MULTISCALE MODELING OF POLYMERS: LEVERAGING REACTION KINETICS FOR STRUCTURE MORPHOLOGY AND PROPERTY PREDICTION

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ABSTRACT

Quantum mechanics (QM) simulation has become a reliable tool for the prediction of structures, chemical mechanisms, and reaction energetics for fundamental reaction steps. Employing automated QM tools, we can identify key reaction steps and their kinetics involved in polymer synthesis and matrix-crosslinking. The information obtained from QM, is often overlooked, but is critical in building realistic polymer systems and condensed phase morphologies.

There are numerous amine and epoxy monomers in use today for composites, adhesives and coatings. In this study we have screened the key reaction barriers of amine/epoxy/accelerant combinations yielding 252 reactive barriers. Utilizing a subset of these with crosslinking tools that are chemically agnostic; we can generate physically meaningful morphologies and efficiently study the properties of crosslinked polymer systems.

In this presentation, we will review the large scale simulation of reactive barriers and discuss the key trends observed. In addition, the connection to physical properties will be reviewed. This presentation will highlight builders, QM and MD simulation workflows, and prediction of properties and data analysis, that provide insight into existing epoxy/amine materials as well provide avenues for developing new chemistries with desired processing performance properties.

1. INTRODUCTION

Thermoset polymers have gained interest in recent years due to their favorable thermomechanical properties for applications in aerospace, automotive, defense and high performance athletics equipment. Materials containing thermosets have numerous applications due to their high performance characteristics [1]. While thermosets are very versatile, the cost to incorporate these polymers into new materials is high. Acceleration of the development process pipeline would not only reduce costs, it would also decrease accumulation of thermoset waste which is difficult to recycle.

Molecular simulation represents a solution to lengthy experiments and long development cycles for new materials [2]. Using physics-based modeling, researchers are able to screen a larger chemical space and predict key properties of molecular systems. The intra and intermolecular interactions in polymeric systems can be modeled, providing insight otherwise not accessible. For thermoset polymers the crosslinking chemistry is an additional step that needs to be incorporated. Specific crosslinking polymer builders need to be capable of mimicking the crosslinking chemistry to build a statistically relevant network architecture. To address this issue, several groups have built crosslinking simulation modules capable of predicting polymer network formation using either Monte Carlo (MC) or molecular dynamics (MD) based methods for both atomistic and coarse grained systems [3 and references within].

While these methods have been used successfully to build and predict thermomechanical properties for thermoset systems, they often require expert knowledge or specialized code. To make these computational methods available to a broader audience, we have developed a user-friendly cross linking module with increased versatility/applicability, allowing users to define the chemistry for their system of interest. Utilizing SMARTS patterns, a language for substructure searching in a molecule, the user can specify the exact chemistry that takes place during the crosslinking process [4]. Additionally, we can provide the activation energies of different reactions during the crosslinking process to accurately build the crosslink network that are practically relevant. The activation energies can be obtained from quantum calculations. These workflows in combination with accurate force fields and GPU accelerated MD code, thermomechanical properties can be predicted quickly. High-throughput prediction of thermoset systems can have a significant impact on lead times to developing new materials.

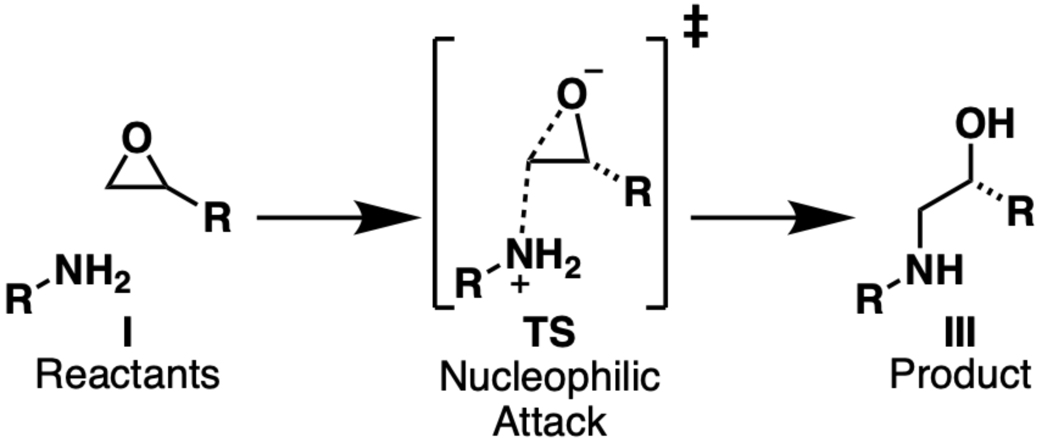


Figure 1. Crosslinking reaction. The initial reaction occurs between a primary amine and a single epoxide. The resulting product contains a secondary amine that can further react with additional epoxide.

In this work, we perform an enumeration of several epoxide and amine groups and compute the activation energies for all the epoxy/amine combinations using an automated reaction workflow. We select the most interesting combinations from this library to perform in-silico crosslinking and report detailed crosslinking analysis. Furthermore, we report the thermophysical properties and water uptake capacity of these selected systems.

