Molecular Dynamics Study of Brittle Fracture in Epoxy-based Thermoset Polymer

Bonsung Koo, Nithya Subramanian, and Aditi Chattopadhyay

School for Engineering of Matter, Transport, and Energy

Arizona State University, Tempe, AZ, 85287

Abstract

A novel molecular dynamics (MD) simulation methodology to capture brittle fracture in epoxy-based thermoset polymer under mechanical loading is presented. The ductile behavior of amorphous polymers has been captured through traditional MD simulation methods by estimating the stress-strain response beyond the yield point; however, brittle fracture in highly crosslinked polymer materials such as epoxy thermoset has not been addressed appropriately and is the primary objective of this work. In this study, a numerically cured epoxy system comprising molecules of epoxy resin and hardener is generated. During the virtual deformation test, it is observed that the inherent molecular vibration due to temperature re-equilibrates the elongated covalent bonds and this molecular vibration impedes further stretching the covalent bond leading to scission. In order to overcome the influence of thermal vibration, an approach that employs deformation tests at absolute zero temperature condition – a concept borrowed from the quasi-continuum method, is developed. Bond dissociation energy is measured to quantify the extent of failure in the system by calculating the bond potentials during the deformation tests. Applying zero temperature condition to the deformation test, however, requires a large amount of computational time due to intermediate energy minimization processes. To improve the computational efficiency, an ultra-high strain rate (UHSR $\approx 10^{13} \text{ s}^{-1}$) approach is developed by which the thermal vibration is decoupled from the deformation test using a strain rate higher than molecular vibration frequency. Note that the deformation test performed by traditional MD simulation methods used strain rates ranging 10^8 - 10^{10} s^{-1} . Simulation results show that the UHSR approach successfully captures brittle fracture in epoxy polymer due to covalent bond dissociation with high computational efficiency.

Keywords

A. Polymer-matrix composites (PMCs); A. Thermosetting resin; B. Embrittlement; C. Computational modelling;

1. Introduction

Although polymer matrix composites (PMCs) have drawn significant attention from the aerospace industry and their recent application in aircraft primary structures have shown significant weight savings and fuel efficiency, the realization of the full potential of these materials demands an improved understanding of damage initiation and progression from the material level. The intermolecular interactions in the polymer matrix, inelastic behavior of matrix/fiber interphase, and the effects of variability of constituent types (epoxy resin and hardener) on material properties must be studied to develop appropriate physics-based damage models. Several experimental studies have been conducted to address the nonlinear plastic response of composites; but the phenomena occurring at the nanoscale require further investigations. Intermolecular interaction in the polymer matrix under complex loading, in particular, needs atomistic scale investigation;

however, the availability of such information is limited by the resolution/sensitivity of experimental tools.

The mechanical deformation/fracture response of epoxy matrix has been studied using computational approach such as molecular dynamics (MD). A significant amount of research has been reported on characterizing the elastic response of amorphous epoxy and epoxy-nanocomposites using MD simulations [1-9]. Li and Strachan [1] estimated thermal and mechanical properties, such as the glass transition temperature, and tensile/shear moduli of the epoxy resin DGEBF (diglycidyl ether of bisphenol f) with hardeners DETDA (diethyl toluene diamine). They also used the MD method to predict mechanical response under cyclic loading using DGEBF and 33DDS (3,3 diamino diphenyl sulfone) [2]. Valavala et al. [3] and Bandyopadhyay et al. [4] studied the effect of crosslinking degree on mechanical properties of the same epoxy matrix. However, the plastic deformation leading to damage initiation and propagation has not been captured effectively because of the implementation of classical force fields. Since classical force fields were developed to analyze system dynamics around equilibrium states, it is difficult to study material degradation due to covalent bond dissociation through classical MD simulations. Pioneering studies were undertaken by employing a special force field, finitely extensible nonlinear elastic (FENE) [10-13], capable of capturing covalent bond dissociation by modifying the Lennard-Jones potential. In addition, Moller et al. [14] recently developed a new approach to capture covalent bond scission by monitoring the covalent bond length during mechanical deformation by employing classical force fields. If the bond length becomes longer than a threshold, the bond is eliminated and the bond information is deleted from the system database during the virtual deformation test. While the two approaches (FENE and Moller's approach) capture fracture behavior successfully, a large deformation (>100% strain) is required to observe this failure. Such a deformation is not realistic since material failure of epoxy polymeric system appears at a small strain (<10% strain) [15-17].

