure linear momentum was conserved in our simulations, and to reduce the computational cost. The volume of our original system was chosen to be of a size that would give a density similar to what is listed in the Material Safety Data Sheet for the commercial epoxy-hardener system; our initial density was 1065 kg/m^3 . Once this initial box for our system was created, we used VMD’s topology commands to create a LAMMPS data file [8]. The forces in our LAMMPS simulations were parameterized under the CHARMM36 General Force Field (See Figure 3) as listed by the CHARMM parameter files. The coefficients for any interactions not listed explicitly were parameterized by analogy for a similar set of atoms.

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

Figure 3: Parameterization of Forces Under the CHARMM36 Force Field.

Cross-linking Procedure

The cross-linking procedure used in this study is based on the typical curing reaction of epoxy-hardener systems. The primary amine group in the amine-functional curative reacts with the epoxide group in the base resin to produce the secondary amine group (Figure 4). Then, the secondary amine groups react with epoxide groups to further cross-link with the epoxy resin (Figure 5).

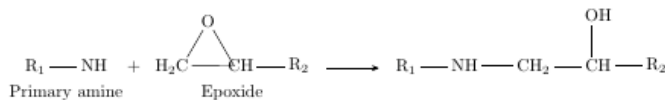


Figure 4: Primary Curing Reaction.

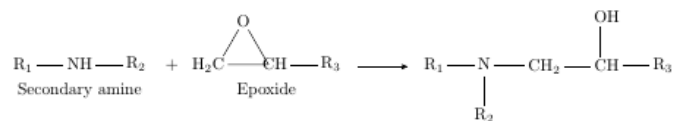


Figure 5: Secondary Curing Reaction.

To construct the cross-linked structure, pre-activation method and cut-off distance were applied without regard for the reaction mechanism that takes place within the curing solution. Under the assumption that the reactivity of the primary amine group and secondary amine group are closed, all amine groups in the packed system were deprotonated thoroughly as shown in Figure 6.

Then, all potential epoxy groups were activated and the ring structure was broken before the cross-linking process to simplify the reaction and bond formation. In experimental conditions, base epoxy and amine hardener are mixed in solution, and hydrogen saturation leads to protonation of the oxygen in each hydroxyl group.

As described before, quantum mechanical calculations in NWChem determined the optimized structures and partial charge of the activated groups again to ensure accuracy since the structure configuration and partial charge distribution will change after activation. In this case, we did not consider self-polymerization of epoxy groups, which means the individual epoxy monomers cannot polymerize. Therefore, the stoichiometric ratio of epoxy groups to amine groups was set to 2:1.

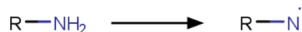


Figure 6: Deprotonation of Functional Amine Group

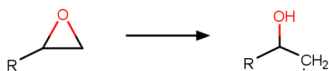


Figure 7: Activation of Functional Epoxy Group

The simulations of the cross-linking process were ran in the LAMMPS software package. The configuration of multiple molecules was rearranged in a local potential energy minimum under the tolerance of 10^{-6} *kcal/mole* before bond creation. During cross-linking we neglected the chemical behavior such as the overlapping of electron orbits, because our purpose in this study is to probe the physical properties of the cross-linked system. We are not focusing on the details of the curing reaction. Instead, at each time step, the distance between a potential reactive pair in the neighbor list was detected and compared with a cutoff distance, whose concept is introduced by the “fix bond/create” LAMMPS command.

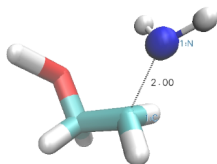


Figure 8: Cutoff Distance for Cross-linking Reaction

If the distance between the two atoms is less than the specified cutoff distance, it will have a certain probability to form the bond and modify the related topological information in the LAMMPS simulation. The probability for the bond creation of both the primary and secondary amine groups was set to 1, again because we are giving more attention to the properties of the cross-linked system than the reaction itself. The cut-off distance of the primary and secondary reactions was set to 2 Angstroms. The simulation was ran in canonical ensemble (NVT) at 600 Kelvin. To describe the stage of cross-linking, the cross-linking percentage is defined as

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

The cross-linking percentage of the molecules in our system is affected by the temperature at which we cross-link, the probability of the reaction, the minimum cut-off distance, and the time duration of the simulation. To increase the cross-linking percentage, we just ran the simulation for a longer time. Finally, cross-linked systems with different cross-linking percentages were generated by the variation of time duration.

