

Predicting Mechanical Response of Crosslinked Epoxy using ReaxFF

Gregory M. Odegard,^{*1} Benjamin D. Jensen,¹ S. Gowtham,² Jianyang Wu,³ Jianying He,³
Zhiliang Zhang³

¹*Department of Mechanical Engineering - Engineering Mechanics, Michigan Technological University, Houghton, MI 49931, USA*

²*Information Technology Services, Michigan Technological University, Houghton, MI 49931, USA*

³*Department of Structural Engineering, Norwegian University of Science and Technology, Trondheim, Norway*

**Corresponding Author, e-mail: gmodegar@mtu.edu*

ABSTRACT: The development of improved epoxy resins can be greatly facilitated using molecular dynamics (MD) techniques. Because molecular-level failure events can play a significant role in epoxy mechanical behavior, the reactive force field (ReaxFF) is an ideal tool for MD simulations of crosslinked epoxies. The results of this study demonstrate that mechanical stiffness and strength values predicted with MD using ReaxFF show close agreement with experiment. The results also indicate that despite the inherently large time-scale differences between experiments and MD modeling, the elastic/yield response from the vastly different characteristic strain rates can be easily correlated.

Keywords: Modeling and simulation, Thermosetting resins, Mechanical properties, Multiscale modeling

1. Introduction

Epoxy resins are thermosetting polymers that are widely used in adhesives, paints, coatings, medical implants, and electrical devices. Epoxy is also widely used as a matrix material in fibrous composites for the aerospace and wind turbine industries. Epoxies are ideal for these applications because of their high specific stiffness, high specific strength, electrical insulating properties, corrosion resistance, chemical compatibility with reinforcing fibers, and relative ease-of-manufacture. Despite the success of epoxies, further improvements in their properties are being sought.

The development of new epoxy materials can be greatly facilitated through computational molecular modeling. Molecular Dynamics (MD) simulations can be used to gain physical insight into the behavior of epoxies exposed to various environmental conditions and mechanical loading. Many studies have addressed the MD simulation of epoxy materials using traditional fixed-bonding force fields [1-8]. These studies have provided some very useful information regarding the structure and thermo-elastic behavior of epoxies. However, because bond scission is a critical step in the initiation of failure in epoxies, a different approach must be used predict the strength and failure resistance of epoxies on the molecular level.

The Reax Force Field (ReaxFF) was initially developed to model bond dissociation and formation in carbon-based materials [9]. In the ReaxFF, the potential energy is defined as a function of bond order with energy penalties for nonequilibrium configurations. Parameters for the ReaxFF functions are developed by first simulating reactions that are expected to occur in a system of interest using computationally demanding ab initio methods. ReaxFF parameters are then determined that minimize differences between the ab initio and ReaxFF potential energies. Although specific ReaxFF parameter sets are typically developed for individual material systems, many parameter sets have been successfully adopted for materials that they were not originally intended for. The ReaxFF has been shown to accurately describe a wide range of carbon-based systems [10-20], including bulk polymer systems [21-23]. However, it has not yet been used to model bulk epoxy polymers.

The objective of this study is to demonstrate that an existing parameter set of the ReaxFF can be successfully used to predict the structure and elastic response of a crosslinked epoxy material. A model epoxy system has been constructed and simulated to predict the elastic properties and yield strength. The predictions have been compared to experimentally-obtained results for the same epoxy system. The results indicate that the ReaxFF can be reliably used to predict the elastic properties and yield point of epoxy-based systems. It is important to note that ideally a new ReaxFF could be developed specifically for the epoxy material system discussed herein. However, this study demonstrates that this is not necessary as the existing parameter used in this study predicts an elastic response and yield point that closely matches experiment.

2. Molecular modeling

The modeled epoxy system was composed of the EPON 862 monomer (Diglycidyl ether of Bisphenol F) and the crosslinking agent DETDA (Diethylene Toluene Diamine). Figure 1 shows the molecular structure of these two molecules before crosslinking. During the crosslink process, each amine group in DETDA can react with two epoxide groups in EPON 862. Therefore, a molar ratio of 2:1 of EPON 862 to DETDA molecules is necessary for a stoichiometric mixture. Details on the crosslinking process for this system can be found elsewhere [1].

