An equation of state for polyurea aerogel based on multi-shock response

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Abstract. The equation of state (EOS) of polyurea aerogel (PUA) is examined through both single shock Hugoniot data as well as more recent multi-shock compression experiments performed on the LANL 2-stage gas gun. A simple conservative Lagrangian numerical scheme, utilizing total variation diminishing (TVD) interpolation and an approximate Riemann solver, will be presented as well as the methodology of calibration. It will been demonstrated that a $p-\alpha$ model based on a Mie-Gruneisen fitting form for the solid material can reasonably replicate multi-shock compression response at a variety of initial densities; such a methodology will be presented for a commercially available polyurea aerogel.

1. Introduction
Polyurea (PU) is a moderately tough polymer that has shown promise in a variety of applications. Furthermore, it has recently been successfully manufactured into an aerogel [1, 2] in the density range of 0.016-0.55 g/cm³. The materials specifically tested here are commercially available [3] at a density of nominally 0.2 g/cm³. In terms of a low density impactor, the unique properties of PUA are that it has a very fine microstructure (see figure 1) and also has a reasonable compressive yield strength near 1.7±0.3 MPa (see figure 2.)

Here, we report on the experimental and subsequent modeling of polyurea, specifically in its aerogel form. Some standard Hugoniot data on fully dense material has been investigated previously [4, 5].

We model the solid PU with a simple Mie-Gruneisen EOS based on a Murnaghan fitting form for an isentrope [6], and the distended aerogel via a $p-\alpha$ model [7, 8] with dynamic compaction [9]. Computational modeling is performed with the use of a 2nd order spatial total variation diminishing, conservative Lagrangian scheme based on an approximate Riemann solver which allows for discontinuous material properties across cell interfaces, without the use of artificial viscosity.

2. Material models
The material properties of the the various components of the experiment are: Lexan, Ta, PUA and LiF (see figure 5.) All these materials, except the PUA, were previously fully described in [10].
The solid PU is modeled with a Mie-Gruneisen EOS based on a Murnaghan form for the isentrope. Thus, the reference pressure, $p_{\text{ref}}$, as a function of the solid density, $\rho_s$, is given by:

$$p_{\text{ref}}(\rho_s) = \frac{K_0}{K_0'} \left[ \left( \frac{\rho_s}{\rho_0} \right) K_0' - 1 \right]$$  \hspace{1cm} (1)$$

where $K_0$ is the isentropic bulk modulus at zero pressure, $K_0'$ is the derivative of the isentropic bulk modulus with respect to pressure at zero pressure and $\rho_0$ is the ambient density of the solid PU. The following equation can be integrated to obtain the reference energy along this reference isentrope, $e_{\text{ref}}$:

$$e_{\text{ref}}(\rho_s) = \int_{\rho_0}^{\rho_s} \frac{p_{\text{ref}}(\rho_s)}{\rho_s^2} d\rho_s$$  \hspace{1cm} (2)$$

which results in:

$$e_{\text{ref}}(\rho_s) = \frac{K_0 \left( 1 - \frac{\rho_s}{\rho_0} \right) - \frac{K_0}{K_0'} \left( 1 - \left( \frac{\rho_s}{\rho_0} \right) K_0' \right)}{(K_0' - 1)\rho_s}$$  \hspace{1cm} (3)$$

and in the standard Mie-Gruneisen fashion, a hydrodynamic EOS for the solid density material, $e_s(\rho_s, p_s)$, can be constructed as:

$$e_s(\rho_s, p_s) = e_{\text{ref}}(\rho_s) + \frac{p_s - p_{\text{ref}}(\rho_s)}{\rho_s \Gamma(\rho_s)}$$  \hspace{1cm} (4)$$

where $\Gamma(\rho_s)$ is an assumption. This equation can easily be inverted to obtain $p_s(\rho_s, e_s)$:

$$p_s(\rho_s, e_s) = p_{\text{ref}}(\rho_s) + (e_s - e_{\text{ref}}) \rho_s \Gamma(\rho_s).$$  \hspace{1cm} (5)$$

From examining the Hugoniot of solid PU, one obtains a reasonable fit with parameters shown in table 1. See figure 3 for comparison between model Hugoniot and experimental data. The previous experiments were all below 10 GPa, so there is some uncertainty in pressures significantly higher than this.

