

ATOMISTIC SIMULATION OF YIELD AND RUPTURE IN POLYMER MATRIX COMPOSITES

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Keywords: molecular dynamics, yield, rupture, progressive damage

Abstract

A multiscale molecular mechanics and quantum mechanics framework is used to investigate thermoset materials at large strain, where classical molecular models produce nonphysical forces. This framework is applied to predict bond scission within the material as well as yield and rupture envelopes. The goal is to produce response laws for polymer material systems, especially for use in damage models at the microstructure scale where chemical variability and crosslinking could play a large role in fracture properties.

1. Introduction

Interfacial properties between the polymer matrix and reinforcements are well-known to affect the failure mode and have large implications on the ultimate strength and fracture toughness of the material system [1]. Because of the tendency for composites to crack along or near interfaces, the interphase region between the bulk matrix and interface is of growing concern. Additionally, micromechanical progressive damage simulations demand a thorough understanding of the material properties and behavior in this region. Although many groups have studied the interphase [2, 3, 4], the community lacks a definitive link between the material structure (3D polymer network, etc.) and the apparent properties (stiffness, strength, etc.).

The present submission builds on the multiscale quantum mechanics/molecular mechanics (QMMM) approach described in [5] to simulate cross-linked systems under high strain and bond stretch, where traditional molecular dynamics force fields produce non-physical forces [6]. A set of criteria for efficient simulation of bond scission events provides capability to develop yield and rupture envelopes in the bulk polymer and interphase regions of the composite. The material behavior, including yield and rupture envelopes, can then be passed to a micromechanics progressive damage simulation to then predict larger scale, homogenized fracture properties.

2. Model Material System

As a model system, diglycidyl ether of bisphenol A (DGEBA) is used with methylene diamine (MDA) as a crosslinking agent (see Fig. 1).

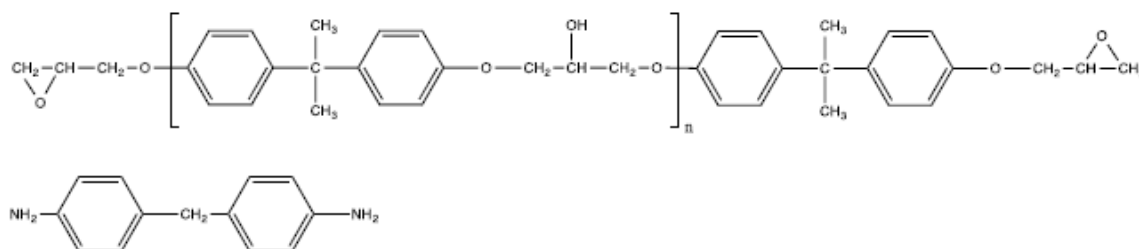


Figure 1: Chemical structure of the diglycidyl ether of bisphenol A (DGEBA) prepolymer (top) and methylene diamine (MDA) (bottom)

The precursors to each system had stoichiometric ratios of epoxide and amine groups. For the purpose of crosslinking, the epoxide groups were opened into alcohol and methyl groups, the latter to be subsequently reacted. System sizes were approximately 30,000 atoms. The equilibrium cell lengths were 70Å, several times greater than the randomly-coiled length of the constituent molecules. In order to have a basis for estimating stochastic variation, each system was constructed five times with different initial randomized coordinates and velocities using the Amorphous Cell module from Materials Studio [7].

3. Stress-strain Simulation

The five independent crosslinked configurations for each system were given Constant-Valence Force Field [7] (CVFF) parameters with harmonic potentials. Systems were equilibrated at T=298 K and P=101,325 Pa using LAMMPS [8] with all cell vector lengths allowed to vary independently. To determine the mechanical properties of the epoxy system, a simulation was started from an equilibrated configuration. Systems were strained at constant true strain rates of 10⁹ s⁻¹ and 10¹⁰ s⁻¹ in one direction, with a barostat of 101,325 Pa applied in the orthogonal directions.

