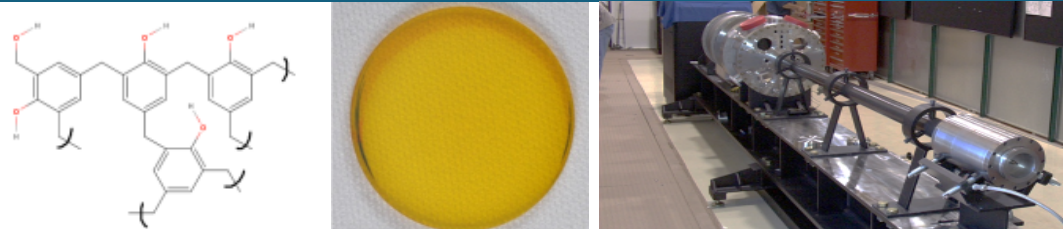


Shock Hugoniot and High Strain-Rate Viscoelastic Behavior of a Phenolic Polymer



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We thank Benjamin Anderson for sample fabrication. Sandia National Laboratories is a multi mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DENA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Introduction

Phenolic polymers are a common binder in industrial composites.

Yet high strain rate mechanical loading has not been extensively studied for phenolics.

Cured phenolic forms large amorphous, crosslinked structures

Dynamic compression known to involve both fast relaxations (e.g., dilation, side-group rotation) and slow relaxations (e.g., chain reptation)

Challenging for relating macroscopic observables to molecular processes

Here, we explore shock behavior of phenolic up to 1.2 GPa using a multifaceted approach:

Plate impact experiments



Dynamic mechanical analysis (DMA)



Continuum model

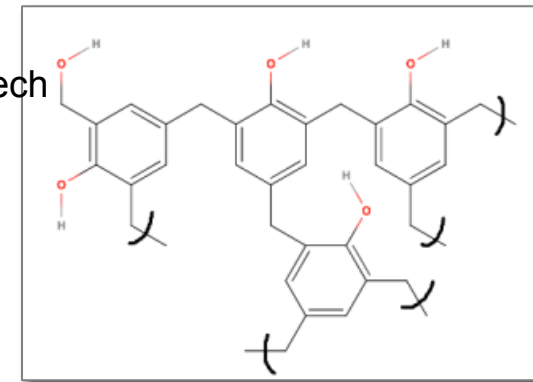


Molecular dynamics (MD) simulation



Mars 2020 Perseverance heat shield

Image credit: NASA/JPL-Caltech



Reproducible Method for Phenolic Sample Synthesis



Resole-type formaldehyde phenolic resin “PSR133” (Barrday Corp.) used for high-temperature applications

Custom sample curing cycle:

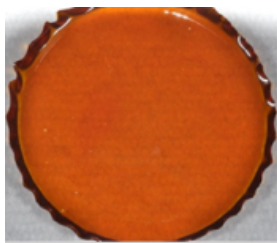
~50 mm x 2 mm “pucks”

Free of visible inclusions

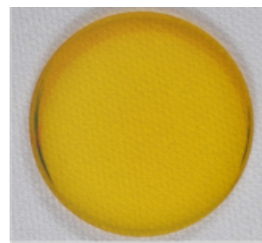
Cure extent ~95–98% (calorimetrically-based)