To extend the EOS model from the solid PU to the PUA, we employ the $p - \alpha$ model. In lieu of $\alpha$, we use the solid volume fraction, $\phi_s$, which is the reciprocal of $\alpha$. In evaluating the porous (aerogel) EOS, we have:

$$p(\rho, e, \phi_s) = p_s(\rho/\phi_s, e)\phi_s$$  \hspace{1cm} (6)$$
Table 1. EOS and compaction parameters for solid PU with $\Gamma(\rho_s) = \Gamma_0(\rho_0/\rho_s)^q$.

| $\rho_0$ | $K_0$ | $K'_0$ | $\Gamma_0$ | $q$ | $A$ | $B$ | $\mu_c$ |
|---------|-------|--------|------------|-----|-----|-----|---------|
| g/cm$^3$ | GPa   | GPa    | GPa        |     | GPa | GPa | $\mu$s  |
| 1.098   | 3.6   | 7.5    | 0.55       | 1   | 0.0048 | 2.5 | 0.01    |

where $e = e_s$ as there is no assumed surface energy nor energy associated with the void region. Likewise, the energy can be written as:

$$e(\rho, p, \phi_s) = e_s(\rho/\phi_s, p/\phi_s)$$  (7)

We assume that $\phi_s$ is an independent state variable modeled by the dynamic compaction equation [9]:

$$\frac{d\phi_s}{dt} = \max\left( \frac{\phi_s (1 - \phi_s)}{\mu_c} (p_s - \beta_s), 0 \right)$$  (8)

where $\frac{d}{dt}$ is the material derivative and $\beta_s$ is the configuration pressure, i.e. the quasistatic pressure at a particular solid volume fraction. The term, $\mu_c$, is the compaction viscosity which controls the timescale of compaction. The max function ensures that the porosity is monotonically decreasing as a function of time. The measured stress-strain relationship, figure 2, can be manipulated to obtain an approximate $\beta_s$. The model:

$$\beta_s = A \left( \frac{\phi_s - \phi^0_s}{1 - \phi^0_s} \right)^{1/4} e^{B\phi_s}$$  (9)

fits the available data well. The terms $A$ and $B$ are parameters used in fitting the data, and $\phi^0_s$ is the initial solid volume fraction. See table 1 and figure 4.

3. Multi-shock experiments

Three multi-shock experiments were performed on the PUA. These were performed at LANL’s two-stage gas gun facility, and the experimental setup is pictured in figure 5. A lexan projectile, with a layered impactor of PUA followed by Ta, is launched and subsequently strikes a LiF buffer and window. The primary diagnostic is a Photonic Doppler Velocimetry (PDV) measurement of the LiF buffer-LiF window interface velocity. The as fired dimensions are listed in table 2, along with the measured flyer velocity, $u_f$, at impact.

The impact results in a shock proceeding into the LiF and a shock traveling back into the PUA. Knowing the flyer velocity, the EOS of LiF and the measured particle velocity, one can determine a Hugoniot point for each of these experiments. These are shown in figure 3. Once the shock in PUA reaches the Ta, a strong reflected shock results in the PUA, and subsequent shocks between the Ta and LiF serve to further compress the PUA. See figures 6, 7 and 8.

4. Computational methodology and results

Here, a brief description of the computational methodology is given for solving the Euler equations with a general equation of state in a conservative Lagrangian framework. In the present modeling, strength effects of the materials are ignored. The finite volume discrete conservation of momentum and energy equations can be expressed as:

$$\frac{\partial}{\partial t} \int_{x_{i-1/2}}^{x_{i+1/2}} \rho u dx = - \left( p_{i+1/2} - p_{i-1/2} \right)$$  (10)
Figure 3. PU and PUA Hugoniot data and Mie-Gruneisen Murnaghan $p - \alpha$ model. These model Hugoniots assume the post-shock state is fully compacted. Note for $U_p < 0.5 \text{ mm/}\mu\text{s}$, the porous material will not be fully compacted.

Figure 4. Model compaction curve: $\beta_s$ versus solid volume fraction, $\phi_s$, for $\phi^0_s = 0.1, 0.2, 0.3, 0.4, 0.5$ (left to right).

Figure 5. Schematic of multi-shock experiments showing the multicomponent impactor (left) and buffer-window assembly (right).