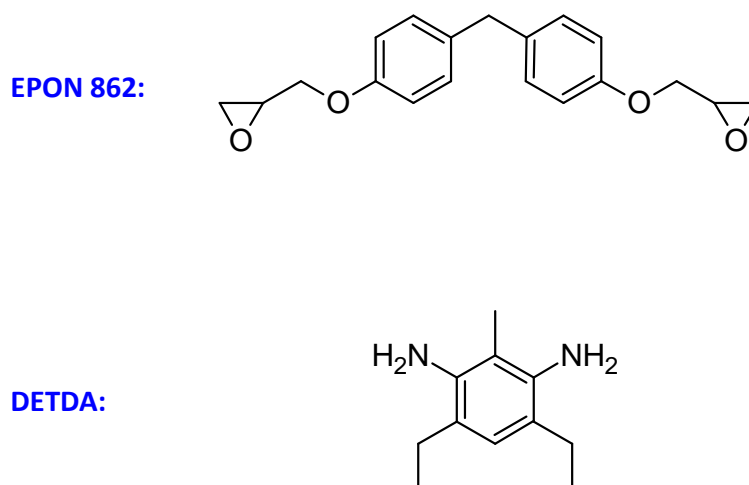


Figure 1 - Molecular structures of EPON 862 and DETDA monomers

Five independent samples of equilibrated and cross-linked EPON 862/DETDA MD models were established with the ReaxFF. Each model contained 72 EPON 862 molecules and 36 DETDA molecules, for a total of 4,284 atoms. The MD models were constructed using a multi-step procedure using the LAMMPS MD simulation software package [24]. First, modified versions of the EPON 862 and DETDA molecules were placed inside a simulation box at a very low mass density (0.004 g/cc). The modified versions of the molecules are shown in Figure 2, and represent the pre-crosslinked configurations. The EPON 862 and DETDA molecules were modified in this way to more easily simulate the complex crosslinking process. The modified molecules were slowly compressed to a bulk density of 1.2 g/cc at 300 K in the NVT ensemble over a period of 4 ns. This densification occurred over a simulated time of 4 ns using the OPLS all-atom force field [25].

Second, The R^1 and R^2 groups shown in Figure 2 (representing carbon and nitrogen radicals, respectively) were crosslinked using the “fix bond/create” command in LAMMPS with a crosslinking cut-off radius of 7.0 Angstroms. After a 1 ns simulation in the NVT ensemble, this resulted in an average crosslink density of 85%.

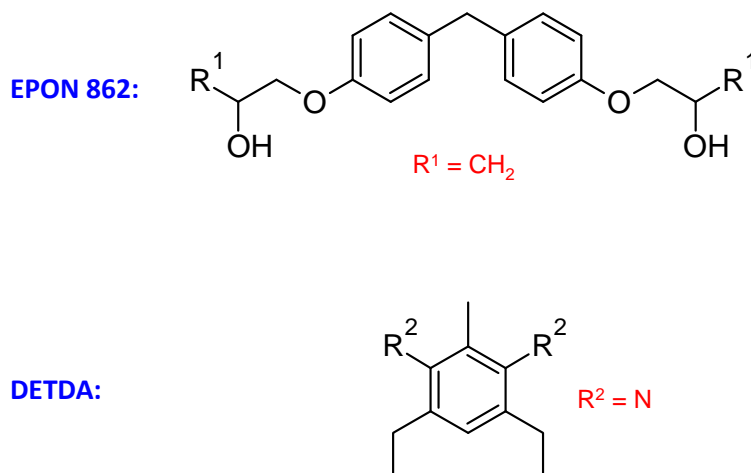


Figure 2 - Molecular structures of pre-crosslinked EPON 862 and DETDA monomers

For the third step, the five samples were slowly equilibrated in the NVT ensemble using the ReaxFF with the parameterizations of Liu et al [26]. The temperature was increased during these simulations from 0 to 300 K over 100 ps to ensure stability in the model after the change in force fields. Time steps of 0.1 fs were used [11]. Finally, the five samples were equilibrated in the NPT ensemble for 100 ps at 300 K using the Berendsen barostat [27]. The average density of the five samples after this step was 1.2 g/cc.

