Atomistic Modeling Framework for a Cyclobutane-based Mechanophore-embedded Nanocomposite for Damage Precursor Detection

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Abstract

An atomistic modeling framework is developed to simulate mechanophore activation and evaluate the sensitivity of cyclobutane-based mechanophores. Mechanophores are force-responsive functional units, which when embedded in an epoxy-based thermoset polymer matrix provide self-sensing capability in polymeric composites. In the presence of damage or damage precursors, covalent bond dissociation of the mechanophore generates fluorescence, which is referred to as the mechanophore activation. A Tris-(Cinnamoyloxymethyl)-Ethane (TCE) monomer is used to synthesize the cyclobutane structure through ultra-violet (UV) dimerization; the synthesized cyclobutanes are incorporated into the thermoset polymer matrix. A hybrid molecular dynamics (MD) simulation framework is developed by integrating two force-fields: a classical force-field, Merck Molecular Force Field (MMFF) and a bond-order based force-field, Reactive Force Field (ReaxFF). The hybrid MD methodology enables construction of the molecular model of the cyclobutane-based mechanophore embedded nanocomposite and simulation of the mechanophore activation. The synthesis of epoxy network and cyclobutane structure is numerically simulated by a covalent bond generation method employing MMFF. Through this numerical synthesis, the physical entanglement between the epoxy network and cyclobutane chain is also captured, which determines the local force distribution within the novel nanocomposite. Covalent bond dissociation due to the applied local force on the mechanophore is simulated using ReaxFF and results from the virtual deformation tests show successful mechanophore activation. A local work analysis method is developed to evaluate the sensitivity of mechanophore. Results from the simulation framework show increment in the number of activated cyclobutanes during the deformation test. Good agreement is observed with experimental results: the intensity of fluorescence was found to be directly proportional to the deformation.

Keywords: Molecular dynamics, Cyclobutane-based mechanophore, Reactive Force Field, Epoxy-based thermoset, Local work analysis

1. Introduction

Understanding damage precursors in complex materials and systems remains a critical issue in structural health monitoring. Although a significant amount of research has been reported on developing techniques for damage detection, sensor development to track damage initiation and

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progression in complex heterogeneous material systems such as polymer matrix composites (PMC), still remains a critical challenge. Damage initiation in PMC occurs at the molecular level (interphase between fiber and polymer matrix, or covalent bond dissociation in polymer matrix); therefore, the development of nanoscale sensing technologies is desired. Recently, there has been significant interest in developing mechanophores which are activated by covalent bond dissociation leading to their color change when they are exposed to mechanical stimulation; hence, molecular level damage detection becomes feasible. Davis et al. [1] developed a mechanophore called spiropyran and observed color changes with the onset of yielding in spiropyran-embedded thermoplastic polymer matrix. Chen et al. [2] studied bis (adamantyl)-1,2-dioxetane as a mechanophore which allows real-time monitoring of thermoplastic polymer deformation by observing a momentary color change. Cho et al. [3] observed UV-excited fluorescence from induced cracks on the surface of a thermoplastic thin film using a cyclobutane-based mechanophore. In recent research, the authors successfully integrated the cyclobutane-based mechanophore ('smart' material) into epoxy-based thermoset polymer matrix ('smart' polymer) [4]. Compression test results indicated successful capture of crack nucleation by exhibiting a color change immediately following the yield point. Unlike previous mechanophore studies, which used thermoplastic or elastomer as host materials, the authors' recent experimental work offers an important advantage of using thermoset polymer matrix which is prevalent in most applications where high temperature and stiffness are important. A complementary modeling effort is currently underway to obtain in-depth understanding of mechanophore activation and local force in the nanocomposite. It is important to note that development of such models, requiring a thorough understanding of the mechanochemistry interactions at the atomistic scale, is still at its infancy.

