Shock Hugoniot Behavior of Mixed Phases with Widely Varying Shock Impedances

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The shock velocity dependence on shock pressure in composite explosive materials containing polymeric binders is known to exhibit marked non-linear behavior in the $U_s - u_p$ plane at low pressures. This is in addition to the non-linear behavior noted in pure polymeric materials. The precise description of this behavior is important in analyzing the response of energetic materials to impact shocks. We will show that the mismatch of the shock impedances in materials such as rocket propellants composed of polymer binder, aluminum, and ammonium perchlorate can be expected to exhibit a very large initial slope of the shock velocity, $U_s$ dependence on the particle velocity, $u_p$. This slope is simply a result of the equilibration of Hugoniot pressure amongst the phases. With accurate descriptions for the equations of state of the individual components, we successfully predict the extreme slope at low compression. The effect is primarily due to the very large change in compressibility of the polymeric phase at relatively low volumetric compression of the whole mixture. Examples are shown and compared with available experimental results.

INTRODUCTION

Our studies of the consequences of high-velocity impacts on solid-fuel rocket motors require an accurate description of the shock response of the propellant as an inert, composite solid. Direct measurements of the Hugoniot of a number of propellants have been performed (1,2,3), but it would be convenient to have an accurate model. Many of the propellant formulations use the same constituents, but differ in proportions. In that case, an accurate model would permit the use of fewer impact shock experiments to define the Hugoniot of a new composition.

The shock front in a composite material exhibits a structure that corresponds to the particle-size distribution of the constituents. Typical solid rocket propellants use particles with various size distributions, as large as 300 microns, and as small as 20 microns. Although our interest is in propellant pieces with much larger dimension, so that we are not interested in wave structure with that much detail in time or space resolution, we wish our model to be consistent with the microscopic picture.

With these immiscible mixtures, the specific volume that is occupied by a constituent on an isotherm is the same as that occupied by the constituent alone at the same pressure and temperature. We estimate the time to reach thermal equilibrium behind the shock front by noting that most of the mass of these propellants is ammonium perchlorate (AP). The smallest size will equilibrate in the shortest time. For a spherical particle with the surface held at temperature $T$ that differs from the initial temperature, the center point gets half-way to that temperature in the characteristic time $0.12 \frac{a^2}{\kappa}$ (4) where $a$ is the radius and $\kappa$ the thermal diffusivity, which for AP is 0.0023 cm$^2$/s. The characteristic time for a 20 micron particle is 50 microsec, which is long after the passage of the shock front. Thus our model needs to consider that the constituents will be at different temperatures.

We chose to assume that the constituents are at pressure equilibrium behind the shock front, and that they each got to that state by a single shock. We realize that this assumption is not precise. The low-impedance binder, for example, must reach its final pressure with multiple shocks, because the outrun-
ning shocks in adjacent particles will drive bow waves into the plastic that then reflect off each other. Nevertheless, our assumption simplifies our work, and is a good approximation. A similar method was used by Bernecker. (5) The entropy difference between the Hugoniot and the adiabat, which is the limiting case of compression by multiple shocks, is only third order in the pressure jump (6).

THE INVERTED HUGONIOT EOS

With a model that describes the composite by a sum over the constituent volumes, it is convenient to describe the constituents by a Hugoniot that can be solved explicitly for the volume. We found an effective way to express the volume as a function of pressure on the Hugoniot, which simplifies the volume summation for mixtures. The expression is based on an empirical relation for the modulus of the Hugoniot, $K_h$, where

$$K_h = V\frac{\partial p}{\partial V},$$

and $K_h$ is a specific function of the Hugoniot pressure

$$K_h = K_0(l + \lambda \rho_v / K_o)^n$$

where $K_0$ is the initial modulus and $\lambda$ and $n$ are parameters used to fit the experimental data. We can integrate this expression to obtain

$$V_h = V_0 \exp \left[ \frac{l - (1 + \lambda \rho_v / K_o)^n}{\lambda (l - n)} \right]$$

Having determined values for $\lambda$ and $n$ for each component, the Hugoniot of the mixture is obtained by the weighted sum of the various component volumes,

$$V_h = \sum_{n} a_i V_{h,i}$$

where $a_i$ is the initial volume fraction of the $i$-th component. The shock velocity and particle velocity are given by the usual expressions

$$U_s = p_h / [\rho_v (1 - V_h)]$$

and

$$u_p = p_h / (\rho_v U_s).$$

We can now use this to illustrate the behavior of mixtures. The weight composition of several rocket propellants is 69% AP, 19% aluminum, and 12% Hydroxy-terminated polybutadiene (HTPB) binder. The equation of state for aluminum metal is well known and widely documented. With the parameters $\lambda$ and $n$ taken to be 6 and 0.82 respectively, and $K_o$ 0.743 Mbar we recover the linear equation of state given by Steinberg (7) for 1100 aluminum with density 2.71 g/cm$^3$.