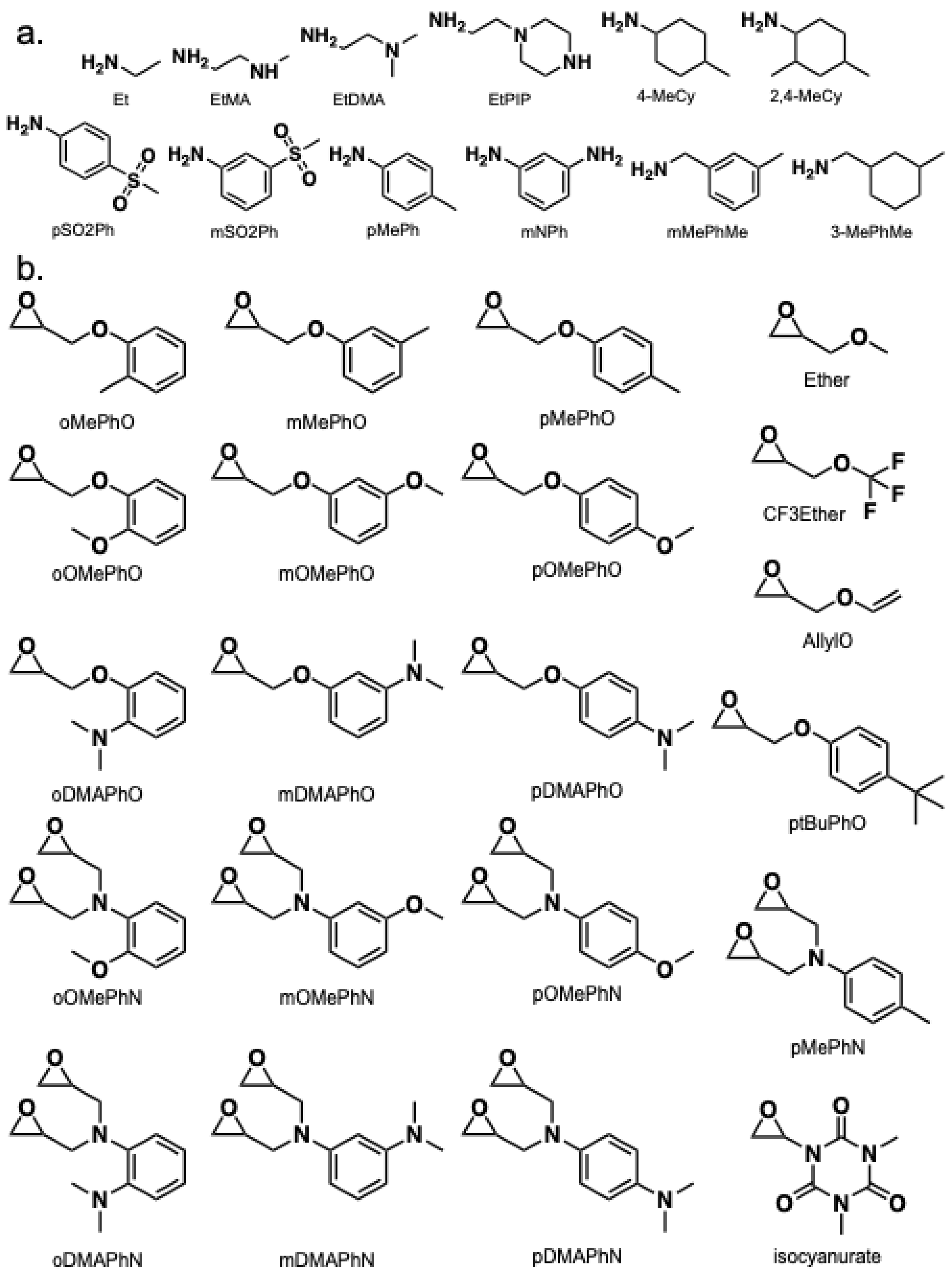


Figure 2. Epoxide and Amine Libraries. Library of both amines (a) and epoxides (b) studied with DFT to compute the relative reaction barriers.

2. METHODS

To study the thermomechanical properties of a thermoset system, molecular dynamics (MD) simulations can be utilized. Using physics based modeling, molecular systems can be studied in detail without any training data for a particular system of interest [5]. For thermoset polymers, prediction of the network architecture at the molecular level is done by simulating the curing process. During this process, a number of reactions can occur between two chemical groups, forming new bonds. In the case of an epoxy-amine system, the amine reacts with the epoxide ring (Figure 1).