Fig. 2 shows example results of the strain simulation when only a classical force field is used for the entire simulation. At small strain, properties such as Young's modulus and yield strength can be determined. At larger strains, however, the classical force field leads to unphysical results with no limit on the stress that can be maintained by the systems due to the harmonic bond potentials. While the use of Morse bond potentials would limit maximum stress, the system dynamics would also be unphysical because, while energy associated with broken bonds would decline, energy associated with angle and dihedral potentials which include the broken bond would not.

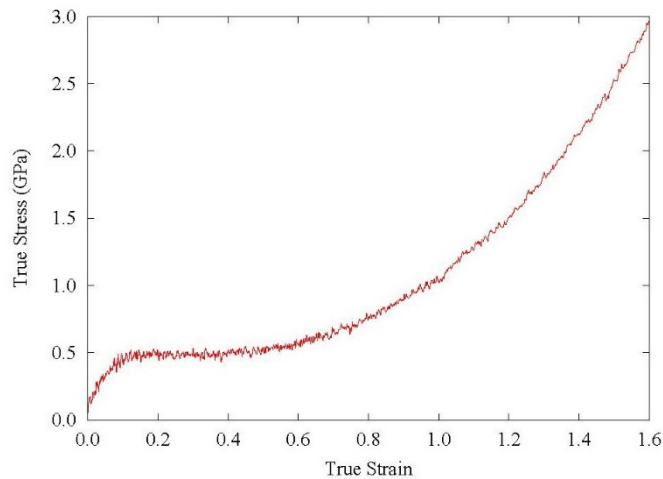


Figure 2: Example of a stress-strain curve for DGEBA at a strain rate of 10^9 s^{-1} using only a classical force field. Properties agree at small strain, but no failure is observed at larger strains since bonds are not allowed to break.

4. Combined QMMM Method

In order to efficiently include QM-informed bond scission with classical MD simulations, the following method was developed, enhancing the framework described in [5]. A prescribed true strain rate is applied to an initially equilibrated system. At every time step, all backbone bond lengths compared with preset threshold values according to bond type. When any single length reaches or exceeds the value, the MD simulation is paused. The atom coordinates in a zone surrounding the stretched bond are used as inputs to a QM geometry optimization. In this, the outermost atoms in the zone are fixed to maintain positional compatibility with the surrounding molecular network and to maintain the strain on the inner atoms. Once the optimization completes a comparison is made with the bonds as defined when the MD simulation was paused and the occurrence of any bond scission and subsequent reactions are determined. Any dangling bonds are capped with hydrogen atoms since classical force fields do not handle radicals. The classical MD system is then updated with the new atom coordinates, types, charges, and bond information. Velocities are assigned to atom in the QM zone using a Maxwell-Boltzmann distribution at the target temperature. The MD simulation continues to deform the system at the prescribed strain rate until another bond is sufficiently stretched to trigger a subsequent QM calculation. Simulation continues until a true strain of 2.0 is reached. There are three main concerns in the method which have been studied thus far. First, the selection of the quantum method is paramount as it will be used for optimization of the structure for highly strained bonds. Second, the physical dimensions of the region around the highly strained bond which will be ported from the molecular dynamics simulation into the quantum framework must be determined. Finally, an appropriate bond stretch criterion which triggers quantum calculations to begin must be set. The following three subsections discuss these points.

4.1. QM Method Selection

Bond breaking is a fundamental part of thermoset composite damage and failure. However, accurately modeling this is challenging, especially for large systems. In order to accurately capture subsequent reactions after bond breaking occurs in the polymer matrix, large systems containing 10s to 100s of atoms will be required. Therefore, a reliable and efficient method for modeling bond breaking is needed. For the purpose of this contribution, we selected the N12 functional [9] for its accuracy and computational efficiency. For a detailed discussion of the QM methods which were surveyed, see [6].

