MODELING THERMOSET POLYMERS AT THE ATOMIC SCALE: PREDICTION OF CURING, GLASS TRANSITION TEMPERATURES AND MECHANICAL PROPERTIES

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ABSTRACT

Thermoset polymers have gained interest in recent years due to their low cost, ease of processing and unique physical properties. Molecular simulation represents an avenue to explore the chemical structure-function relationship of these polymers by leveraging advances in the speed and accuracy of molecular dynamics (MD) simulations, due to high performance computing (CPU/GPU), efficient algorithms and modern force fields. We have developed a cross linking algorithm that allows for any chemistry to be defined to break two bonds and form new ones. This feature greatly increases the applicability in forming polymers with different crosslinking chemistries. System properties can be monitored during a cross linking simulation within a single interface, allowing the user to estimate properties like theoretical gel points and reactive group concentrations as curing occurs. After curing, glass transition temperatures (T_g) can be predicted using long MD cooling simulations in excess of 1 microsecond made possible with the GPU-enabled Desmond MD engine. Mechanical response properties can also be predicted. In this work, several different types of crosslinking chemistries will be explored, including epoxies, benzoxazines and polyurethanes

1. INTRODUCTION

Materials containing thermoset polymers are an integral part of the composites industry and comprises ~25 % of the global plastics market [1]. Polymeric materials based on thermosets have a wide range of applications including aerospace, military, marine and high performance consumer products. Typically, composite materials with a specific range of physical properties are required in the design process. With the advances in computational modeling, due to technological breakthroughs in CPU and GPU-based computing, costly experimental methods can be reduced by prediction of relevant thermoset properties. Using atomistic simulations, the relationship between microscopic and macroscopic properties can be addressed, with the potential for "materials by design" [2].

Molecular dynamics simulations allow users to simulate materials at the molecular level in a thermodynamically rigorous manner. Accurate force fields, based on a combination of high level quantum mechanical calculations and experimental data, can be used to describe the key interactions in polymeric systems [3]. Previously, the lack of polymer builders capable of generating highly crosslinked networks based on specific chemical reactions of multifunctional groups was a major barrier to simulation thermoset polymers. To overcome this problem, several groups have built crosslinking modules to predict the network formation first by coarse-grained MD and Monte Carlo based methods then later fully atomistic methods [4–8].

While several methods exist to build thermoset networks, most are hardwired for a particular chemistry or require expert-level knowledge of the underlying simulation code. For property prediction of thermoset materials to be accessible to a larger audience, we developed a crosslinking module that is not only accessible non-experts but also increased the versatility/applicability by 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 step [9]. Once a networked system is built, user-friendly workflows can be incorporated to predict properties including: solubility, glass transition temperatures and mechanical response. By leveraging high throughput MD simulations with GPU acceleration, researchers and engineers can explore more chemical space to designing new materials.

2. EXPERIMENTATION

Molecular dynamics (MD) simulations enable researchers to simulate molecular systems to predict thermomechanical properties at the atomic level [3]. In order to prepare a thermoset polymer structure for such simulations, a polymerization process is required to build the network structure. During this process, a limited number of reactions can occur between to chemical groups, forming a new bond(s). Reaction sites 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 a new set of bonds is formed, using the search criteria and potentially limiting the number of new bonds formed in a single iteration, an equilibration MD simulation can be performed. All of these steps are necessary to form a highly crosslinked thermoset system that can then be used for subsequent simulations to predict physical properties.

All polymer building, molecular dynamics and analysis were performed using the Schrödinger Materials Science suite [10]. All of the MD results discussed in this work was obtained using the GPU-enabled highly efficient Desmond MD engine [11,12]. The initial monomer systems were built using the *Disordered System Builder* module with the OPLS3 force field [13]. For the TGDDM/3,3-DDS system, the total number of molecules was set to 256 (11,520 total atoms) with a stoichiometry of 1:1. The resulting amorphous systems were then equilibrated using the following protocol: 2000 minimization step using steepest decent then switching to conjugate gradient for the final 500 steps. Then the system is heated to 300K for 24ps using a NVT ensemble followed a high temperature step at 700 K for 240 ps with a NVT ensemble to allow electrostatic reorganization. The system is then rapidly cooled to 300 K for 24 ps at 1 atm with a NPT ensemble, then extended for an additional 240 ps. A high compression step is performed

next at 300 K, NPT ensemble with the pressure set to 1000 atm. This step is used to condense and pack the system, removing unwanted inner volume. After the compression step, the system is relaxed back to 1 atm using a NPT ensemble at 300 K for an additional 30 ns.