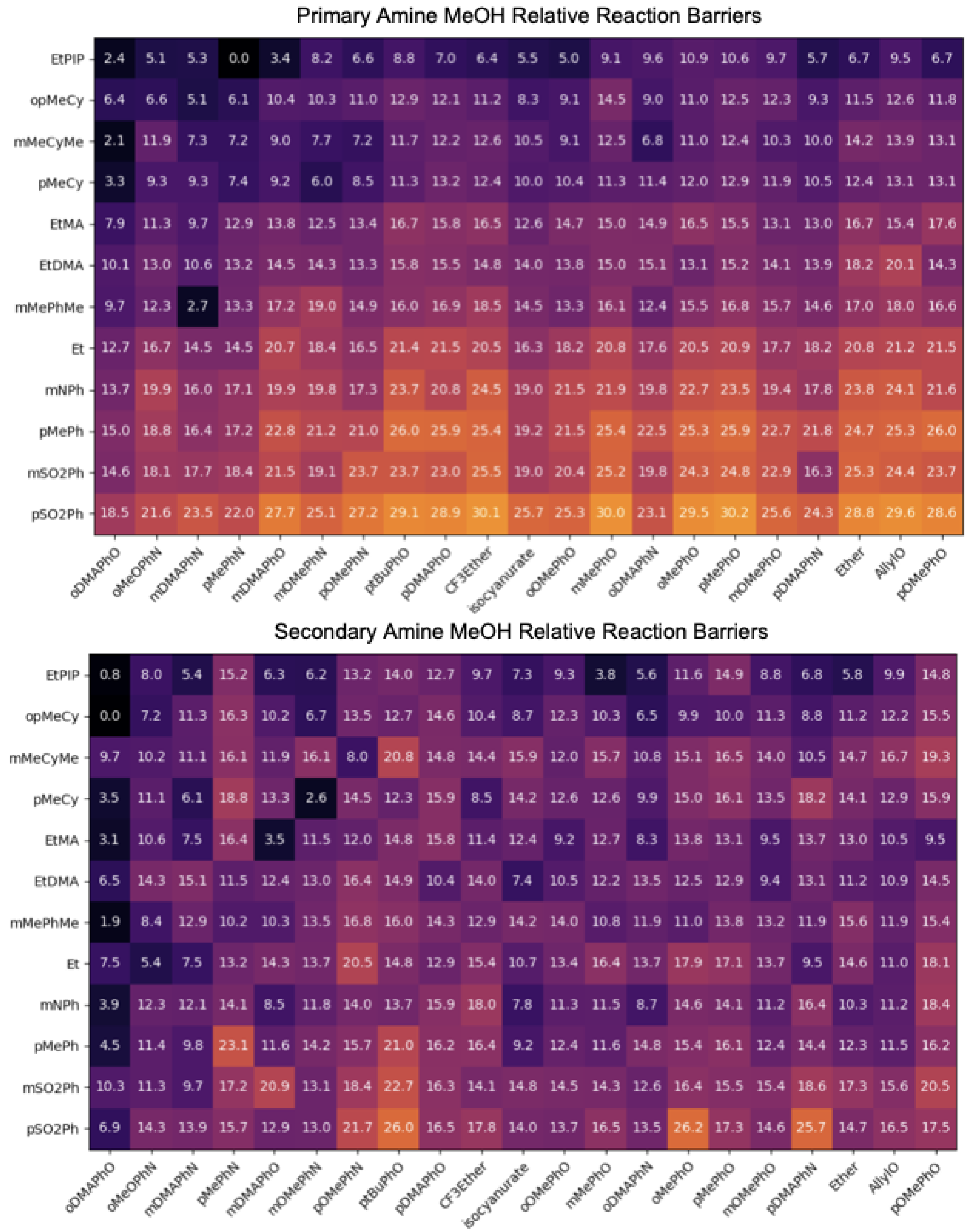
Relative reaction rates of various amines and epoxides can be predicted using density functional theory (DFT) simulations. Using an automated reaction workflow a library of amines and epoxides were studied (Figure 2). In addition, several catalysts were employed to determine their effect on relative reactivities.

Reaction sites when crosslinking can be determined by separation distance in space and controlled in each bond formation step. To specify the bonds that will be broken, this information is generally required at the beginning of each simulation. After each set of product bonds is formed an equilibration MD simulation can be performed. All of these steps are necessary to form a highly crosslinked thermoset system that mimics experiment and can be used for subsequent physical property prediction.

The Schrödinger Materials Science Suite version 2020-4 was used to build the monomer molecules, compute the reaction barriers, build the thermoset polymer, perform MD simulations, and perform data analysis [6]. The reaction structures and barriers were built and computed with the Reaction Workflow. An epoxy-amine reaction library was built to include starting materials, intermediates, transition states (TS), and products for the uncatalyzed reaction as well as water, methanol, and BF3 catalyzed versions. The libraries were then enumerated onto the parent reaction library generating 252 reaction libraries of all epoxide and amine combinations. The Reaction Workflow was then used to automate the conformational search using MacroModel[7] for all structures in each reaction library and subsequently optimize and locate transition states using Jaguar.[8] Several tests are then performed to confirm that all structures are true stationary points on the reaction profile including no negative frequencies for ground state structures and a single negative frequency that corresponds to the active atoms in the TS of interest. Finally the relative energies for each reaction step is computed and saved. This output was used to compute the relative barriers for each of the 252 epoxide amine combinations.

The initial monomer systems were built using the Disordered System Builder tool with the OPLS3e force field [9]. For the thermoset systems, the total number of atoms was set to ~20,000 atoms with a reactive stoichiometry of 1:1. We created ten different replicates for each of the epoxy-amine systems considered. The resulting amorphous systems were then equilibrated using the following protocol: the Materials relaxation protocol was used, followed by 20 ns of final NPT simulation at 300K/1atm. Thermoset networks were created using the crosslinking polymers builder. The input parameters for the simulation are the SMARTS patterns to define the bond breaking and forming steps along with an equilibration protocol. The SMARTS pattern for primary and secondary amine bonds was defined for all the reactions . The number of crosslinks was limited to 20 per iteration (less than 5% cure). After each crosslinking iteration, a MD equilibration stage was performed (800K, 50ps NPT at 1 atm). Analysis of the crosslinked structures was performed using the cross link polymers analysis module.