4.2. Optimal QM Region Size

With efficiency in mind, it is essential to find the smallest region size which still yields accurate results. In addition to having a sufficient number of atoms, it is also important for the region to maintain the strain on the stretched bond. This is accomplished by fixing some atoms in the outer shell of the region and only allowing inner atoms to move during the geometry optimization. If this shell thickness is too small, an insufficient number of atoms will be available to maintain the strain on the inner atoms, allowing the inner atoms to relax toward equilibrium bond lengths. If the number of mobile atoms is too small, an unphysical amount of strain will be placed on them, leading to unphysical forces. As the total region size is increased the calculation becomes more time consuming with a small increase in accuracy. Thus, two distances must be determined, r_{act} , the radial distance from the geometric center of the stretched bond in which atoms are unconstrained, and r_{tot} , defining the total region size including the atoms which are fixed to maintain strain and compatibility with the broader molecular network.

In order to determine the optimal region size, systems were strained until the largest bond length was stretched to 2.0 Å. Based on a series of trial simulations, this was determined to be a large enough distance to cause the bond to break in all cases. Then, different candidate regions were formed by including all atoms within a radius, r_{tot} , varying from 2 Å to 10 Å. For each region, all incomplete ring structures were completed and all dangling bonds capped with a hydrogen atom. For each value of r_{tot} , various candidate were further created by varying, r_{act} from 0.5 Å to $(r_{tot} - 0.5)$ Å.

For each candidate system, the energy was then minimized using the QM method previously discussed. Energy minimization was chosen since it yields a deterministic result and will break a bond if it lowers the energy. To determine the optimal region size, the root mean square deviation (RMSD), given by

$$\text{RMSD} = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i^{\text{test}} - x_i^{\text{ref}})^2} \quad (1)$$

is computed for the N mobile atoms in a candidate system, where x_i^{test} is the position of atom, i , in the candidate system and x_i^{ref} is the corresponding coordinate of the reference system. In this way a lower value of the RMSD indicates the coordinates of the candidate system are closer to the reference system, and is therefore more accurate. The reference system was chosen to be $r_{tot} = 10$ Å and $r_{act} = 8.5$ Å. This system contains 483 atoms, and the computational expense of this renders it unfeasible for use in the QM/MM simulation. RMSD results for the system investigated are shown in Fig. 3. For the largest values of r_{tot} (6 Å and 8 Å), RMSD generally decreases with increasing r_{act} and then increases as the fixed shell thickness becomes less than 1 Å, thus indicating a minimum required frozen shell thickness to provide the mobile atoms a representative chemical environment and adequate constraints for maintaining strain. With $r_{tot} = 8.0$ Å having a clear minimum at 6.5 Å, this combination of values is considered optimal for our purposes. The reference configuration with $r_{tot} = 10$ Å contained 483 atoms and took about twice as long to compute as $r_{tot} = 8.0$ Å, which had 230 atoms. For all cases with $r_{tot} \geq 6$ Å, the same bond was broken.

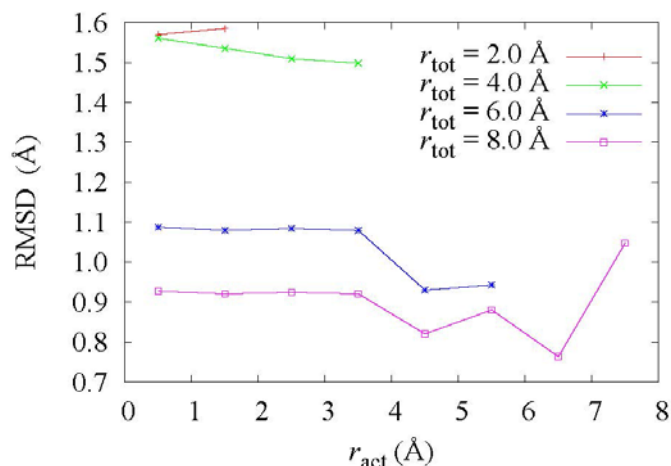


Figure 3: RMSD as a function of r_{act} for different values of r_{tot} using $r_{tot}=10\text{\AA}$, $r_{act}=8.5\text{\AA}$ as a reference

4.2. QM Trigger

Because there are multiple types of bonds in the system, it is convenient to have a single criterion that works well for all bond types. For this, the ratio of the bond length to the equilibrium bond length, L_{check}/L_{equil} , is used as the test metric for all backbone bonds.

