

SHOCK COMPRESSION OF HYDROCARBON POLYMER FOAM USING MOLECULAR DYNAMICS

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Abstract. Organic polymers and nanocomposites are increasingly being subjected to extreme environments. Molecular-scale modeling of these materials offers insight into failure mechanisms and response. In previously published work, we used classical molecular dynamics (MD) and density functional theory (DFT) MD simulations to determine the principal shock Hugoniot for two hydrocarbon polymers, polyethylene (PE) and poly(4-methyl-1-pentene) (PMP). DFT was in excellent agreement with experiment, and one of four classical MD potentials, ReaxFF, was found to be suitable for studies up to 50 GPa. Here, we extend these results to include low-density polymer foams using NEMD techniques. We find good quantitative agreement with both experiment and hydrocode simulations. Further, we have measured local temperatures to investigate the formation of hot spots and polymer dissociation near foam voids.

Keywords: shock, foam, polymer, molecular dynamics, simulation

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INTRODUCTION

Polymer foam is a crucial part of the dynamic hohlraum platform used to generate intense x-ray radiation at Sandia's Z-machine [1, 2, 3] and designs for Inertial Confined Fusion (ICF) often involve foams. As experimental designs are being refined – primarily as a result of an interplay between radiation-hydrodynamics modeling, improved diagnostics, and improved drivers – the importance of having accurate material models based on a fundamental understanding of the material's behavior is becoming increasingly clear. Modeling both the qualitative and quantitative aspects of shock propagation in polymers and polymer foams is therefore of significant importance.

In previously published work in this area, we [4] showed that both DFT and MD could be highly effective tools for quantitative analysis of shock compression of dense polymers. 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 found that DFT captured the shock response up to 300 GPa. Further, of four classical MD potentials, ReaxFF [5, 6] did the best in capturing the quantitative response up to 50 GPa. ReaxFF is a reactive potential which allows for chemical dissociation. However, most of the potentials diverged from experimental results at pressure substantially below the pressures at which dissociation was observed in DFT calculations.

In expanding our work to foams, we note the 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 model these larger scales drove us to shift our modeling from DFT/MD to MD/Mesoscale. Thus, although

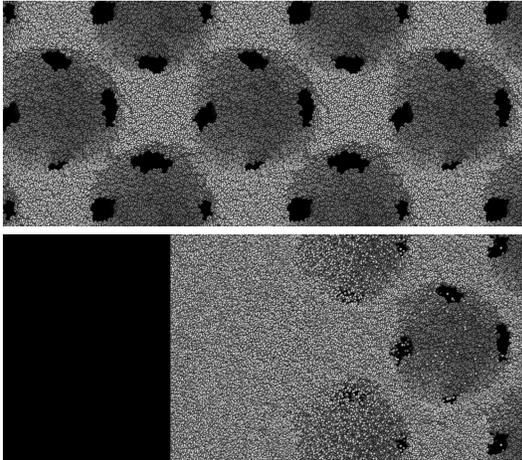


FIGURE 1. Simulation snapshots of the initial foam structure (top) and of the propagating shock front (bottom). The shock shown is strong enough to dissociate the atoms of the polymer, which can be seen vaporized within the void space ahead of the front. The snapshots are shaded to indicate depth. Black spaces are areas in which void mergers allow unobstructed views through the entire sample.

DFT was notably successful in modeling dense polymers, we did not apply these techniques to foam systems. On the mesoscale we report briefly on continuum hydrocode results for comparison with MD. Complete continuum analysis [7] and experimental [8] results will be reported elsewhere.

METHODOLOGY

PMP foam samples of several densities were created by introducing appropriately sized voids into a dense polymer sample. Our construction methods for the dense polymer have been previously reported [4]. Voids were introduced by growing spherical inclusions at a temperature of 400 K. The system was run at constant pressure in an NPT ensemble. This allowed the overall dimensions of the simulation cell to expand as the inclusions grew. The samples used in this work contained 400 chains of 50 repeat runs or 360,800 atoms. The voids were formed in a regular face center cubic lattice. When the void expansion was completed, the samples were cooled to 300 K over 1 ns, the inclusions were removed and the systems were allowed to equilibrate. The final densi-

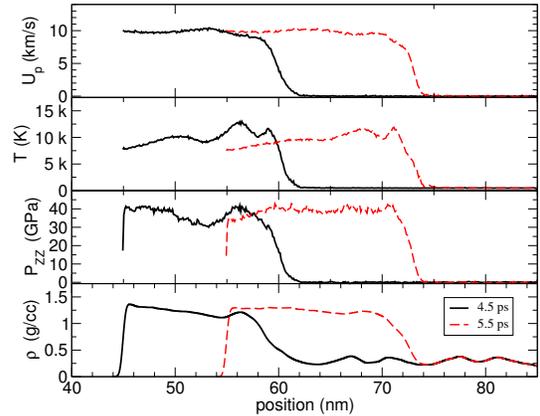


FIGURE 2. One-dimensional spatial profiles of the propagating shock, with piston velocity of 10 km/s, in 0.3 g/cc PMP foam after 4.5 ps (solid) and 5.5 ps (dashed).

ties of foam used in this study were 0.245 g/cc and 0.300 g/cc, compared to a bulk polymer density of 0.801 g/cc [4]. The final size of the foam sample was approximately 20 x 20 x 20 nm. Larger samples, of 1.44 million atoms, suitable for shock propagation were produced by replicating these cubical foams to produce elongated samples with dimensions of approximately 20 x 20 x 80 nm. A sample system is shown in Figure 1.

The 0.300 g/cc foam, on which we will concentrate, had voids of radius of 8 nm. During equilibration, these voids shrunk slightly, and opened into each other, so that both the void and the polymer were contiguously connected across the samples.