Residual volatiles est. < 3 wt%

Diamond turning also removed exterior oxide from cure

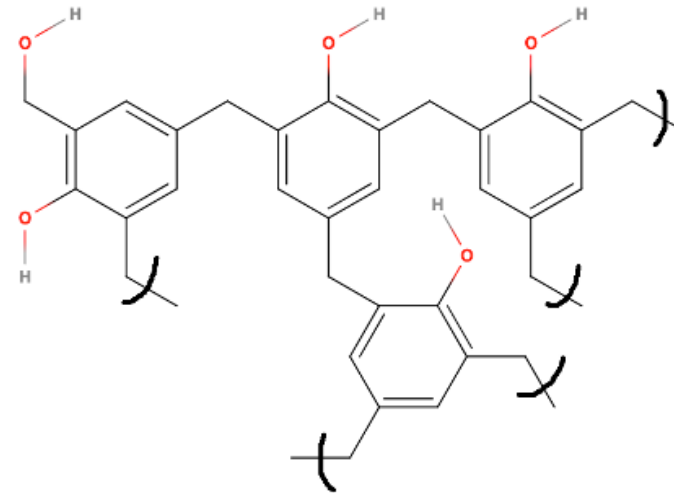


Phenolic Puck



Phenolic Target

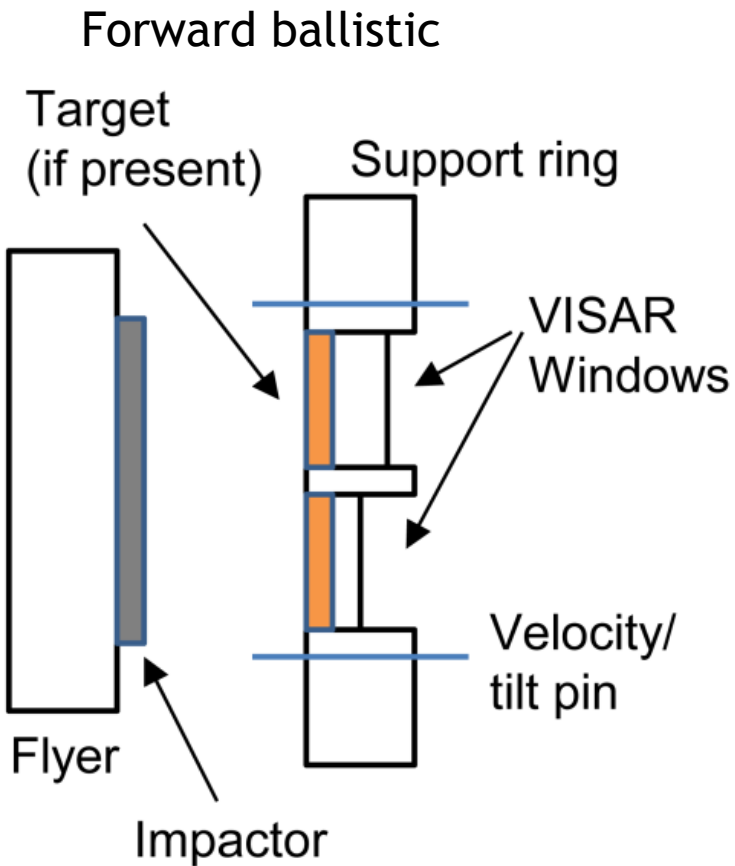
→ *Reproducible, uniform phenolic gas gun targets*



	Avg. (\pm s.d.)
Density	1.252 \pm 0.004 g/cm ³
Sound speed (longitudinal)	3.05 \pm 0.02 km/s
(transverse)	1.41 \pm 0.01
Poisson's ratio	0.364 \pm 0.003
Shear modulus (shear)	2.50 \pm 0.03 GPa
(bulk)	8.34 \pm 0.15

Plate Impact Experiments

Light gas gun at Dynamic Integrated Compression Experimental (DICE) Facility (Sandia National Laboratories)



Shot	Impactor	Target	Windows	Flyer velocity (m/s)
Forward #1	Sapphire	Phenolic	PMMA (2x) +blank for spall	106
Forward #2	Sapphire	Phenolic	PMMA (3x)	299
Reverse #1	Phenolic	---	LiF PMMA Sapphire	106
Reverse #2	Phenolic	---	LiF PMMA Sapphire	301

Reverse ballistic (not shown):

