

MOLECULAR MODELING OF THERMOSETTING POLYMERS: EFFECTS OF DEGREE OF CURING AND CHAIN LENGTH ON THERMO-MECHANICAL PROPERTIES

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Introduction

We use molecular dynamics (MD) both at the atomistic and coarse-grained level to predict the mechanical and thermal properties of thermosetting polymers. The coarse-grained simulations, where the polymer network is treated as a bead-spring system, can capture several important “general” behaviors of thermosets such as the role of chain length of the resin strands, degree of curing, strain rate and temperature on the thermo-mechanical response of a cured polymer system. Atomistic simulations, on the other hand, can provide detailed microscopic information on the physical properties of thermosetting polymers and can lead to predictions in “quantitative” agreement with experiments. Recently a number of MD models of thermosets were developed and investigated by some researchers [1-7]. While generating useful insight into the dependence of the physical properties of thermosetting polymers on their cross-link networks, these studies have either not been able to provide specific correlation with the chemical structure of the resin system (in the case of the coarse-grained simulations) or been significantly affected by the small system size used and the short time simulations (in the case of the atomistic studies).

In this proceeding paper, we will first briefly discuss our recent results, using coarse-grained bead-spring model, on the dependence of failure stress and failure strain of highly cross-linked polymers on chain length of the resin strands. But, the majority of the paper will focus on our work on understanding the mechanical properties of one particular thermosetting polymer, DGEBA/DETDA epoxy system using atomistic molecular dynamics simulations. A series of atomistic simulations were

carried out to examine and predict thermo-mechanical properties at different extents of reaction. In addition, the effect of crosslink density and system size on the properties of the thermosets was also studied using atomistic simulations.

Coarse-grained simulations of Thermosets

We have used a coarse-grained bead-spring model to study the dependence of the mechanical properties of thermosets on chain length of the resin strands. In the coarse-grained model used here the polymer network is treated as a bead-spring system. To create highly cross-linked networks similar to epoxy networks, a liquid mixture consisting of strand beads, that represent resins, and one-bead molecules, representing cross-linkers, was cross-linked dynamically. In this investigation the strand length was varied between 2 and 6 beads while the cross-linkers had a functionality of 6. The network was dynamically formed during a constant temperature simulation until at least 95% of all possible bonds between crosslinkers and resin strands were made. Details about the coarse-grained simulation protocol can be found in [3].

The result from coarse-grained simulation, shown in Figure 1, demonstrates the relation between mechanical properties of thermosetting polymers and resin chain length. This result clearly shows that while the failure behavior of a highly cross-linked network depends strongly on resin chain length, the elastic response of the system does not show any observable dependence on resin chain length. Since the main objective of our present work is to understand the elastic response of the DGEBA/DETDA epoxy system, the atomistic simulation part described below will only consider a DGEBA monomer as the resin.

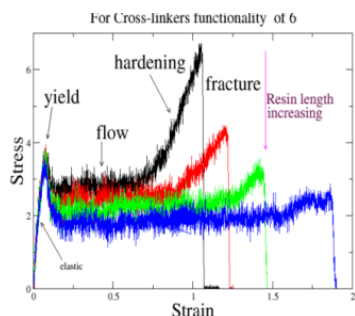


Figure 1: Tensile stress-strain curves for resin strands with chain length 2 beads (black), 3 beads (red), 4 beads (green) and 6 beads (blue).

Building of the Atomistic models

The rest of the paper will focus on the atomistic-scale investigation of the thermosetting materials based on the reaction of the DGEBA (diglycidyl ether of bisphenol A) monomers with curing agent EPI-Cure-W (diethylenetoluenediamine, DETDA) (Figure 2).

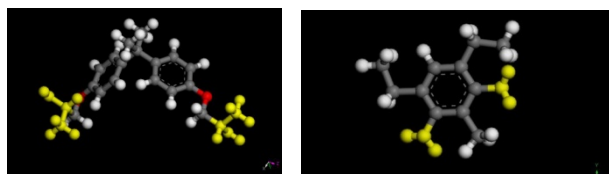


Figure 2: Reactants used for curing epoxy-amine system. (left) Epoxy resin monomer DGEBA (diglycidyl ether of bisphenol A); (right) Aromatic amine hardener DETDA (diethylene toluene diamine). The reaction sites are highlighted by yellow.

