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Coarse-Grained Molecular Dynamics Study of the Curing and Properties of Highly Cross-Linked Epoxy Polymers

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ABSTRACT: In this work, a coarse-grained model is developed for highly cross-linked bisphenol A diglycidyl ether epoxy resin with diaminobutane hardener. In this model, all conformationally relevant coarse-grained degrees of freedom are accounted for by sampling over the free-energy surfaces of the atomic structures using quantum mechanical simulations. The interaction potentials between nonbonded coarse-grained particles are optimized to accurately predict the experimentally measured density and glass-transition temperature of the system. In addition, a new curing algorithm is also



developed to model the creation of highly cross-linked epoxy networks. In this algorithm, to create a highly cross-linked network, the reactants are redistributed from regions with an excessive number of reactive molecules to regions with a lower number of reactants to increase the chances of cross-linking. This new algorithm also dynamically controls the rate of cross-linking at each local region to ensure uniformity of the resulting network. The curing simulation conducted using this algorithm is able to develop polymeric networks having a higher average degree of cross-linking, which is more uniform throughout the simulation cell as compared to that in the networks cured using other curing algorithms. The predicted gel point from the current curing algorithm is in the acceptable theoretical and experimental range of measured values. Also, the resulting cross-linked microstructure shows a volume shrinkage of 5%, which is close to the experimentally measured volume shrinkage of the cured epoxy. Finally, the thermal expansion coefficients of materials in the glassy and rubbery states show good agreement with the experimental values.

INTRODUCTION

Epoxy resins are widely used as adhesives for a wide range of applications in electronic packaging, automotive, and aerospace industries due to their unique set of properties, including excellent thermal and mechanical stabilities, which are unmatched to those of other thermoset resins.^{1–3} Despite recent experimental advances in the microstructural characterization of these materials, experimental investigations of the dominant molecular mechanisms still suffer from complications and difficulties associated with collecting conformation-specific data, especially during deformation.^{4–6}

Molecular dynamics (MD) simulations have been recently utilized to deduce molecular details of the plastic flow, glassy response, and pressure and temperature dependences of polymeric systems.^{7,8} However, MD simulations typically suffer from severe limitations on the spatial and temporal scales. These limitations are also more pronounced in simulations of polymeric materials, especially when comparatively large simulation cells are needed to simulate statistically independent material properties. One way to overcome these limitations is to reduce the number of degrees of freedom in the atomic simulations by mapping the atomic structure to a group of coarser particles, called "super atoms", while properly averaging the high-frequency internal degrees of freedom of the molecule. This process leads to a lower number of degrees of freedom and softer

interparticle potentials compared with MD potentials, which can dramatically decrease the effective time of the simulation.

Coarse-graining approaches can be typically grouped into two techniques. In the first technique, coarse-graining is achieved by optimizing the interparticle potentials to match certain macroscopic physical properties. Examples of this include coarsegraining the force fields by optimizing the potential fields for partitioning of free energy between the polar and apolar phases of the lipid and surfactant^{9,10} or optimizing them for density and surface tension of the surfactant/water systems.¹¹ In this technique, the exact one-to-one mapping of atomic groups to super atoms introduces a large number of parameters to be optimized. Thus, for systems with different monomers, the optimization becomes impractical. Instead, simplified potential fields are often used,^{4,12} which poorly simulate the conformation of chains in the network. In the second technique, the focus is on matching the structural aspects of the material, such as the centroid, mass, and angular momentum, through adjusting the mean forces derived from the Boltzmann inversion¹³⁻¹⁸ or inverse Monte Carlo methods.¹⁹ The coarse-grained potential fields developed in this technique must be used for simulations

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 $A \qquad (b) \qquad (b) \qquad (b) \qquad (b) \qquad (b) \qquad (b) \qquad (c) \qquad$

Figure 1. Chemical structure of (a) DGEBA and (b) DAB. (c) The chemical reaction between reactants during the curing process.