- Phenolic sample impacts several windows

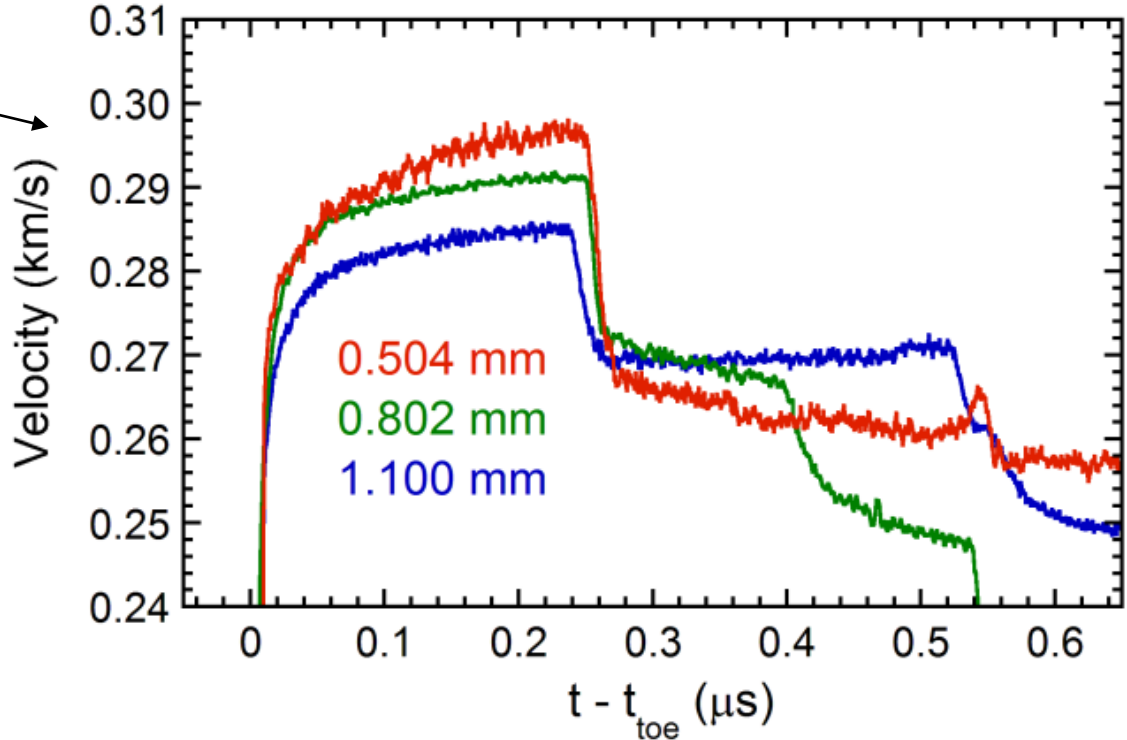
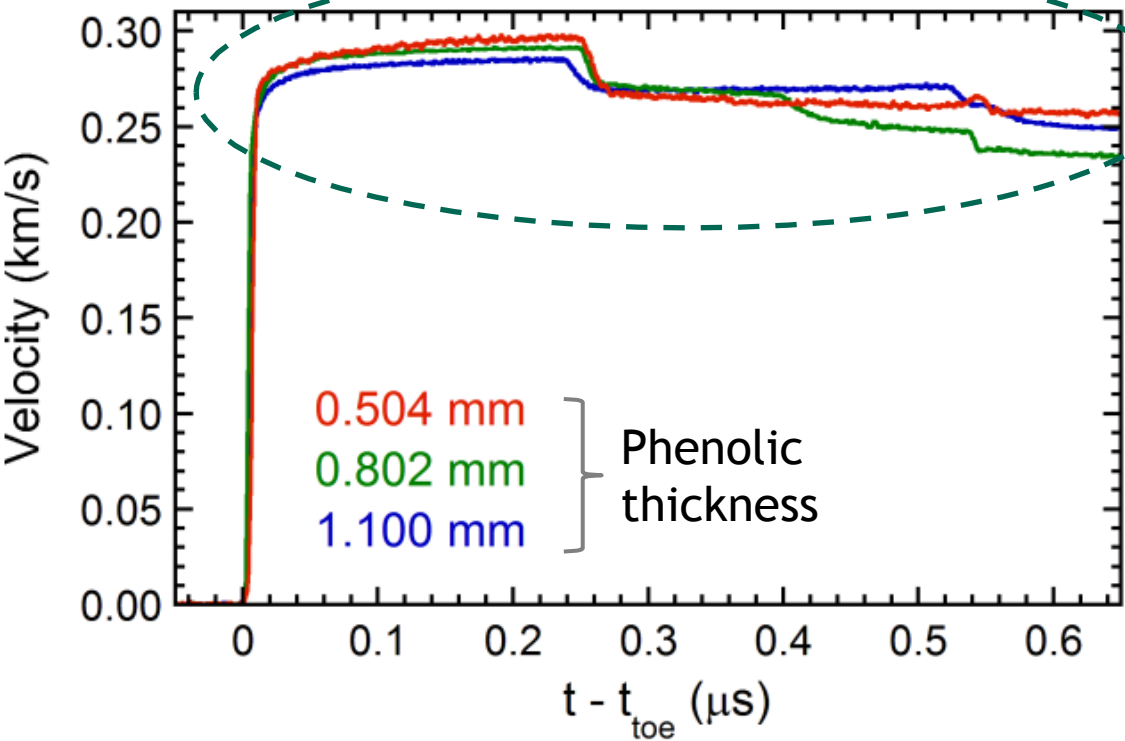