To obtain thermomechanical properties, the resulting crosslinked systems were first subjected to a thermophysical properties calculation. These calculations mimic the kinetic process of



Primary Amine MeOH Relative Reaction Barriers

	oDMAPhO	oMeOPhN	mDMAPhN	pMePhN	mDMAPhO	mOMePhN	pOMePhN	ptBuPhO	pDMAPhO	CF3Ether	isocyanurate	oOMePhO	mMePhO	oDMAPhN	oMePhO	pMePhO	mOMePhO	pDMAPhN	Ether	AllylO	pOMePhO
EtPIP	2.4	5.1	5.3	0.0	3.4	8.2	6.6	8.8	7.0	6.4	5.5	5.0	9.1	9.6	10.9	10.6	9.7	5.7	6.7	9.5	6.7
opMeCy	6.4	6.6	5.1	6.1	10.4	10.3	11.0	12.9	12.1	11.2	8.3	9.1	14.5	9.0	11.0	12.5	12.3	9.3	11.5	12.6	11.8
mMeCyMe	2.1	11.9	7.3	7.2	9.0	7.7	7.2	11.7	12.2	12.6	10.5	9.1	12.5	6.8	11.0	12.4	10.3	10.0	14.2	13.9	13.1
pMeCy	3.3	9.3	9.3	7.4	9.2	6.0	8.5	11.3	13.2	12.4	10.0	10.4	11.3	11.4	12.0	12.9	11.9	10.5	12.4	13.1	13.1
EtMA	7.9	11.3	9.7	12.9	13.8	12.5	13.4	16.7	15.8	16.5	12.6	14.7	15.0	14.9	16.5	15.5	13.1	13.0	16.7	15.4	17.6
EtDMA	10.1	13.0	10.6	13.2	14.5	14.3	13.3	15.8	15.5	14.8	14.0	13.8	15.0	15.1	13.1	15.2	14.1	13.9	18.2	20.1	14.3
mMePhMe	9.7	12.3	2.7	13.3	17.2	19.0	14.9	16.0	16.9	18.5	14.5	13.3	16.1	12.4	15.5	16.8	15.7	14.6	17.0	18.0	16.6
Et	12.7	16.7	14.5	14.5	20.7	18.4	16.5	21.4	21.5	20.5	16.3	18.2	20.8	17.6	20.5	20.9	17.7	18.2	20.8	21.2	21.5
mNPh	13.7	19.9	16.0	17.1	19.9	19.8	17.3	23.7	20.8	24.5	19.0	21.5	21.9	19.8	22.7	23.5	19.4	17.8	23.8	24.1	21.6
pMePh	15.0	18.8	16.4	17.2	22.8	21.2	21.0	26.0	25.9	25.4	19.2	21.5	25.4	22.5	25.3	25.9	22.7	21.8	24.7	25.3	26.0
mSO2Ph	14.6	18.1	17.7	18.4	21.5	19.1	23.7	23.7	23.0	25.5	19.0	20.4	25.2	19.8	24.3	24.8	22.9	16.3	25.3	24.4	23.7
pSO2Ph	18.5	21.6	23.5	22.0	27.7	25.1	27.2	29.1	28.9	30.1	25.7	25.3	30.0	23.1	29.5	30.2	25.6	24.3	28.8	29.6	28.6

Secondary Amine MeOH Relative Reaction Barriers

	oDMAPhO	oMeOPhN	mDMAPhN	pMePhN	mDMAPhO	mOMePhN	pOMePhN	ptBuPhO	pDMAPhO	CF3Ether	isocyanurate	oOMePhO	mMePhO	oDMAPhN	oMePhO	pMePhO	mOMePhO	pDMAPhN	Ether	AllylO	pOMePhO
EtPIP	0.8	8.0	5.4	15.2	6.3	6.2	13.2	14.0	12.7	9.7	7.3	9.3	3.8	5.6	11.6	14.9	8.8	6.8	5.8	9.9	14.8
opMeCy	0.0	7.2	11.3	16.3	10.2	6.7	13.5	12.7	14.6	10.4	8.7	12.3	10.3	6.5	9.9	10.0	11.3	8.8	11.2	12.2	15.5
mMeCyMe	9.7	10.2	11.1	16.1	11.9	16.1	8.0	20.8	14.8	14.4	15.9	12.0	15.7	10.8	15.1	16.5	14.0	10.5	14.7	16.7	19.3
pMeCy	3.5	11.1	6.1	18.8	13.3	2.6	14.5	12.3	15.9	8.5	14.2	12.6	12.6	9.9	15.0	16.1	13.5	18.2	14.1	12.9	15.9
EtMA	3.1	10.6	7.5	16.4	3.5	11.5	12.0	14.8	15.8	11.4	12.4	9.2	12.7	8.3	13.8	13.1	9.5	13.7	13.0	10.5	9.5
EtDMA	6.5	14.3	15.1	11.5	12.4	13.0	16.4	14.9	10.4	14.0	7.4	10.5	12.2	13.5	12.5	12.9	9.4	13.1	11.2	10.9	14.5
mMePhMe	1.9	8.4	12.9	10.2	10.3	13.5	16.8	16.0	14.3	12.9	14.2	14.0	10.8	11.9	11.0	13.8	13.2	11.9	15.6	11.9	15.4
Et	7.5	5.4	7.5	13.2	14.3	13.7	20.5	14.8	12.9	15.4	10.7	13.4	16.4	13.7	17.9	17.1	13.7	9.5	14.6	11.0	18.1
mNPh	3.9	12.3	12.1	14.1	8.5	11.8	14.0	13.7	15.9	18.0	7.8	11.3	11.5	8.7	14.6	14.1	11.2	16.4	10.3	11.2	18.4
pMePh	4.5	11.4	9.8	23.1	11.6	14.2	15.7	21.0	16.2	16.4	9.2	12.4	11.6	14.8	15.4	16.1	12.4	14.4	12.3	11.5	16.2
mSO2Ph	10.3	11.3	9.7	17.2	20.9	13.1	18.4	22.7	16.3	14.1	14.8	14.5	14.3	12.6	16.4	15.5	15.4	18.6	17.3	15.6	20.5
pSO2Ph	6.9	14.3	13.9	15.7	12.9	13.0	21.7	26.0	16.5	17.8	14.0	13.7	16.5	13.5	26.2	17.3	14.6	25.7	14.7	16.5	17.5

