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MODELING SHOCK-DRIVEN REACTION IN LOW DENSITY, NON-ENERGETIC POLYMERIC MATERIALS

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ABSTRACT

Shock experiments on low density polyurethane foams reveal evidence of reaction at low impact pressures. However, these reaction thresholds are not evident over the low pressures reported for historical Hugoniot data of highly distended polyurethane at densities below 0.1 g/cc. To fill this gap, impact data for PMDI foam with a density of 0.087 g/cc were acquired for model validation. An equation of state (EOS) was developed to predict the shock response of these highly distended materials over the full range of impact conditions representing compaction of the inert material, low-pressure decomposition, and compression of the reaction products. A tabular SESAME EOS of the reaction products was generated using the JCZS database in the TIGER equilibrium code. In particular, the Arrhenius Burn EOS, a two-state model which transitions from an unreacted to a reacted state using Arrhenius kinetics, as implemented in the shock physics code CTH, was modified to include a statistical distribution of states. Hence, a single EOS is presented that predicts the onset to reaction due to shock loading in PMDI-based polyurethane foams. This methodology was also used to predict the anomalous compaction of PMDI foams over published data sets from 0.087 to 0.87 g/cc, and solid Polyurethane at a theoretical maximum density (TMD) of 1.264 g/cc. Likewise, similar modeling techniques were used to predict the performance of SX-358 foam, an RTV-based stress cushion material at a nominal density of 0.41 g/cc, and the matrix material, with properties similar to Sylgard, at 1.1 g/cc. At the start of this study, data were only available at a single impact condition below the threshold for reaction; hence, the decomposition of this material at higher pressures was revealed as a significant finding of this work. The decomposition of SX-358 at higher impact pressures to product species including solid, liquid, and gaseous molecules was estimated with thermochemical equilibrium calculations using TIGER. This modeling approach, developed for PMDI foam, was shown to predict gas gun data, acquired as part of this study, up to pressures of 14 GPa. Furrthermore, additional phase transitions were predicted in the product species under shock compression. To date, this study is the first known to the authors that demonstrates and successfully predicts the decomposition of these low-density polymer-based foams using a single model applicable to a broad range of impact loading conditions.

INTRODUCTION

Polymeric foams are ubiquitous in society and used almost universally for packaging, insulation, and cushioning [1]. Although foam is a well-known engineering material, the response of low-density polymeric foams under shock loading is poorly understood. Foams are effective as energy absorbers due to their ability to undergo large strains under a nearly constant pressure. Under shock compression and release to the same initial pressure, assuming the foam remains a solid, the net *Pv* work done during this cycle is converted into stored internal energy, which is manifested as material temperature. For the low-density polymeric foams investigated in this study, as long as the interface pressure remained under a 1 GPa, the foam remained a solid. However, beyond these impact pressures, the foam experienced a large volume *increase* at a nearly constant pressure, which is counter to the normal compression behavior of most materials to have a *decrease* in volume with increased pressure. Here, the shock temperatures experienced were sufficient to cause the foam to change phase from a solid to a multiphase gaseous mixture. Although this abrupt change in volume during compression was present in historical data for PMDI foams provided within the Marsh compendium [2] at densities of 0.3 g/cc and above, an explanation of this anomalous compaction was provided by the joint computational and experimental study published by a team of Los Alamos National Laboratory (LANL) scientists, Dattelbaum *et al.* [3]. This team generously provided their data and offered technical insight during the span of this study reported herein. Using a Hayes EOS for the solid material and a separate EXP-6 potential for the products EOS, they showed an abrupt transition from the solid phase at low pressures. This transition pressure monotonically increased with solid volume fraction over a wide range of initial foam density.

At a density of approximately 0.096 g/cc, the historical data presented in Marsh [2] show normal compaction behavior over the experimental range of impact pressures. One aim of this work is to fill in the gap at higher pressures by providing new data at or near this density, and to predict the response to impact using a single model that is valid for compaction, transition, and reaction product compression regimes. For practical applications where multidimensional stress waves propagate large chunks of foam bounded by irregularly shaped boundaries, and the state of the material under loading is unknown and cannot be assumed *a priori*, a model that is applicable in any of the aforementioned shock regimes is needed for predictive simulation of the bulk response. Furthermore, the cellular structure of the foam, the spatial distribution of the porosity, and the EOS of the matrix must also be known.

Validation experiments are vital for characterizing these foams and obtaining requisite information for computational simulation. This work covers series of validation experiments conducted for both PMDI foam and SX-358 foam. Historical data from shock experiments on the individual matrix materials were vital for the equation of state calculations. According to Carter and Marsh [4], solid polymeric materials also decompose under shock loading, but at much higher pressures.