It was necessary to initially create the model with a traditional fixed-bonding force field (OPLS) in order to efficiently establish the crosslinked structure. With OPLS, the “fix bond/create” command could be used to create the crosslink bonds for specified distances between reactive groups. This command could not be used with ReaxFF. By varying the distance for bond formation in this manner between 2 and 10 Angstroms, it was determined that crosslink formation distances between 2 and 7 Angstroms resulted in covalent bond distributions in the model that were nearly identical with the uncrosslinked systems. For higher values of crosslink

formation distances (8 - 10 Angstroms), the resulting covalent bonds were relatively large compared to the covalent bonds in the rest of the model. After these equilibration steps were complete, the five samples had uniform mass densities and zero-valued residual stresses (determined with the “fix ave/spatial” command in LAMMPS), which indicated that the change in force fields and subsequent equilibration resulted in a well-equilibrated system with no residual effects. Figure 3 shows a typical molecular structure of the equilibrated and crosslinked model.

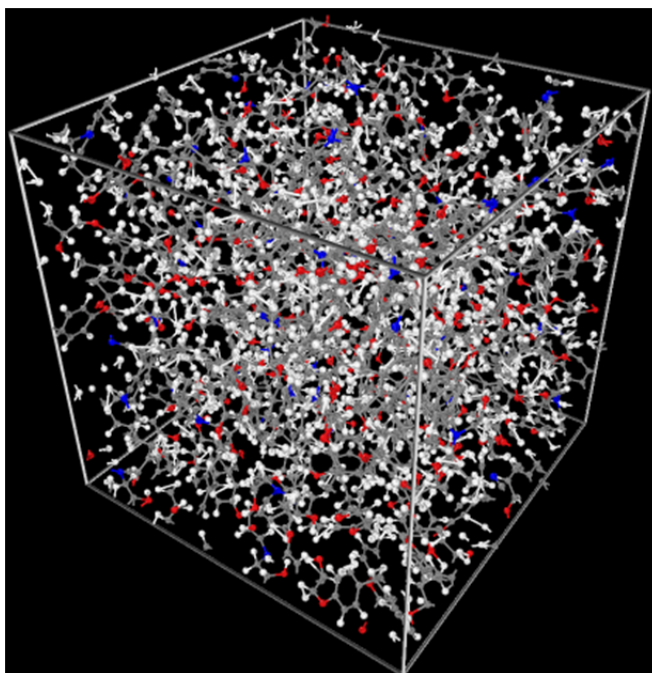


Figure 3 - Molecular structure of equilibrated and crosslinked MD model with ReaxFF. Coloring scheme: white - hydrogen, gray - carbon, blue - nitrogen, red - oxygen

Once the five crosslinked epoxy model samples were established, they were subjected to simulated tensile deformations along the x-, y-, and z- directions at two different strain rates. A 20% axial tensile strain (~18% true strain) was applied with zero-valued pressures applied in the lateral directions with the Berendsen barostat [27] to allow for the natural Poisson contraction. Using 0.1 fs time steps, the deformations were applied gradually over 1 ns and 2 ns, resulting in a strain rates of $2 \times 10^8 \text{ s}^{-1}$ and $1 \times 10^8 \text{ s}^{-1}$, respectively.