Forward Ballistic Plate Impact

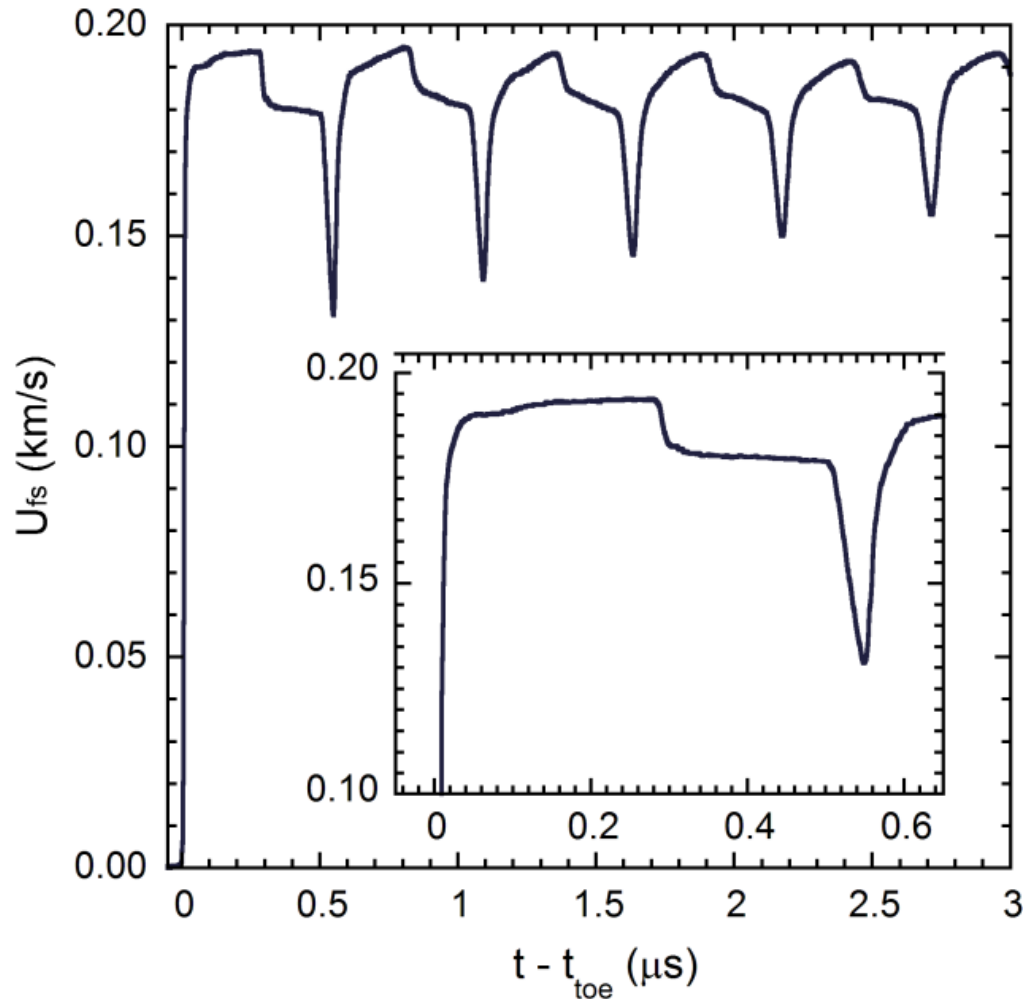
Comparison of three thickness indicates shock dampening through the sample thickness