In this paper, a novel atomistic simulation methodology is developed to accurately simulate the brittle behavior of epoxy-based thermoset polymer. An appropriate bond order based force field is necessary to capture bond dissociation during the deformation test. Odegard and his co-workers [18] used a bond order based force field to capture material degradation of an epoxy polymer system during deformation test; however, it was inconclusive whether the material degradation is due to conformational change (molecular sliding) or covalent bond dissociation. In addition to the selection of an appropriate force field, a method to decouple molecular thermal vibration from mechanical deformation is explored in this paper. Two deformation methods are hypothesized to suppress the effect of thermal vibration: zero-temperature deformation and ultra-high strain rate (UHSR $\approx 10^{13} \text{ s}^{-1}$) deformation. The energy minimization process in the zero-temperature method maintains the system at ground state-free of thermal effects, whereas the UHSR method allows molecular vibration, but deforms the simulation volume with a higher strain rate than the bond vibration frequency of the covalent bonds. These two methods (zero-temperature and UHSR) implicitly produce time-independent behavior resembling quasi-static systems because the thermal activation of molecular motion is decoupled from the virtual mechanical deformation [19]. The virtual mechanical deformation results show that the two deformation methods with the appropriate bond order based force field captures brittle fracture in epoxy-based polymer system at a small strain (~10%), which correlate well with experimental results [15-17].

2. Molecular Model and Simulation Method

Molecular structures of Di-Glycidyl Ether of Bisphenol F (DGEBF, epoxy resin) and Di-Ethylene Tri-Amine (DETA, hardener) are used to construct a simulation volume based on the weight fraction ($M_{\text{DGEBF}}:M_{\text{DETA}}=100:27$). Table 1 contains the number of molecules in the simulation volume (66,560 atoms) and Figure 1 shows a schematic of the 3D molecular structure of the volume. A classical force field - MMFF (Merck Molecular Force Field), is implemented to equilibrate the epoxy system and perform the curing simulation (crosslink formation) [20]. MD simulations are conducted by Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) developed by Sandia National Laboratory [21]. A stochastic crosslink formation approach, based on a cutoff distance for covalent bond generation between active sites is adopted to simulate the epoxy curing process [22]. It is noteworthy that MD simulations with a classical force field are very effective to study processes in a system around its equilibrium state (e.g., curing); however, they are not appropriate for investigating covalent bond dissociation occurring away from the equilibrium state (e.g., deformation tests). **The classical force field, MMFF shows an asymptotic increase in bond energy with elongation of bonds whereas bond order based force field is capable of capturing bond dissociation beyond a critical bond length [23]. ReaxFF, a popular bond order based force field, was developed for hydrocarbon compound by van Duin and co-workers [23-27] and many parameter sets have been reported to describe the nonlinear response of diverse materials including zinc oxide [28], Vanadium oxide [29], fuel cell [30], Li/Si alloys [31], etc. The most suitable ReaxFF parameter set for the epoxy-based polymer system is determined by a bond dissociation energy (BDE) calculation of a specific C-C bond highlighted by the red box in Figure 2. The BDE calculation is performed by the constrained geometry external force (COGEF) method developed to estimate the strength of covalent bonds by Beyer et al. [32]. The BDEs calculated by different ReaxFF parameter sets (Table 2) are compared with the C-C bond energy obtained by pyrolysis experiments [33]; the bond energy was measured to be 389kJ/mol at 298K. Based on the values presented in Table 2, the force field parameters reported by Singh and co-workers [27] show the best correlation with the pyrolysis experimental result; therefore, this parameter set is used for the virtual deformation tests performed in this study.**

Figure 1. Schematic of the MD simulation volume containing DGEBF (epoxy resin) and DETA (hardener).