Figure 3. MeOH catalyzed relative reaction barriers. Each box denotes the relative reaction barrier to the lowest barrier denoted in black and at 0.0 kcal/mol. All energies in kcal/mol B3LYP-D3/6-31G**.[10]

cooling of a molecular system to obtain the glass transition temperature. By measuring the density as a function of temperature, the T_g can be estimated by nonlinear fitting of the data to a hyperbola [11]. Thermophysical properties simulations were performed over a temperature range of 800K to 100K for all the systems, at a rate of 1 ns per 10K step using an NPT ensemble for all simulations. The resulting density profile was analyzed using the thermophysical properties analysis module. This module performs an automated estimation of T_g by fitting the density data as a function temperature to a hyperbolic curve. The peak of the hyperbola is then used to determine the T_g value.

Once the simulation is equilibrated at the temperature of interest, during the T_g prediction; the thermoset system can then be used for evaluation of additional properties. For example, we evaluated the maximum water uptake capacity of the systems using GCMC approach. The GCMC simulations were performed for 50 ns at 300 K and 100 % humidity.

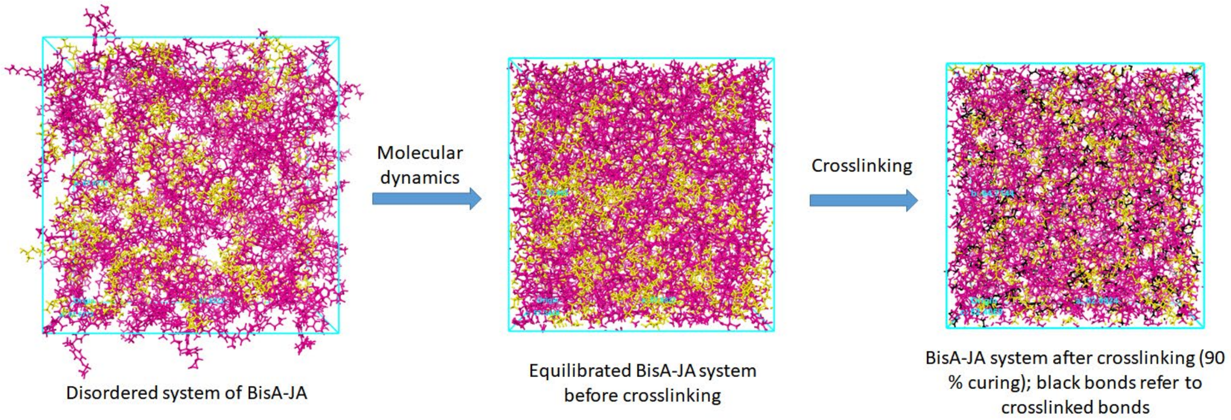
Table 1: Epoxy-amine systems considered for molecular dynamics simulations

System #	**epoxide**	**epoxide abbreviation**	**amine**	**amine abbreviation**
1	bisphenol A	BisA	4,4-diamino diphenyl sulphone	44DDS
2	bisphenol A	BisA	Jeffamine	JA
3	bisphenol A	BisA	tris(2-aminoethyl)amine	TEAE
4	bisphenol A + p-triglycidyl aminophenol	BisA-pTGAP	4,4-diamino diphenyl sulphone	44DDS
5	bisphenol A + p-triglycidyl aminophenol	BisA-pTGAP	Jeffamine	JA
6	bisphenol A + p-triglycidyl aminophenol	BisA-pTGAP	tris(2-aminoethyl)amine	TEAE
7	bisphenol A + ether	BisA-nPG	4,4-diamino diphenyl sulphone	44DDS
8	bisphenol A + ether	BisA-nPG	Jeffamine	JA
9	bisphenol A + ether	BisA-nPG	tris(2-aminoethyl)amine	TEAE

3. RESULTS

Before performing the crosslinking simulation, the relative reaction rates need to be computed. Using a reaction library that contains the uncatalyzed epoxy-amine TS as well as the H2O, MeOH, and BF3 catalyzed TSs for both primary and secondary amines, a library of epoxides and amines were enumerated. Each epoxy/amine combination was subjected to the Reaction Workflow to locate all stationary points in the reaction as well as compute energetic barriers for all reaction steps. The relative rates for MeOH catalyzed epoxy-amine reactions is presented as a heat map in Figure 3.