Figure 2. Mapping atoms to coarser super atoms. The DGEBA coarse-grained coordinates are indicated. (a) DGEBA and DAB molecules. (b) Coarsegrained cross-linked DGEBA/DAB.

having identical thermodynamic conditions to those they were fitted to.⁴ It should be noted that one limiting factor in most coarse-grained simulations is that the approach does not account for the dihedral coarse-grained coordinates.^{4,12,15} However, the dihedral degrees of freedom are known to have a significant role in the conformational changes of polymer chains.¹

For realistic simulations of epoxy polymer systems, the starting chain network in the simulations should represent a realistic cross-linked amorphous microstructure, with the correct degree of cross-linking. The curing process is typically modeled by allowing a mixture of curing agents and epoxy monomers to diffuse in a heated melt. When a curing agent is in the bond-forming vicinity of a reactive epoxy monomer, a bond is created. This process is terminated when the desired degree of cross-linking is obtained.^{4,20,21} In the literature, two methodologies are commonly used to develop such cross-linked microstructures. In the first method, an iterative MD/molecular mechanics

procedure is used to create the desired cross-linked microstructures.²⁰ In the second method, the cross-linking algorithm dynamically increases the bond-forming radius during the curing process to facilitate the formation of bonds at higher degrees of cross-linking.²² Both approaches have been utilized to successfully reproduce the curing process in relatively small simulation cells. However, both methods are bound to have severe computational limitations for larger simulation cells due to the need for complete relaxation of the polymeric network after a new topology is created. Furthermore, it has been shown that the rate of reaction in curing larger epoxy network systems dramatically decreases and cross-linking reaches a saturated state when the system converts to a gel after the first several thousands of steps in the simulation.²³ Thus, there is a need to develop a new methodology that is efficient to be able to create highly cross-linked networks.

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Figure 3. Coarse-graining process of the interparticle potentials (from left to right bond, angle, and dihedral coordinates) at T = 300 K. (a) Histogram of the relaxed coarse-grained coordinate conformations. (b) PDF of the relaxed coarse-grained coordinates. (c) The coarse-grained bond, angle, and dihedral potentials calculated by inverting the PDF of the relaxed coarse-grained coordinates.

In this article, a new coarse-grained model is developed for bisphenol A diglycidyl ether (DGEBA) epoxy monomers with diaminobutane (DAB) curing agents. In this model, all conformationally relevant coarse-grained degrees of freedom, including the angles and dihedrals formed during the curing process, were accounted for by sampling over the free-energy surfaces of DGEBA and DAB monomers using quantum mechanical (QM) simulations. The pair potential is also optimized to predict an experimentally realistic density and glass-transition temperature of the system. A new curing algorithm is also developed to model the creation of crosslinked polymer networks with a high degree of cross-linking. This algorithm significantly improves the performances of current curing algorithms and also creates a uniformly cross-linked microstructure that mimics the microstructure more realistically.

MATERIAL SYSTEM

The chemical structures of the DGEBA epoxy monomer and DAB curing agent are shown in Figure 1. The curing reaction between DGEBA and DAB takes place by the release of a hydrogen atom from the curing agent and breaking of one of the oxygen bonds in the DGEBA monomer, as shown in Figure 1c. A carbon atom in the epoxy monomer is thus freed such that a nitrogen atom in the curing agent, DAB, can bond to the DGEBA monomer, whereas the released hydrogen atom forms a bond with the oxygen atom in the DGEBA monomer. The resulting polymer chain can subsequently cross-link with other monomers



Figure 4. Calculated coarse-grained potentials from QM simulations at different temperatures. (a) Bond potential energy, (b) A–C–A angle potential energy, (c) C–A–C angle potential, and (d) dihedral angle potential.

to create a cross-linked network on the basis of the availability of reactive functional groups in the monomers. It should be noted that the curing agent, DAB, can bond to a maximum of four DGEBA monomers.

COARSE-GRAINING MODEL

Although there are many different approaches for coarse-graining of polymers, they all share two common steps: (1) mapping of the atomic structure into coarse-grained particle systems and (2) defining new interparticle interactions between these coarse-grained particles. The coarse-grained model adopted here follows broadly the model proposed by Tschop et al.¹⁸ However, unlike that model, the pair potential is optimized to predict the experimental density and glass-transition temperature. The details of the model are discussed in the following two subsections.

Mapping and Intrachain Potentials. Here, the group of atoms that belongs to the repetitive chemical units of DGEBA monomers and curing agent DAB is mapped to coarser particles, called super atoms, as shown in Figure 2b. The interactions between these connected super atoms are represented by springlike bond, angular, and torsional potentials that properly average the high-frequency internal degrees of freedom of the molecules. These potentials are calculated by inverting the Boltzmann distribution density function of their coarse-grained coordinate.