A mechanophore activation modeling framework for the spiropyran-embedded thermoplastic polymer was developed by Silberstein et al. [5] to analyze local force distribution and mechanophore activation. A quantum theory-based method, a traditional molecular dynamics (MD) simulation method and finite element approach were employed to analyze kinetics of the spiropyran, local force distribution on the molecules, and macroscopic stress in the polymer specimen, respectively. Local forces applied on spiropyran were estimated using a classical force-field, Dreiding [6], and a reference force, which is a critical force required to transform the spiropyran to the merocyanine, was calculated by the quantum theory-based method. The mechanophore activation was observed when the estimated local force exceeded the reference force during the virtual deformation tests. This study proposed a pioneering modeling framework to simulate mechanophore activation; however, several issues need to be addressed to improve reliability of the local force analysis. First, the traditional MD method using classical force-fields is limited to the study of a system around its equilibrium state [7-10]; it is not appropriate for investigating plastic deformation pertaining to covalent bond dissociation which occurs away from the equilibrium state. Since external forces propagate through polymer network during the deformation test and polymer network might be disconnected due to covalent bond dissociation, local force applied on the mechanophore will vary as polymer network deforms. Therefore, capturing covalent bond dissociation during the virtual deformation test is critical for the accurate estimation of local force. Furthermore, the MD model used in their framework ignored spiropyran molecule and only considered poly(methyl-methacrylate) (PMMA) as thermoplastic backbone and ethylene glycol dimethylacrylate (EGDMA) as a crosslinker; hence, their local force information was estimated from the crosslinker (EGDMA), not from the mechanophore. In

order to address these two issues, a unique force-field capable of capturing covalent bond dissociation should be considered. Furthermore, a method to construct a molecular model of the experimental sample (smart polymer) with high accuracy must be developed.

This paper presents an atomistic modeling framework integrating a hybrid MD simulation method and a local work analysis method. The hybrid MD simulation methodology is developed by combining two force-fields: a classical force-field and a bond-order based force-field. Merck Molecular Force Field (MMFF) [10, 11], one of the classical force-fields, is implemented to simulate covalent bond generation which is directly related to both epoxy curing and UV dimerization; this enables to construct accurate molecular model of the smart polymer. Since the classical force-field itself cannot simulate covalent bond generation, a curing simulation method is adopted from the author's previous work [12]. This curing simulation using a cut-off distance-based covalent bond generation approach was developed primarily for a neat epoxy system. In the present study, the cutoff distance-based curing simulation is extended to simulate numerical UV dimerization. Reactive Force Field (ReaxFF) [13], one of the bond-order based force-fields, is employed to effectively capture covalent bond dissociation during the virtual deformation tests. By addressing the two deficiencies in Silberstein's modeling framework, the hybrid MD technique provides an effective simulation tool for mechanophore activation. Furthermore, a local work analysis is also developed within the modeling framework to evaluate the performance of mechanophores in the smart polymer.

2. Numerical UV Dimerization

In experiments, the cyclobutane-based mechanophore is synthesized by Tris-(Cinnamoyl oxymethyl)-Ethane (TCE) monomer at room temperature in a thermoset polymer matrix through UV dimerization. The energy equilibrium of the cinnamoyl group ($C=C$) breaks after UV-absorption which leads to a four carbon atoms' ring structure called 'cyclo'-butane. It is noted that epoxy curing occurs while the cyclobutanes are synthesized; hence, epoxy curing simulation and numerical UV dimerization must be performed simultaneously. Through this curing process, physical entanglement between epoxy network and TCE polymer chain also can be constructed. The realization of this physical entanglement in MD simulation is very critical, because the physical entanglement directly affects mechanical property of the system as well as local force distribution. As mentioned before, the cut-off distance-based covalent bond generation method was developed previously for epoxy curing simulation. Therefore, this method is extended to perform the numerical UV dimerization. In addition to covalent bond generation, the following two issues should be addressed: i) structural conversion from cinnamoyl group to cyclobutane; ii) transformation of topology information (parametric conversion) between two structure. Figure 1 shows the difference in structure and bond length between the TCE monomer and polymer; it is found that there are huge differences in bond potential energies in spite of small difference in bond length between a carbon single bond (348 kJ/mol) and double bond (614 kJ/mol) according to Ref. [14]. Therefore, it is important to assign the correct topology information after generating the cyclobutane structures. Furthermore, the $C=C$ double bonds of the cinnamoyl group affect neighbor atoms' topology; hence the neighbor atoms' topology should be changed correctly when the double bond changes to a single bond. The numerical UV dimerization method includes the following standard steps: i) put two TCE monomers in a simulation unit cell (approximated size of the unit cell is $3 \times 3 \times 3 \text{ nm}^3$); ii) equilibrate the unit cell using NPT