Thermoset networks were created using the *Crosslink Polymer* builder. The workflow for iteratively building a network is shown in figure 2. The input parameters for the simulation are the SMARTS patterns to define the bond breaking and forming steps along with an equilibration protocol. The primary and secondary amine bonds corresponding SMARTS pattern was defined as "N[H]" while C-O bond in the epoxy ring is defined as "[C;r3;H2]O". The number of crosslinks was limited to 2 per iteration. After crosslinking iteration, a MD equilibration stage was performed (800 K, 50 ps NPT at 1 atm). Analysis of the crosslinked structures was performed using the crosslink polymers analysis panel.
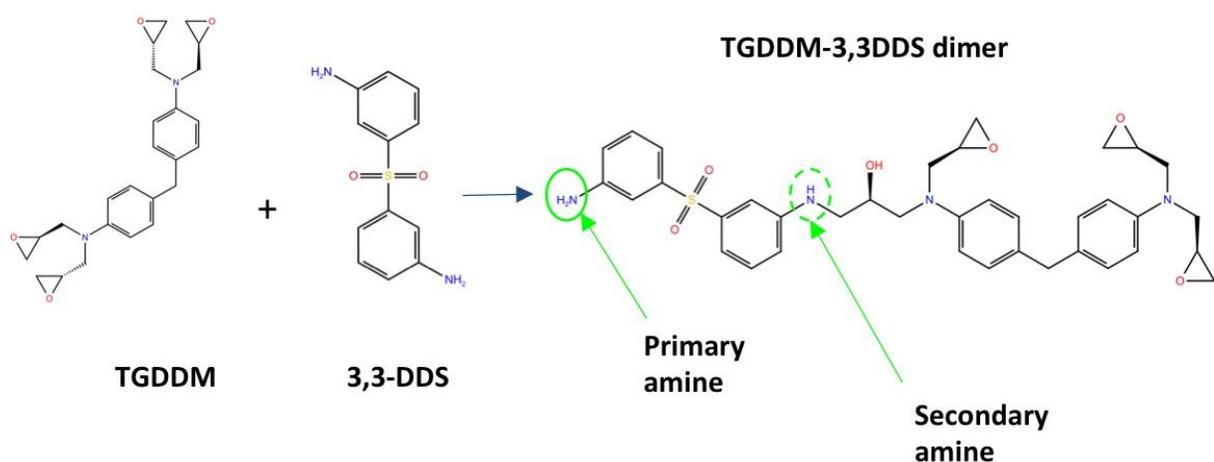

Figure 1. Epoxy and amine reaction for polymerization

To obtain thermomechanical properties, the resulting crosslinked systems were first subjected to an automated MD protocol using the *Thermophysical Properties* module. These calculations mimic the cooling process of a molecular system to obtain the glass transition temperature. By monitoring the density as a function of temperature, the T_g can be estimated by nonlinear fitting of the data to a hyperbolic function[14]. The iterative MD simulation cycle was performed over a temperature range of 700 K (800 K to 100 K) for TGDDM/3,3-DDS at a rate of 20 ns per 10 K step using an NPT ensemble for all simulations. The resulting density profile analysis was facilitated using the dedicated *Thermophysical Property Analysis* tool. This panel performs an automated estimation of T_g by fitting the density/temperature data to a hyperbolic curve. The intersection of the high and low temperature hyperbolic asymptotes corresponds to the estimated T_g value.

Once the simulation is equilibrated 300 K during the T_g prediction; the thermoset system can then be subjected to a series of strained controlled tensile test simulations. The stress-strain driver was utilized to perform the strain calculations by deforming the cell iteratively and running NVT equilibrations at each step. For this type of calculation, the strain was defined as volume conserving uniaxial with a step size of 0.002 and a total of 125 steps. At each step, the system is equilibrated for 100 ps at the desired temperature. The resulting stress for each step is