All the atomistic MD simulations were conducted using Discover modulus of the Materials Studio (Accelrys Inc.) software. The COMPASS force field was employed in these simulations. The Velocity Verlet algorithm was used for integration of classical Newton's equations. To build the thermosetting material, first, stoichiometrically perfect mixtures of the epoxy monomers and curing agent molecules were packed into a simulation cell with 3D periodic boundary conditions using the Amorphous Cell modulus of the Materials Studio package and were followed by energy minimization of the obtained structures. To study the effect of system size on the

thermo-mechanical properties of the thermoset material under consideration, we built mixtures of several sizes varying between 2000 and 8000 atoms.

After energy minimization of these mixtures, many topologically independent structures were generated from each of the mixtures by saving the configuration at every 100 ps during isothermal and isochoric (NVT) equilibration of the mixtures at elevated temperature (673 K). Crosslinking was then carried out on each of the newly generated structures (mixtures) using the approach described below. In order to enhance molecular mobility and hence to accelerate the crosslinking, the curing was done at a higher temperature, 473 K.

During the cross-linking cycle chemical reactions occur based on the distance criterion. Bonds are formed between reactive atoms within a cutoff distance and then appropriate hydrogen atoms are deleted. To identify cross-linking sites during the curing process, the capture sphere growth approach of Eichinger et al. [8], which allows specifying both minimum and maximum cutoff radii of the chemical reaction, was used. To mimic real cross-linking reactions, that is reactive groups have to diffuse slowly to each other, the model systems after each cross-linking cycle were subjected to a cascades of both energy minimization and constant volume and temperature MD equilibrations according to the procedure used in Insight Polymer software. The polymerization cycle was repeated until either the maximum number of cycles is reached or all sites have reacted.

In order to minimize the presence of defects and stresses in a given structure, energetic and structural information were extracted at each cross-linking cycle. Unusually high bond stretching energy in the model system is a sensitive measure of distortion and usually happens when the cross-linking process introduces a defect. In the present study, structures that showed a dramatic increase in the maximum bond stretching energy at high extensions of the reaction were rejected in favor of stress-free structures.

In this work we generated batches of many topologically independent structures for each of the

four different system sizes studied (each containing 2000, 4000, 6000, or 8000 atoms). During the curing stage of each of these structures, new structures with conversion degrees from 50% to 100% were selected and their thermo-mechanical response was characterized.

Annealing

As described above, to enhance molecular motions and reduce stresses in the models, curing reaction was conducted at the elevated temperature (473 K) which is above the glass transition region for this material. An annealing simulation procedure was used to cool down the systems with various extents of reaction to predefined temperature values. In this study we chose two temperatures for mechanical characterization of the systems, 298 K and 480 K which are above and below the glass transition temperature of a given structure, respectively.

(i) Prediction of Equilibrium Properties. Glass Transition Temperature:

To determine the glass transition temperature of a given cross-linked model, we calculated the volume-temperature curve using constant pressure and temperature MD simulations. Cooling of the model systems was carried out in steps of 10 K with 100 ps equilibration run at each temperature. Figure 3 shows specific volume-temperature plot that was determined by averaging results from 5 randomly picked epoxy structures that were cured to the 100% extent of reaction and each containing 8000 atoms.

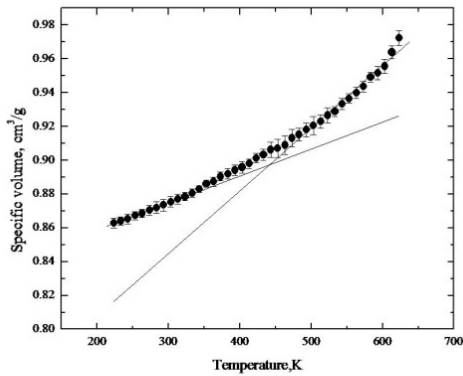


Figure 3: *Specific volume-temperature plot for fully cured epoxy structure containing 8000 atoms.*

The volume increases with increase in temperature and a change in slope is observed for each cooling cycle. The glass transition temperatures were

determined at the point of the change in the slope between high and low temperature regions (represented by the intersection of the solid lines in the above figure). The results of our glass transition investigation are presented in Figure 4 where the glass transition temperature is plotted as a function of the extent of the reaction for the four different system sizes studied. As expected [9] we observe an increase in glass transition temperature with increase in degree of curing. However, the increase in T_g with degree of curing is not smooth probably an indication of finite system size effect. The experimental values of the glass transition temperature for this material found in the literature [10-13] range from 441 K to 476 K and are also shown in figure 4 as filled circles. We see that our simulation results for extent of reactions higher than 90% are within the range of the reported experimental values.