Results

Thermal Expansion Coefficient and Glass Transition Temperature

The coefficient of thermal expansion is a measure of how the volume of a system changes in response to a change in temperature, with the pressure held constant. To measure this quantity it is essential that the volume of our system is in equilibrium for a given temperature and pressure. In our LAMMPS simulations, we used thermodynamic ensemble commands to fix the external temperature and pressure of

our system. We used the canonical ensemble (NVT) when we wanted to keep the volume and temperature of the system to remain constant and the isothermal-isobaric ensemble (NPT) when we wanted to allow the volume of our system to fluctuate in response to an externally applied pressure.

After we obtained our fully cross-linked system with the method described above, we ran an energy minimization of our system with both force and energy stopping tolerances of 1.0e-6. The purpose of this minimization is to remove excess energy that was in our original system or that was generated in the cross-linking process. We then ran 500 ps of NVT at 600 Kelvin followed by 500 ps of NPT at 600 Kelvin and 1 atmosphere to equilibrate first the temperature and then the pressure of our system to the desired external constraints. The NVT ensemble was ran first to allow the temperature of the system to reach 600 Kelvin without any effects of volume change, and then the NPT was ran when the temperature was already equilibrated to allow the volume to change due only to the external pressure. The volume of the system was averaged over the last 0.5 ps of NPT equilibration and we took the standard deviation of the volume in that time. We then began the process of gradually cooling our system in a similar method as that implemented by Wu and Xu [10] and also by Wang et. al [11], and at each 20 Kelvin interval, 1 ps of NVT equilibration and then 1 ps of NPT equilibration was done to allow the system's volume to equilibrate at that temperature and a constant 1 atmosphere pressure. The volume for the last 0.5 ps of each NPT equilibration was averaged and the standard deviation was taken. This incremental cooling and equilibration was done to cool the system from 600 Kelvin to 100 Kelvin.

The thermal expansion coefficient is defined as

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

meaning it is the slope of the graph of the natural log of the volume vs. the temperature at a constant pressure. However, this is not a fixed value at all temperatures. For a thermoset polymer such as we have observed, there is a phase transition in the material that causes a significant change in the thermal expansion coefficient and heat capacity. This phase transition is marked at what is known as the glass transition temperature T_g . Below this temperature the epoxy resin system is said to be in a stiff, "glassy" state, and above this temperature the resin is considered to be in the more flexible "rubbery" state [1]. The glass transition temperature is another essential quantity we would like to measure for our model system because in a practical application the stiffness of the material at expected temperatures needs to be considered in determining the benefits of one resin over another. Figure 9 shows the graphed results of the natural log of our equilibrated volume with respect to the fixed temperature at a constant pressure of 1 atmosphere.

The left side of the graph shows the system in the glassy state, and the right side shows the rubbery state. We calculated a linear regression for both of these phase states to measure the thermal expansion coefficient for both. The data points from 240 Kelvin to 340 Kelvin were ignored for the linear fits to ignore the effects of the actual phase transition on the slope of either phase. The temperature at which these two linear fits intersect was measured as the glass transition temperature. In this study, our measured thermal expansion coefficient was 1.88e-4 K^{-1} in the glassy state and 4.93e-4 K^{-1} in the rubbery state, with a glass transition temperature of 314.21 Kelvin. The average standard deviation for the volume measurements were around 1% of the measured value, so we believe these are accurate characteristics of our system in equilibrium.

Isothermal Compressibility

We followed a similar procedure for our measurement of the isothermal compressibility coefficient of our system. Our cross-linked system that had been equilibrated to 1 atmosphere and 600 Kelvin was used as the initial state, and then we increased the isotropic external pressure exerted on the system box at a rate of 5 atmospheres/ps. At each 5 atm interval the system was subjected to 1 ps of NPT equilibration at that pressure and a constant 600 Kelvin, and the volume for the last 0.5 ps of the simulation was averaged to find the equilibrium value.