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then calculated using the final 20% of each simulation trajectory. Stress-strain curves were generated using the stress strain analysis panel.
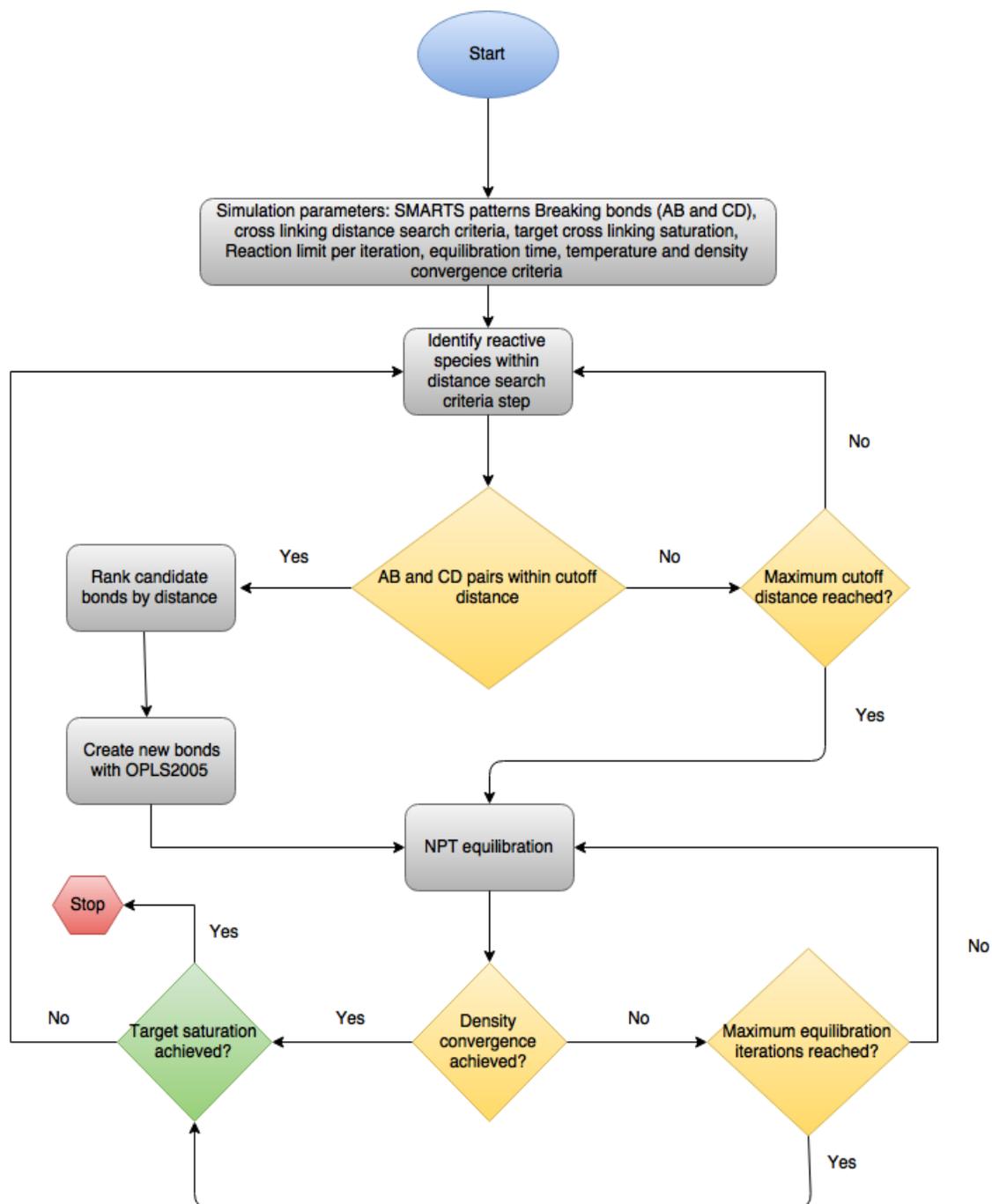
Figure 2. Crosslinking algorithm workflow diagram

3. RESULTS

To demonstrate the utility of using automated workflows for generating atomistic models for thermosets with subsequent property prediction, we chose to illustrate this process for a well-known epoxy/amine system: TGDDM and 3,3-DDS. Before building a highly crosslinked network for the system, we first generated an amorphous system then equilibrated using a MD protocol. Once the system is equilibrated, the crosslinking step can be performed. During the crosslinking, instabilities can arise from the formation of unphysical structures due to the fact that the chemistry is being driven by distance separations alone.