(isobaric-isothermal) ensemble (300K and 1 atm) with Nose-Hoover thermostat/barostat using MMFF; iii) Generate covalent bonds when the carbon atoms belonging to the cinnamoyl group are within a pre-defined cutoff distance of 6 Å (four times the length of a C-C bond); and iv) Assign correct topology information to the newly generated cyclobutane structure. All the MMFF force-field information for cinnamoyl group and cyclobutane are generated by Swiss Institute of Bioinformatics [11]. The force-field information of cyclobutane is used when the cinnamoyl groups are transformed to cyclobutane through this dimerization approach. Note that the purpose of this simulation is to show that the numerical UV dimerization enables the synthesis of two cinnamoyl groups into one cyclobutane structure correctly; therefore, only two TCE monomers are involved in this simulation, which result in small size of unit cell. In the following section, large system comprising multiple molecules of epoxy resin, hardener, and TCE monomers will be used to construct the simulation unit cell of the smart polymer and to perform the epoxy curing simulation and numerical UV dimerization simultaneously. In addition to the transformation of the structure/topology, the numerical UV dimerization method should be able to construct two possible types of cyclobutane structures, as shown in Figure 2(a), head-to-head and head-to-tail. This is very important because not only do they lead to a variety of numerical dimerization products but they also allow generation of a consecutive TCE polymer chain (smart material chain) which leads to physical entanglement with epoxy network chain (see Figure 2(b)). In the following section, this numerical UV dimerization method is verified using a bond dissociation energy (BDE) calculation method.

Figure 1. Topological difference between a) cinnamoyl group in TCE monomer and b) cyclobutane in TCE polymer.

Figure 2. a) Two types of possible cyclobutane structures: 1) head-to-head, 2) head-to-tail and b) schematic of entanglement between the smart material network and epoxy network ('TCE': TCE polymer chain, 'E': epoxy network).

3. Verification of Numerical UV Dimerization and Characterization of Cyclobutane

The accuracy of the developed numerical UV dimerization method needs to be established, since incorrect topology information leads to inaccurate dynamic behavior. In order to verify the numerical UV dimerization method, BDE of two molecules (pre-dimerized and numerically dimerized TCE polymers) are compared. BDEs are calculated using the constrained geometry external force (COGEF) method, developed by Beyer et al. [15], to estimate the strength of covalent bonds. This COGEF method is implemented using ReaxFF in this study. Since many ReaxFF parameter sets were reported to describe nonlinear response of polymers [13, 16-19], a process to determine the most suitable ReaxFF parameter set for the smart polymer is required before proceeding the comparative study. A dicyano-substituted cyclobutane (DSC) whose structure is similar to cyclobutane in TCE polymer is chosen. Kryger et al. [20] estimated the BDE of DSC to be 239 kJ/mol using the density functional theory. Table 1 presents the BDEs of DSC calculated using COGEF with different ReaxFF parameter sets. The ReaxFF parameter set reported by Singh et al. [13] yields a BDE value of 245.71 kJ/mol and shows the best correlation with Kryger's results. Therefore this parameter set is implemented in the COGEF method and all the virtual deformation tests in this study.

