Quantitative Comparison of Atomistic Simulations with Experiment for a Cross-Linked Epoxy: A Specific Volume−Cooling Rate Analysis

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Steps for preparing the molecular models of the cross-linked epoxy network

1. Molecular model of Epon 1001F and 4,4'-DDS

Models of a single molecule each of Epon 1001F and 4,4'-DDS were created in the Chem3D 16.0 software, which is part of the PerkinElmer Informatics ChemOffice Professional Ultra software package.[1, 2] In the case of Epon 1001F, we used the *active* form of the molecule (shown in **Figure S1**). The advantage of using this active form is that the topological modifications needed to transform the model from the unreacted mixture of Epon 1001F and 4,4'-DDS to the cross-linked network are drastically simplified. We note that the use of such an active form of the epoxy monomer has been the standard practice in creating the molecular models of cross-linked epoxy networks since the earliest of studies in literature[3] and has no effect on the chemistry of the cross-linked network. The two molecules were saved in the SYBYL2 file format (mol2).

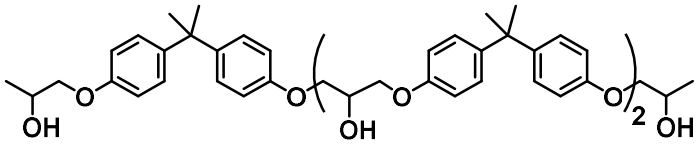

Figure S1: Chemical Structure of 'active' Epon 1001F

2. Force-Field, Partial Charges, and Topology

We used the AmberTools16[4] suite to apply the partial charges and force-field parameters to the models of Epon 1001F and 4,4'-DDS. Specifically, we used the Antechamber tool to identify the appropriate atom types for the general AMBER force-field[5, 6] (GAFF) and apply the partial charges using the Austin Model 1 with bond charge correction[7, 8] (AM1-BCC). Then, we used the LEaP program to generate files containing the coordinates and the topology of the molecular model in formats that were compatible with AMBER[4] simulation package. Finally, we then used the amber2lammps.py python script, which is distributed with the LAMMPS[9] simulation package, to obtain data files for the models of Epon 1001F and 4,4'-DDS which were compatible with LAMMPS.[9]

3. Preparing the Reaction Mixture

Two molecules of the epoxy monomer Epon 1001F and one molecule of the cross-linker 4,4'-DDS were merged in a simulation box using LAMMPS and this box was then replicated nine times in each of the three cartesian dimensions, such that the resulting simulation box comprised of 1,458 molecules of

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Epon 1001F and 729 molecules of 4,4'-DDS. Five replicas of this reaction mixture were then simulated. Simulations were performed for each replica at a temperature of 800 K and a pressure of 10.13 MPa (100 atm) for a simulation time of about 10 ns. In order to obtain five independent replicas, we varied the seed for the random number generator that was used to obtain the initial velocities of the trajectory. Additionally, the exact simulation time for the replicas was varied in steps of 200 ps, such that the first replica of the mixture was simulated for 10 ns and the fifth replica was simulated for 11 ns.

4. Simulated Annealing to Identify Connectivity Sequence

We used the simulated annealing (SA) method to identify and optimize the connectivity sequence between each of the nitrogen atoms of the cross-linker molecules (4,4'-DDS) and the end carbon atoms of two epoxy monomers molecules (Epon 1001F) in the five independent replicas of the mixture. The details of the simulated annealing technique[10] and the applications[11-13] of the technique for preparing models of cross-linked models has been described in detail elsewhere. The formation of short cycles (rings or loops) was explicitly prohibited by allowing only a single connection between a given pair of Epon 1001F and 4,4'-DDS molecules, since the probability of such cyclizing reactions is known to be negligible.[14] In **Figure S2**, the probability distribution for the distances of the 2,916 connections in the reaction mixture is shown. Initially, these connections were made using a random number generator, which was then subjected to SA optimization for the purpose of minimizing the sum of the squares of the individual distances of each of the connections. As can be seen in that figure, the simulated annealing optimization technique drastically minimizes the average connection length from a value of about 70 Å to 10 Å.

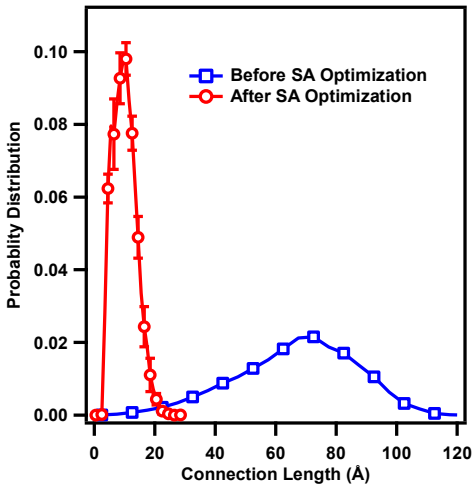

Figure S2: Probability distribution of the 2,916 connections between molecules of Epon 1001F and 4,4'-DDS before and after simulated annealing based optimization.