Using the automatic *Crosslink Simulation Analysis* tool, the evolution of simulated crosslinked cell structure can be monitored, along with the physical properties of the system like volume and density; giving insight into the quality of the simulation. As the system of TGDDM/3,3-DDS monomer is heated, a change in the density and volume of the simulation cell is observed (Figure 3.). As more crosslinked are formed, the volume begins to decrease by 7.4% at the final cure percentage of 95%. In addition to volume shrinkage and density information, the gel point can also be obtained from the crosslinking simulation. By tracking the molecular weight of the two largest structures, the gel point can be estimated by the inflection point of the second largest molecular weight species. For the TGDDM/3,3-DDS system, the gel point is between 40-45% (Figure 4).
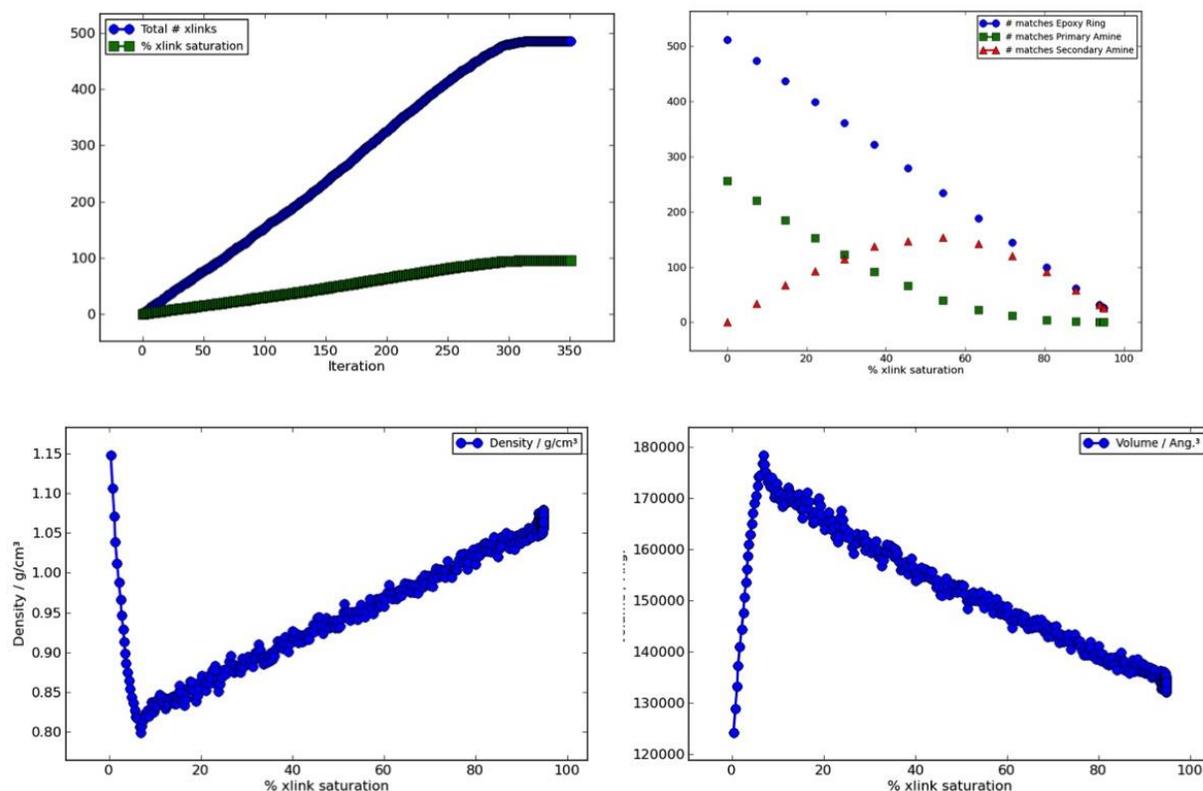
Figure 3. Cure properties measured during crosslinking job. Upper Left: The number of crosslinks formed and saturation as a function of crosslinking attempts (iterations). Upper right: Concentration of reactive groups (primary and secondary amines, epoxy rings) as a function of crosslink saturation. Lower left: Density fluctuations and volume fluctuations (lower right) during the simulation.

One of the most important properties of amorphous polymers, including thermosets, is the glass transition temperature (T_g). It is key to determining the processing and application temperatures for a particular polymeric material. MD simulations can be used to estimate several thermodynamics properties, like density and internal energy, necessary to determine T_g computationally. The simulation workflows typically employed to determine T_g involve cooling or heating up a model system at a constant rate with a thermostat to control the temperature of the system.