Following the numerical UV dimerization of the TCE polymer, a pre-dimerized TCE polymer which has the same structure as the numerically dimerized TCE polymer is generated for the BDE comparative study. The COGEF method follows the standard steps: i) energy minimization using the conjugate gradient method with MMFF; ii) NVT (isovolume-isothermal) ensemble at 300K equilibration for 50 ps where the potential energy of the system reaches a certain value with small variance; and iii) deformation by moving each carbon atom with constant velocity (0.0005 Å/fs) in opposite x-direction until the bond breaks (displacement control) using ReaxFF. Figure 3 illustrates the boundary condition in terms of the moving directions of atoms (red arrows). No constraint is imposed in the y- and z-directions while the COGEF method is performed. Note that this simulation is performed in non-periodic boundary condition, since pair potentials caused by molecules in the 'images' (copy of original unit cell) can affect the BDE calculation indirectly. Throughout the COGEF simulation, the trajectories of the atoms are collected every 100 fs, and time averaged values of every state are stored every 1 fs (0.1 fs timestep). The total energy of the system is measured as the geometry deforms, as shown in

Figure 4. The first drop in total energy is observed around 56 ps, which implies covalent bond dissociation. The simulation results reveal a BDE of 315.05 kJ/mol from the pre-dimerized TCE polymer (Figure 4(a)) and 315.4 kJ/mol from the numerically dimerized TCE polymer (Figure 4(b)). The percentage error between the two systems is less than 0.001%; it indicates that the numerical UV dimerization method transforms the cinnamoyl groups to cyclobutane correctly. In addition, COGEF method provides the critical bond length (2.16 Å) and the magnitude of bond rupture force (BRF) (6.8nN) at the bond dissociation moment (see Figure 5). These results will be used as reference values for mechanophore activation in the following section.

Table 1. BDEs of dicyano-substituted cyclobutane (DSC).

ReaxFF Parameter Sets	BDE (kJ/mol)
Chenoweth et al. [17]	150.83
Mattsson et al. [18]	519.72
Newsome et al. [19]	258.88
Singh et al. [13]	245.71

Figure 3. Schematic of boundary condition for tensile test (cyclobutane structure is emphasized with bigger sphere): constant velocity (0.0005 Å/fs) in opposite x-direction.

Figure 4. BDEs obtained from a) pre-dimerized cyclobutane structure and b) numerically dimerized cyclobutane structure (elongation starts at 50ps with 0.0005 Å/fs and bond scission occurs around 56ps).

Figure 5. a) C-C bond lengths of cyclobutane and total energy of the TCE polymer and b) BR force of cyclobutane (≈ 6.8 nN).

4. Local Force and Work Analysis

A representative volume element (RVE) of the smart polymer consists of randomly distributed molecules of the constituents, as shown in Figure 6. The weight percentages of the constituents, which are determined in experiments, are: 70 wt% DGEBF, 20 wt% DETA, and 10 wt% TCE monomers. A 100-TCE monomer system is prepared and the number of resin/hardener molecules are determined accordingly as shown in Table 2 (84700 atoms). The use of a large number of TCE monomers is ideal since it would improve the likelihood of generating more cyclobutane structures; however, the analysis of a large system requires a large computational time. Given that reason, the 100-TCE monomer system reveals a good number of cyclobutane structures and the simulation time is reasonable. Epoxy curing/UV dimerization simulations are first performed with MMFF force-field; this is followed by virtual deformation tests using ReaxFF. Periodic boundary conditions are applied to the boundaries of the RVE (approximate

