MOLECULAR DYNAMICS SIMULATION OF SHOCK-COMPRESSED HYDROCARBON POLYMERS AND FOAMS

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Abstract

Hydrocarbon polymers, foams and nanocomposites are increasingly being subjected to extreme environments. Molecular scale modeling of these materials offers insight into failure mechanisms and complex response. Classical molecular dynamics (MD) simulations of the principal shock Hugoniot were conducted for two hydrocarbon polymers, polyethylene (PE) and poly(4-methyl-1-pentene) (PMP). We compare these results with recent density functional theory (DFT) calculations and experiments conducted at Sandia National Laboratories. Here, we extend these results to include low-density polymer foams using nonequilibrium MD techniques. We find good quantitative agreement with experiment. Furthermore, we have measured local temperatures to investigate the formation of hot spots and polymer dissociation near foam voids.

1 Introduction

Understanding of the high-pressure, high-temperature response of polymers and polymer foams is necessary to better predict shock propagation and wave shape evolution in a variety of applications, such as Inertial Confined Fusion (ICF) research. More generally, doped foams allow the exploration of the equation of state of mixed high-Z / low-Z systems. We have shown in previous work [1] that both DFT and MD could be highly effective tools for quantitative analysis of shock compression of dense polymers. In those studies, we found good agreement with experiment for both linear chains such as polyethylene, as well as branched chain polymers such as poly(4-methyl-1-pentene) (PMP). In particular, we showed that DFT captured the shock response up to 300 GPa. Of four classical MD potentials, ReaxFF [2, 3] did the best in capturing the quantitative response up to 50 GPa. ReaxFF is a reactive potential that allows for chemical dissociation. Here, we extend our work on dense polymers to study the shock response of foams constructed from these same polymers. It should be noted that there is inherent difficulty presented by the multiple length scales responsible for the shock response in foams. In addition to the atomic length scale response, which we have shown DFT and MD can capture well, foams introduce the larger scale of the void structure, wall thickness, and even longer-range density inhomogeneity within samples. The likely need to capture the response at these larger scales drove us to shift our modeling from DFT/MD to MD/Mesoscale. The emphasis here will be on molecular dynamics results, however, we briefly allude to mesoscale continuum hydrocode results and experimental results, which have been recently conducted at...
Sandia for comparison. Complete continuum analysis [4] and experimental results [6] have been reported elsewhere.

![Simulation snapshot showing the initial foam structure before shock propagation for a 0.245 g/cc density PMP foam sample. Both voids and polymer are continuously connected across the sample.](image)

**Figure 1.** Simulation snapshot showing the initial foam structure before shock propagation for a 0.245 g/cc density PMP foam sample. Both voids and polymer are continuously connected across the sample.

## 2 Methodology

We have previously reported on our methods of constructing both the dense polymer [1] and the foam [5] polymer samples. Briefly, an initially ordered sample of PMP was constructed with 200 chains of 50 repeat units. This system made up a periodic unit sample that is later replicated to form a larger sample for shock propagation. The sample unit cell consists of 360,800 atoms with a final size of approximately 20 nm x 20 nm x 20 nm. This PMP was heated to 500 K and allowed to equilibrate into an amorphous polymer structure. Voids were then introduced into the sample in a face-center-cubic arrangement to approximate the densities of experimental foams. The systems were cooled to 300 K, and final densities of 0.300 g/cc and 0.245 g/cc foam were achieved by adjusting the radius of the voids. The dense PMP polymer at 300K has a density of 0.801 g/cc [1]. Most of the results presented here are for the 0.300 g/cc foam, which is most closely matched the experiment. The final arrangement was replicated four-fold in the z direction to create a system of 20 nm x 20 nm x 80 nm with 1.44 million atoms, so that shock waves could propagate in z. A sample of the 0.245 g/cc sample is shown in Figure 1. The spherical voids shown are approximately 16 nm in diameter.

The shock waves were driven by a nonequilibrium molecular dynamics (NEMD) method using a momentum mirror, with co-moving thermostat, moving into the stationary sample. The sample was initially thermalized at 300 K and had periodic boundary conditions in the directions transverse to the shock propagation. The simulation duration was set based on the system traversal time for each wave, but was typically on the order of tens of picoseconds. The free surface opposite the piston was frozen to prevent surface relaxation. Simulations were run on 800 processors of Sandia's Red Sky supercomputer for four days per Hugoniot point. The shock strength was controlled by setting the piston velocity, which was held constant throughout the simulations, after a short acceleration to reduce transient waves. Final piston velocities ranged from 10 to 30 km/s. These velocities produced pressures ranging from tens to hundreds of GPa. All observables were calculated by averaging per-atom quantities over 1 Angstrom wide bands perpendicular to the propagation direction.

A local temperature of each carbon atom was calculated and assigned to each atom in the simulation by analysis of the velocity distribution of all atoms within a 2 nm diameter sphere around. These per-atom temperatures were then averaged within bins, as above, and also visualized directly to investigate the local temperature during void collapse. A simple measure of dissociation was made by comparing the instantaneous carbon bonding to the
initial bonds of the unshocked foam. Atoms with altered bond neighbors were considered dissociated.

All MD simulations were run with the LAMMPS parallel molecular dynamics code [7] with ReaxFF [2, 3]. The numerical integration was performed using the velocity Verlet algorithm with a time step of 0.025 fs.

Figure 2. Hugoniot response of 0.300 g/cc PMP foam, showing both molecular dynamics (red circles) and experimental results [6] (black squares). Data are plotted in shock velocity versus particle velocity space (left), and in shock pressure versus density space (right). These experimental results were reanalyzed from previous reports [5].

