Shock Compression of Hydrocarbon Polymers: A Molecular Dynamics Approach with Comparison to DFT, Continuum and Experiment

J. Matthew D. Lane*, Gary S. Grest*, Aidan P. Thompson*, Kyle Cochrane†, Michael Desjarlais*, Thomas R. Mattsson*

* Sandia National Laboratories, Albuquerque, NM USA
† Raytheon Ktech Corporation, Albuquerque, NM USA

Introduction

Organic polymers and nanocomposites are increasingly being subjected to extreme environments. Molecular-scale modeling of these materials offers insight into failure mechanisms and response. Density functional theory (DFT) molecular dynamics (MD) and classical MD simulations of the principal shock Hugoniot are presented for two hydrocarbon polymers, polyethylene (PE) and poly(4-methyl-1-pentene) (PMP). DFT results are in excellent agreement with experiment data, which is currently available up to 80 GPa. Further, we predict the PE and PMP Hugoniots up to 350 GPa and 200 GPa, respectively. For comparison, we studied two reactive and two non-reactive interaction potentials. For the latter, the exp-6 interaction of Borodin et al. showed much better agreement with experiment than OPLS. For the reactive force fields, ReaxFF displayed decidedly better agreement than AIREBO. For shocks above 50 GPa, only the DFT results are of high fidelity, establishing DFT as a reliable method for shocked macromolecular systems.

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.

Results and Discussion

Our PMP Hugoniot results (see Figure 1) demonstrate that the DFT simulations are in excellent agreement with experimental data, effectively capturing even the subtle curvature in Us-Up. The ReaxFF potential is the most accurate classical potential, followed by the exp-6 potential. These are quantitatively accurate to within 10% at experimental pressures of 30 GPa and 15 GPa, respectively. The OPLS and AIREBO potentials have too stiff of a response in both hydrocarbon polymers even for very weak shocks. Since the OPLS potential does very well in describing normal and branched alkanes at ambient pressures, this result suggest that the LJ 12-6 is in general too stiff to model shocks; softer potentials such as the exp-6 appear to be more appropriate.

Figure 1: Hugoniot for poly(4-methyl-1-pentene) in Us-Up (right) and P-ρ (left). Experiment: shock handbook (black filled circle). Simulations: AIREBO (gray square), OPLS (purple filled triangle down), exp-6 (magenta circle), ReaxFF (brown diamond), DFT-AM05 geometry 1 (red filled square), and DFT-AM05 geometry 2 (blue filled triangle up).

Figure 2 shows the Hugoniot response of 0.3 g/cc PMP foam. For comparison, we include both experimental and hydrocode simulation. We find good quantitative agreement with both experiment and the hydrocode results in the range of piston velocities explored.

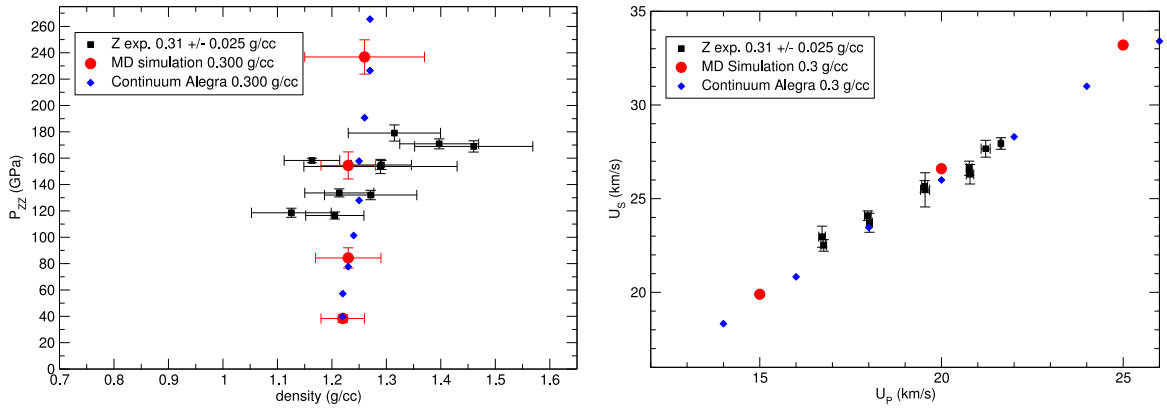

Figure 2: Hugoniot for 0.3 g/cc PMP foam in Us-Up (right) and P-ρ (left).

In conclusion, we have used NEMD to study the shock propagation and material response of dense polymer and polymer foams. We have shown that molecular dynamics, using the ReaxFF interaction, can quantitatively capture the Hugoniot response in hydrocarbon. 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 pressures at which polymers dissociate.

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