Glass Transition Temperature of Cross-Linked Epoxy Polymers: a Molecular Dynamics Study

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Recently, epoxy polymers have been used in different applications and research fields due to their superior properties. In this study, the classical molecular dynamics (MD) was used to simulate formation of the epoxy polymer from cross linking of the EPON 828 with DETA curing agent, and calculate the glass transition temperature (T_g) of the material. A series of MD simulations were independently carried out on the cross-linked epoxy polymer in a range of temperatures from 600 K down to 250 K, and the density of the materials was calculated at the end of each run. Through the linear fitting between temperature and density above and below the glass transition temperature, T_g was estimated. The glass transition temperature of the pure DGEBA were also estimated through the same procedure and compared with those of the cross-linked polymer. Molecular simulations revealed significant increase in T_g of the cross-linked epoxy polymer as a result of newly created covalent bonds between individual chains.

Keywords: Cross linking; Epoxy polymers; Glass transition temperature; Molecular dynamics.

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1. INTRODUCTION

Epoxies are thermosetting polymers with cross-linked structures, obtained from reaction between epoxy resins and hardeners. Epoxies with 3D cross-linked structures have superior properties, making them attractive materials for different applications including coatings, composite materials, adhesives, electronic packaging, etc. The cross links are irreversible covalent bonds and the cross-linked polymers cannot be re-melted and re-shaped.

Previously, the study of cross-linked polymers was mainly based on experimental trials, while in recent years, considerable attention has been paid to using the modeling and simulation approaches for development of polymers and polymer (nano)composites [1], using simulation methods in different length and time scales. In this context, there are few studies related structure and properties of cross-linked polymers and their composites. [2-11].

The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) also known as EPON 828, can be cross-linked in presence of diethylenetriamine (DETA) curing agent to yield one of the most important members of epoxy polymers.

In this study, molecular dynamics, as one of the most effective and popular simulation methods, was used for the first time to simulate the cross linking of the DGEBA resin with DETA curing agent, and estimate the glass transition temperature of the yielded epoxy polymer.

2. MODELING AND SIMULATION DETAILS

2.1 Molecular Structures of DGEBA and DETA

The molecular structures of DGEBA or EPON 828 resin ($C_{21}H_{24}O_4$) and DETA curing agent ($C_4H_{13}N_3$) are schematically represented in Fig. 1.
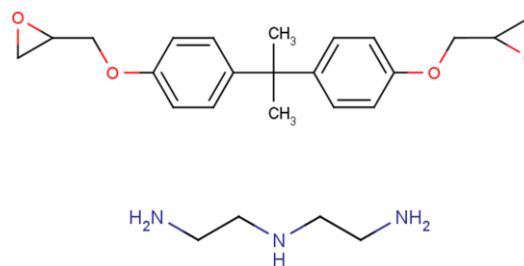
Fig. 1 – Molecular structures of EPON 828 (top), and DETA (bottom).

DGEBA is a bi-functional reactant with two epoxide groups at two ends, while DETA has five reactive sites and hence is a multi-functional (fivefold-functional) reactant. DGEBA and DETA are able to produce 3D cross-linked epoxy polymers.

Each DETA molecule can react at most with five DGEBA molecules, each of which capable of being connected to another DETA molecule through its opposite epoxide head. Thus, the ideal composition ratio of DGEBA/DETA in the blend is 5/2.

2.2 Cross Linking Mechanism

In the previous subsection, the molecular structures of the molecules and also the potential curing sites were introduced. The C−O bond in each epoxide group need to be broken in order to form a reactive −CH2 site (Fig. 2), capable of being cross-linked to DETA molecule.

Fig. 2 – Conversion of an original epoxide group to a reactive one through breaking the C−O bond

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In the blend of resin and hardener, under appropriate circumstances, the molecules start to move around and the curing sites will have the chance of getting sufficiently close to each other, so that the covalent bonds could be created between C and N atoms. A convergence of 100% will be achieved if all potential covalent bonds are created, though it is rare in natural conditions. Fig. 3 shows a fully cross-linked epoxy polymer, in which one DETA molecule is connected to five DGE-BA molecules through covalent bonds.
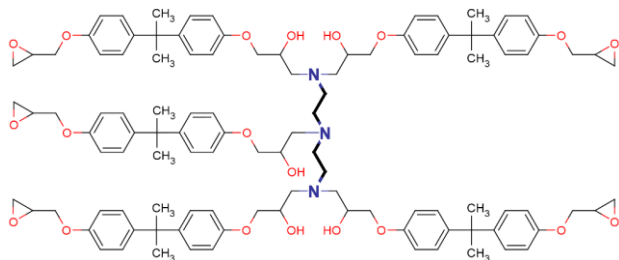
Fig. 3 – Schematic representation of a fully cross-linked set of DETA and EPON 828 molecules

However, in actual reactions, the degree of cross linking (convergence) is usually less than 100%.