Several experimental methods are available to estimate T_g and are widely used by engineers/researchers. Time scales of the experiments are generally much longer, on the order of minutes, than accessible by even the fastest MD codes. Given the well-known kinetic dependence of T_g, MD cooling simulations will tend to overestimate experimental T_g values[15]. Despite the different in time scales, several studies have shown molecular simulations do have predictive power when estimating T_g values. Typically, most MD simulations overestimate the T_g by ~ 20K, due to differences between experimental and simulated cooling rates [15].
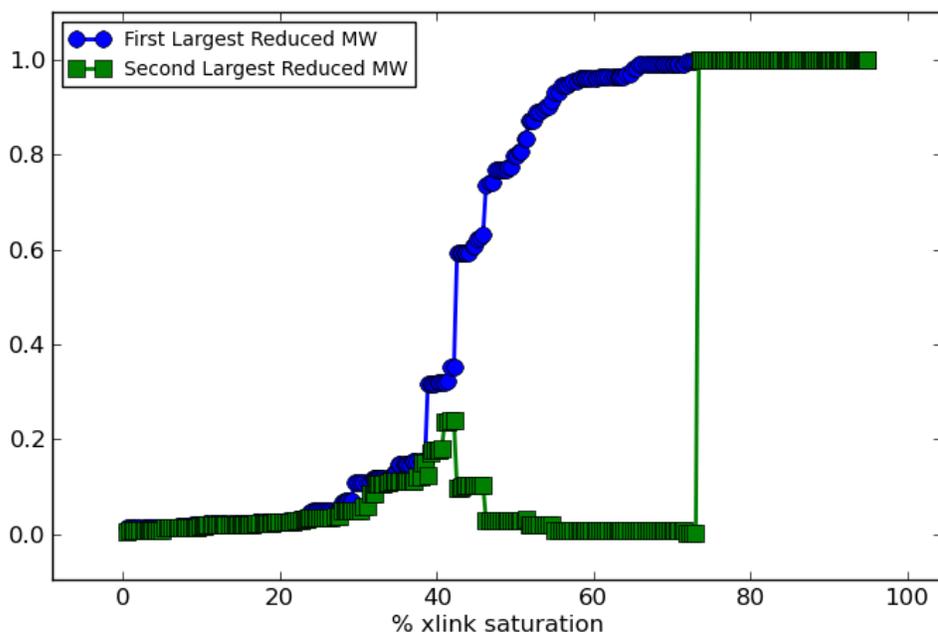

Figure 4 Gel point curve for TGDDM/3,3-DDS crosslinking simulation

To automate a workflow that incorporates a cooling rate for a defined temperature range, we developed the *Thermophysical Properties* module. This allows for full control over the temperature range, cooling rate and density convergence criteria. Density convergence is an important factor for accessing the system's response to cooling and quality of simulations. In the case of TGDDM/3,3-DDS we cooled the system down from the curing temperature from the

crosslinking simulation (800 K) to 100 K. The cooling rate was set to 20ns per 10 K steps, resulting in a 1.44 μs cooling simulation. From the density values determined at each temperature, the hyperbolic fitting process identified the T_g as 534 K (Figure 5), which is in agreement with the experimental dry T_g of 504 K reported by Huntsman[16]. The 30 K difference can be rationalized by the accelerated cooling rate from the cooling simulations being on the order of microseconds. In addition to T_g, the coefficient of thermal expansion can also be determined by fitting to the linear region of the glassy region and was found to be 110.14 10^{-6} K^{-1} at 298.15 K.
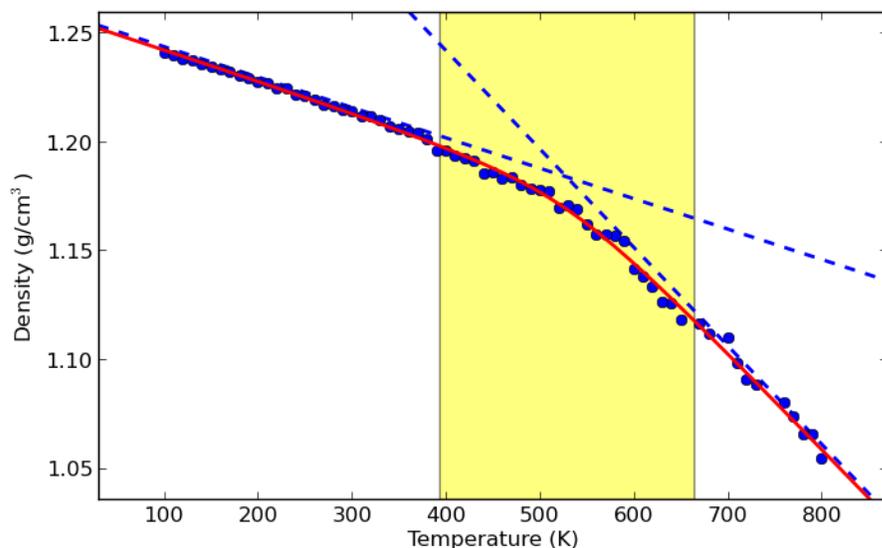