Based on the reaction barriers, we selected nine epoxy amine systems for evaluation using molecular dynamics (see Table 1). We created amorphous cells of these nine systems and equilibrated using the protocol mentioned in the methods section. The equilibration step is necessary to densify the system, packing all the molecules in the cell. As a final equilibration step, the system was heated to 800K, the target temperature for running the crosslinking protocol. The high temperature allows the system to sample a large portion of phase space and minimize the residual strain that occurs during the bond forming step (Figure 1). This allows the system to reach a high degree of conversion, typically greater than 90%. In this work, we stopped the crosslink procedure once the curing reaches 90%.



Disordered system of BisA-JA

Equilibrated BisA-JA system before crosslinking

BisA-JA system after crosslinking (90 % curing); black bonds refer to crosslinked bonds

Figure 4: Schematic for obtaining a crosslinked simulation cell in MSS. The pink and yellow molecules represent BisA and JA molecules, respectively. The black bonds represent crosslinked bonds.

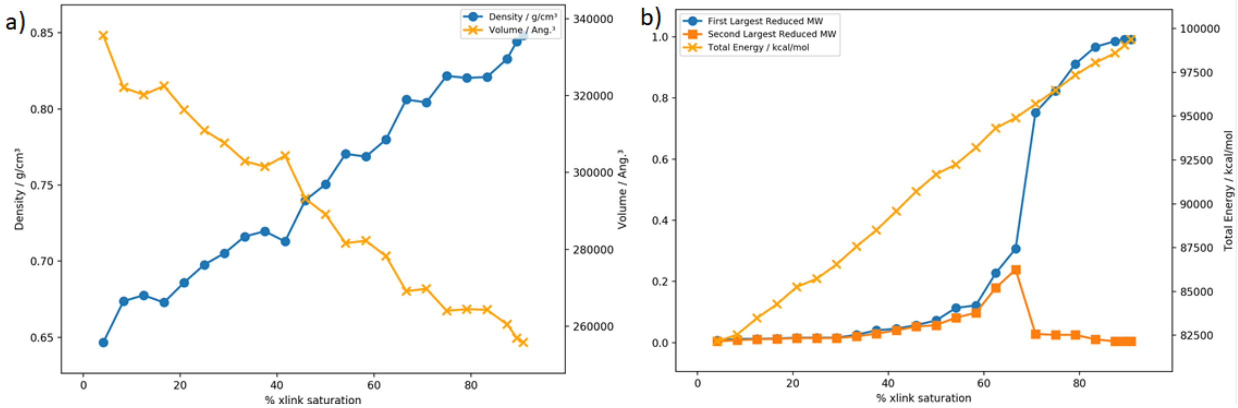


Figure 5. Monitoring evolution of the crosslinked polymer system. During the crosslinking simulation of BisA-JA, system properties can be monitored including: a) density and volume , b) total energy of the MD simulation from each iteration and theoretical gel point using the first and second reduced molecular weight species.