Shock waves were driven by moving a warm momentum mirror into the sample. The sample was initially thermalized at 300 K and had periodic boundary conditions in the directions transverse to the shock propagation. The free surface opposite the piston was frozen to prevent surface relaxation. The simulation duration depended on the speed of shock propagation, but was typically on the order of tens of picoseconds. 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. Piston velocities ranged from 10 km/s 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 Å wide bands per-

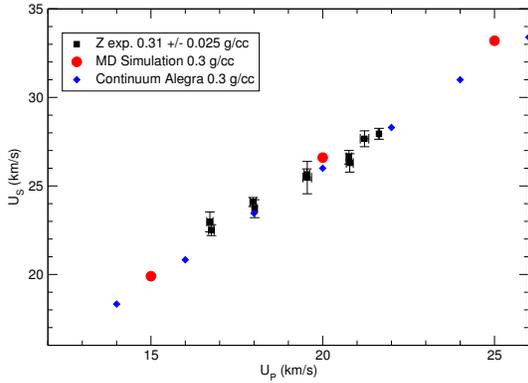


FIGURE 3. Hugoniot response of PMP foam, showing shock velocity, U_S , vs particle velocity, U_P . Results of experiment, continuum and MD simulation are plotted together.

pendicular to the propagation direction.

All MD simulations were run with the LAMMPS parallel molecular dynamics code [9, 10]. The numerical integration was performed using the velocity Verlet algorithm with a time step of 0.025 fs. Even at the highest temperatures, our 0.025 fs was sufficiently small. Select simulations which were rerun with a 5 times smaller timestep, showed identical results. Polymers were maintained at a temperature of 300 K. Long-range Coulomb interactions were calculated using the PPPM method [11].

RESULTS AND DISCUSSION

Our nonequilibrium molecular dynamics (NEMD) simulations were limited in duration because our samples were relatively small. Thus, total shock propagation times were limited to tens of picoseconds. It is not clear whether the shock profiles have reached true steady state profiles, in the sense required by the Hugoniot-Rankine equations. However, we do observe profiles, such as those presented in Figure 2 which are spatially homogeneous behind the shock front. This allows us to compute average values for the thermodynamic variables, such as uniaxial pressure, density, temperature, etc.

Figure 3 shows the Hugoniot response in U_S versus U_P space. For comparison, we include both experimental and hydrocode simulation results which will be thoroughly reported elsewhere [7, 8]. As seen

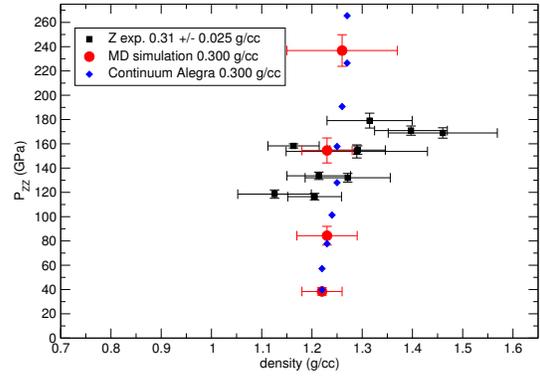


FIGURE 4. Hugoniot response of PMP foam, showing uniaxial pressure, P_{zz} , vs density, ρ . Results of experiment, continuum and MD simulation are plotted together.

in Figure 3 we find good quantitative agreement with both experiment and the hydrocode results in the range of piston velocities explored.

Figure 4 shows the Hugoniot response in P_{ZZ} versus ρ space. MD results are plotted along with both experimental and hydrocode simulation results. Here we find good agreement with the hydrocode simulations, but 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 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 center of the spread in experimental values.

Showing good agreement with experimentally observable quantities gives us confidence in using MD to explore quantities which are not easily measured experimentally. Primary among these, is the local temperature of the samples. In Figure 2 we show a profile of the temperature at two simulation times. In Figure 5 we show the average final shock temperature behind the shock front for several shock pressures and for two different initial foam densities. Temperatures are much higher than for comparable shock pressures in dense polymer. In fact, the introduction of voids causes an order-of-magnitude increase in shock temperatures.

Our measured temperatures are high enough that

one should begin to question whether molecular dynamics can properly model the physics – which is likely to increasingly depend on the electronic degrees of freedom. At 100,000 K, for instance, one would expect that nearly every atom would be ionized to form a plasma. At that temperature, clearly MD would not capture the important physics. It is reasonable to assume that MD results much above 50,000 K would be suspect.

Unlike in the dense polymer case, we see significant dissociation of the PMP polymer in shocked foams. The lower image in Figure 1 shows the vaporized atoms which 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 produced by local heating and hot spot formation is an area that we plan to pursue further.

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 which 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 pres-

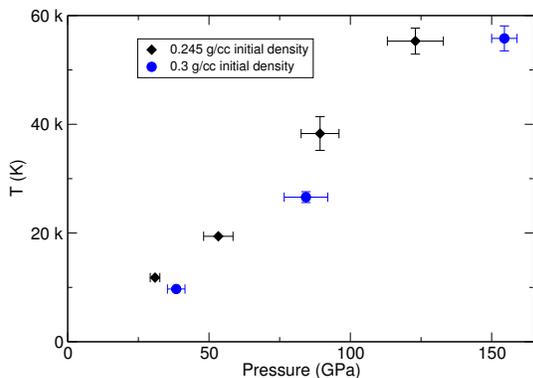


FIGURE 5. Plot of average temperature vs average uniaxial pressure, P_{zz} , of states behind the shock for two PMP foam densities.

ures at which polymers dissociate.

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