Table 1. Components in the simulation volume ($M_{\text{DGEBF}}:M_{\text{DETA}}=100:27$).

	Weight	Formula	Number of Molecules
DGEBF	313 g/mol	$\text{C}_{19}\text{H}_{20}\text{O}_4$	1120
DETA	103 g/mol	$\text{C}_4\text{H}_{13}\text{N}_3$	920

Figure 2. Molecular structure of the resin (DGEBF) and C-C bond used for BDE calculation.

Table 2. Calculated BDE with different parameter sets.

ReaxFF Parameter Sets	BDE (kJ/mol)
Chenoweth et al. [24]	330.2
Weismiller et al. [25]	333.9
Aryanpour et al. [26]	359.4
Singh et al. [27]	409.6

3. Effect of Thermal Vibration on Potential Energy under Deformation Test

Temperature is directly related to the kinetic energy of the molecular system. However, temperature also causes potential energy variation in MD simulations. Temperature changes affect not only the frequency but also the amplitude of molecular vibration leading to changes in the potential energy. This phenomenon is verified in the following simulations. The potential energy of 100 ps NPT (isobaric-isothermal) ensemble of the epoxy-based thermoset polymer at different temperatures (0K, 100K, and 500K) is measured with MMFF force field after epoxy curing process. As mentioned before, epoxy curing process is performed using the cutoff distance based covalent bond generation method, reported by the authors [22], after performing energy minimization (conjugate gradient method) and subsequent equilibration for 10 ns with the NPT ensemble (300K and 1atm, Nose-Hoover thermostat/barostat) on the initial system (size of the volume is $15 \times 15 \times 15 \text{ nm}^3$) with periodic boundary conditions. The timescale discrepancy between experiments and simulation is addressed with an assumption that once the system reaches a steady state of potential energy through equilibration, it will stay at the same state. The NPT simulation time of 100 ps was sufficient to equilibrate the potential energy of the molecular systems to their steady states. Figure 3(a) shows that temperature affects variations in potential energy. It is noted that the ensemble simulations with absolute 0K setting cause instability in LAMMPS; therefore, near-zero temperature ($\approx 1\text{K}$) is used for equilibration. As shown in Figure 3(a), the system equilibrated at 500K has higher potential energy than others. In the following simulations, the effect of simulation volume deformation on the potential energy is addressed. It is initially hypothesized that the potential energy increases as the simulation volume deforms because the covalent bonds, angles, dihedrals, and impropers deform during this deformation test.

The epoxy-cured simulation volume is deformed gradually at a constant rate. During the deformation, the atoms in the volume get remapped to new positions at each timestep. This deformation of the simulation volume and subsequent remapping of atoms causes the bond length between atoms to vary based on the local force experienced by the atoms. The simulation volume

is deformed along x-axis with a strain rate of 10^{10} s^{-1} in the NPT ensemble (three different temperatures and zero pressure on y and z-axis). Interestingly, it is observed that the deformation of the simulation volume does not vary the potential energy for all three cases, indicating that the hypothesis made initially is incomplete. This observation also implies that the deformation test fails to capture plastic behavior of the material system. Two possible interpretations emerge: i) the bond length is being re-equilibrated between timesteps due to thermal vibration of molecules during the deformation test; ii) the re-equilibration occurs because the frequency of bond vibration is significantly higher than the deformation strain rate. Using these two interpretations, the previous hypothesis is updated as follows: *the potential energy increases as the simulation volume deforms when the inherent molecular thermal vibration is decoupled*.

The renewed hypothesis is evaluated by studying the frequency of bond vibration at different temperatures, especially for the molecular vibration at near-zero temperatures. Table 3 shows the frequencies of bond vibration estimated from MD simulations by performing NPT equilibration at room temperature (300K) and near-zero temperatures ($\approx 1\text{K}$) at 1 atm. The bond vibration frequency analysis is conducted on three typical bonds of the constituent molecules in the epoxy system (DGEBF and DETA): carbon-carbon (C-C), carbon-nitrogen (C-N), and carbon-oxygen (C-O) bonds. The frequency is calculated using fast Fourier transform (FFT) by plotting the fluctuation in bond length about its equilibrium value. The peak value of frequency determines the primary vibration frequencies of the corresponding bonds. Since the molecular system is at a near-equilibrium state throughout the equilibration, MMFF force field used to extract the bond vibration frequency.