size: $50 \times 50 \times 50 \text{ nm}^3$ at the initial state) along all three directions. Conjugate gradient energy minimization is performed. Subsequently, NPT (isobaric-isothermal) ensemble equilibration is conducted on the RVE at 300K and 1atm (laboratory environment) for 10 ns using the Nose–Hoover thermostat and barostat to control the temperature and pressure, respectively. The 10 ns equilibration of the system allows the potential energy to converge to a mean value with small variance. After equilibration, the simulation of epoxy curing and UV dimerization are performed simultaneously; degrees of epoxy curing and UV dimerization have reached to around 52% (the number of new bonds/the maximum possible number of bonds between carbon atoms of DGEBF and nitrogen atoms of DETA) and around 28% (the number of new cyclobutane structures/the maximum possible number of cyclobutane structures), respectively. This is followed by system stabilization using NPT ensemble again (300K and 1atm) to reduce the augmented potential energy caused by the newly generated bonds. After system stability is confirmed by checking the potential energy with a mean value and small variance, the virtual deformation tests are performed with ReaxFF. The quasi-static deformation method, which is originally developed by Theodorou et al. [21] and adopted by Mott et al. [22] to capture plastic deformation of glassy polymer, is employed for this virtual deformation tests of the crosslinked smart polymer unit cell. The atoms in the volume get remapped to new positions at each timestep (‘change_box’ in LAMMPS) while the simulation volume deforms. During the deformation, the cyclobutane ring-structures are stretched depending on the magnitude of applied force on the carbon atoms of cyclobutane. The atomic forces experienced by the mechanophore molecules are also stored for the local force analysis. It is important to emphasize that the TCE polymer does not generate any covalent bond with epoxy network; as mentioned before, the physical entanglement between the epoxy network and TCE polymer chain allows load transfer which leads to mechanophore activation (covalent bond dissociation).

After the virtual deformation test, the mechanophore activation is simulated using atoms’ trajectory data by monitoring the C-C bond lengths of cyclobutanes. The color change from red (healthy cyclobutane) to green (damaged cyclobutane) is triggered when the C-C bonds are stretched beyond the critical bond length ($2.16 \text{ \AA}$) as shown in Figure 7; however, this is based on a purely qualitative visualization approach. For quantitative simulation of the mechanophore activation the atomic forces applied on the carbon atoms of cyclobutanes need to be analyzed. The local force is defined as amplitude of an internal force which contributes to deformation of the C-C bonds. For example, if bond stretching forces, $\vec{F}_1$ and $\vec{F}_2$, are applied on the cyclobutane in opposite direction as shown in Figure 8, the local force is specified by $\min\{|\vec{F}_1|, |\vec{F}_2|\}$ and the bond will move with an acceleration due to net force, $\vec{F}_{\text{net}} = \vec{F}_1 + \vec{F}_2$. $\vec{F}_1$ and $\vec{F}_2$ are pair forces and cancel out if they are equal; however, the zero net force only implies zero acceleration of the bond, and the internal force ($|\vec{F}_1| = |\vec{F}_2|$) contributes to the deformation of the bonds. The local force definition is summarized in Table 3. Using this local force analysis approach, mechanophore activation is said to occur when one of the local forces of four bonds in the cyclobutane becomes greater than RBF (6.8 nN). In order to verify whether local force information of cyclobutanes can be used as a criterion in mechanophore activation, local force information of two different cyclobutanes in the RVE was monitored, whose activation states were already known. The first cyclobutane chosen for this analysis had no activation and the second cyclobutane activated at 50% strain. Figure 9 shows the local force trends of the two cyclobutanes. However, the results indicate that local force analysis is not a relevant way to

identify mechanophore activation, because the amplitudes of forces of the first cyclobutane (no activation) spike higher than the BRF (6.8nN) as the strain increases. In order to compensate for the local force analysis, a local work analysis approach is developed by considering displacement of C-C bonds. The concept is equivalent to strain energy calculation used in structural analysis. The local work is defined as the work ($\int \vec{F} \cdot d\vec{L}$) done by the applied local force ($\vec{F}$) on the bond with a small deformation, $d\vec{L}$. This can be stated as $\int \min\{|\vec{F}_1|, |\vec{F}_2|\} \cdot d\vec{L}$ using the same example as shown in Figure 8. The results of local work analysis show that the dashed line AC (green) in Figure 10(b), in the case of the second cyclobutane, starts to increase at 50% strain. Essentially, a certain amount of force needs to be maintained over a certain amount of time to elongate a covalent bond until it breaks. Therefore, it is reasonable to claim that the local work is a key factor governing mechanophore activation, instead of local force. Five samples with different initial locations of molecules and the same weigh fraction of constituents are generated and tested to see if this method shows consistent results. The results show that the mechanophores in all the samples are consistently activated at a strain of approximately 25% and the number of activated mechanophores increases as the strain increases (see Figure 11).