NOMENCLATURE

A	Frequency factor (1/s)
C_s	Bulk sound speed (cm/s)
C_v	Specific heat at constant volume (J/kgK)
n	Exponent
P	Bulk pressure (GPa)
P_c	Fitting parameter (GPa)
p_g	Gas pressure (GPa)
p_s	Solid pressure (GPa)
s	Hugoniot slope
t	Time (s)
T	Temperature (K)
u_p	Particle velocity (cm/s)
U	Bulk shock velocity
U_c	Convective shock velocity (cm/s)
z	Ordinate of Cumulative Distribution Function

Greek Symbols

α	Distension parameter
ε	Strain
ϕ_{s0}	Initial solid volume fraction
ϕ_s	Solid volume fraction
Γ_s	Grüneisen coefficient
λ	Extent of reaction
ρ_{s0}	Initial solid density (g/cm^3)
ρ_s	Solid density (g/cm^3)
θ	Activation temperature (eV)
σ	Standard deviation of A (1/s)

MATRIX EOS MODELING

Polyurethane EOS

Solid Polyurethane (PU), the matrix material in the rigid PMDI foam investigated herein, decomposes at high pressures, beyond 20 GPa. Historical data given by Marsh [2] and van Thiel [5], when plotted in U-u_p or P-u_p Hugoniot space, show a kink or a change in slope at the threshold pressure. Hence, the unreacted U-u_p shock Hugoniot data [2,5] were fit with a simple linear relationship is given by

$$U = C_s + su_p \tag{1}$$

The least squares fit to the shock Hugoniot data was slightly different than the values published in Marsh [2], and gave the best fit to the data ($R^2 = 0.994$) , especially at higher pressures. Using the coefficients C_s and s, and additional thermodynamic data [3], the solid EOS was described with an analytic Mie-Grüneisen (MGR) relationship [6]. At pressures above the threshold, a tabular SESAME EOS was constructed. The JCZS EOS database in TIGER was used to calculate the equilibrium composition of polyurethane given by the formula $C_{36}H_{44}N_6O_{12}$ [7, 8]. Transition from the unreacted solid state to the reaction products EOS was accomplished with the Arrhenius Reactive Burn (ARB) model. This is a two-state model based upon Arrhenius kinetics where the extent of reaction progress variable is computed from a rate equation that depends upon two kinetic parameters, the frequency factor and the activation temperature. This model was originally developed for homogeneous explosives, but it has also been applied to very fine-grained solids, single crystals, and some non-explosive materials such as liquids or polymers. The ARB model was adapted for the shock decomposition of polymers, adding an additional parameter to account for a distribution of states, as has been shown by the work of Hobbs and Lemmon [9] for the thermal decomposition of PU foam. Here, the transition from the solid to the reacted phases is governed by a state relationship--a chemical kinetics rate law, avoiding *ad hoc* methods for pairing Hugoniot curves, and eliminating the need of picking between a solid or products EOS depending upon a guess of the end state. Furthermore, use of a tabular equation of state allows for the prediction of off-Hugoniot states.

The Mie-Grüneisen, Arrhenius Reactive Burn, and SESAME equations of state are models which are available in the shock physics code, CTH [6, 10]. CTH is an Eulerian, finite volume, multidimensional shock propagation code that solves the conservation equations for mass, momentum, and energy for up to 98 multimaterials including gases, fluids, solids and reactive mixtures. A summary of the model parameters obtained for PU are given in Table 1.

TABLE 1. Equation of state and thermophysical property data for PU.

Variable (cgs units)	**Value**
θ (eV)	0.8
A (s^{-1})	5.0×10^{9}
ρ_{s0} (g/cm^{3})	1.264
C_v (erg/g-eV)	1.97×10^{11}
$\Gamma_s\rho_s$ (g/cm^{3})	0.91
s	1.63
C_s(cm/s)	2.38×10^{5}

A comparison of the reactive PU model to available high-strain rate shock data to nearly 50 GPa is provided in Fig. 1. The boundary between the inert and products regimes is nearly indistinguishable; transition occurs at approximately 20 GPa. Having a products EOS that fits shock Hugoniot data over a wide pressure range is critical to predicting the decomposition of foams where presumably, the matrix consists of solid PU, regardless of the initial porosity.

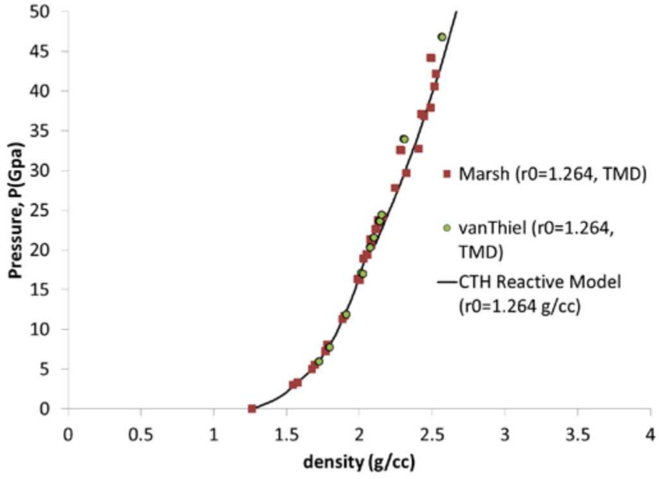

FIGURE 1. Shock Hugoniot data for PU and predicted response with CTH using a reactive model that transitions from a solid to products EOS above a threshold pressure.