Table 3. Comparison of bond vibration frequencies at different temperatures ($1\text{THz}=10^{12}\text{s}^{-1}$).

Bond Type	Bond Vibration Frequency (THz)	
	300K	$\approx 1\text{K}$
C-C	33.4	0.65
C-N	37.3	0.68
C-O	38	0.71

Figure 3. Potential energies of epoxy-cured system at different temperatures during (a) Equilibration, and (b) Uniaxial deformation.

4. Deformation Test at Zero Temperature

Deformation tests at zero-temperature are performed to decouple thermal vibration from mechanical deformation. As mentioned in the previous section, NPT ensemble simulations with absolute 0K setting makes the system unstable in LAMMPS. Introducing an energy minimization step into the virtual deformation test maintains the system temperature at zero. This idea is borrowed from the quasi-continuum method, which was originally developed as a multiscale modeling method to bridge molecular scale to continuum scale by decoupling temperature effect [34]. The simulation volume is deformed by gradually varying strain using ReaxFF and the atom coordinates in the volume are remapped from a previously stored box shape to a new deformed one based on an affine transformation followed by energy minimization [35, 36]. Through this simulation method, the absolute zero temperature condition successfully allows to decouple thermal vibration from MD simulations and plastic deformation induced by covalent bond breakage is observed. However, the energy minimization conducted at every small strain deformation makes the method computationally expensive. This method is applied to the epoxy-cured system (66,560 atoms) for 1000 tensile strain steps resulting in 50% final strain. This simulation is performed on a computing node with Intel(R) Xeon(R) CPU E5-2640 v2 @ 2.00GHz processors using eight CPU cores and the total CPU hours for a single simulation were well over 1000 hours. The prohibitively large computational time associated with energy minimization warrants the development of a numerical framework that can simulate fracture in epoxy-based thermoset polymer reliably and efficiently.

5. Deformation Test with Ultra-High Strain Rate

The feasibility of performing deformation tests at USHRs ($\gg 10^{10} \text{ s}^{-1}$) is explored as an alternative to the computationally intensive zero-temperature method. The average bond vibration frequency ($0.68\text{THz}=0.68\times 10^{12} \text{ s}^{-1}$) is calculated to be higher than deformation strain rates, $10^8\text{-}10^{10} \text{ s}^{-1}$, which are normally used in literature pertaining to MD simulations [1-4]. Hence, it is expected that these UHSRs, higher than the average vibration frequency of the bonds present in the molecular system of interest, deform the simulation volume faster than bond vibrations. Therefore, elongated bond lengths overcome thermally-induced re-equilibration during the deformation test. Here, the term UHSR is used to differentiate from the 'high strain rate' used in the current MD research field [1-4].

Tensile deformation simulations are performed at different temperatures with different strain rates to analyze the effect of strain rate and temperature on potential energy. After the equilibrations of the system for 100 ps at two different temperatures ($\approx 1\text{K}$ and 100K), tensile deformations are performed until 100% strain at these two temperatures with multiple strain rates ranging from $1\times 10^{10} \text{ s}^{-1}$ to $2\times 10^{13} \text{ s}^{-1}$. Figures 4(a) – (d) show the variation of potential energy along the strain. As mentioned in the previous section, the systems that were equilibrated at two different temperatures have different potential energies (see Figure 4(a)). The trends observed from Figures 4(a) – (d) indicate the interplay of two important phenomena causing variation in potential energy: 1) the increase in temperature causes geometric distortions in the molecular system and indirectly leads to an increase in potential energy; 2) the application of strain to the simulation volume leads to bond elongation and a corresponding increase in potential energy. Depending on the values of temperature and the applied strain rate, one of these phenomena dominates over the other. In Figure