Table 2. Components in the smart polymer (DGEBF:DETA:TCE=70%:20%:10%)

	Weight	Formula	Number of Molecules
DGEBF	313 g/mol	$C_{19}H_{20}O_4$	1300
DETA	103 g/mol	$C_4H_{13}N_3$	1100
TCE	510 g/mol	$C_{32}H_{30}O_6$	100

Figure 6. Schematic of RVE: a) epoxy resin (DGEBF), b) hardener (DETA), and c) mechanophore (TCE monomer).

Figure 7. Procedure for simulation of mechanophore activation: a) prepare dimerized smart polymer RVE, b) start the deformation test (atoms in red represents healthy cyclobutanes, atoms in green represents damaged cyclobutanes), and c) observe atoms in green as the RVE deforms.

Figure 8. Schematic of cyclobutane under the applied atomic forces ($\vec{F}_1$ and $\vec{F}_2$); $d\vec{L}$ is displacement.

Table 3. Definition of local force due to $\vec{F}_1, \vec{F}_2$ along x-axis in opposite direction (Figure 8)

Condition of Atomic Force ($\vec{F}_1, \vec{F}_2$)	Local Force	Motion
$ \vec{F}_1 = \vec{F}_2 $	$\min\{ \vec{F}_1 , \vec{F}_2 \}$	zero acceleration
$ \vec{F}_1 \neq \vec{F}_2 $		acceleration due to $\vec{F}_1 + \vec{F}_2$

Figure 9. Local force plots of two cyclobutanes in the polymer matrix: a) cyclobutane with no activation and b) activated cyclobutane at 50% strain (dotted black line represents the threshold of 6.8nN).

Figure 10. Local work plots of two cyclobutanes in the polymer matrix: a) cyclobutane with no activation and b) activated cyclobutane at 50% strain (dotted black line represents the threshold of 315kJ/mol (2,615 pN-Å)).

Figure 11. Mechanophore activation vs. strain obtained from five samples.

5. Conclusion

A novel atomistic modeling framework for a cyclobutane-based mechanophore embedded thermoset polymer matrix was developed to accurately simulate mechanophore activation and to evaluate the sensitivity of mechanophore. A Tris-(Cinnamoyloxymethyl)-Ethane (TCE) monomer was synthesized to develop the cyclobutane-based mechanophore; this was incorporated into the thermoset polymer matrix to develop a self-sensing nanocomposite system. A hybrid MD simulation approach, comprising a classical force-field, MMFF, and a bond-order-based force-field, ReaxFF, was successfully developed to emulate the experimental processes, from sample preparation to mechanical loading tests. Epoxy curing and UV dimerization were simulated to construct the RVE of the smart polymer using MMFF. Through the numerical curing and dimerization process, the RVE successfully captured physical entanglement between the epoxy network and TCE polymer chain. Local forces experienced by the mechanophores in the smart polymer were estimated by capturing covalent bond dissociation using ReaxFF. In addition, local work analysis was performed, within the modeling framework, to obtain a quantitative assessment of the sensitivity of mechanophores to mechanical stimulation. Simulation results showed good agreement with experimental results performed previously [4]; the number of activated mechanophores increased as the RVE deformed. Five samples with different initial configuration of molecules but the same weight fraction, curing condition, and types of epoxy and mechanophores were analyzed. The results confirmed the robustness of this modeling framework by exhibiting consistent strains of first activation from the five samples. It is anticipated that the modeling framework could be used to provide design guidelines for further improvements in mechanophore sensitivity and mechanical properties of the smart polymer without resorting to a large number of experiments.

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References

- [1] Davis, D. A., Hamilton, A., Yang, J., 2009, "Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymeric Materials," *Nature*, **459**(7243) pp. 68-72.
- [2] Chen, Y., Spiering, A., Karthikeyan, S., 2012, "Mechanically Induced Chemiluminescence from Polymers Incorporating a 1, 2-Dioxetane Unit in the Main Chain," *Nature Chemistry*, **4**(7) pp. 559-562.
- [3] Cho, S., Kim, J., and Chung, C., 2008, "A Fluorescent Crack Sensor Based on Cyclobutane-Containing Crosslinked Polymers of Tricinnamates," *Sensors and Actuators B: Chemical*, **134**(2) pp. 822-825.