3. Results

Stress-strain plots were examined for each loading direction and each sample. A representative stress-strain plot is shown in Figure 4. When considering all of the plots, a common theme was discerned. There was a linear-elastic response up to a strain of between 3 to 5%, at which point the slope of the curves immediately changed, signifying the first characteristic yield event. After the first yield event, the stress-strain responses exhibited a reduced slope up to the second characteristic yield event, which, similar to the first yield event, is likely associated with changes in molecular conformation or bond scission. In some cases, multiple yield events occurred after the first yield event. Regardless, the stress-strain responses of the systems typically exhibited a

nearly zero-valued tangent stiffness at the higher strain levels (greater than 10% true axial strain), as shown in Figure 4. Although the data in Figure 4 could be fit in many different ways, the three strain-line fits shown in the figure were representative of the entire set of stress-strain plots.

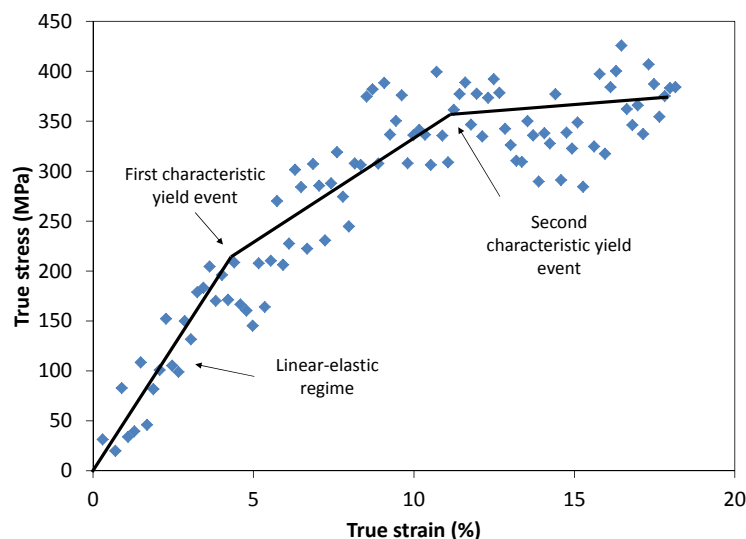


Figure 4 - Representative stress-strain curve for EPON862/DETDA

It is important to note that the response shown in Figure 4 is for a nano-scale system, and cannot be compared directly with the stress-strain responses of bulk epoxy specimens. In bulk samples, individual yield events at the molecular level (e.g. conformational changes and bond scissions) contribute to an observed overall non-linear response that does not exhibit clearly-defined individual yield events [28]. It is also important to note that ideally the exact cause for the changes in slope could be determined from the MD simulation. However, two factors made the nature of failure difficult to discern. First, the bond order values for the entire models fluctuated throughout the simulation process such that the changes in slope could not be directly correlated with bond scission. Second, because of the highly amorphous nature of the model, it could not be clearly determined by visual inspection of the structure if conformational changes or bond scission events lead to the sudden changes in the stress-strain slope.

The Young's modulus was determined for each axial deformation over all five samples by calculating the slope of the initial portion of the stress-strain plots (up to the first characteristic yield event). Figure 5 shows the resulting average values for the two simulated strain rates and those obtained experimentally [28] at three lower strain rates. The line shown in Figure 5 is a power law least-squares fit of the experimental data points. As expected, the predicted Young's modulus is higher than the experimental values. However, considering the experimental trend in modulus with strain rate, the range and trends of predicted values agrees closely with the experimental data, considering the scatter in the predicted values.

The yield strength from the MD simulations was defined as the stress at the first characteristic yield event. The average value of the predicted yield stress (189 MPa) and experimental values of yield stress [28] for the same epoxy system are shown in Figure 6 with their corresponding strain rates. Because of the different shape of nano-scale and bulk-scale stress strain curves of

epoxies (discussed above), it was assumed that the first characteristic yield event at the nano-scale corresponded to the 1% yield offset in the bulk-level experiments. The value of 1% was chosen because it approximately corresponds to the onset of nonlinearity in the bulk-scale tests [28]. As in the case of Figure 5, a power-law least-squares fit of the experimental data is shown in Figure 6. From this comparison there is excellent agreement between predicted and measured values of yield stress considering strain rate effects and the scatter in the predictions.