3 Results and Discussion

NEMD simulations were used to produce Hugoniot states within the polymer foam. From the material response, the Hugoniot state variables, final pressure, density, particle velocity, shock velocity and temperature were extracted. Although these systems were run for relatively short times, the profiles appear to have reached a spatially uniform steady state. Further, the final variable states behind the shock are consistent with the Hugoniot-Rankine equations for a steady-state shock front. We, however, cannot rule out the possibility of a slow relaxation behind the front, which these simulations could not capture.

The left panel of Figure 2 shows the Hugoniot response in $U_S$ versus $U_P$ space. For comparison, we include recently published experimental results [6] from Sandia’s Z-machine. We found good quantitative agreement with experiment (shown) and continuum-based modeling results [4, 5] (not shown, see reference) in the range of piston velocities explored.

The right panel of Figure 2 shows the Hugoniot response in $P$ versus $\rho$ space. Again, MD results are plotted along with experimental results. The experimental results demonstrate significantly more spread in the final shock density of the foam. This is almost certainly due to significant variation in the initial foam’s ambient densities -- both between samples, and even within individual samples. The foam's final shocked density and pressure are both affected by this variation in initial density. In contrast the foams produced for simulation are uniform on the nanometer scale, and densities are precisely known. The MD results run through the spread in experimental values, although a systematic shift to higher pressures and densities is not completely resolved. These experimental results have been reanalyzed [6] since there initial publication [5].

Good Hugoniot data agreement with experiment gives confidence that the ReaxFF potential and MD methods are capturing the dominant physics of the compression, allowing exploration of quantities that are not easily measured experimentally. Local temperature was measured within the samples and final average temperatures were also calculated. Figure 3 shows the average final temperature behind the shock front as a function of shock pressure for the dense polymer and for two different initial foam densities. The temperatures are much
higher than for comparable shock pressures in dense polymer and the temperatures rise as the initial foam density drops. Linear trend lines have been added for each data set. We see that the introduction of voids causes an order-of-magnitude increase in shock temperatures. In fact, these average temperatures are high enough that electronic degrees of freedom, which MD does not capture, may become important. We believe that ionization and significant electron energy partition would reasonably become a factor between above 60 kK. Several of the strongest shock simulations were repeated with time steps as small as 0.01 fs. We found that even at the highest temperatures, our 0.025 fs was sufficiently small, to assure that energy was conserved.

![Figure 3](image)

**Figure 3.** Temperatures as a function of final shock pressure for three densities of polymer. All three samples are identical, except for the void size introduced. Void space increases final temperatures dramatically.

Figure 4 shows the snapshots of the local temperature response at two early times with approximately half a picosecond separation. These are taken from a simulation with 10 km/s impactor. The two vertically stacked images for each time step show the same side view of the propagating wave. The top image shows all atoms colored in gray to show depth, while the bottom shows only the hottest carbon atoms in the system. The images in the bottom right for each time step shows the same atoms but in the axial view. By comparing the snapshots between the two times, we can see that the carbon atoms are thermalizing on the time scale of picoseconds. We see clearly that the hottest atoms are always in the collapsing void, but cool quickly. This indicates that the significantly increased average final temperature in the foams is due to energy released at the collapse of voids, which takes the form of significantly higher temperature regions. These local hot spots, however, very quickly distribute heat to their atomic neighbors. In the axial views, one can see a complete spatial inversion of the hot spot regions, which correlates directly to the current areas of void collapse in each. Although the temperature spikes are extremely transient, we note that these temperatures produce vaporization, ejecta, and polymer dissociation, which is long-lived in the material.
Figure 4. Snapshots of void collapse at two time steps in a 10 km/s shock impact, showing vaporization and hot spot formation. The top images are side views of the shock. Directly below each is an identical view in which only the highest-temperature particles are visualized. To the bottom right for each time step is an axial view of the hot spots. Orange and red particles have temperature of >15,000 and >20,000 K, respectively.

Unlike in the dense polymer case, we see significant dissociation of the PMP polymer in shocked foams. The snapshot image in Figure 5 shows the vaporized atoms that are blown out as ejecta as the shock propagates through each void. These ejecta can travel faster than the shock speed, and therefore can blur the front for cases where the void spaces are contiguous. In the dense polymer we observed dissociation only above 180 GPa, but in foams, it is observed at our lowest pressures, approximately 50 GPa. This dissociation is produced by local heating and hot spot formation, and thus offers something of a time-integrated view of the hotspot history.

Figure 5. Snapshot from the side view of a 25 km/s shocked polymer foam showing only the dissociated carbon atoms. Significant vaporization is clearly shown where hot spots have traveled through the material. Moreover, ejected carbon can be seen impacting the far side of collapsing voids, and even propagating ballistically ahead of the shock front within the percolating void space.
4 Conclusions
In conclusion, we have used NEMD to study the shock propagation and material response of polymer foams. Building on the findings of previously published work in dense polymers, we have shown that molecular dynamics using the ReaxFF interaction, can quantitatively capture the Hugoniot response in foam. Moreover, MD allows us to explore aspects that are elusive in experimental studies, such as the measurement of local temperatures and the formation of hot spots around voids. We see qualitatively different response in foams, most notably in the pressures at which polymers dissociate. We were able to map out the hot spots in the compressed foam, and see that they correspond directly with the collapsing voids. The hottest temperatures, above 15 kK, thermalize below this threshold on the picosecond timescale, although the overall average temperature is driven up by as much as an order of magnitude over that of the dense polymer by the presence of voids. Future work will include the incorporation of nanoparticles into void space to look at the effect of polymer and foam dopants on the Hugoniot, as well as on the microscopic response at the internal interfaces.

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References