In order to obtain cross-linked epoxy polymers from resin and curing agent using MD method, one can either use a previously created cross-linked molecule with a certain degree of cross linking to construct the simulation box with given density and number of representative molecules, or alternatively create a simulation box including primary molecules of resin and curing agent without any cross link, and perform a cyclic set of minimization, equilibration and dynamics runs to reach a satisfactory cross-linked structure.

The second method is complicated and time consuming to establish, especially in the case of large systems. Nevertheless, it is much more accurate and realistic than the first one, and hence, is absolutely recommended to be used rather than the first method. Moreover, it can be applied flexibly with respect to many parameters such as, cross linking cut-off distance, content of curing agent, etc. Here, the second method with the same priority for the primary and secondary reactions was applied in this study.

Another important concern is final attainable degree of cross linking (convergence), i.e. the ratio of reacted sites to all possible reactive ones. It can be controlled through the cross linking cut-off distance, temperature, and to some extent, content of the curing agent.

Cross linking cut-off distance is a crucial factor in obtaining desirable degrees of cross linking, and subsequently reasonable cross-linked structures. Taking small cut-off values will lead to small degrees of cross linking, and vice versa. In other words, the maximum attainable convergence will be restricted by the cut-off value, as the creation of covalent bonds can occur solely within a predefined cut-off distance around the reaction sites. Therefore, in order to achieve high degrees of convergence, large or even no cut-off values must be imposed. In such cases, on the other hand, the resulted polymer will be excessively strained and difficult to get equilibrated. These issues should be taken into account for assigning appropriate cut-off distances.

The attraction force between pair of atoms beyond the large distances can be ignored. Different cut-off values, e.g. 4-10 Å [12, 13, 14-16], 5-10 Å [17], 7-8 Å [18] and 6 Å [7], have been applied in previous studies. Regardless of the attainable degree of cross linking, a cut-off value of 5.64 Å, four times the C−N bond length [19], was adopted in our scheme to avoid highly strained structures.

2.3 Software and Force-Field

All simulations were performed using Accelrys Materials Studio 5.5 software package [20]. The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force-field was employed in all minimization and dynamics simulations. COMPASS, as the new version of Polymer Consistent Force-Field (PCFF), is an ab-initio force-field parameterized for different molecules including most common organics, small inorganic molecules, and polymers to predict various properties of the materials [21-26].

The total energy function in COMPASS force-field is composed of 12 terms including valence and non-bonded interaction terms [21]. Valence terms fall into two categories: diagonal (bond stretching, bending, torsion, and out-of-plane potentials), and off-diagonal cross-coupling terms (describing the interactions between diagonal terms). The non-bonded interactions, including relatively short range van der Waals (vdW) and long range electrostatic interactions, are described by Lennard-Jones (LJ) 9-6 and Coulombic functions, respectively.

The atom-based summation method with cut-off radii of 15.5 and 18.5 Å, respectively for minimization and dynamics tasks, was used in calculation of the vdW interactions. Long range corrections was also applied on the cut-off radii to smoothly eliminate the non-bonded interactions over a range of distances and avoid the discontinuities caused by direct cut-offs. The electrostatic interactions, on the other hand, were dealt with through the Ewald summation method [27] with the accuracy of 10-4 and 10-5 kcal/mol for minimization and dynamics tasks, respectively.

3. SIMULATION AND DATA COLLECTION

The simulation of cross linking process and data collection were carried out in five main steps, as follows:

I. construction and energy minimization;
An amorphous cell composed of 10 DGEBA and 4 DETA molecules with a low density of 0.5 g/cm3 was constructed at room temperature and under periodic boundary conditions. The weight fraction of DGEBA:DETA in simulation box was chosen to be 100:12, based on the composition ratio (5/2) and the molecular weights of DGEBA (340.41) and DETA (103.17).

The system was subjected to 1000 steps energy minimization to reach the nearest local minimum. The task employed both steepest descent and conjugate gradient (Fletcher-Reeves) algorithms, with the convergence criteria of 1000 and 10 kcal/mol.Å, respectively.

II. pre-equilibration;

To reach the global minimum of potential energy, 2 ns isothermal-isobaric (NPT) dynamics with time step of 1 fs at 298 K and 1 atm was performed. The Nose-Hoover thermostat [28, 29] and Andersen barostat [30] were used to control, respectively, the temperature and pressure of the system during the simulation.

The time evolution of the energy and temperature of the system was monitored so that the equilibration condition could be judged.

