Rubbers under high triaxial loads

PJ Gould
Impact against propellant – Insensitive Munitions

• We have a duty of care for our armed forces

• Our weapons should only explode when and where we want them to

• NATO standard for Insensitive Munitions response
  – Fragmenting munitions attack (Fragment Impact)
  – No response more severe than Type V (Burning)
  – Steel fragment from 15 g with velocity up to 2600m/s and 65 g with velocity up to 2200m/s.

• These tests are really expensive and a cost-effective approach to assurance is needed

• Small-scale approach using highly-instrumented tests on small amounts of material
  – Still expensive and needs material to be available

• Ideally we would be able to predict response from chemistry and physics
Impact against propellant

• Shock-to-Detonation Transition and No reaction
Impact against propellant

• Unknown (X) to Detonation Transition
Impact against propellant

• Need to predict – consider the material response

• Impact conditions
  – Uniaxial strain
    – Implies Poisson’s ratio is zero but these are large volumetric deformations
  – Sub microsecond response: strain rates $10^7$/s
  – Pressure 6 GPa
  – Temperature?
    – Mechanical work with heat capacity
    – Entropic effects with high hoop strain at rear of block

• What are the things we need to predict?
Group Interaction Modelling

• Group Interaction Modelling (GIM) is a group contribution method for predicting properties of polymers without need for synthesis or measurement.
  – Originated in polymer industry
  – Significant evidence of predictive capability
  – Can predict physical and mechanical properties as a function of rate and temperature through the glass transition

• Mean Field description of energy-deformation response
  – Van der Waals and Hydrogen bonding
  – Can be predicted via quantum mechanics codes
  – Account for vibrational modes and conformational state
  – Equivalence of thermal and mechanical energy

• Interacting groups have characteristic contributions to parameters used:
  – $M$ molecular weight of a group
  – $V_w$ (cc/mol) van der Waal’s volume of a group
  – $E_{coh}$ (J/mol) cohesive energy of intermolecular forces
  – $\theta_D$ (K) 1-D Debye reference temperature related to polymer chain stiffness
  – $N$ skeletal degrees of freedom per group
GIM

• Potential function method
  – Lennard-Jones and self-similar
  – Born criterion for instability
  – Stress and bulk modulus from derivatives of $E(V)$
  – Put $P$ vs $V$ into Rankine-Hugoniot equations
    – Shock equation of state
  – Also get tensile response which is hard to measure

\[ P = -\frac{dE}{dV} \]

• Point of inflection correlated with glass transition
  – Is L-J sufficient for this?
Pressure vs volume

- Rubbers are not incompressible
- Hugoniot from GIM potential function
  - Allows shock propagation to be predicted
- Some questions arise about volumetric loss through glass transition
  - In particular: how does one predict the factor 2 in bulk modulus change?
  - Link to thermal expansion
  - Further questions then about thermal expansion coefficient of plasticized rubbers
Pressure vs volume

• Validation against ring-down
Pressure vs volume

- Comparison of VISAR and HetV with numerical simulation (GRIM)
- The differences reflect details of the experimental arrangement not being included in the simulation and known physics missing from the material model
Heat Capacity

• 1-D Debye Theory
  – VV Tarasov, Russian Journal of Physical Chemistry 39 (1965) 1109
  – B Wunderlich: ATHAS database

• Chain skeletal modes contribute directly to potential function and thermal energy

• At glass transition need extra 0.5N degrees of freedom

• Group optical modes treated as Einstein oscillators

\[
C \approx NR \left( \frac{6.7T}{\theta_D} \right)^2 \frac{1}{1 + \left( \frac{6.7T}{\theta_D} \right)^2}
\]

\[
C_E = \frac{R \left( \frac{\theta_E}{T} \right)^2 \exp\left( \frac{\theta_E}{T} \right)}{\left[ \exp\left( \frac{\theta_E}{T} \right) - 1 \right]^2}
\]

\[
H_T = \int_0^T C \, dT
\]
Heat Capacity – pressure effect on heat capacity

- Movement of T_g as a function of pressure can be seen in poly(styrene) data*
  - Isothermal data
  - Loss peak appears to broaden
  - If T_g moves above current temperature then extra degrees of freedom should be suppressed
  - Would have a significant effect on heat capacity
  - What happens adiabatically?
  - How does this tie in with instability condition for glass transition?
  - HTPB would require imposed pressure of 400 MPa to move T_g above room temperature
  - Heat capacity would drop from 2 J/kg/K to 1.5 J/kg/K
  - Needs verification

\[
\frac{dT_g}{dP} = 4 \frac{P}{B Nk}
\]

*Ougizawa, GD Dee, DJ Walsh, Polymer, 30 (1989) 1675
Heat Capacity – pressure effect on heat capacity

- Should be working with volume but this has practical issues
- Pressure/volume affects Debye $\theta$ temperatures which changes the vibrational modes
- This reduces heat capacity
- Use QM to calculate new vibrational modes for different pressures and new $\theta$ temperatures
- Additional to movement of glass transition but there is a feedback
  - Need to avoid double counting

Debye temperatures can be included into model to suggest heat capacities at high pressures.

At 5 GPa and 300K

HTPB $C_v = 1.0 \text{ J g}^{-1} \text{K}^{-1}$, RDX $C_v = 0.79 \text{ J g}^{-1} \text{K}^{-1}$

Can use Dreger & Gupta measurements under same conditions to give RDX $C_v = 0.81 \text{ J g}^{-1} \text{K}^{-1}$

Strength of rubber

• Good capability to predict rubber extension and failure in uniaxial tension

• Entropic stiffening treated as loss of degrees of freedom in modulus calculations

• Fracture when all degrees of freedom associated with glass transition have been lost

• Good prediction of silk properties – Vollrath & Porter

• How does this extend to 3D strain?
  – Particularly tensile

• How does it tie in to fracture mechanics and fragmentation?
  – And temperature?

Fragmentation

- There is an obvious lengthscale from microstructure

- So use a percolation model with energy-based failure criterion
  - Site percolation: bond is either failed or not
  - Site size is microstructural length
  - Energy gives probability of failure which translates to number of failure sites in 3D lattice
  - When there is no fully-bonded path material is fragmented
  - Gives fragment size distribution

- Allows other capability such as burn area calculation

- What happens if there is no obvious lengthscale?
  - Comminution limit of rubbers?
  - Link to fracture mechanics
Fragmentation

- Validation against soft capture
- Compare model predictions with measured fragment distributions and shape of fragment cloud
- Importance of numerical scheme
Summary

• Some predictive capability

• Some fundamental questions still to be answered
  – Temperature
  – Time-dependence of volumetric properties
  – Configurational entropy in triaxial stress states
    – Particularly tensile