4(a), the applied strain rate is less than the value of bond vibration frequencies at $\approx 1\text{K}$ and 100K ; therefore, case (1) dominates in this range of strain rate. In Figure 4(b), the applied strain rate is higher than bond vibration frequencies at $\approx 1\text{K}$ but lower than the bond vibration frequencies at 100K . This indicates that case (2) is dominant in the $\approx 1\text{K}$ simulations whereas case (1) plays a more important role in the 100K simulation. At higher strain rates ($\approx 10^{13}\text{ s}^{-1}$), as shown in Figures 4(c) and (d), the influence of temperature is reduced significantly because the applied strain rate is higher than the bond vibrational frequencies in both the $\approx 1\text{K}$ and the 100K simulations. If the strain rate of the deformation is faster than the bond stretching vibration, the effect of re-equilibration of the stretched bond due to thermal vibration is reduced. Therefore, the applied strain is transferred completely to the atomic bonds and case (2) dominates over case (1). Figure 4(d) shows that the potential energy values almost converge in spite of the difference in temperature, indicating that the potential energy is invariant to temperature at UHSRs. Thus, the effects of temperature on the deformation test are reduced at UHSRs, and the variation in potential energy can be fully attributed to the increase in strain in the system causing bond elongation and bond dissociation.

Figure 4. Effect of temperature on potential energy at different strain rates: (a) $1 \times 10^{10}\text{ s}^{-1}$, (b) $1 \times 10^{12}\text{ s}^{-1}$, (c) $1 \times 10^{13}\text{ s}^{-1}$, and (d) $2 \times 10^{13}\text{ s}^{-1}$.

A. Compatibility between Zero-Temperature and UHSR Methods

The equivalence of the UHSR approach with zero-temperature method is verified by comparing the deformation test results using a small system comprising 3 DGEBF and 1 DETA molecules (149 atoms). The resin and hardener are connected by carbon-nitrogen (C-N) covalent bonds.

Subsequent to energy minimization and NPT equilibration with periodic boundary conditions, the tensile deformation tests are performed by the two methods. Figure 5 shows the variation in bond energy calculated by (a) zero-temperature and (b) UHSR methods using ReaxFF; in both cases, the bond energies increase until bond dissociation occurs. The strain value at which bond dissociation occurs is called ‘critical strain’. The critical strains are different for the zero-temperature ($\approx 80\%$) and the UHSR ($\approx 60\%$) cases, since the energy minimization at every small deformation step in the zero-temperature method brings the geometry of the system to its ground state abruptly, and thereby ‘hot spots’ where stresses are concentrated in the system are periodically relaxed. Therefore, the critical strain in the zero-temperature case is slightly higher than that in the UHSR case. Morphological transformation along the strain in two cases is also studied using snapshots taken at specific strains (see Figure 6). Two systems are stretched in a similar way at the beginning of the strain, while they shows different locations of hot spots as the strain increases. Consequently, UHSR method does exhibit the potential to capture plastic deformation of covalent bond as the zero-temperature method by showing that the tendency of variation in bond energy is very similar for the two methods. Through this small system test, UHSR method also confirms higher computational efficiency over the zero-temperature method.

Figure 5. Bond energies calculated by (a) zero-temperature and (b) UHSR methods during the deformation test; strain rate for the UHSR method is 10^{13} s^{-1} .

Figure 6. Snapshots of deformation tests from zero-temperature and UHSR methods; the strain information corresponds to the plots in Figure 5.

B. Results from the UHSR Method

The UHSR method is employed on the same epoxy system that was used in the application of the zero-temperature approach (described in the previous section). The simulation volume containing cured epoxy is deformed along x-axis in the NPT ensemble ($\approx 1\text{K}$ and zero pressure on y and z-axis) at a strain rate of 10^{13} s^{-1} with ReaxFF. During the deformation, the atoms in the volume get remapped to new positions based on the local atomic forces at each timestep. In order to investigate the effect of spatial randomness, five simulation unit cells with stochastic initial configuration of molecules are constructed and the virtual deformation test for each unit cell is performed. The engineering stress-strain response, presented in Figure 7, clearly exhibit an average yield strain below 10%. The yield stress is over-estimated due to the strain rate discrepancy between experiments and MD simulations [37]; however, the yield strains show a good correlation with experimental results found in literature [15-17].