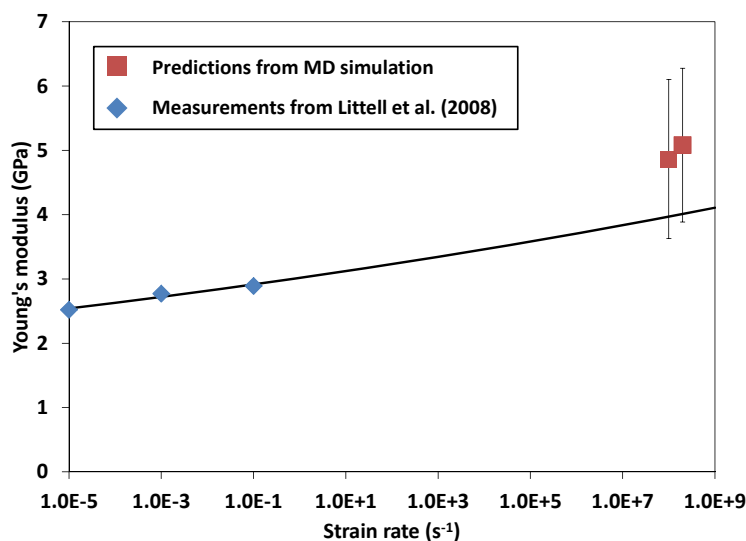


Figure 5 - Predicted and measured Young's modulus vs strain rate. The superposed line indicates the trend of the experimental values. Uncertainty in predicted values is from the standard deviation for all samples and loading conditions

The Poisson's ratio of each system was determined by examining the negative slope of the transverse/axial strain curves for up to the first characteristic yield event. An example plot of the transverse/axial strain response is shown in Figure 7. As can be seen from the plot, the average transverse strain values (calculated from the two transverse strains of the simulation box) show an expected amount of scatter and a clear trend of decreasing value with increasing axial strain. The average predicted Poisson's ratio from the simulations was 0.35 ± 0.08 and 0.35 ± 0.05 for simulated strain rates of $1 \times 10^8 \text{ s}^{-1}$ and $2 \times 10^8 \text{ s}^{-1}$, respectively. The average value from experiments on the same epoxy system is 0.41 [28]. The Poisson's ratio is not generally dependent on strain rate [28], and thus shows moderate agreement between prediction and experiment.

It is important to note that typical MD-based predictions of elastic properties of polymers typically ignore the influence of simulated strain rate, even though strain rate effects in polymers are well-documented [29]. The likely reason for this omission is because the Young's moduli of polymers for wide ranges of strain rates are on the same order (see Figure 5) and the simulation of laboratory strain rates is nearly impossible to achieve for fully atomistic models. Differences between predicted and experimentally-determined values of modulus are sometimes justified by statistical scatter in the predicted modulus values from different simulated samples (see, for

example, reference [30]). However, because of the availability of experimental data for the particular epoxy system studied herein, the results of this research indicate that predictions in modulus and strength can agree with experiments when the strain rate discrepancy is carefully considered.