The Boltzmann distribution density function of a monomer, *P*, can be expressed in terms of its atomic coordinates, as follows

$$P(l, \theta, \phi) \propto e^{-U(l, \theta, \phi)}$$
(1)

where U is the internal potential energy of the system and l, θ , and ϕ represent the bond lengths, angles, and dihedral angles, respectively, of chemically bonded atoms in a fully atomic structure. As the energy of the systems must be conserved after coarse-graining, the coarse-grained representation of the probability density function (PDF) is equal to the Boltzmann distribution function of the fully atomic model

$$P(l, \theta, \phi) = P(L, \Theta, \Phi)$$
⁽²⁾

where for the coarse-grained structure *L* represents the length of the coarse-grained bond between super atoms (e.g., L_{AC} in Figure 2a), Θ represents the coarse-grained angle between super atoms (e.g., $\Theta_{\overline{CAC}}$ and $\Theta_{\overline{ACA}}$, as shown in Figure 2b), and Φ represents the coarse-grained dihedral angle between bonded super atoms (e.g., $\Phi_{\overline{CACA}}$ in Figure 2b). This PDF is calculated by sampling over the free-energy surface of the DGEBA monomer at a constant temperature, *T*. It should be noted that the flexibility of polycarbonate structures is mostly due to the rotational degrees of freedom along the carbon backbone structure. Therefore, a random conformation of a monomer can be achieved by disturbing a random dihedral angle on the backbone of its atomic structure and then relaxing the monomer accordingly.

The first step in this sampling process is to optimize a randomwalk atomic structure at the force-field level at a constant temperature. This optimized geometry will later serve as the initial structure for semiempirical QM simulations by the Hartree–Fock method. The sampling begins by setting one dihedral angle on the backbone of the atomic structure to a random angle; the energy of the system is then minimized while keeping this angle constant. The coarse-grained coordinates are

then calculated by computing the distances and angles between the centers of geometry of the super atoms over the relaxed atomic structure. This relaxed atomic structure will be adopted for the next sampling step. This process is repeated by selecting another random dihedral angle on the backbone of the relaxed atomic structure. This sampling process is terminated when a statistically reliable collection of equilibrated coarse-grained conformations of the monomer is achieved. These calculations were performed using the Gaussian90 software,²⁴ with the 6-31 G* basis. For the case of the DGEBA monomer, as shown in Figure 2a, assuming that these coarse-grained coordinates are independent, the PDF of the monomer can be rewritten as¹⁸

$$P(L, \Theta, \Phi) = P(L_{AC})P(\Theta_{\widehat{CAC}})P(\Theta_{\widehat{ACA}})P(\Phi_{\widehat{CACA}})$$
(3)

Thus, by computing the PDF of each coarse-grained coordinate, the coarse-grained potential functions can be predicted, after accounting for the respective volume elements of the density functions, as follows

$$U^{L_{AC}}(L) = -k_{B}T \ln\left(\frac{P(L)}{L^{2}}\right)$$

$$U^{\Theta_{\widehat{CAC}}}(\Theta) = -k_{B}T \ln\left(\frac{P(\Theta)}{\sin(\Theta)}\right)$$

$$U^{\Theta_{\widehat{ACA}}}(\Theta) = -k_{B}T \ln\left(\frac{P(\Theta)}{\sin(\Theta)}\right)$$

$$U^{\Phi_{\widehat{CACA}}}(\Phi) = -k_{B}T \ln(P(\Phi))$$
(4)

Examples of the histogram, PDF, and coarse-grained potential calculated from the QM simulations for a coarse-grained bond, dihedral, a bending angle, and a dihedral angle of the DGEBA monomer at 300 K are shown in Figure 3. The computations were repeated for a range of temperatures from 150 K \leq *T* \leq 500 K, and the coarse-grained potential functions for the different coordinates of the DGEBA monomer are shown in Figure 4. These potentials are parametrized for the coarse-grained MD simulations by fitting the curves using harmonic functions for the bond and angular potentials and an OPLS²⁵ function for the dihedral potentials. These simulations were also performed on curing agent DAB and cross-linked DGEBA/DAB polymers on a system, as shown in Figure 2b, to parameterize all conformationally relevant coarse-grained degrees of freedom. Table 1 summarizes all of the optimized parameters calculated for the DGEBA/DAB polymer networks at room temperature (see also Tables 2 and 3 in the Appendix).