Figure 7. Stress-strain response from simulations with different initial location of molecules.

The BDE of the system is calculated through additional deformation tests in order to investigate material failure due to covalent bond breakage. The BDE is normalized by the system volume to obtain the BDE density. Figure 8 illustrates the variation of BDE density for bulk thermoset polymer matrix as the simulation volume deforms at two different strain rates (10^{12} s^{-1} and 10^{13} s^{-1}). The increment in BDE density verifies that covalent bond breakage causes material failure. The curve pertaining to 10^{12} s^{-1} deformation test in Figure 8 exhibits only slight increment in BDE density owing to most of the elongated bonds affected by thermal equilibration. However, the deformation test conducted at strain rate 10^{13} s^{-1} successfully overcomes thermal vibration and substantial increment in BDE density is observed at low strains.

The snapshots shown in the Figure 8 were taken at specific strain values (20%, 40%, 60%, and 80%), and the highlighted dots represent atoms of damaged bonds. The plot shows significant increment in BDE density from the initiation of deformation to 50% strain, which is correlated with ‘burst of bond breakage events’ also observed in experiments [38]. The results also reveal that bond breakage events initiate around yield strain and get accelerated subsequently until complete material failure. Furthermore, the comparisons show that strain rate 10^{13} s^{-1} is appropriate for observing brittle fracture in the epoxy-based thermoset polymer matrix. The BDE density and yield strain information estimated by the physics-based molecular simulations are expected to provide valuable insight and input in continuum level fracture analyses.

Figure 8. Variation of BDE density with strain at near-zero temperature with different strain rates.

6. Conclusion

A novel atomistic simulation methodology was developed to capture brittle failure in epoxy-based thermoset polymers using ReaxFF. This study primarily addressed the effects of temperature on potential energy during the virtual deformation tests, since it was observed that thermal vibrations led to relaxation of bonds and subsequent bond elongation was impeded. In order to decouple the thermal effects, a computationally prohibitive zero-temperature method was first explored. An

alternative approach to the zero-temperature method was then devised to improve computational efficiency while maintaining accuracy. The alternative approach, the UHSR method, enabled the study of bond dissociation (brittle behavior) of bulk polymer system (large system size) using ultra-high strain rates ($\approx 10^{13} \text{ s}^{-1}$) which are higher than the average vibration frequency of the bonds present in the molecular system of interest. The UHSR method produced very similar results as the zero-temperature method, but with significant computational benefits using a combination of low temperature ($\approx 1\text{K}$) and ultra-high strain rate. The UHSR method also provides a platform to quantify both the BDE and BDE density in a bulk polymer system; these parameters are capable of describing the extent of damage in continuum level fracture analysis of thermoset polymer systems.

Acknowledgements

This research is supported in parts by the U.S. Army Research Office, technical monitor: Dr. David Stepp (Agreement Number: W911NF-15-1-0072) and the Office of Naval Research, technical monitor: Mr. William Nickerson (Agreement Number: N00014-14-1-0068).