Isothermal compressibility is defined as

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\left(\frac{\partial \ln(V)}{\partial P} \right)_T \quad (2)$$

Again, it can be found via the slope of the natural log of volume, but in this case with respect to a change in pressure with temperature constant, and then the negative sign to make the coefficient itself positive

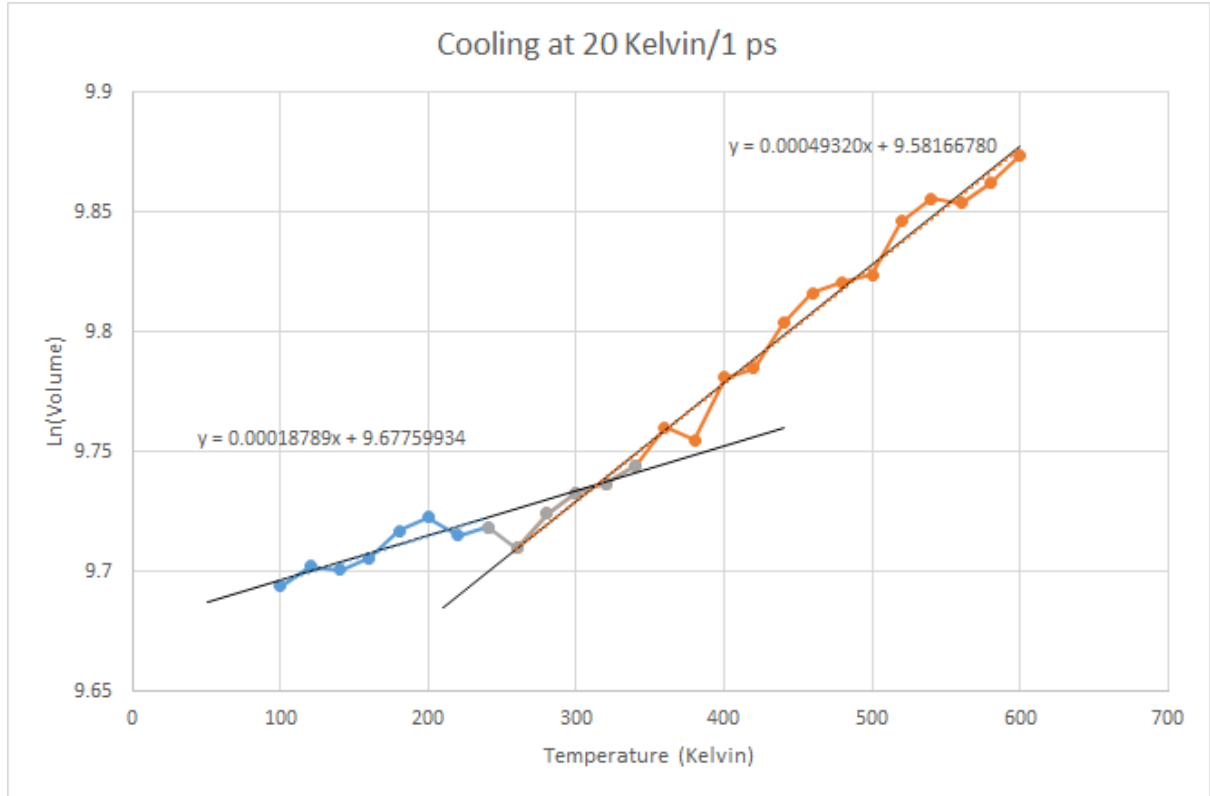


Figure 9: Thermal Expansion and Glass Transition Temperature

(because an increase in external pressure generally causes a decrease in volume). Below is our results for the natural log of the equilibrated volume of our system for a range of 1 atm to 40 atm (Figure 10)

Our measured isothermal compressibility coefficient is $1.92e-4 \text{ atm}^{-1}$ or in SI units $1.89e-9 \text{ Pa}^{-1}$. The standard deviation of each average volume was greater for this simulation than for our measurement of thermal conductivity; the standard deviation was on average 5% of the measured value for each measurement, and a linear fit seemed less accurate for this data. We attribute this difficulty in measurement to the fact that the changes in volume in response to a change in pressure are much smaller in magnitude compared to a change in temperature, and this has to do with the fact that our system is a solid and does not expand or contract as significantly as a gas would due to an external pressure. The fractional changes in volume (roughly 2%) make it much more difficult to measure. To improve upon this result in the future, the system could be equilibrated for a longer number of time steps and volumes measured over a larger range of pressures.

Thermal Conductivity

Thermal conductivity is a significant thermophysical property for materials science. In engineering applications, the thermal conductivity of epoxy resins is an important parameter to be considered when it is coated or adhered between two materials at different temperatures. Therefore, we measured the thermal conductivity of our epoxy resin systems and explored the relation between it and cross-linking percentage. By strict definition, thermal conductivity is the amount of heat per unit time per unit area that can be conducted through a plate of unit thickness of a given material. The general equation for thermal conductivity is

$$\vec{q} = -k\vec{\nabla}T \quad (3)$$

'q' is the energy cross unit cross section area per unit second. 'T' is the temperature. 'k' is thermal conductivity.