- [4] Zou, J., Liu, Y., Shan, B., 2014, "Early Damage Detection in Epoxy Matrix using Cyclobutane-Based Polymers," *Smart Materials and Structures*, **23**(9) pp. 095038.
- [5] Silberstein, M. N., Min, K., Cremer, L. D., 2013, "Modeling Mechanophore Activation within a Crosslinked Glassy Matrix," *Journal of Applied Physics*, **114**(2) pp. 023504.
- [6] Mayo, S. L., Olafson, B. D., and Goddard, W. A., 1990, "DREIDING: A Generic Force Field for Molecular Simulations," *Journal of Physical Chemistry*, **94**(26) pp. 8897-8909.
- [7] Pearlman, D. A., Case, D. A., Caldwell, J. W., 1995, "AMBER, a Package of Computer Programs for Applying Molecular Mechanics, Normal Mode Analysis, Molecular Dynamics and Free Energy Calculations to Simulate the Structural and Energetic Properties of Molecules," *Computer Physics Communications*, **91**(1) pp. 1-41.
- [8] Kaminski, G. G. A., 2001, "Evaluation and Reparametrization of the OPLS-AA Force Field for Proteins Via Comparison with Accurate Quantum Chemical Calculations on Peptides," *The Journal of Physical Chemistry.B*, **105**(28) pp. 6474; 6474-6487; 6487.
- [9] Jorgensen, W. W. L., 1996, "Development and Testing of the OPLS all-Atom Force Field on Conformational Energetics and Properties of Organic Liquids," *Journal of the American Chemical Society*, **118**(45) pp. 11225; 11225-11236; 11236.
- [10] 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.
- [11] Zoete, V., Cuendet, M. A., Grosdidier, A., 2011, "SwissParam: A Fast Force Field Generation Tool for Small Organic Molecules," *Journal of Computational Chemistry*, **32**(11) pp. 2359-2368.
- [12] 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.
- [13] Singh, S. K., Srinivasan, S. G., Neek-Amal, M., 2013, "Thermal Properties of Fluorinated Graphene," *PRB*, **87**(10) pp. 104114.
- [14] McNaught, A.D., and McNaught, A.D., 1997, "Compendium of chemical terminology," Blackwell Science Oxford, .
- [15] 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.

- [16] An, Q., Zybin, S. V., Goddard III, W. A., 2011, "Elucidation of the Dynamics for Hot-Spot Initiation at Nonuniform Interfaces of Highly Shocked Materials," *Physical Review B*, **84**(22) pp. 220101.
- [17] 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.
- [18] Mattsson, T. R., Lane, J. M. D., Cochrane, K. R., 2010, "First-Principles and Classical Molecular Dynamics Simulation of Shocked Polymers," *Physical Review B*, **81**(5) pp. 054103.
- [19] Newsome, D. A., Sengupta, D., Foroutan, H., 2012, "Oxidation of Silicon Carbide by O₂ and H₂O: A ReaxFF Reactive Molecular Dynamics Study, Part I," *The Journal of Physical Chemistry C*, **116**(30) pp. 16111-16121.
- [20] Kryger, M. J., Munaretto, A. M., and Moore, J. S., 2011, "Structure–mechanochemical Activity Relationships for Cyclobutane Mechanophores," *Journal of the American Chemical Society*, **133**(46) pp. 18992-18998.
- [21] Theodorou, D. N., and Suter, U. W., 1986, "Atomistic Modeling of Mechanical Properties of Polymeric Glasses," *Macromolecules*, **19**(1) pp. 139-154.
- [22] Mott, P., Argon, A., and Suter, U., 1993, "Atomistic Modelling of Plastic Deformation of Glassy Polymers," *Philosophical Magazine A*, **67**(4) pp. 931-978.

Virtual Deformation Test