5. Directed Diffusion to Accelerate the Diffusion of Epon 1001F and 4,4'-DDS

We used the directed diffusion (DD) protocol to accelerate the diffusion of the Epon 1001F and 4,4'-DDS molecules based on the connectivity sequence identified in the previous step. This protocol has been described elsewhere.[15] In experiments, the diffusion of reactants in epoxy networks slows down drastically with an increase in the degree of conversion or curing of the network. As a result, the curing of epoxy networks is typically performed for several hours at temperatures above the glass transition.[16]

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Since such time-scales are inaccessible via atomistic simulations, we accelerate the diffusion process by applying weak harmonic restraints that are gradually strengthened in 12 stages by increasing the harmonic force constant and reducing the equilibrium length.[15] The application of such adaptive restraints in 12 stages (see **Table S1**) allows the connection length to evolve from an average distance of about 10 Å to the bond length prescribed by the GAFF[5, 6] force-field (1.458 Å). Since Van der Waals forces would ordinarily limit the distance between the terminal carbon atom of Epon 1001F and the nitrogen atom of 4,4'-DDS to no less than 3.3 Å, pairwise interactions between these connecting atoms are excluded. At each stage of the DD technique, the models were simulated at a temperature of 700 K and a pressure of 10.13 MPa (100 atm) for a simulation duration of 37.5 ps.

Table S1: Schedule of the Directed Diffusion Protocol

Stage	1	2	3	4	5	6	7	8	9	10	11	12
Harmonic Force Constant (kcal mol^{-1} Å^{-2})	0.0625	0.125	0.25	0.25	0.25	0.25	0.5	1	5	25	125	333.27
Equilibrium Length (Å)	15	12	9	6	3	1.5	1.5	1.5	1.5	1.5	1.5	1.458

In **Figure S3**, we show the average connection length and the associated variance at the beginning and at the end of each of the 12 stages. As can be seen in that figure, the combination of the harmonic restraints and the elevated temperature allows a rapid diffusion of the Epon 1001F and 4,4'-DDS molecules. Conceptually, the use of such harmonic restraints to accelerate diffusion bears similarity to the use of umbrella sampling for biasing the sampling of a given set of order parameters.

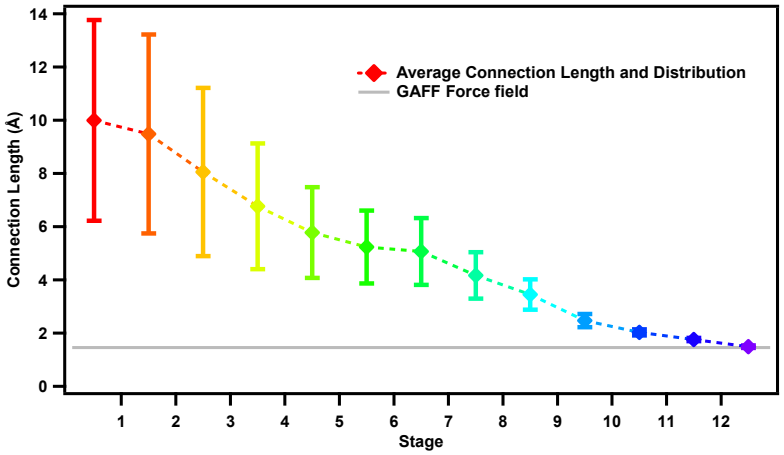

Figure S3: Evolution of the connection length and distribution before and after each stage the DD technique

6. Transformation of the Topology to Obtain Cross-linked Network

In this work, we made no attempt to study or simulate the reaction mechanism underlying the formation of the cross-linked network. The classical methods used in this work are unsuitable for such a purpose. Instead, we simulate the diffusion of Epon 1001F and 4,4'-DDS molecules to obtain a well-packed amorphous state for preparing models of the cross-linked network. In experiments, stochastic encounters of the epoxy group on the Epon 1001F molecule and the amine group on the 4,4'-DDS

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molecule result in a chemical reaction. In this work, we substitute the reaction mechanism with a transformation of the connections optimized (SA) and relaxed (DD) in previous steps by: (1) deleting a hydrogen atom bonded to each of the two terminal carbon atoms of the Epon 1001F molecule and the two hydrogen atoms bonded to each of the two nitrogen atoms of the 4,4'-DDS molecule; (2) changing the values of the partial charges on the atoms in the vicinity of the new bonds to those calculated by the AM1-BCC model; and (3) modifying the local topology (angles, dihedrals, and impropers) as necessary to be consistent with GAFF. A custom code was used for this purpose.

7. Final Relaxation

The model of cross-linked epoxy for each of the five replicas obtained above were relaxed for 10 ns using MD simulations at a temperature of 820 K and a pressure of 5 MPa. As an additional check, we show the distribution of the end-to-end distances of the relatively flexible Epon 1001F molecules in the reaction mixture and after the relaxation of the cross-linked network in **Figure S4**. As can be seen in this figure, the distribution of the end-to-end distances is essentially unchanged before and after the cross-linking protocol, showing that the application of the harmonic restraints during the directed diffusion does not lead to any unphysical stretching or deformation of the Epon 1001F molecules.

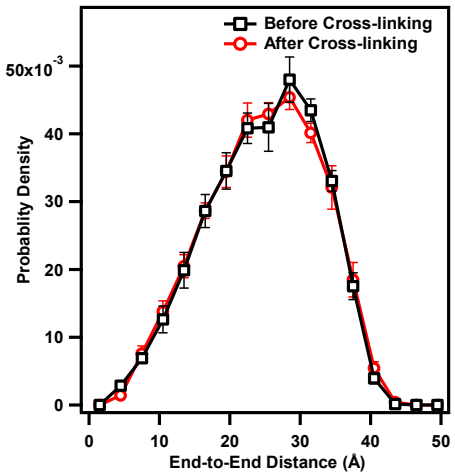

Figure S4: Distribution of the end-to-end distances of the Epon 1001F molecules in the reaction mixture and the relaxed structure before and after cross-linking respectively.

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