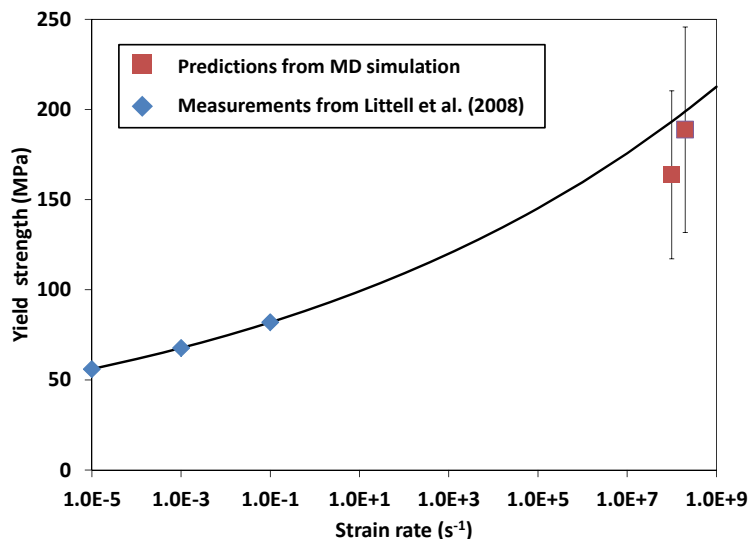


Figure 6 - Predicted and measured yield strength vs strain rate. The superposed line indicates the trend of the experimental values. Uncertainty in predicted values is from the standard deviation for all samples and loading conditions

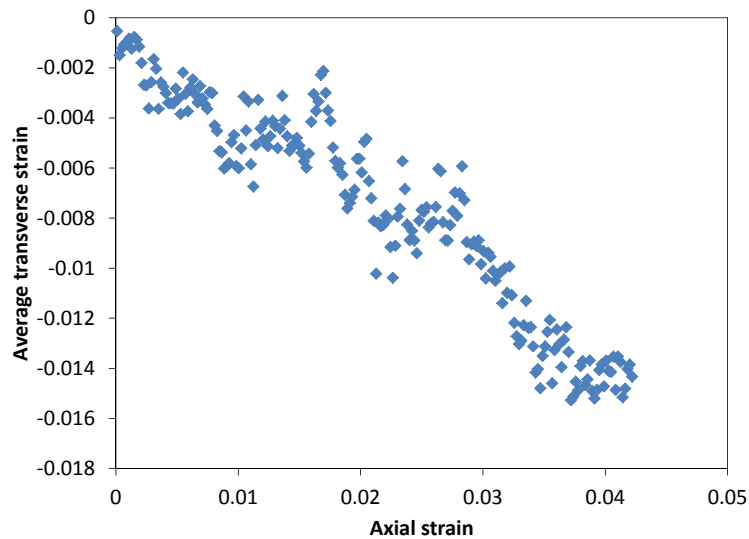


Figure 7 - Representative transverse strain vs axial strain from the MD simulations. The negative slope of this curve is the Poisson's ratio.

A wide range of methods are available to simulate the crosslinking of epoxy systems in the molecular dynamics framework [1-8]. The various methods have a large range of level of difficulty and rigor. The crosslinking method described herein is relatively efficient. The results

shown in Figures 5 and 6 indicate that this method yields molecular structures that accurately describe the elastic/yield response of the system. Therefore, this method is reliable and can be used to establish crosslinked structures for a wide range of thermosetting resins.

4. Conclusions

The results of this study indicate that the ReaxFF with the Liu parameter set is an excellent tool for predicting the elastic response and yield point of epoxy polymer resins. This is important for the use of MD to facilitate the development of more advanced epoxies and epoxy-based composites. Unlike with traditional fixed-bonding force fields, the ReaxFF will allow for the prediction of strength-related parameters of epoxies at the molecular level. Secondly, this study demonstrates that when predicted elastic properties are compared with experiment, the influence of strain rate should be considered. The results described herein show that a slight over-prediction of elastic properties occurs if the strain rate discrepancy between simulation and experiments is ignored. Finally, a newly-developed method to simulate the crosslinking process in epoxy materials was utilized in this study. This method is efficient and the results indicate that the resulting molecular structures can be used to accurately predict the elastic response and yield point of crosslinked epoxy systems.

ACKNOWLEDGMENTS

This research was funded by the U.S. - Norway Fulbright Foundation, the U.S. Air Force Office of Scientific Research under the Light Weight Materials Program (Grant No. FA9550-13-1-0030), NASA under the Revolutionary Technology Challenges Program (Grant No. NNX09AM50A), and NASA under the Subsonic Fixed Wing Program (Grant No. NNX11AO72A). SUPERIOR, a high performance computing cluster at Michigan Technological University, was used in obtaining results presented in this publication.