Rounded velocity profile suggests a subsequent dynamic process (e.g. viscoelasticity)

Identical impact conditions



Forward Ballistic Plate Impact (continued...)



Free surface velocity of windowless sample indicates classic spall signature

Spall strength from pull-back:

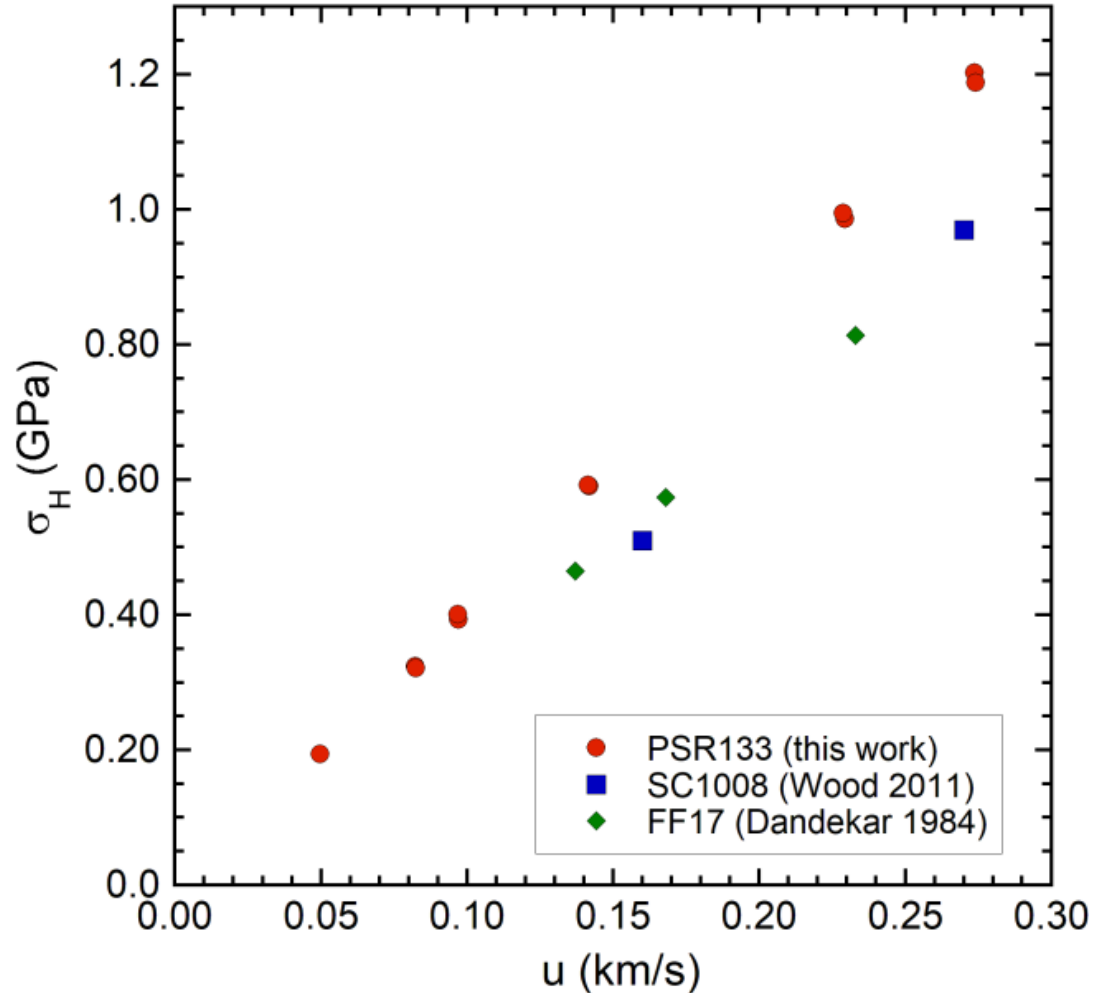
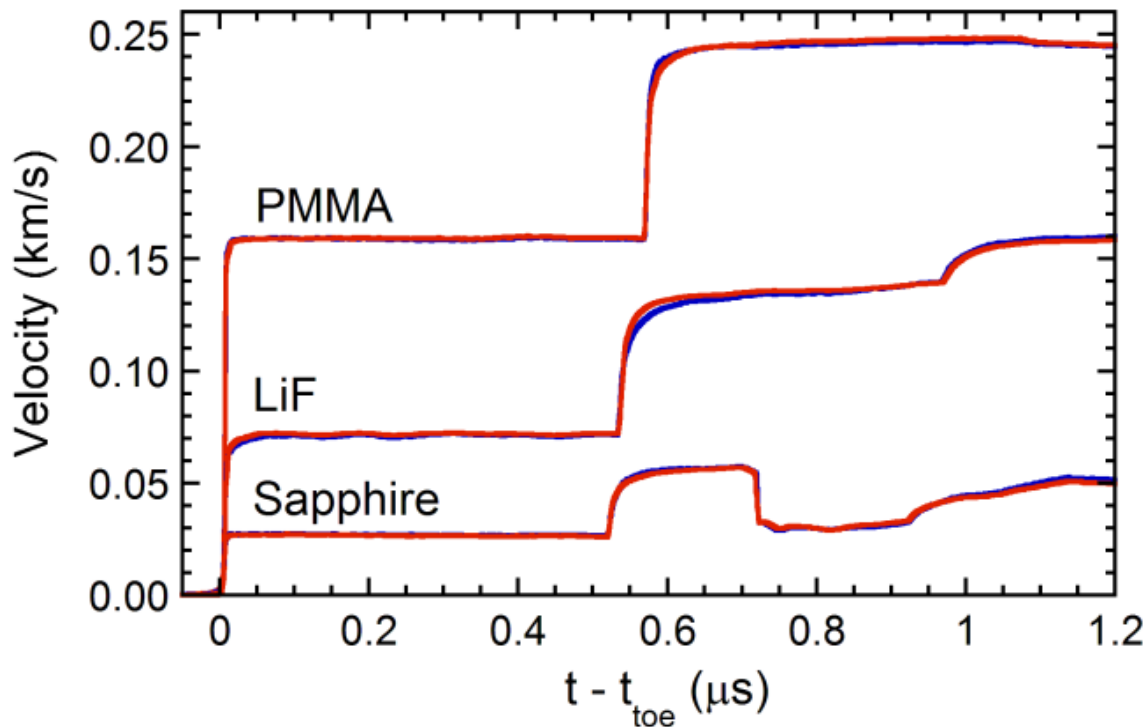
$$\sigma_{spall} = (1/2)\rho_0 C_L \Delta u_{fs}$$

→ 92 MPa

Shock Hugoniot Measurements

Measurement redundancy from dual recording along a common fiberoptic path (separate velocity-per-fringe constants)

Reverse ballistic



Wood, D. C., et al., J. Mater. Sci. 46 (9), 5991-5999 (2011).

Dandekar, D.P. and R.M. Lamothe, in Shock Waves in Condensed Matter, ed. J. R. Asay, R. A. Graham and G. K. Straub, 125-128 (1984).

Mulliken-Boyce Viscoelastic / Viscoplastic Model

Pressure-dependent viscoelastic response across:

α -transitions (main-chain segment rotations)

β -transitions (side group rotations)

Accounts for large, high-rate strains in glassy polymers through time-temperature superposition of transition temperature:

$$G(\dot{\epsilon}, T_{eff}) = C_{\beta,1} + C_{\beta,2}T_{eff} + C_{\beta,3}T_{eff}^2 + \dots$$