III. creation of covalent bonds;

Once the structure got equilibrated, the distances between pairs of reactive atoms were measured, and covalent bonds were created between appropriate atoms (those within cross linking cut-off distance). Thereafter, a smart minimization task with 1000 iterations was performed, in order to release the stress imposed on the system. After minimization, the system was subjected to 100 ps high temperature canonical (NVT) dynamics at 500 K and 1 atm, in order to give enough kinetic energy to the molecules and increase the probability of curing sites to fall within the reaction cut-off distance. Again, the distances between pair of remaining reactive atoms were measured, and new covalent bonds were created, if possible. After each bond creation stage, the degree of cross linking could be calculated. The step 3, as a cyclic combination of bonding-minimization-dynamics, was repeated until 13 new covalent bonds from 20 potentially possible bonds were created, i.e. the convergence of 65% was achieved. The simulation boxes before and after cross linking are represented in Fig. 4. For clarity, the DETA molecules in non-cross-linked structure, and created bonds in cross-linked structure are shown in CPK and Ball-Stick styles, respectively.
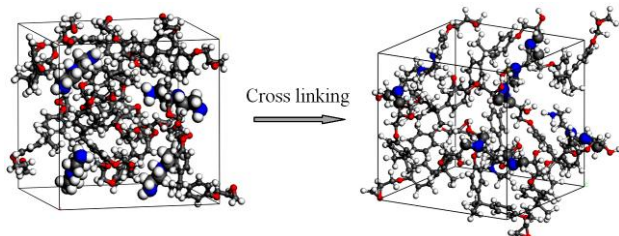
Fig. 4 – Conversion of uncured blend containing 10 EPON 828 and 4 DETA molecules (left) to final cross-linked epoxy polymer with convergence of 65% (right).

It should be noted again that the relatively small cut-off distance (5.64 Å) restricted the maximum attainable degree of cross linking.

IV. post-equilibration;

The final cross-linked structure was equilibrated through 2 ns NPT dynamics, with the same procedure as in step 2, to achieve the most stable configuration for calculation of the properties.

V. data collection;

The equilibrated structure was subjected to 8 independent NPT dynamics for 50 ps in 8 different temperatures from 250 K to 600 K. the time step and pressure were set to 1 fs and 1 atm, respectively. The final density at the end of each run was determined for further analyses.

4. RESULTS AND DISCUSSION

The densities of the final structure in different temperatures, calculated in previous section, are plotted with respect to temperature in Fig. 5. The glass transition temperature is the indicated point where the two trend lines intersect, i.e. about 396 K.
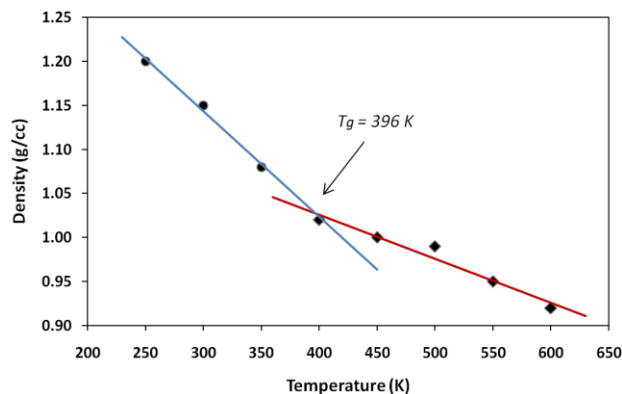
Fig. 5 – Variation of the density in terms of temperature. The intersection of the trend lines indicates the glass transition temperature (T_g)

In order to validate the simulation results, the calculated T_g and density (at room temperature) were compared to some reported experimental data for the same epoxy polymer (DGEBA+DETA). The comparisons are summarized in Table 1.

Table 1 – Comparison of the obtained T_g and density with reported experimental values.

Density (@ 300 K), g/cc			T_g, K		
Current study	Ref. [31]	Ref. [32]	Current study	Ref. [33]	Ref. [34]
1.15	1.16	1.19	396	402	402

As can be seen, there is excellent agreement between the simulation results and experimental data.

The density and glass transition temperature of the pure DGEBA were also estimated through the same procedure, and compared with those of the cross-linked polymer in Table 2.

Table 2 – The simulated values of the density at room temperature and T_g for both uncured DGEBA and cross-linked epoxy polymer

Property	Pure DGEBA	Cross-linked polymer
Density (@ 300 K), g/cc	1.08	1.15
T_g, K	348	396

It is evident from Table 2 that the glass transition of cross-linked polymer occurs in considerably higher temperatures in comparison to the uncured DGEBA.

5. CONCLUSIONS

In this study, the molecular dynamics method with COMPASS force-field was used for simulation of cross linking between epoxy EPON 828 with DETA curing

agent. Tracking the density variation with temperature, the glass transition temperature of both cross-linked epoxy polymer and uncured epoxy were estimated. The comparisons demonstrated the accuracy of presented cross linking scheme, and usefulness of molecular dynamics in prediction of the material properties of the cross-linked epoxy polymer.

The simulation results revealed considerable increase in glass transition temperature of the cross-linked epoxy polymer in comparison to the pure DGE-BA, due to new covalent bonds. The glass transition is also expected to take place at even higher temperatures by increasing the degree of cross linking through assigning larger reaction cut-off distances and using more contents of curing agent.

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