Pair Potential. The interactions between nonbonded super atoms in the network are described using a Lennard-Jones (LJ) potential function in the form

$$U^{\rm LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$
(5)

where *r* is the distance between a pair of nonbonded super atoms, σ is the finite distance at which the interparticle potential is zero, and ϵ is the depth of the potential wall.²⁶ The LJ potential is chosen as it results in a temperature independent self-diffusion coefficient at a constant density.¹⁸ The cutoff radius of the LJ potential is 2.5 σ . Here, the values of σ and ϵ are optimized to reproduce the experimentally measured density and glasstransition temperature of the material. In the optimization procedure, the initial values for these parameters are chosen as ϵ

Table 1. Parameters f	or Coarse-Grained	Potentials	Calculated
at <i>T</i> = 300 K (Figure	e 2b)		

bond potential		$K_{\rm d}$		$d_{\rm eq}$	
$C \rightleftharpoons A$		5.5903	7.04		
$F \rightleftharpoons F$		6.942		5.89	
$F \rightleftharpoons C$		6.652		4.67	
angular potentia	al	$K_{ heta}$		θ_{eq}	
ĈAĈ		6.741	1	36.969	
ÂCĂ		3.499	143.125		
FFC		10.944	150.84		
CFC		11.995	65.132		
F CA		8.875		75.13	
torsional potential	K_1	K_2	K_3	K_4	
CACA	289.674	-161.759	57.656	-10.1758	

= 2.5 kcal mol⁻¹ and $\sigma = \left(\frac{\Psi M_m}{3\rho}\right)^{1/3}$, where Ψ is number density,

 ρ is the real density, and $M_{\rm m}$ is mass of each monomer in grams. A number of simulations, with different LJ potential parameters in the range of $\pm 25\%$ of the initial guess, were performed. In these simulations, the temperature of the simulation cell is decreased from 700 to 100 K and the density is constantly calculated to find the glass-transition temperature. The optimum parameters that are selected for the LJ potential in the current model are those that minimize the objective function

$$f(\mathbf{x}) = \sum_{i=1}^{N=2} \left[\frac{g(\mathbf{x})}{X_i} - 1 \right]^2$$
(6)

where $\mathbf{x} = \{\epsilon, \sigma\}, g(\mathbf{x})$ are the predicted values, and $X_i(i = 1, 2)$ are the known experimentally measured glass-transition temperature and density. The optimized values are computed to be $\epsilon = 1.519$ kcal mol⁻¹ and $\sigma = 5.382$ Å, as they predict a density of 1.21 g cm⁻¹ at room temperature and a glass-transition temperature of 388.15 K, which are in good agreement with the experiments.²⁷

CURING ALGORITHM

The curing process of highly cross-linked polymer networks involves mixing of curing agents and polymer monomers in a heated liquid melt until they form the required chemical bonds. The resulting unique structure of these polymer networks should be properly captured in the initial microstructure of fully atomic or coarse-grained MD simulations.

Traditionally, in simulations of the curing process, a melt composed of a mixture of the prepolymer and curing agent is randomly placed in a cubical simulation cell having periodic boundary conditions imposed along all directions. The constituents are then allowed to diffuse in the simulation cell at a constant high temperature and pressure. A bond is formed with a certain probability every time the reactive end of the epoxy monomer is at a critical distance from the curing agent. The simulation is terminated when the required degree of crosslinking is achieved in the network.²⁰

This cross-linking algorithm typically generates good representative epoxy networks in systems having a small number of atoms. However, for systems having a large number of atoms, or if a high degree of cross-linking is required, this algorithm results in a system that reaches a saturated state at a degree of cross-linking lower than the desired value within several thousand simulation time steps.²³ Furthermore, this algorithm typically leads to a nonuniform distribution of cross-linked

monomers inside the simulation cell for networks with high degrees of cross-linking. On the other hand, in simulations in which lower degrees of cross-linking are required, the short chains that were initially generated inside the simulation cell form bonds with their neighbors and nearest neighbors, which may result in the formation of chains that are comparatively longer than the desired average length of cross-linking.¹²