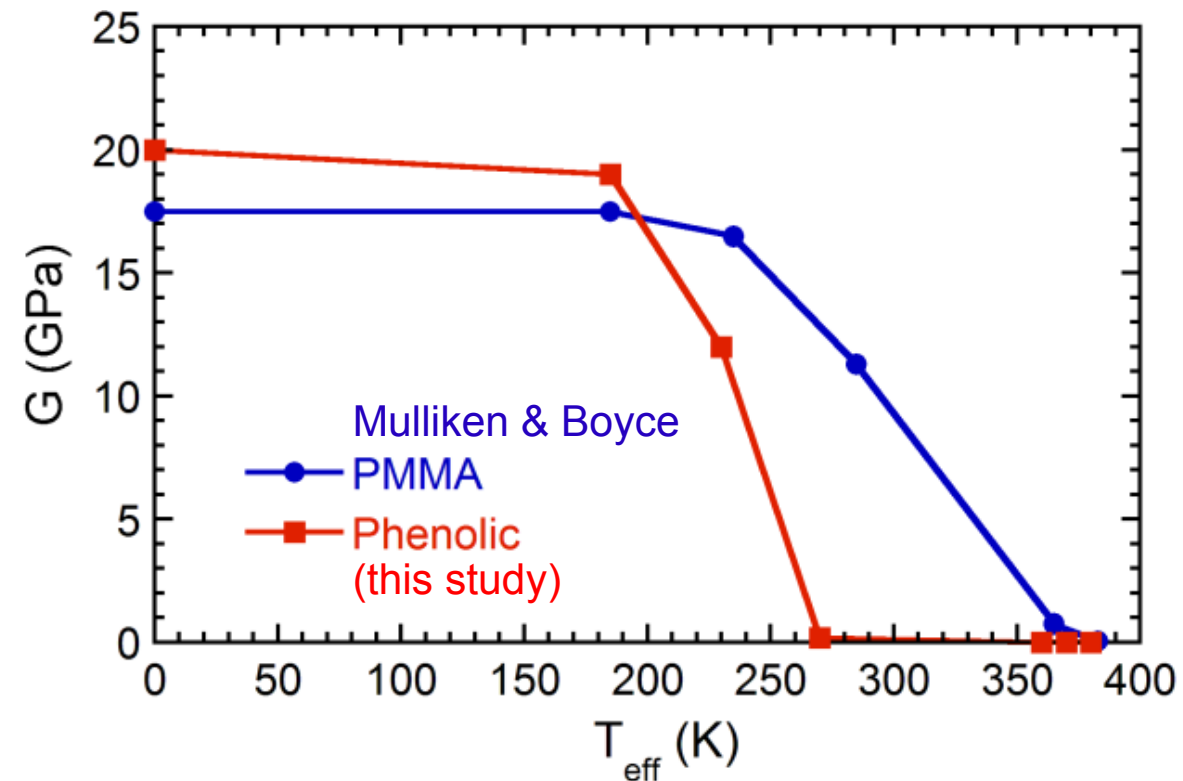
$$T_{eff} = T - \mu_{\beta}^{shift} \log_{10}(\dot{\epsilon}/\dot{\epsilon}_{\beta,0})$$

Model form previously implemented in CTH hydrocode

Shear modulus (G) calibrated to Dynamic Mechanical Analysis (DMA) measurements

Temperature ~ 140 – 280 K

Frequency ~ 0.2 – 20 Hz



Viscoelastic model in hydrocode reproduces shock dynamics



Mulliken-Boyce viscoelastic model (calibrated to DMA)

CTH shock hydrodynamics code

Density and Hugoniot as-measured

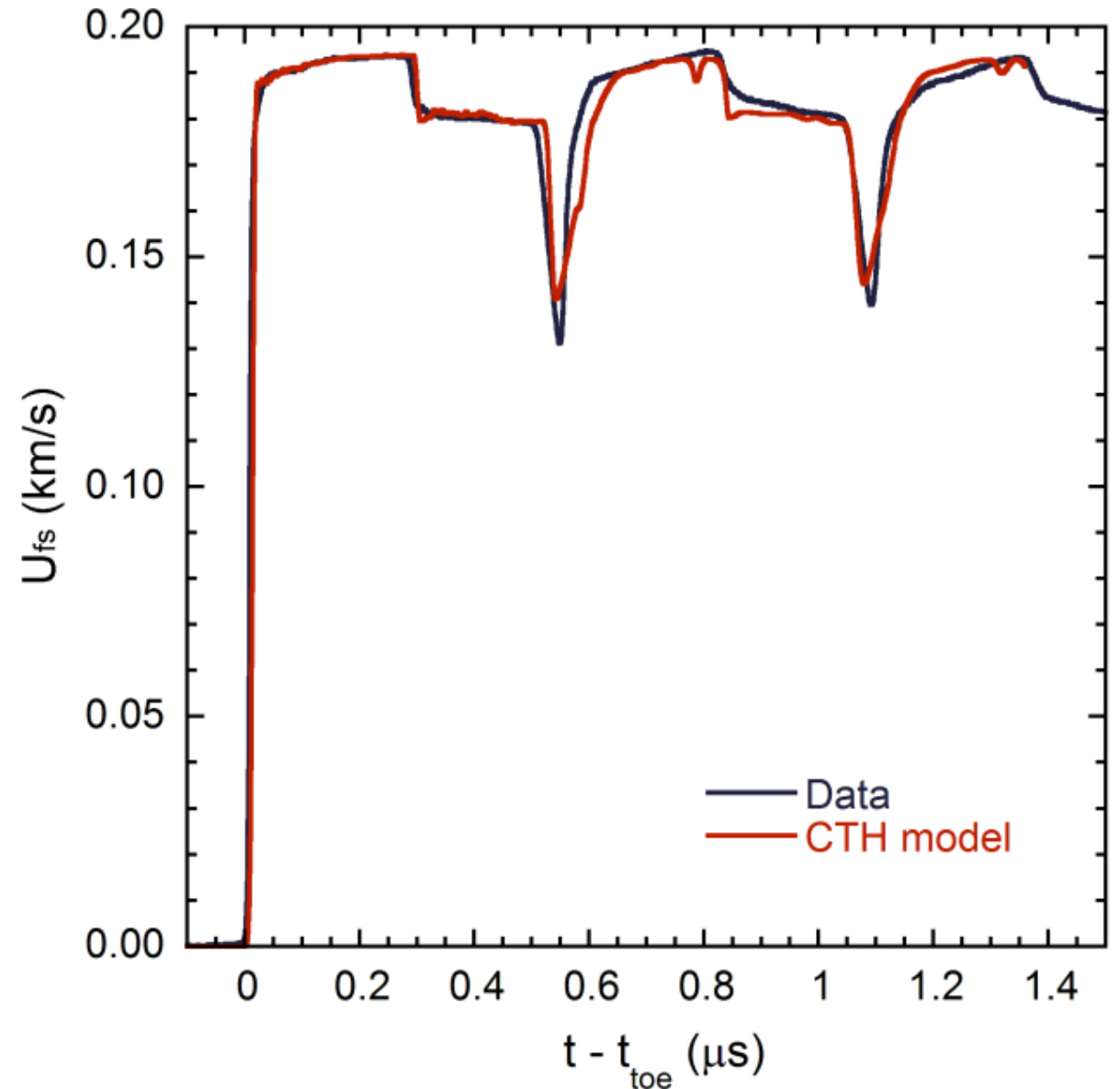
Dynamic spall strength:

102 MPa from fitting CTH model

92 MPa measured from pull-back

Other shots exhibited similar agreement (omitted for brevity)

Congruence across DMA/shock strain rates suggests viscoelastic behavior



Molecular Dynamics Simulations of Phenolic Shock Compression



Simulations by Keith Jones using analogous methods
(see previous talk)

“Hugonostat method” (Ravelo 2004)

Non-propagating, constant uniaxial stress with density equilibration

Temperature controlled to satisfy Rankine-Hugoniot conditions

Previous success with polyethylene in ReaxFF (Mattson 2010).

Structures tuned to match experimental density

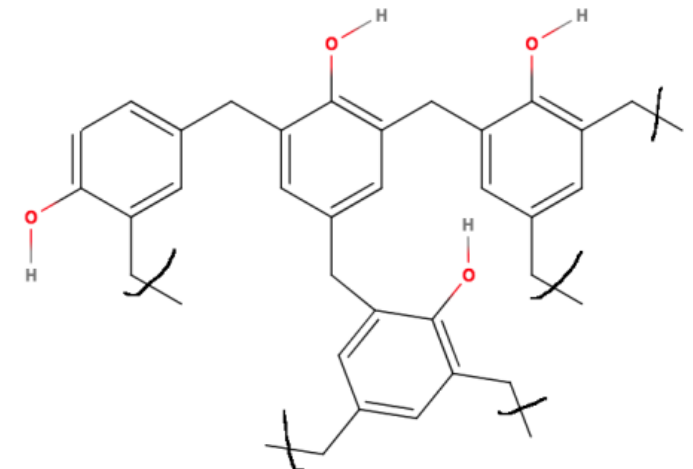
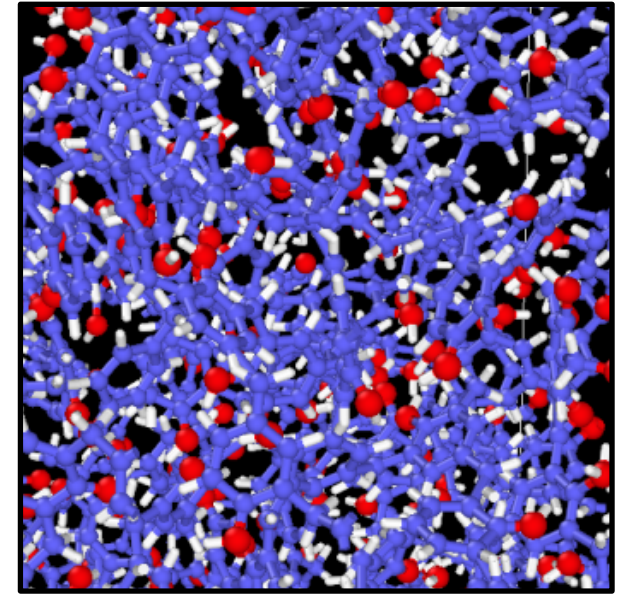
LAMMPS molecular dynamics 3D atomistic simulation code

ReaxFF force field – hybrid potential (K. Jones, 2020)