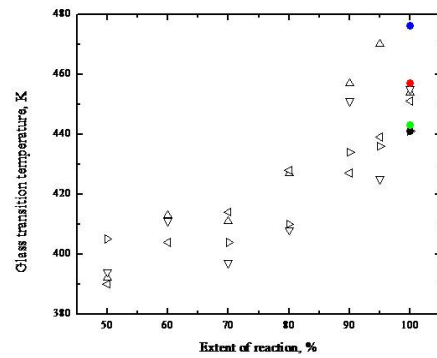


Figure 4: *Glass transition temperatures as a function of the extent of the reaction. Triangles pointing up: 2000 atom structure; triangles pointing down: 4000 atom structure; triangles pointing left: 6000 atom structure; triangles pointing right: 8000 atom structure. Experimental values of glass transition temperature: black filled circle [12]; green circle [10]; red circle [11]; blue circles [13].*

(ii) Coefficient of Thermal Expansion:

The slopes in the glassy and rubbery regions in the specific volume-temperature plot correspond to the volumetric coefficients of thermal expansion (CTE) of the two regions. Figure 5 represents the results on coefficients of thermal expansion calculations for the glassy and rubbery regions for different degrees of reaction. In both the glassy and rubbery regions, the CTE monotonically decreases with the increase in degree of polymerization. Experimental value for fully cured structure at room temperature [13] is also shown in figure 5 as a black filled circle. The

CTE values obtained from our simulations for high degrees of curing are below the experimental value but are still in a reasonable agreement with experiment.

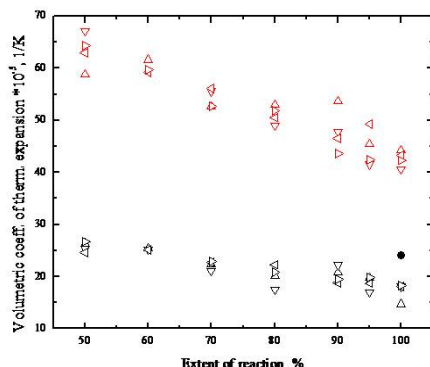


Figure 5: Volumetric coefficients of thermal expansion as a function of the extent of the reaction in glassy state (black triangles) and rubbery state (red triangles). The directions of the triangles correspond to the same model sizes as described in the Figure 4. The filled circle represents experimental value [13].

(iii) Density:

In figure 6, the dependence of density on the extent of curing reaction at temperatures below and above T_g is shown. As expected the density increases in the course of the reaction and the rate of increase shows strong dependence on temperature. Densities of highly cured systems at room temperature are below but within 2% of the experimental value [14].

Mechanical properties

Elastic Coefficients and Poisson's ratio

Any small volume element of an amorphous material in nanoscopic scale can be characterized by unique distribution of matter within it and individual elements can be viewed as regions of a nanoscopically heterogeneous composite material. In this sense we can talk about distribution of the material properties in the macroscopic sample. In the present work statistical variation of the elastic constants was studied by estimation of upper and lower bounds of the material properties using Voigt, Reuss and Hill-Walpole approaches [15-18]. For this purpose we generated butches of up to 60 topologically distinct thermosets for each extent of the reaction.

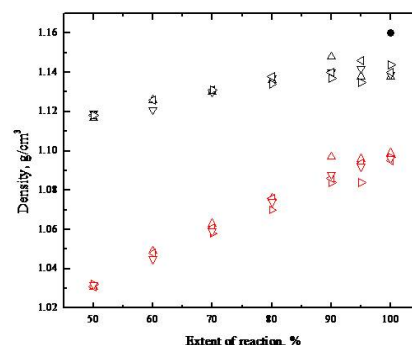


Figure 6: Density as a function of the extent of the reaction at 298K (black triangles) and 480K (red triangles). The directions of the triangles correspond to the same model sizes as described in the Figure 4. Filled circle represents experimental value [14].