The aim is to select a length ratio trigger value that minimizes the frequency of two types of errors. Type I errors are due to performing a QM calculation when a bond not will break using the geometry minimization scheme, and type II errors are due to not performing a QM calculation when a bond is past the length at which it will break. If L_{check}/L_{equil} is too small, then the bond will not break and many unnecessary QM calculations will occur. If L_{check}/L_{equil} is too large, the classical bond potential will be used for bonds stretched well past where the classical force field is valid, leading to unphysical behavior.

To identify the length ratio which results in the minimum errors, the strains at which a QM calculation is first triggered and at which a bond is first broken were examined. This is shown in Fig. 4 for a strain rate of 10^9 s^{-1} and $n=0$. At a length ratio of $L_{check}/L_{equil}=1.16$, bonds are checked at a strain of 0.043 less than the first instance of a broken bond. Conversely, at a ratio of 1.19, the first time a bond is checked it is broken, indicating that this value is too large. Intermediate values do show bonds being checked before they break, albeit at a strain slightly less than the strain at which a bond is broken. There is however, a moderate increase in the strain value at which a bond is first broken compared with $L_{check}/L_{equil}=1.16$.

By examining the fraction of bonds which are checked and result in a broken bond, it is possible to estimate the cost associated with type I errors. This is shown in Fig. 5 for a strain rate of 10^9 s^{-1} and $n=0$. It should be noted that while the total number of bonds checked varies for different length ratios there are on the order of 100 bonds checked for each value, which more bonds being checked for smaller ratios. For $L_{check}/L_{equil}=1.16$, over 80% of QM calculations do not result in a broken bond, causing the simulation to spend 5 times longer performing QM calculations than strictly necessary. A value of 1.20 results in all checked bonds being broken, thereby performing no unnecessary QM calculations. From examining the associated stress-strain curves and the strain at first break, however, it is clear that values of 1.19 or greater lead to type II error and therefore yield unphysical results. A value of $L_{check}/L_{equil}=1.17$ to 1.18 reduces the number unnecessary QM calculations while yielding similar results to a value 1.16 when considering the stress-strain behavior and the strain at first break.

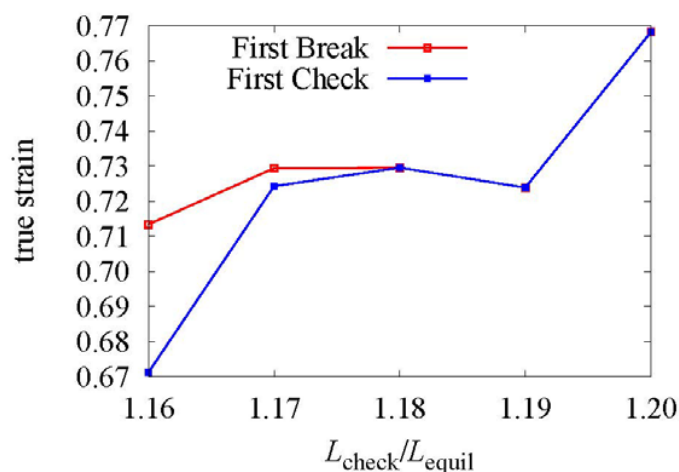


Figure 4: True strain value at which the first QM calculation was triggered (blue) and at which the first bond was broken (red) as a function of $L_{\text{check}}/L_{\text{equil}}$.