REFERENCES

1. Bandyopadhyay, A., P.K. Valavala, T.C. Clancy, K.E. Wise, and G.M. Odegard, *Molecular modeling of crosslinked epoxy polymers: The effect of crosslink density on thermomechanical properties*. *Polymer*, 2011. **52**(11): 2445-2452.
2. Doherty, D.C., B.N. Holmes, P. Leung, and R.B. Ross, *Polymerization molecular dynamics simulations. I. Cross-linked atomistic models for poly(methacrylate) networks*. *Computational and Theoretical Polymer Science*, 1998. **8**(1-2): 169-178.
3. Fan, H.B. and M.M.F. Yuen, *Material properties of the cross-linked epoxy resin compound predicted by molecular dynamics simulation*. *Polymer*, 2007. **48**(7): 2174-2178.
4. Heine, D.R., G.S. Grest, C.D. Lorenz, M. Tsige, and M.J. Stevens, *Atomistic simulations of end-linked poly(dimethylsiloxane) networks: Structure and relaxation*. *Macromolecules*, 2004. **37**(10): 3857-3864.
5. Li, C.Y. and A. Strachan, *Molecular dynamics predictions of thermal and mechanical properties of thermoset polymer EPON862/DETDA*. *Polymer*, 2011. **52**(13): 2920-2928.
6. Varshney, V., S. Patnaik, A. Roy, and B. Farmer, *A Molecular Dynamics Study of Epoxy Based Networks: Cross-linking Procedure and Prediction of Molecular and Material Properties*. *Macromolecules*, 2008. **41**(18): 6837-6842.

7. Wu, C.F. and W.J. Xu, *Atomistic Molecular Modelling of Crosslinked Epoxy Resin*. Polymer, 2006. **47**: 6004-6009.
8. Yarovsky, I. and E. Evans, *Computer simulation of structure and properties of crosslinked polymers: application to epoxy resins*. Polymer, 2002. **43**(3): 963-969.
9. van Duin, A.C.T., S. Dasgupta, F. Lorant, and W.A. Goddard, *ReaxFF: A reactive force field for hydrocarbons*. Journal of Physical Chemistry A, 2001. **105**(41): 9396-9409.
10. Chenoweth, K., A.C.T. van Duin, and W.A. Goddard, *ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation*. Journal of Physical Chemistry A, 2008. **112**(5): 1040-1053.
11. Jensen, B.D., A. Bandyopadhyay, K.E. Wise, and G.M. Odegard, *Parametric Study of ReaxFF Simulation Parameters for Molecular Dynamics Modeling of Reactive Carbon Gases*. Journal of Chemical Theory and Computation, 2012. **8**(9): 3003-3008.
12. Jiang, D.E., A.C.T. van Duin, W.A. Goddard, and S. Dai, *Simulating the Initial Stage of Phenolic Resin Carbonization via the ReaxFF Reactive Force Field*. Journal of Physical Chemistry A, 2009. **113**(25): 6891-6894.
13. Lummen, N., *ReaxFF-molecular dynamics simulations of non-oxidative and non-catalyzed thermal decomposition of methane at high temperatures*. Physical Chemistry Chemical Physics, 2010. **12**(28): 7883-7893.
14. Mueller, J.E., A.C.T. van Duin, and W.A. Goddard, *Development and Validation of ReaxFF Reactive Force Field for Hydrocarbon Chemistry Catalyzed by Nickel*. Journal of Physical Chemistry C, 2010. **114**(11): 4939-4949.
15. Mueller, J.E., A.C.T. van Duin, and W.A. Goddard, *Application of the ReaxFF Reactive Force Field to Reactive Dynamics of Hydrocarbon Chemisorption and Decomposition*. Journal of Physical Chemistry C, 2010. **114**(12): 5675-5685.
16. Nielson, K.D., A.C.T. van Duin, J. Oxgaard, W.Q. Deng, and W.A. Goddard, *Development of the ReaxFF reactive force field for describing transition metal catalyzed reactions, with application to the initial stages of the catalytic formation of carbon nanotubes*. Journal of Physical Chemistry A, 2005. **109**(3): 493-499.
17. Qian, H.J., A.C.T. van Duin, K. Morokuma, and S. Irle, *Reactive Molecular Dynamics Simulation of Fullerene Combustion Synthesis: ReaxFF vs DFTB Potentials*. Journal of Chemical Theory and Computation, 2011. **7**(7): 2040-2048.
18. Salmon, E., A.C.T. van Duin, F. Lorant, P.M. Marquaire, and W.A. Goddard, *Early maturation processes in coal. Part 2: Reactive dynamics simulations using the ReaxFF reactive force field on Morwell Brown coal structures*. Organic Geochemistry, 2009. **40**(12): 1195-1209.
19. Srinivasan, S.G. and A.C.T. van Duin, *Molecular-Dynamics-Based Study of the Collisions of Hyperthermal Atomic Oxygen with Graphene Using the ReaxFF Reactive Force Field*. Journal of Physical Chemistry A, 2011. **115**(46): 13269-13280.
20. Zhang, L.Z., S.V. Zybin, A.C.T. van Duin, S. Dasgupta, W.A. Goddard, and E.M. Kober, *Carbon Cluster Formation during Thermal Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and 1,3,5-Triamino-2,4,6-trinitrobenzene High Explosives from ReaxFF Reactive Molecular Dynamics Simulations*. Journal of Physical Chemistry A, 2009. **113**(40): 10619-10640.
21. An, Q., S.V. Zybin, W.A. Goddard, A. Jaramillo-Botero, M. Blanco, and S.N. Luo, *Elucidation of the dynamics for hot-spot initiation at nonuniform interfaces of highly shocked materials*. Physical Review B, 2011. **84**(22).