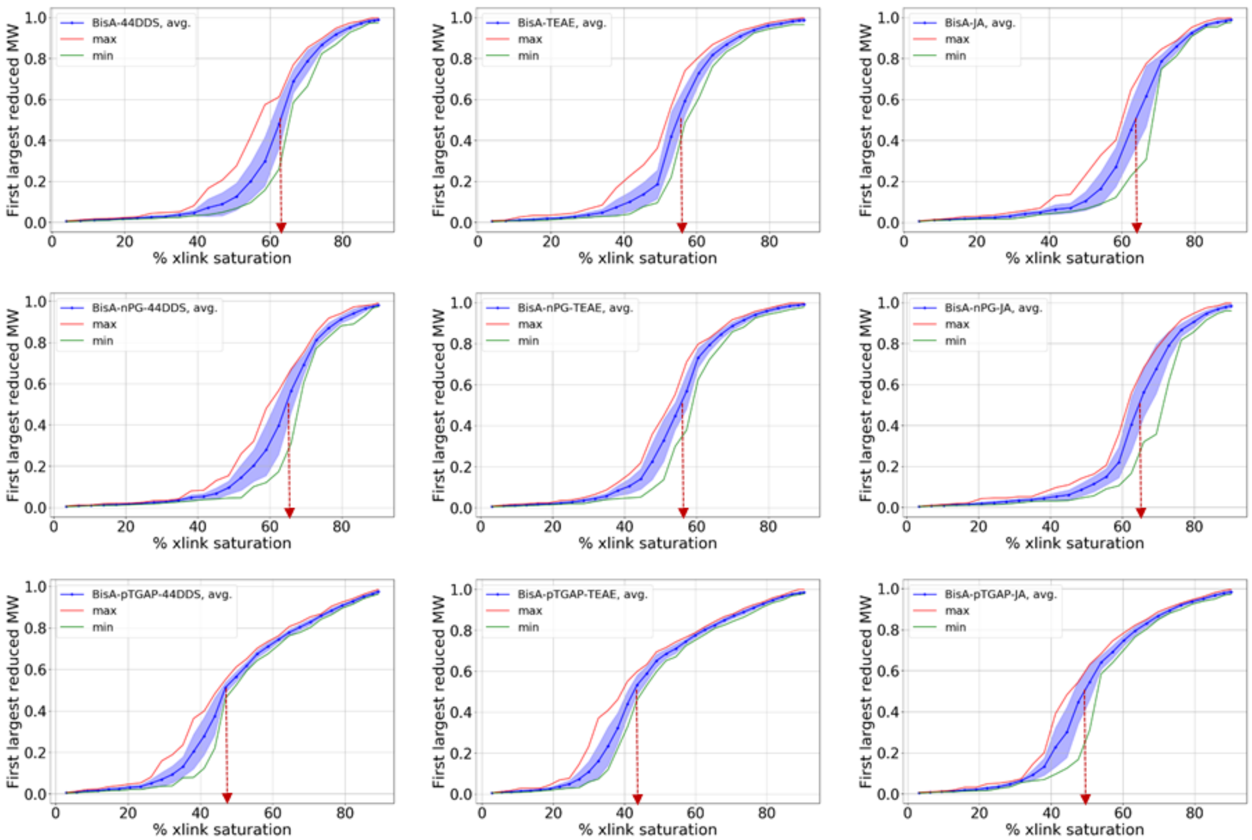


Figure 6: Tracking of first largest reduced molecular weight during the crosslinking of all nine systems. The red arrows in each plot refers to the get point (the point where a single structure is at least 50 % of the system).

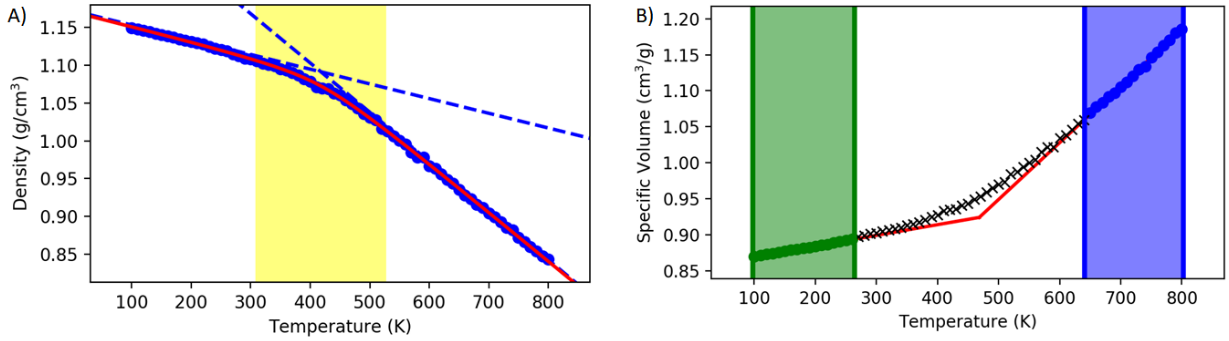
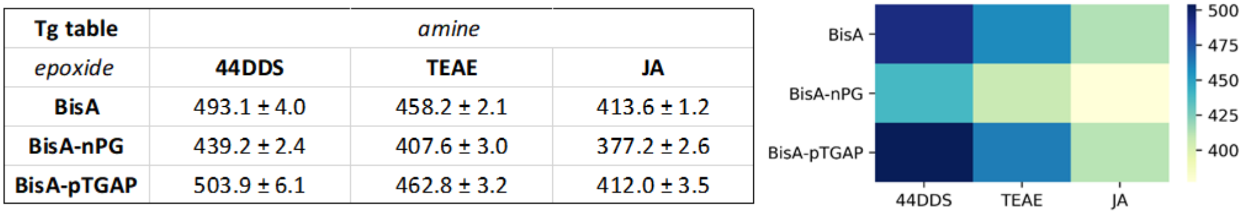


Figure 7: Estimation of T_g and volumetric CTE. A) The T_g is determined by a hyperbolic fit of the density of the crosslinked BisA-JA system as a function of temperature. Volumetric CTEs above and below the T_g were determined using the bilinear fit method (green shaded regions indicates glassy region fit while the blue shaded region represents the rubbery region).

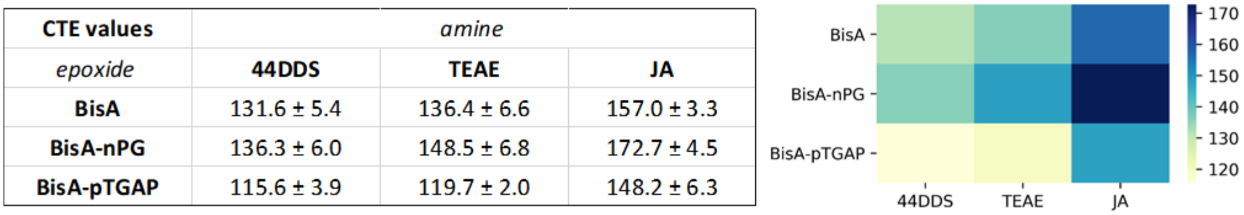
As the curing process evolves, the system undergoes several physical changes. In Figure 4, we show a schematic of obtaining a crosslinked simulation cell from a disordered system. As crosslinks are formed the system volume decreases while the total energy of the system increases as more strain is introduced from the bonds formed between the amine and the epoxide ring. Real time analysis of the physical evolution of these parameters allows researchers to gain insight to the process of curing, not just the resulting polymer network. Utilizing the built-in analysis functionality, these properties can be monitored as the simulation progresses. Using the BisA-JA system as an example, we monitored changes in density, volume, total energy and estimated the theoretical gel point (Figure 5). Volume shrinkage is a well known effect of crosslinking epoxy resins, and can be estimated from a single crosslinking simulation [9].