References

- [1] Li, C., and Strachan, A., 2011, "Molecular Dynamics Predictions of Thermal and Mechanical Properties of Thermoset Polymer EPON862/DETDA," *Polymer*, **52**(13) pp. 2920-2928.
- [2] Li, C., Jaramillo, E., and Strachan, A., 2013, "Molecular Dynamics Simulations on Cyclic Deformation of an Epoxy Thermoset," *Polymer*, **54**(2) pp. 881-890.
- [3] Valavala, P., Odegard, G., and Aifantis, E., 2009, "Influence of Representative Volume Element Size on Predicted Elastic Properties of Polymer Materials," *Modelling and Simulation in Materials Science and Engineering*, **17**(4) pp. 045004.
- [4] Bandyopadhyay, A., Valavala, P. K., Clancy, T. C., 2011, "Molecular Modeling of Crosslinked Epoxy Polymers: The Effect of Crosslink Density on Thermomechanical Properties," *Polymer*, **52**(11) pp. 2445-2452.
- [5] Shiu, S., and Tsai, J., 2014, "Characterizing Thermal and Mechanical Properties of Graphene/Epoxy Nanocomposites," *Composites Part B: Engineering*, **56**pp. 691-697.
- [6] Shin, H., Chang, S., Yang, S., 2016, "Statistical Multiscale Homogenization Approach for Analyzing Polymer Nanocomposites that Include Model Inherent Uncertainties of Molecular Dynamics Simulations," *Composites Part B: Engineering*, **87**pp. 120-131.
- [7] Rahman, R., and Haque, A., 2013, "Molecular Modeling of Crosslinked Graphene–epoxy Nanocomposites for Characterization of Elastic Constants and Interfacial Properties," *Composites Part B: Engineering*, **54**pp. 353-364.

- [8] Ionita, M., 2012, "Multiscale Molecular Modeling of SWCNTs/Epoxy Resin Composites Mechanical Behaviour," *Composites Part B: Engineering*, **43**(8) pp. 3491-3496.
- [9] Zhang, J., Koo, B., Subramanian, N., 2015, "An Optimized Cross-Linked Network Model to Simulate the Linear Elastic Material Response of a Smart Polymer," *Journal of Intelligent Material Systems and Structures*, pp. 1045389X15595292.
- [10] Panico, M., Narayanan, S., and Brinson, L., 2010, "Simulations of Tensile Failure in Glassy Polymers: Effect of Cross-Link Density," *Modelling and Simulation in Materials Science and Engineering*, **18**(5) pp. 055005.
- [11] Sliozberg, Y. R., Hoy, R. S., Mrozek, R. A., 2014, "Role of Entanglements and Bond Scission in High Strain-Rate Deformation of Polymer Gels," *Polymer*, **55**(10) pp. 2543-2551.
- [12] Hoy, R. S., and Robbins, M. O., 2007, "Strain Hardening in Polymer Glasses: Limitations of Network Models," *Physical Review Letters*, **99**(11) pp. 117801.
- [13] Rottler, J., and Robbins, M. O., 2003, "Growth, Microstructure, and Failure of Crazes in Glassy Polymers," *Physical Review E*, **68**(1) pp. 011801.
- [14] Moller, J., Barr, S., Schultz, E., 2013, "Simulation of Fracture Nucleation in Cross-Linked Polymer Networks," *Jom*, **65**(2) pp. 147-167.
- [15] Kinloch, A.J., 2013, "Fracture behaviour of polymers," Springer Science & Business Media.
- [16] Cook, W. D., Mayr, A. E., and Edward, G. H., 1998, "Yielding Behaviour in Model Epoxy thermosets—II. Temperature Dependence," *Polymer*, **39**(16) pp. 3725-3733.
- [17] Dlubek, G., Pointeck, J., Shaikh, M. Q., 2007, "Free Volume of an Oligomeric Epoxy Resin and its Relation to Structural Relaxation: Evidence from Positron Lifetime and Pressure-Volume-Temperature Experiments," *Physical Review E*, **75**(2) pp. 021802.
- [18] Odegard, G. M., Jensen, B. D., Gowtham, S., 2014, "Predicting Mechanical Response of Crosslinked Epoxy using ReaxFF," *Chemical Physics Letters*, **591**pp. 175-178.
- [19] Mott, P., Argon, A., and Suter, U., 1993, "Atomistic Modelling of Plastic Deformation of Glassy Polymers," *Philosophical Magazine A*, **67**(4) pp. 931-978.
- [20] Halgren, T. A., 1996, "Merck Molecular Force Field. I. Basis, Form, Scope, Parameterization, and Performance of MMFF94," *Journal of Computational Chemistry*, **17**(5-6) pp. 490-519.
- [21] Plimpton, S., 1995, "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *Journal of Computational Physics*, **117**(1) pp. 1-19.