The one dimensional temperature gradient across the simulation system was generated by adding energy to hot reservoir and subtracting energy from cold reservoir, which are located in the middle and two sides along the x-axis respectively. When the energy flux and temperature are distributed uniformly

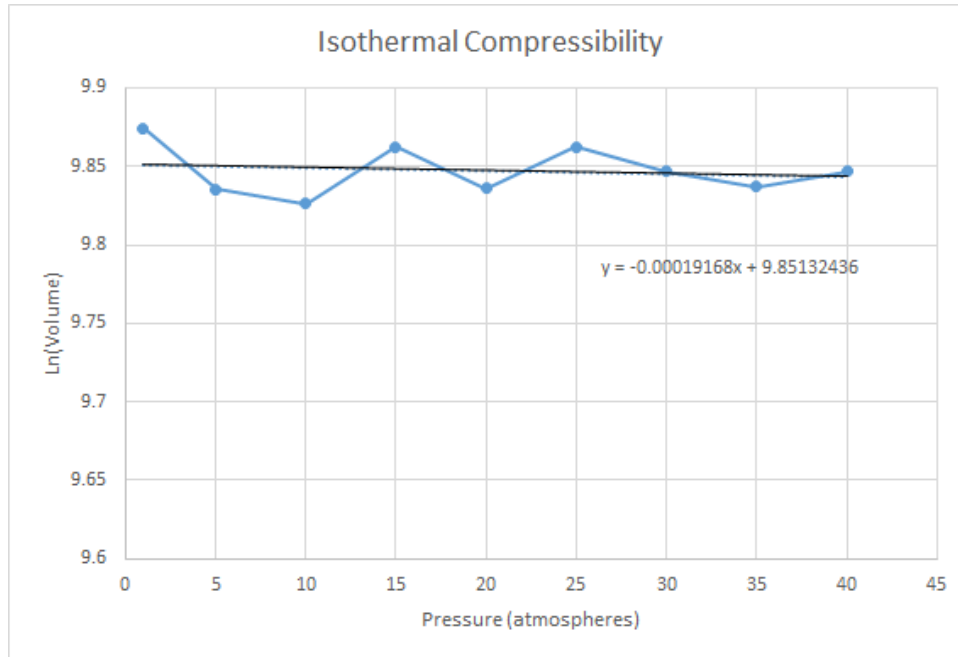


Figure 10: Isothermal Compressibility

from the cold reservoir to the hot reservoir, the energy addition in the hot reservoir and subtraction from the cold reservoir per unit time will be the same with energy flux across any cross section in the experiment domain and the thermal conductivity can be determined. The energy flux here is defined as the rate of energy transfer per unit area.

We ran simulations for cured epoxy resin systems with six different cross-linking percentages, which are 5%, 20%, 35%, 50%, 65% and 80%, and at two different temperatures, 300 K (in the glassy state) and 550 K (in the rubbery state). Before generating the temperature gradient, the systems were minimized in potential energy for 1 ps, ran in canonical ensemble for 5 ps and in isothermal-isobaric ensemble for 5 ps for relaxation. The energy flux was set to $2.7e13 \text{ W/m}^2$ and performed for 130 ps for equilibration. We read temperature distribution during final 5 ps. We can easily tell that the temperature decrease linearly from the hot reservoir to cold reservoir as shown in figure. We neglect the data whose temperature is beyond the glass state or rubbery state temperature region as well as the data at hot reservoir and cold reservoir when linear fitting them to measure the thermal conductivity. The thermal conductivities with respect to different cross-linking percentages in 300 K and 550 K were analyzed and shown in Figure 11. As you can see, thermal conductivities of the epoxy resin system in glassy state are generally greater than those in rubbery state. Thermal conductivity in 300 K and 550 K reach local maxima at 35% and 50% in terms of cross-linking percentage respectively. We noticed that the epoxy resin system with 5% cross-linking degree has a similar thermal conductivity at the two different temperatures. The reason could probably be no glass transition or low transition temperature if the epoxy resin is not cured enough and both of them are in the rubbery state.