To overcome these issues, here, a new algorithm is developed that not only prevents the formation of long un-cross-linked chains but also guarantees uniformity of distribution of crosslinked monomers. In this approach, groups of partially crosslinked chains of epoxy monomers and curing agents, as shown in Figure 5, are used. These prepolymers are DGEBA monomers



Figure 5. Partially cross-linked molecules used for cross-linking: (a) partially cross-linked epoxy (nonactive), (b) partially cross-linked epoxy with curing agents at its ends (active). The red beads are the cross-linker super atoms, whereas the green and blue beads represent the A and C epoxy super atoms, respectively.

with a random degree of polymerization between 3 and 6, bonded through curing agent DAB. A mixture of these groups is randomly positioned within the simulation cell having periodic boundary conditions imposed along all directions. These partially cross-linked chains ensure that long un-cross-linked chains are not created.

In addition, to create a uniform cross-linked network, first, the simulation cell is divided into smaller regions. The inhomogeneity of each region is then determined by subtracting the number of active curing agents from the number of reactive DGEBA monomers. To increase the likelihood of bond formation in each region, the velocities of super atoms in regions with an excessive number of reactive monomers or active curing agents are modified to move active super atoms to neighboring regions having less available reactive super atoms. The velocities of the super atoms in each region are then corrected to conserve the temperature of the premodified system, while removing the spurious translation or rotation that the modified velocities may cause. After each redistribution step, the system is equilibrated to maintain the energy state of the system. This redistribution algorithm prevents the locking of reactive monomers in one region when there is a higher chance of bond formation in other regions and mimics the process of shaking or stirring of the system. Furthermore, if bond formation is allowed without any control of the rate of bond formation in different local regions, regions with a higher number of reactive super atoms will exhibit a much faster rate of cross-linking. This will lower the mobility of un-cross-linked super atoms in these regions. Therefore, the redistribution of these super atoms becomes harder and requires a significantly longer time, which might not be attainable in the simulation time frame. To avoid this, the rate of curing is

controlled in every region by enforcing a probability of bond formation for a chemically reactive pair of epoxy and curing agents in every region as a function of the local degree of crosslinking, such that

$$a = a_{\min} + \mathcal{H}(\chi_{\text{target}} - \chi_{\text{local}}) \times \left(\frac{\chi_{\text{cell}}}{\chi_{\text{target}}}\right) \times a_{\max} \times \left(\frac{\chi_{\text{cell}}}{\chi_{\text{local}}}\right)$$
(7)

where *a* is the acceptance rate, \mathcal{H} is the Heaviside function, γ is the degree of cross-linking, which is calculated as the ratio of the number of available pairs of reactive super atoms to the number of bonds formed in that region. Equation 7 increases the probability with which available pairs of reactive super atoms successfully form bonds, as the average degree of cross-linking of the simulation cell becomes closer to the target degree of crosslinking. It also decreases the local probability of bond formation for a region that has a higher local degree of cross-linking compared to the average degree of cross-linking of the simulation cell. This adaptive acceptance rate function leads to a uniform degree of cross-linking over the entire simulation cell, even for networks with a low degree of cross-linking. It should also be noted that when a bond is created during the curing process, several angles and dihedral angles are formed between the two super atoms at the ends of the bond and their neighboring super atoms. These newly formed angular and dihedral coordinates are usually neglected in most coarse-grained models due to the complication in assigning the correct type of potential for each coordinate during the simulation. This new algorithm was submitted to be included in the updated baseline libraries of LAMMPS (MC, and USER MISC).²⁸ These libraries include dynamic detection of the type of each coordinate on the basis of the type of its forming atoms.

RESULTS AND DISCUSSION

In the following, all simulations are conducted using LAMMPS.²⁸ An epoxy network is created by randomly generating a mixture of partially cross-linked DGEBA/DAB reactive (33% mol) and active (66.7% mol) molecules in a cubical simulation cell having an edge length of 75 nm. Periodic



Figure 6. Comparison between the traditional²⁰ and new cross-linking algorithms. Numbers in squares indicate the steps at which the microstructure in Figure 8 was generated.