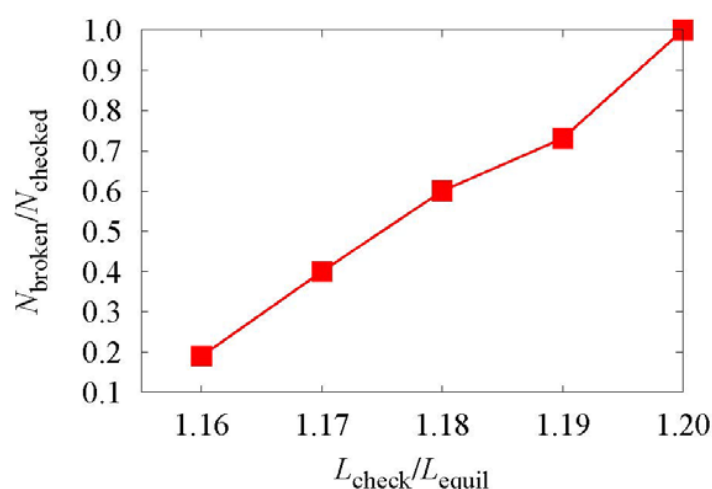


Figure 5: The fraction of times a QM calculation results in a broken bond as a function of $L_{\text{check}}/L_{\text{equil}}$.

5. Discussion/Conclusions

A novel integrated QM/MM method for determining an upper bound to the strain for which covalent bond breaks in an amorphous polymer system and for determining the locations of the bonds that break first has been developed. QM calculations are employed to determine if a bond breaks during a classical atomistic strain simulation by using a simple minimization technique that is computationally feasible. The QM calculations are only performed on a subset of atoms surrounding a stretched bond identified on-the-fly as likely to break. Three primary considerations needed for efficient and accurate use of this method have been determined. The QM method that provides the speed and accuracy needed was determined to be DFT with the N12 functional. This was compared with many other methods on small test systems and found to most accurately follow the CAS results, deemed to be the gold standard. A reasonable QM region size was found to be an approximate sphere of radius 8.0 Å around the stretched bond with atoms within 6.5 Å free to move in the optimization, while those in the outer 1.5 Å margin were held fixed to maintain strain and provide a representative chemical environment. While precise values of the optimal size may vary for different systems, it is important to note that, in addition to having a sufficient number of atoms free to optimize, it is also critical to ensure the outer, fixed region,

is also sufficiently large. These radii defining the regions serve as a starting point for determining the optimal values for other systems.

The bond stretch ratio monitored to trigger a QM calculation was also determined to be 1.17 Å for this system. This value, especially, may not represent the optimal choice as much as a compromise among type I and type II errors. With a value too small, many QM calculations are performed, which impacts the cost negatively and thereby limits the strain rates to higher values. If $L_{\text{check}}/L_{\text{equil}}$ is too large, however, bonds are stretched well past where classical force fields are valid and lead to unphysically high stress values. For a value 1.18 the first bond checked is broken, indicating that this value is too large. More sophisticated schemes to trigger a QM calculation could be imagined, but would require additional computations at each classical MD step.

While this work represents a step forward in modeling the fracture of epoxies, there are still many opportunities to advance this capability. For instance, one could use the DFT functional and a set of small molecules designed to parameterize ReaxFF for polymer systems. Additionally, a more advanced QM/MM implementation is possible with a QM calculation being spawned and then running concurrently with MD as in conventional QM/MM, before being turned off. This poses a number of additional difficulties, however, both from a thermodynamic and computational perspective. While, the coupling between QM and MM regions in concurrent QM/MM simulations has been extensively studied, the possibility of multiple QM regions interacting, when they can begin and end, possibly overlapping, independently is a challenge. Computationally, the challenge is to find the proper load balancing required to efficiently utilize the computational resources with multiple QM regions which do not persist for the entire simulation. However, the work presented here, the QM method, the region size, and the QM trigger, would all be directly applicable to such an implementation. These also provide excellent starting points to implementing this for a variety of different material systems.

Acknowledgments

Funding was provided by the Air Force Office of Scientific Research Low Density Materials Program.

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