To calculate elastic constants we used the static approach [19]. Three tensile and three shear deformations of magnitude ± 0.0005 were applied to the systems. The obtained stress tensor is then used to estimate stiffness and compliance matrices C_{ij} and S_{ij} of the material as well as Young's, Shear, Bulk moduli and Poisson's ratio.

The dependence of elastic moduli on the extent of reaction and at two temperatures for the system containing 6000 atoms is shown in Figure 7. As expected the results from our simulation demonstrate the pronounced increase in Young's, bulk and shear moduli with extent of curing at both temperatures. However, the values of the Young's modulus determined from our simulation are above the experimental values (2.71 GPa) even at the highest extent of the cross-linking reaction [20]. One of the possible reasons of high tensile modulus of the structures we built for our simulations is that our models are free of defects while various kinds of defects are usually present in real macroscopic samples that tend to reduce the measured values of the elastic moduli of the material. As can be seen in figure 7, the Poisson's ratio does not show any strong dependence on the extent of reaction. From our simulation we determined an average Poisson's ratio value of 0.3 for all extensions, which is lower than the experimental value [21].

There seems to be a systematic dependence of the elastic constants (determined as the average values of the upper and lower bounds) on system size, where the bounds were observed to narrow significantly with increase in system size from 2000 to 8000 atoms. We plan to study large systems to

minimize the effect of system size so that the characteristics of the dependence of elastic moduli and other properties of the thermoset on the extent of the reaction can be determined more precisely.

Conclusions

In the present study we were able to generate a set of stress-free thermoset models with high degree of cure. We studied the dependence of the thermo-mechanical properties of highly cross-linked polymers on the extent of curing reaction, temperature and size of the model. We found densities and glass transition temperatures of the systems in good agreement with experimental data. However, the mechanical values from our model systems were found to be higher than in real macroscopic samples. Size effect on the material properties was observed. Further increase in the size of the model could help to obtain more accurate simulation results.

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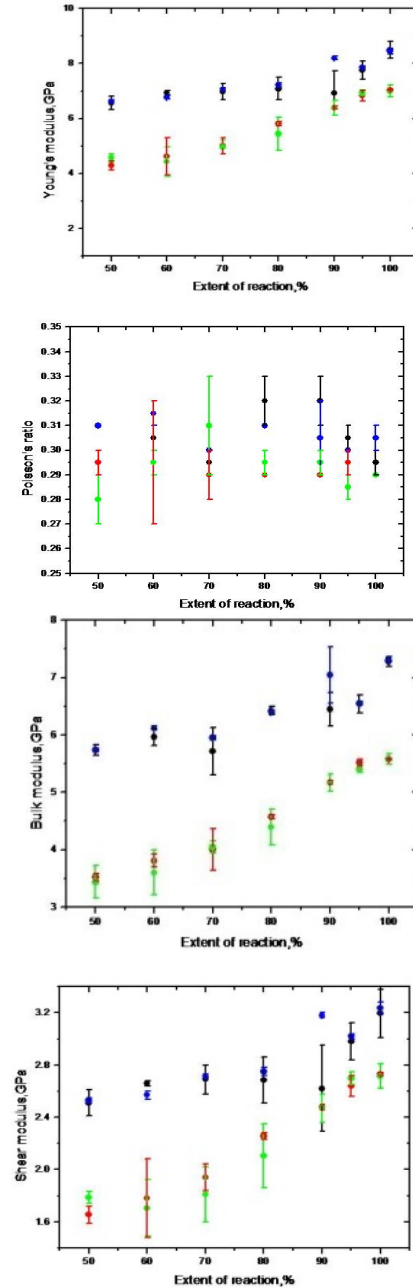


Figure 7: Elastic moduli as a function of the extent of the reaction: (a) Young's modulus; (b) Poisson's ratio; (c) bulk modulus; (d) shear modulus. Black: Voigt and Reuss bounds at $T=298K$; blue: Hill-Walpole bounds at $T=298K$; green: Voigt and Reuss bounds at $T=480K$; red: Hill-Walpole bounds at $T=480K$.

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