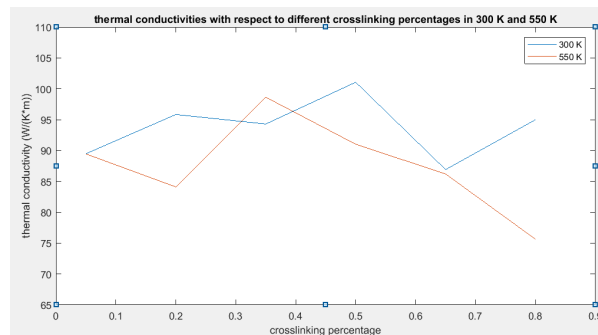


Figure 11: Thermal Conductivity for Different Cross-linking Percentages at Two Different Temperatures.

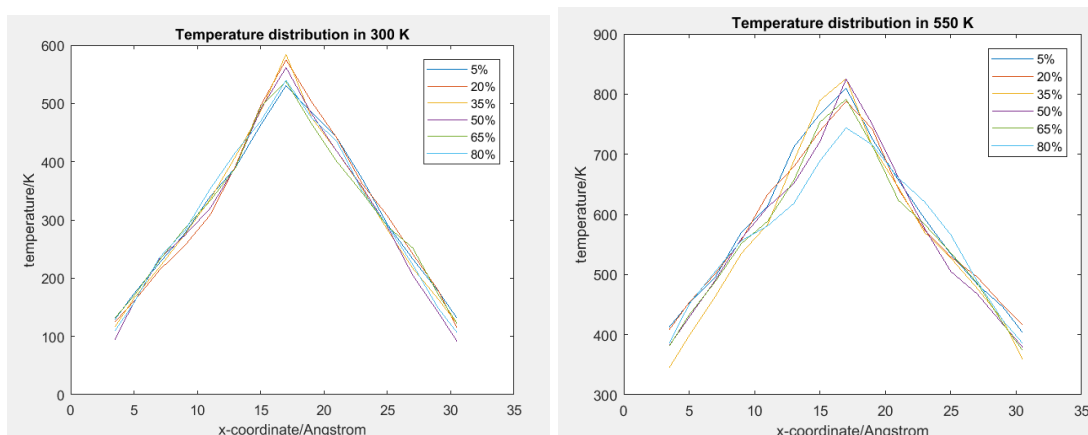


Figure 12: Distribution of Temperatures for Different Cross-linking Percentages

However, compared with the thermal conductivity measured by real experiments, 0.221 W/Km in powder filled epoxy resin by Lin et. al [12] and 0.35 W/Km in common, our results, nearly 90 W/Km , are much larger than those. The potential reasons for the inaccuracy in molecular dynamics could be the length of simulation domain (which is 3 nm) is too small and the temperature gradient is too high (10^1 K/m) so that the atoms in the system do not behave according to real conditions and the heat transfer cannot be described by the general equation above.

Methods to Improve the Accuracy of Our System

For the measurement of physical properties, we have placed high importance on the improvement of accuracy of our system. The easiest way to do this is to extend the size of our system. It can reduce random error and decrease the sensitivity of our system to fluctuate. However, the size of the system domain is limited in molecular dynamics simulations; the simulation of a large number of atoms may waste large amounts of computational resources. We need to make a trade-off between accuracy and cost while choosing the size of our simulation. Moreover, we can still improve the accuracy of our systems by regenerating the functional groups. All amine and epoxy groups in this study were activated thoroughly before cross-linking, and the functional groups in the molecules that were not involved in cross-linking need to be modified back into an unactivated state.

The method we are currently researching and trying to implement to regenerate the functional groups is as follows. The epoxy groups are regenerated by bond formation. Hydrogen atoms are created randomly through the system, bonded into amine groups and hydroxyl groups and the remaining are removed from the system. Before each step, minimization is performed for 5 picoseconds for relaxation. Finally, the partial charge of each atom is updated, which is obtained by quantum mechanics calculations using NWChem.

Conclusion

The thermoset epoxy resin systems with different cross-linking percentages were generated successfully using VMD, NWchem, Packmol, and LAMMPS software packages. Under the CHARMM36 force field, we are able to simulate the molecular dynamics behavior of our epoxy resin systems. The numerical results we have obtained except for thermal conductivity in this study are comparable to those determined by real experiments. Further simulations of this type need to be conducted to measure the thermal conductivity. The epoxy resin model also needs to be improved for accuracy by regeneration of functional groups.

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