22. Chenoweth, K., S. Cheung, A.C.T. van Duin, W.A. Goddard, and E.M. Kober, *Simulations on the thermal decomposition of a poly(dimethylsiloxane) polymer using the ReaxFF reactive force field*. Journal of the American Chemical Society, 2005. **127**(19): 7192-7202.
23. Mattsson, T.R., J.M.D. Lane, K.R. Cochrane, M.P. Desjarlais, A.P. Thompson, F. Pierce, and G.S. Grest, *First-principles and classical molecular dynamics simulation of shocked polymers*. Physical Review B, 2010. **81**(5): 054103
24. Plimpton, S., *Fast Parallel Algorithms for Short-Range Molecular-Dynamics* Journal of Computational Physics, 1995. **117**(1): 1-19.
25. Jorgensen, W.L., D.S. Maxwell, and J. Tirado-Rives, *Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids*. Journal of the American Chemical Society, 1996. **117**: 11225-11236.
26. Liu, L.C., Y. Liu, S.V. Zybin, H. Sun, and W.A. Goddard, *ReaxFF-g: Correction of the ReaxFF Reactive Force Field for London Dispersion, with Applications to the Equations of State for Energetic Materials*. Journal of Physical Chemistry A, 2011. **115**(40): 11016-11022.
27. Berendsen, H.J.C., J.P.M. Postma, W.F. van Gunsteren, A. DiNola, and J.R. Haak, *Molecular Dynamics with Coupling to an External Bath*. Journal of Chemical Physics, 1984. **81**(8): 3684-3690.
28. Littell, J.D., C.R. Ruggeri, R.K. Goldberg, G.D. Roberts, W.A. Arnold, and W.K. Binienda, *Measurement of epoxy resin tension, compression, and shear stress-strain curves over a wide range of strain rates using small test specimens*. Journal of Aerospace Engineering, 2008. **21**(3): 162-173.
29. Ferry, J.D., *Viscoelastic Properties of Polymers* 1980, New York: John Wiley & Sons, Inc.
30. Bandyopadhyay, A. and G.M. Odegard, *Molecular modeling of crosslink distribution in epoxy polymers*. Modelling and Simulation in Materials Science and Engineering, 2012. **20**(4).