In addition to the above mentioned properties, we can also obtain insight into the gel point, a property which is often difficult to measure experimentally. From the simulations, we can easily gel point by measuring the concentrations of the largest two molecule species in the system. It can be estimated from the maximum molecular size for the first largest molecule generated. In this work, we consider the gel point as the %crosslink where the first largest molecular weight reaches 50% of the system. We first compute the average curve of the first largest molecular weight from ten replicates and select the 50% point as shown in Figure 6. Among the three amines considered, TEAE amine exhibits the lowest gel point. Addition of nPG epoxide to BisA does not impact the gel point, whereas, addition of pTGAP decreases the gel point significantly.



Tg table	*amine*		
epoxide	**44DDS**	**TEAE**	**JA**
BisA	493.1 ± 4.0	458.2 ± 2.1	413.6 ± 1.2
BisA-nPG	439.2 ± 2.4	407.6 ± 3.0	377.2 ± 2.6
BisA-pTGAP	503.9 ± 6.1	462.8 ± 3.2	412.0 ± 3.5

Figure 8: Comparison of T_g values of all nine epoxy-amine systems. The unit of T_g is K.



CTE values	*amine*		
epoxide	**44DDS**	**TEAE**	**JA**
BisA	131.6 ± 5.4	136.4 ± 6.6	157.0 ± 3.3
BisA-nPG	136.3 ± 6.0	148.5 ± 6.8	172.7 ± 4.5
BisA-pTGAP	115.6 ± 3.9	119.7 ± 2.0	148.2 ± 6.3

Figure 9: Comparison of CTE values of all nine epoxy-amine systems. The unit of CTE is $10^{-6}K^{-1}$.

With the resulting crosslinked polymer system, subsequent simulation methods can be used to predict thermomechanical properties. One of the most attractive properties of thermoset systems are the relatively high glass transition temperatures (T_g). MD simulation protocols can mimic the cooling process, capturing the kinetic dependence of T_g [12]. Although the timescales for measuring T_g experimentally are far outside the time domain of MD simulations, these simulations can be used to predict T_g with some degree of overestimation (typically 20-40K) [13]. Using the thermophysical properties prediction module, the crosslinked systems were heated to 800K and then cooled down to 100K at a rate of 5 ns per 10K. The wide range of temperatures is necessary to collect sufficient data points in both the glassy and rubbery regions for the hyperbolic fitting process [11]. The hyperbolic center, obtained from the data fitting of density data as a function of temperature, is the T_g. Figure 7 shows the method we use to compute T_g values using hyperbolic fitting method and CTE values from the linear fitting method. We report the T_g results in Figure 8. The results indicate that the T_g values are dependent on the type of amine - it decreases as we go from 44DDS to TEAE to JA. Aromatic amine 44DDS exhibits higher T_g compared to aliphatic amines. Addition of nPG to BisA decreases the T_g value, and addition of pTGAP to BisA increases it.

In addition to T_g, we can also estimate the volumetric coefficient of thermal expansion (CTE) for the thermoset system. In order to do this, a bilinear fit is performed on the specific volume data as a function of temperature. For the model system, CTE was determined above and below the T_g by linear fitting to both regions (Figure 6). In Figure 9, we report the CTE values below the T_g region, i.e. in the glassy region. The trend in CTE values is the opposite of T_g trends.

Next, we computed the water uptake capacity of these nine epoxy-amine systems. Figure 10 shows the percentage of water uptake. Water uptake is the highest for BisA-pTGAP/44DDS system and lowest for BisA-JA system. Addition of nPG or pTGAP epoxides to BisA allows for more water uptake, with the latter showing a higher uptake. In the case of amines, the water uptake order is 44DDS>TEAE>JA. Thus, the aliphatic amines show a lower uptake than the aromatic amine 44DDS.

4. CONCLUSIONS

Molecular modeling of thermosets is an active area of research. Previously, these simulation methods required expert knowledge and custom algorithms to generate thermoset networks. By developing user friendly workflows within the Schrödinger Materials Science suite, the entire process from calculating relative reaction barriers to generating crosslinked structures to thermomechanical property prediction is accessible to both experts and non-experts alike; enabling analysis from a few systems to many via high throughput screening. In this work, we took nine epoxy formulations, BisA alone or combined with either pTGAP or nPG and crosslinked with 44DDS, TEAE, or JA, and were able to generate molecular networks, predict T_g and mechanical response, while also gaining insight toward the structure-function relationship.

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