Hugoniot data for AP with initial porosity averaging 3.8% are given by Sandstrom et al. (8). They also give a few points on the isotherm for fully dense AP, 1.95 g/cm$^3$. Since our interest is in the low-pressure behavior, and their lowest Hugoniot pressure was 40 kbar, we incorporated their room-temperature isothermal data and that of Bridgman for AP (9) with the shock wave data to develop the equation of state of the constituents. The method we use to estimate the Hugoniot from the isotherm is described by McQueen, et al. (10) as they sought to extract the isothermal compression from shock wave data and other thermomechanical properties. In summary, we calculate the energy on the isotherm by integrating the differential equation obtained from the thermodynamic law,

$$dE = T dS - pdV$$

and the thermodynamic identity (10),

$$dT = -\gamma T dV / V + T dS / C_v$$

resulting in

$$dE_T = (\gamma C_v T / V - p) dV$$

on the isotherm. Here $E$ is the internal energy density, $C_v$ is the specific heat, and $\gamma$ is the Grüneisen parameter,

$$\gamma = V \left( \frac{\partial p}{\partial E} \right)_v.$$

We use the general pressure-energy equation,

$$E = E_T + (p - p_T) / (\gamma)$$

together with the Hugoniot condition for energy

$$E_h = E_0 + \frac{1}{2} (p_h + p_T) (V_h - V_0)$$

(12)

to calculate the Hugoniot points consistent with the measured isotherms. The procedure used by (8) ignored the increase in energy and pressure of the Hugoniot over the isotherm at the same volume. The methods are identical in the limit of small Grüneisen coefficient. The fit to the AP data with the parameters $\lambda$ and $n$ given by 7 and 0.77, and the initial modulus $K_0$ to be 0.153 Mbar is shown in Figure 1.

A limited amount of low-pressure (less than 10 kbar) Hugoniot data for HTPB is reported by Gupta and Gupta (11). The initial modulus for HTPB was based on data from (11) and (12). Hugoniot data for polyethylene at the same initial density for pressures above 28 kbar are given by Carter and Marsh (13). In addition, we incorporated Bridgman’s isothermal data on polyethylene (14) to 40 kbar in the same way as for AP. With parameter values 11 and 0.9 for
\( \lambda \) and \( n \), and the value 0.025 for the initial modulus, the fitted curve is shown in Figure 2 for polymer density 0.90 g/cm\(^3\). With the constituents, we apply Eq. 4-6 to obtain the Hugoniot of the mixture. For the composition given above, we compare experimental Hugoniot points with the mixture result in Figure 3. The method is seen to capture the essential non-linear behavior of the composite.

**GENERAL METHOD**

We wished to apply this method for combining constituents on the Hugoniot to arbitrary equations of state. We developed a simple computer program that solves for the constituent volume on the Hugoniot by numerical iteration. For these well-behaved materials, any simple iteration scheme converges rapidly. We used Steinberg’s linear \( U-U_p \) relation for aluminum, with his recommended Grüneisen coefficient for off-Hugoniot points. A convenient and simple equation of state form is a polynomial in the compression, \( p \), where

\[
p = K\mu + A\mu^2 + B\mu^2 + \gamma(1 + \mu)\rho_0
\]

(13)

where \( K \) is the bulk modulus, and \( A \) and \( B \) are fitting parameters. For pressure in Mbar, the specific energy \( e \) has units of \( 10^7 \) J/g.

We fit the Hugoniot data for AP by selecting \( \gamma \) to be 1.0, the bulk modulus, \( K=0.15 \), and used linear least squares to obtain the coefficients \( A \) and \( B \) 0.225 and 0.1863 shown in Figure 1. We fit the binder, \( p=0.916 \), with \( \gamma=0.7 \), \( K=0.02 \), \( A=0.294 \), and \( B=0.0196 \) as shown in Figure 2. The resulting combination of the constituent volumes (Equation 4) is shown for the propellant in Figure 3. In addition, we can fit the same polynomial equation of state form to the calculated mixture Hugoniot, for more convenient use in shock wave analysis programs.

The model results show significant curvature in shock-velocity particle-velocity space. This curvature is a direct result of the significant change in the modulus of the compressible polyethylene at low pressure. Figure 4 shows the comparison of the propellant Hugoniot to experimental pressure-volume. We compress the scale in figure 5 to illustrate the changing contribution of the three constituents to the composite volume. It is clear that the binder compresses more easily at first, but is stiffer at high pressure.

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**FIGURE 1.** Experimental Hugoniot points for AP (solid circles) and transformed isotherms of Bridgman (open squares) and Sandstrom et al. (open triangles). Dotted line is the fit using the inverted Hugoniot model. Solid line is from the more general method to be described.

**FIGURE 2.** Experimental Hugoniot points for HTPB (solid triangle), polyethylene (solid circle), and transformed isothermal compression of polyethylene (open square). The inverted Hugoniot fit (dashed line) is shown with the fit using a more general method to be described.

**FIGURE 3.** Comparison of propellant Hugoniot data from (1), circle, (2), square, and (3), triangle, with inverted Hugoniot model (dotted line). The solid line is from the more general method to be described.
CONCLUSIONS

An example of a typical solid-fuel rocket propellant has been used to illustrate the general shock behavior of composite materials that incorporate low-modulus polymers or plasticizers. These rather common materials cannot be adequately represented by a linear shock velocity dependence on particle velocity. For such composite materials, the shock velocity has a rapid increase over a small particle velocity range at low stress levels, and bends over to a more normal value of the slope at higher stress. We found an inverted Hugoniot functional form to be useful, and which we recommend for investigating such behavior. A conventional and more general equation of state method was then used to confirm the results.

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