Figure 7. Contours showing the degree of cross-linking throughout the simulation cell from the (a) traditional²⁰ and (b) new cross-linking algorithms at different steps, as indicated in Figure 6.

boundary conditions are imposed along all directions to mimic the bulk properties of an epoxy network. The molecules are modeled using the coarse-grained bead-spring model, as discussed previously. The initial system is a liquid mixture of the different molecules at a density of 1.16 g cm^{-3} . It should be noted that, in general, variations in the chain lengths, degree of cross-linking, and/or prepolymer structures chosen can affect the final predicted properties of the polymer. However, these effects are beyond the scope of the current study and have been thoroughly investigated separately.²⁹ The LJ potential is disabled at this stage of the simulation to avoid the high repulsive forces if two atoms are placed very close to each other, which would severely decrease the integration time step in the simulations. Instead, a soft cosine pair potential is employed

$$U_{\rm soft} = A + A \, \cos\!\left(\frac{\pi r}{r_0}\right) \tag{8}$$

where $r_0 = 2^{1/6}$. Amplitude *A* is linearly increased from 0.0 to 100.0 over the first 50 000 time steps to gradually move overlapping molecules away from each other. The system is then

relaxed using the NVE ensemble, with the displacement of super atoms limited to 1 Å for 500 000 steps. Finally, the network is relaxed at the simulation temperature for 1 million time steps. The simulations are conducted using the NPT ensemble, in which the Nosé–Hoover thermostat and barostat are employed to control the temperature and pressure during the simulations. The temperature and pressure damping parameters are set to 200 and 1000, respectively. The same simulation parameters are used for each simulation, unless otherwise stated.

In simulations of the cross-linking process, the simulation cell is randomly populated with prepolymers and curing agents and is initially relaxed at 600 K. These molecules are then allowed to diffuse inside the simulation cell under constant temperature and pressure conditions. When a reactive super atom of DGEBA is in the bond-forming vicinity of a reactive super atom of the curing agent, a chemical bond is formed. The bond-forming radius was chosen as 1.6σ . The intrachain potentials used during this step of the simulations are 100 times stiffer than the ones previously calculated for the bonds, angles and dihedral angles to avoid bonds from passing through each other or and forming long



Figure 8. (a) Simulation cell volume as a function of the degree of cross-linking. (b) Comparison of the densities between un-cross-linked and tightly cross-linked (95% cross-linking) networks.



Figure 9. Molecular mass build up as a function of cure conversion. The shaded area indicates the experimentally observed range of gel point, and the dash-dot line indicates the theoretical predicted value.

bonds in the cross-linking simulations. After the desired degree of cross-linking is achieved, the system is relaxed for 1 000 000 time steps with the correct potentials to remove any artifacts caused by the stiffer intrachain potentials during the cross-linking simulation. The average degree of cross-linking in the simulation cell as a function of the number of simulation time steps for both the traditional²⁰ and newly proposed curing algorithms are shown in Figure 6. In addition, the distributions of the local degrees of cross-linking throughout the simulation cell are shown for both algorithms at three different time steps in Figure 7. After 200 000 time steps, marked as 1 in Figure 6, the traditional algorithm shows a 63% degree of cross-linking compared to 56% for the new algorithm. In the new algorithm, the bond formation reaction is decreased in regions with a higher degree of cross-linking, whereas the reaction rates are increased in other regions

with a lower degree of cross-linking to create a uniformly crosslinked network. Therefore, during the early stages of the simulation, a lower average degree of cross-linking is reached compared to that in the traditional algorithm, where the reaction rates are uniform throughout the simulation cell. After 325 000 time steps, marked as 2 in Figure 6, the degree of cross-linking in both algorithms is equal to 78%; however, as shown in Figure 7b, the new algorithm shows a much more uniformly distributed cross-linked network as opposed to that in the traditional algorithm, where a wider distribution of cross-linking is observed across the simulation cell. After 750 000 time steps, marked as 3 in Figure 6, the average degree of cross-linking from the new algorithm is 95%, whereas in the traditional algorithm, the degree of cross-linking did not change much above the 78% value reached in 2. This is due to the fact that the cross-linking rate in the traditional algorithm drops markedly as reactive super atoms are trapped in areas with a higher degree of cross-linking, whereas there is a lack of reactive units in other regions to form bonds. On the other hand, the new algorithm shows a better performance, as it redistributes reactive super atoms from areas with a higher degree of cross-linking to areas with a lower degree of crosslinking.