- [22] Koo, B., Liu, Y., Zou, J., 2014, "Study of Glass Transition Temperature (T_g) of Novel Stress-Sensitive Composites using Molecular Dynamic Simulation," *Modelling and Simulation in Materials Science and Engineering*, **22**(6) pp. 065018.
- [23] Van Duin, A. C., Dasgupta, S., Lorant, F., 2001, "ReaxFF: A Reactive Force Field for Hydrocarbons," *The Journal of Physical Chemistry A*, **105**(41) pp. 9396-9409.
- [24] Chenoweth, K., Cheung, S., Van Duin, A. C., 2005, "Simulations on the Thermal Decomposition of a Poly (Dimethylsiloxane) Polymer using the ReaxFF Reactive Force Field," *Journal of the American Chemical Society*, **127**(19) pp. 7192-7202.
- [25] Weismiller, M. R., Duin, A. C. v., Lee, J., 2010, "ReaxFF Reactive Force Field Development and Applications for Molecular Dynamics Simulations of Ammonia Borane Dehydrogenation and Combustion," *The Journal of Physical Chemistry A*, **114**(17) pp. 5485-5492.
- [26] Aryanpour, M., van Duin, A. C., and Kubicki, J. D., 2010, "Development of a Reactive Force Field for Iron– Oxyhydroxide Systems," *The Journal of Physical Chemistry A*, **114**(21) pp. 6298-6307.
- [27] Singh, S. K., Srinivasan, S. G., Neek-Amal, M., 2013, "Thermal Properties of Fluorinated Graphene," *Prb*, **87**(10) pp. 104114.
- [28] Raymand, D., van Duin, A. C., Baudin, M., 2008, "A Reactive Force Field (ReaxFF) for Zinc Oxide," *Surface Science*, **602**(5) pp. 1020-1031.
- [29] Chenoweth, K., Duin, A. C. v., Persson, P., 2008, "Development and Application of a ReaxFF Reactive Force Field for Oxidative Dehydrogenation on Vanadium Oxide Catalysts," *The Journal of Physical Chemistry C*, **112**(37) pp. 14645-14654.
- [30] van Duin, A. C., Merinov, B. V., Jang, S. S., 2008, "ReaxFF Reactive Force Field for Solid Oxide Fuel Cell Systems with Application to Oxygen Ion Transport in Yttria-Stabilized Zirconia," *The Journal of Physical Chemistry A*, **112**(14) pp. 3133-3140.
- [31] Fan, F., Huang, S., Yang, H., 2013, "Mechanical Properties of Amorphous Li_xSi Alloys: A Reactive Force Field Study," *Modelling and Simulation in Materials Science and Engineering*, **21**(7) pp. 074002.
- [32] Beyer, M. K., 2000, "The Mechanical Strength of a Covalent Bond Calculated by Density Functional Theory," *The Journal of Chemical Physics*, **112**(17) pp. 7307-7312.
- [33] Dean, J.A., 1985, "Lange's handbook of chemistry," McGraw Hill Book Co., New York, NY.

- [34] Tadmor, E. B., Ortiz, M., and Phillips, R., 1996, "Quasicontinuum Analysis of Defects in Solids," *Philosophical Magazine A*, **73**(6) pp. 1529-1563.
- [35] Sommer, J., and Lay, S., 2002, "Topological Structure and Nonaffine Swelling of Bimodal Polymer Networks," *Macromolecules*, **35**(26) pp. 9832-9843.
- [36] Basu, A., Wen, Q., Mao, X., 2011, "Nonaffine Displacements in Flexible Polymer Networks," *Macromolecules*, **44**(6) pp. 1671-1679.
- [37] Fratzl, P., 2008, "Collagen: structure and mechanics, an introduction," Springer.
- [38] Zhurkov, S., Zakrevskiy, V., Korsukov, V., 1972, "Mechanism of Submicrocrack Generation in Stressed Polymers," *Journal of Polymer Science Part A-2: Polymer Physics*, **10**(8) pp. 1509-1520.