Crosslinked then equilibrated at STP for ≥ 100 ps

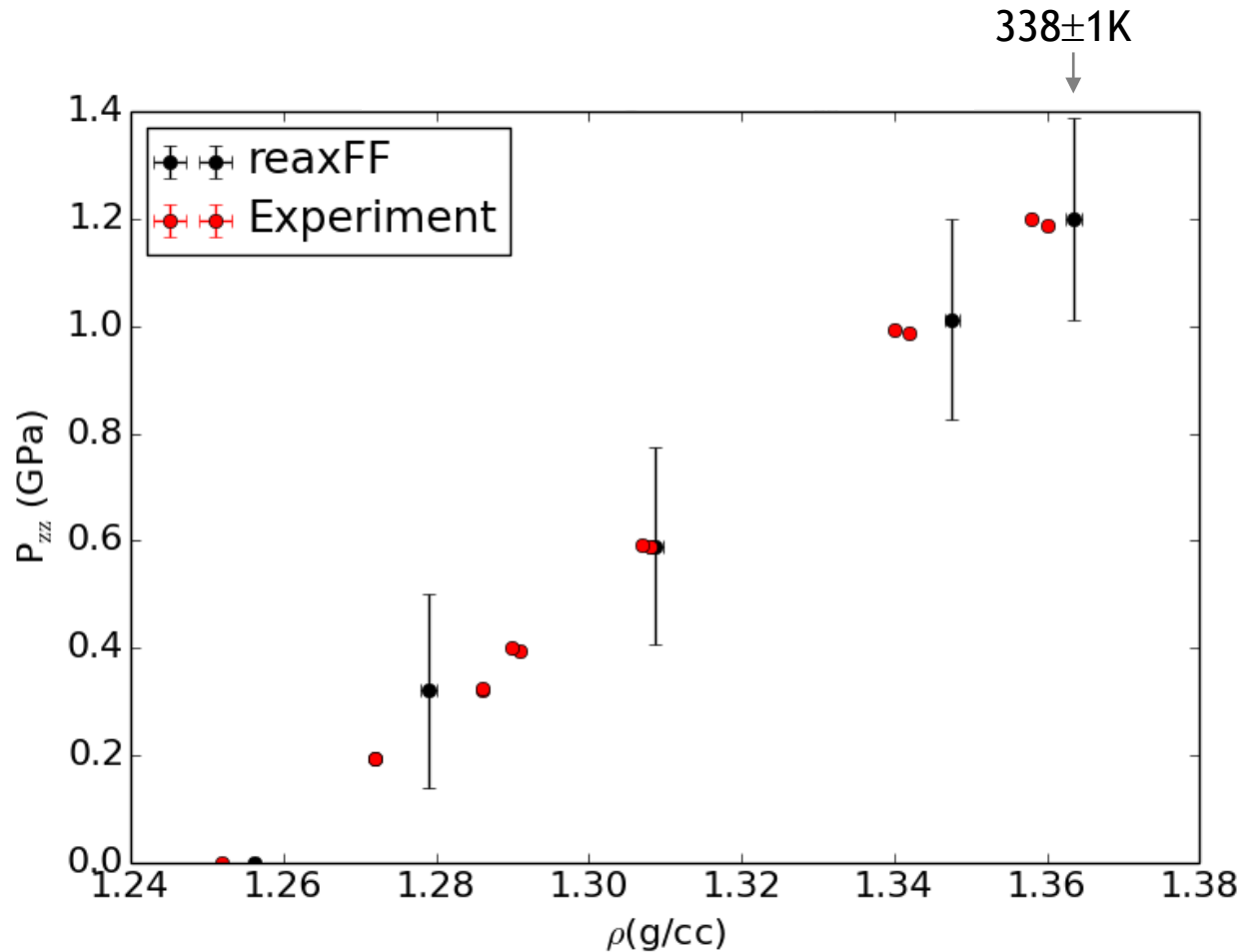
$4-5 \times 10^4$ atoms, 0.05 fs timestep

Periodic boundary conditions



R. Ravelo et al., *Phys. Rev. B* **70**, 014103 (2004).
T. R. Mattsson et al., *Phys. Rev. B* **81**, 054103 (2010).
K. Jones et al., *AIP Conf. Proc.* **2272**, 070018 (2020).
Gissinger et al., *Polymer* **128**, 211-217 (2017)

MD simulations reproduce observed Hugoniot states



No chemical reactions observed

Temperature and pressure below chemical onset (≥ 40 GPa or ~ 1600 - 2000 K; see Keith Jones, et al., previous talk)

Hugoniot elastic limit ~ 6 – 10 GPa from comparison of axial stress and pressure

Error bars represent statistical fluctuations (standard deviations) among individual simulations.

Conclusions

Plate impact experiments, continuum model and atomistic model were developed for a phenolic polymer up to 1.2 GPa.

Observed shock dynamics are consistent with viscoelastic properties from benchtop (DMA) experiments when extended with the Mulliken-Boyce model.

Molecular Dynamics simulations reproduce observed Hugoniot states and suggest the viscoelastic regime extends up to ~6–10 GPa.

Molecular Dynamics simulations will provide an opportunity to explore fast relaxation mechanisms.