The simulation volume during the cross-linking process as a function of the degree of cross-linking, as predicted by the new algorithm, is shown in Figure 8a. The decrease in volume during the curing simulation is in good agreement with the increase in density predicted by the MD simulations.³⁰ The volumes of the relaxed microstructure as a function of time before and after curing are shown in Figure 8b. The cured network is observed to result in a volume shrinkage of 5% at a degree of cross-linking of 95%, which is in accordance with volume shrinkage observed for the cured microstructure.³¹ Furthermore, the molecular mass of the largest polymer block is shown in Figure 9. It is observed that most of the molecular mass build up occurs during 65-70% cure conversion percentages. The calculated gel point during the curing process is at a cure conversion percentage of 67%, which is in good agreement with the theoretical cure conversion percentage of 58% as well as the experimental measures, which are in the range of 50–80%.^{32,33}

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Figure 10. (a) Density and (b) specific volume as a function of temperature.

To study the temperature dependence of the cross-linked network, a simulation was performed to calculate the glasstransition temperature. By definition, the glass-transition temperature, T_{g} , is the temperature at which a reversible transition of amorphous materials or amorphous regions within semicrystalline materials from a hard and relatively brittle state to a molten or rubber-like state takes place.¹ The glass-transition temperature is measured as the point at which a kink is observed in the specific volume (ρ^{-1}). To calculate the glass-transition temperature, the epoxy microstructure is first relaxed at 700 K. The simulation temperature is then reduced to 150 K in 4×10^{6} time steps, with a cooling rate of 2.75×10^4 K s⁻¹. Density versus temperature for the DGEBA/DAB cross-linked network is shown in Figure 10a. The calculated glass-transition temperature of the system is predicted by the current simulations to be 389.16 K, which is in a good agreement with the experimentally measured glass-transition temperature of 393.5 K.²⁷ It should be noted that a comprehensive study on the effect of cooling rate on the predicted glass-transition temperature of polymers from MD simulations has been previously performed.³⁴ On the basis of that study, it was shown that the glass-transition temperature from MD simulations is less sensitive to cooling rate than that from experiments. Nevertheless, the predicted glass-transition temperature from MD simulations is always within the error measurements of experimental data. Another important thermodynamics property is the coefficient of thermal expansion, which is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \tag{9}$$

where *V*, *P*, and *T* are volume, pressure, and temperature of the sample, respectively. The change in volume $\left(\frac{d\nu}{V}\right)$ versus temperature, as predicted from the current simulations, is shown in Figure 10b. The kink suggests a glass-transition temperature of 385.0 K, which complies with the experimentally measured glass-transition temperature of the material. On the other hand, the thermal expansion coefficients of the rubbery epoxies are roughly 3 times higher than the thermal expansion coefficients in the glassy region.¹ It is also observed that the slope of the rubbery region is 3.66 times higher than slope of the glassy region, which is in a good agreement with the experimentally observed trend.

CONCLUSIONS

In the current work, a new coarse-grained model has been developed for DGEBA/DAB polymer systems. All of the conformationally relevant coarse-grained degrees of freedom of the system, including the angles and dihedrals created during the curing process, are calculated by sampling over the energy surface of the system using QM simulations. The nonbonded interparticle potential is optimized to provide realistic predictions of the density and glass-transition temperature of the system. In addition, a new curing algorithm was also developed to efficiently create highly cross-linked polymer networks by redistributing the reactive super atoms from regions with a high degree of cross-linking to regions with a lower degree of cross-linking. This algorithm also controls the rate of curing in different regions of the simulation cell by controlling the probability with which bonds are formed between reactive super atoms to ensure uniformity of the resulting cross-linked network. The simulations using this new curing algorithm show a uniform distribution of the local degree of cross-linking throughout the simulation at different time steps, and this algorithm is also shown to be comparatively more efficient in creating highly cross-linked networks. The predicted gel point from the curing simulation is in the experimental range of the gel point of the epoxy polymers and is in good agreement with the theoretically predicted gel point. Furthermore, the predicted glass-transition temperature of the system is close to the glass-transition temperature measured in experiments. The predicted thermal expansion coefficient in the rubbery state is 3.66 times higher than that in the glassy state, which is in a good agreement with the trend observed in experiments. Finally, it should be noted that the coarse-grained method presented here can be extended to other epoxy systems after the appropriate super atoms and coarse-grained potentials are appropriately defined. Furthermore, these simulations can also aid in the development of a physics-based understanding and constitutive rules that can be incorporated into continuum-level simulations. In particular, it is possible to extract relevant information on the evolution of different microstructural features (e.g., evolution of free-volume holes with strain at different temperatures, bond breaking, etc.).²⁹