Figure 5. Glass Transition Temperature estimation using MD simulated cooling

Mechanical response is another property of amorphous polymers that is crucial for performance. Understanding the molecular origins of mechanical properties can provide insight to macroscopic responses measured experimentally. In order to simulate the different types of deformations that a system can experience, MD simulations are typically employed with varying loading conditions. In this scenario, the simulation cell is deformed in small increments followed by MD equilibration at each step. The crosslinked TGDDM/3,3-DDS system was subjected to a strain controlled tensile simulation (Figure 6). Young's modulus can be obtained by the linear fitting of the stress strain curve up to 4% strain. The yield point can also be defined as the maximum stress attained in the curve.
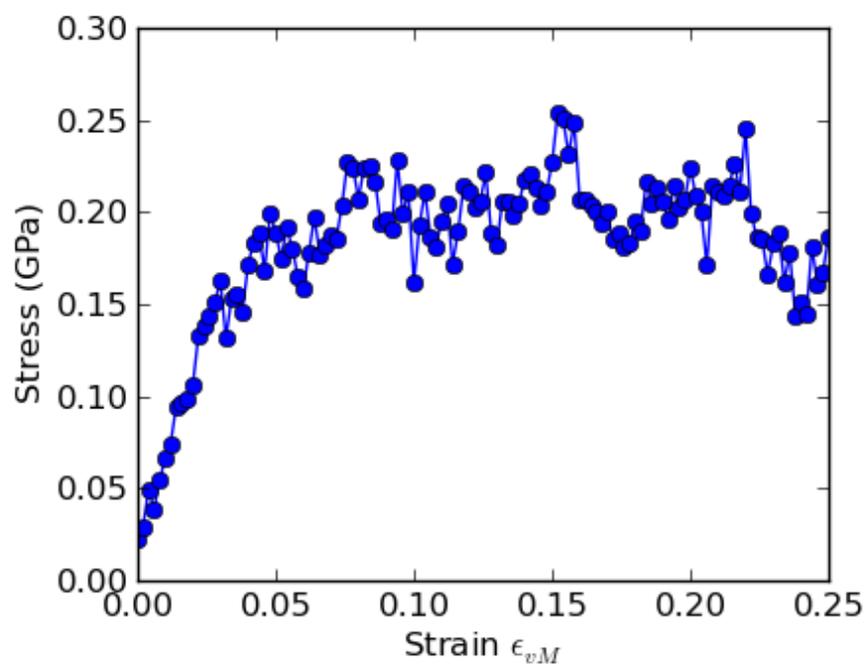
Figure 6. Stress-strain tensile plots for TGDDM/3,3-DDS

4. CONCLUSIONS

The need for a flexible, user friendly crosslinking method to generate equilibrated atomistic models of highly crosslinked thermosets led us to development of a new, versatile *polymer crosslinker.* While most other builders have focused solely on epoxy/amine reaction systems, using a SMARTS based selection criteria for defining the crosslinking chemistry allows for any chemistry to be simulated. This method not only allows for user-defined chemistry, but total control of the crosslinking parameters. When used in conjunction with the *Crosslinking Simulation Analysis* model, simulation quality along with physical/structure characteristics can be monitored in an automated fashion.

In addition to modeling the cure cycle for the thermoset, several other workflows can be utilized to predict both the T_g and mechanical response. Automated MD workflows, modern quantitative force fields, and GPU-accelerated MD increases the accessibility, accuracy and efficiency of thermoset property prediction, which dramatically increases the role of atomistic simulation in accelerating the development of advanced thermoset polymer materials.

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