Table 2. Thicknesses of materials and flyer velocities of multi-shock experiments.

| Shot # | Ta (mm) | PUA (mm) | PUA density (g/cm³) | LiF buffer (mm) | LiF window (mm) | $u_f$ (mm/µs) |
|--------|---------|----------|----------------------|-----------------|-----------------|---------------|
| 2s-724 | 2.429   | 5.139    | 0.202                | 1.131           | 12.802          | 2.094         |
| 2s-722 | 2.517   | 5.296    | 0.199                | 1.120           | 12.844          | 2.659         |
| 2s-723 | 2.569   | 5.416    | 0.199                | 1.152           | 12.761          | 3.020         |

$$\frac{\partial}{\partial t} \int_{X_{i-1/2}}^{X_{i+1/2}} E dx = - \left( p_{i+1/2} u_{i+1/2} - p_{i-1/2} u_{i-1/2} \right)$$  \hspace{1cm} (11)$$

where $X$ represents the initial spatial location, and the $i - 1/2$ and $i + 1/2$ denotes the interface at the edges of the finite volume $i$ which extends from $X_{i-1/2} < X < X_{i+1/2}$. $E = \rho e + \frac{1}{2} \rho u^2$ is the total energy in the cell. The conservation of mass is trivially satisfied in the Lagrangian framework as the mass is a constant. To compute the density in each finite volume cell, one
needs to track the location of $X_{i+1/2}$ in the laboratory frame of reference. This is denoted by $x_{i+1/2}$ (the other interfaces behave similarly.) These laboratory frame locations are simply governed by:

$$\frac{dx_{i+1/2}}{dt} = u_{i+1/2}$$  \hspace{1cm} (12)

Time integration of these equations is performed by a simple explicit forward Euler method. The interfacial approximations to $p_{i\pm1/2}$ and $u_{i\pm1/2}$ require special attention. In general, the solution at the cell interface can be computed from a Riemann problem. For realistic EOSs, this is a rather challenging and time consuming exercise. Instead, an acoustic approximation is made, which can be utilized even across disparate materials, see [11, 12] for discussion. The key results of this approximation are for a first order spatial scheme:

$$p_{i+1/2} = \frac{c_{i+1}c_{i+1}p_i + c_{i}c_{i}p_{i+1} + c_{i}c_{i}c_{i+1}c_{i+1}p_i(u_i - u_{i+1})}{c_{i}c_{i} + c_{i+1}c_{i+1}}$$  \hspace{1cm} (13)

$$u_{i+1/2} = \frac{p_i - p_{i+1} + c_{i}c_{i}u_i + c_{i+1}c_{i+1}u_{i+1}}{c_{i}c_{i} + c_{i+1}c_{i+1}}$$  \hspace{1cm} (14)

where $c_i$ is the sound speed in the cell $i$ (note that [10] had a typo in the subscripts in the first two terms in the numerator for $p_{i+1/2}$). Away from material interfaces, the spatial accuracy can be enhanced to 2nd order, by a conservative MinMod TVD interpolation [13] over the non-uniform Lagrangian grid and replacing the above cell values with 2nd order interpolated values. Although the results are still formally only 1st order, this technique provides enhanced resolution to fine scale structures and discontinuities.

All simulations presented here have an initial spatial resolution (Lagrangian initial spacing) of 10 $\mu$m. Changing the grid by factors of 1/2 and 2 had only minor changes to the computational results (most notably changes to the computed shock thickness, which is on the order of 20 $\mu$m.) Figures 6-8 shows the simulated PDV velocity record at the LiF buffer-LiF window, along with the actual PDV recorded interfacial velocity. As indicated in figure 3, the state of the first shock is reasonably well fit by the model; sans the elastic precursor in the LiF. Subsequent shocks are reasonably modeled by the EOS. The largest errors appear on the reflected shocks at relatively high pressures (above 20 GPa). This is likely due to the extrapolation of the solid Murnaghan EOS at pressures well beyond where it was calibrated.

5. Discussion
A relatively simple $p$-$\alpha$ EOS of a Mie-Gruneisen based on a Murnaghan isentrope fits both the shock and particle speeds reasonably well in the multiple shock experiments as well as in
the single shock experiments. Future work will examine the compaction as well as extend the Hugoniot response to other initial densities including near theoretical maximum density [4, 5]. The chemical decomposition of the PUA as well as higher pressure solid Hugoniots will also be investigated in future work.

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