APPENDIX

Parameters for bond, angular, and torsional potentials calculated at different temperatures are shown in Tables 2 and 3.

Table 2. Parameters for Bond Potential and Angular Potential Calculated at Differen	t Temperatures
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	T = 1	150 K	T =	T = 250 K $T = 300 K$		<i>T</i> = 450 K		
bond potential ^a	K _d	d _{eq}	K _d	d _{eq}	K _d	d _{eq}	K _d	d _{eq}
$C \rightleftharpoons A$	8.323	7.10	5.882	7.06	5.5903	7.04	5.4912	7.03
$F \rightleftharpoons F$	10.311	5.90	7.287	5.85	6.942	5.89	6.803	5.84
$F \rightleftharpoons C$	9.904	4.65	7.000	4.66	6.652	4.67	6.535	4.60
	T = 1	150 K	T = 1	250 K	T = 3	300 K	T = 4	-50 K
angular potential b	$K_{ heta}$	$\theta_{\rm eq}$	K_{θ}	$\theta_{\rm eq}$	K_{θ}	$\theta_{\rm eq}$	$K_{ heta}$	$\theta_{\rm eq}$
ĈAĈ	11.697	135.866	7.525	134.445	6.741	136.969	6.588	136.490
ACA	4.574	140.531	3.545	141.961	3.499	143.125	3.3815	143.388
FFC	13.974	151.73	11.721	150.84	10.944	150.84	9.934	150.84
CFC	14.663	65.046	12.185	65.132	11.995	65.132	10.895	65.132
FCA	11.975	75.01	9.246	75.13	8.875	75.13	7.957	75.13
$a_{TT} = \frac{1}{1} (1 - 1)^{2}$	$2 b_{TT} = 1_1$	$(0, 0)^2$						

 ${}^{a}U_{\text{bond}} = \frac{1}{2}k_{\text{d}}(d - d_{\text{eq}})^{2}. {}^{b}U_{\text{angle}} = \frac{1}{2}k_{\theta}(\theta - \theta_{\text{eq}})^{2}.$

Table 3. Parameters for Torsional Potential Calculated at Different Temperatures

	torsional potential ^a	K_1	K_2	K_3	K_4
T = 150 K	CACA	297.854	-168.0599	60.015	-10.2135
	ACFC	27.125	-16.452	10.325	-1.125
	ACFF	19.345	-14.055	9.744	-1.542
	CFFC	29.233	-16.854	11.123	-1.954
T = 250 K	CACA	296.2	-168.8352	59.8352	-10.74
	ACFC	25.315	-16.021	10.015	-1.045
	ACFF	18.954	-13.532	9.452	-1.235
	CFFC	28.123	-16.123	10.865	-1.684
T = 300 K	CACA	289.674	-161.759	57.656	-10.1758
	ACFC	25.012	-15.851	9.754	-0.985
	ACFF	18.025	-13.132	9.109	-1.0135
	CFFC	25.845	-15.754	10.124	-1.215
T = 450 K	CACA	283.49	-161.1	75.3946	-10.3032
	ACFC	24.856	-15.231	9.422	-0.835
	ACFF	17.954	-12.458	9.033	-0.945
	CFFC	25.423	-15.012	9.333	-0.784

 ${}^{a}U_{dih} = \frac{1}{2}K_{1}[1 + \cos\phi] + \frac{1}{2}K_{2}[1 - \cos2\phi] + \frac{1}{2}K_{3}[1 + \cos3\phi] + \frac{1}{2}K_{4}[1 + \cos4\phi]$

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Notes

The authors declare no competing financial interest.

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