At an equilibrium thermodynamic state near the shock Hugoniot at $T = 3480$ K, $P = 26$ GPa and $\rho = 2.23$ g/cc, TIGER was used to compute the decomposition products composition of PU. The results are given in Table 2.

TABLE 2. Equilibrium products composition of PU predicted with TIGER.

Species	**Mole (%)**
C (s)	58.9
H_2O	19.6
H_2	10.7
N_2	5.4
CH_4	2.2
C_2H_4	1.2
CH_2O_2	1.2

Condensed phase carbon (the polymorph, e.g. graphite or diamond, is unspecified) and water vapor are the primary constituents in the equilibrium mixture at the elevated *PT* state. This is in agreement with the published results by Dattelbaum *et al.* [3] using a different potential for the products, EXP-6. The SESAME EOS developed for the solid PU can also be used for the foam, eliminating the need for developing a separate products table.

SX-358 Matrix EOS

Prior to this study, the performance of SX-358—foam used as a stress cushion-- to shock loading was largely unknown due to the paucity of available Hugoniot data [11]. As shown in Fig. 2, only of handful of valid data existed for the porous material—one datum point at 0.41 g/cc and two data points at 0.73 g/cc. More data were available at the theoretical maximum density (TMD) of 1.12 g/cc; however, it is a poor assumption that the porous samples compact to this density (or to even approach it), as is common for some distended metals, ceramics, or heterogeneous energetic materials [12, 13, 14]. This gaping lack of data, and poor understanding of the response of this material to impact over a wider pressure range, motivated the collection of new experimental data and a unique EOS modeling approach. A key finding of this work, one which had not been previously documented (or likely even known), was that the SX-358 decomposed at higher shock pressures. Concomitantly, available EOS models simply were not adequate for predicting this anomalous behavior.

Accordingly, SESAME 7980 recovers the response of full density SX-358, although it includes a tensile region to extend to lower densities near 0.5 g/cc. The inert EOS for SX-358 at TMD was reconstructed with the Mie-Grüneisen model in CTH. These models, and the available compression data, are shown in the *P*-ρ plane in Fig. 2.

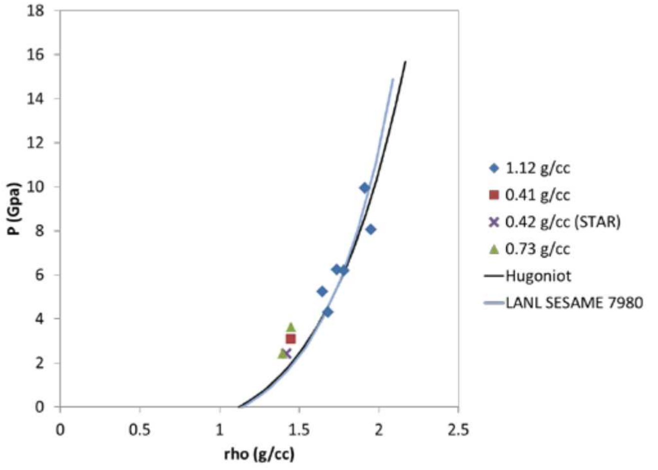

FIGURE 2. Shock Hugoniot data for SX-358 at various densities and predicted responses with CTH using a Mie-Grüneisen and a SESAME EOS.

A products EOS is needed to represent the decomposed state of the SX-358 foam. The matrix material has a molar composition (normalized per mol of H) of $C_{0.362}HO_{0.237}Si_{0.197}$ that is similar to Sylgard 184^{TM} (hereafter, Sylgard) with composition $C_{0.351}HO_{0.203}Si_{0.184}$ [11]. Sylgard is a silicone polymer produced by the Dow Corning Corporation, having a TMD of 1.05 g/cc. It is used widely in industry as an encapsulant for electronic and electrical applications, and has been characterized under high strain rate loading conditions to pressures in excess of 50 GPa [15, 16]. Given the similarity between Sylgard and SX-358 at full density, a products EOS can be constructed for Sylgard and validated over a wide pressure range, and applied as a products EOS for SX-358 at TMD. Hence, a tabular EOS is assembled with the JCZS EOS in TIGER following the same process described for PU. The parameters used in the two-state reactive model are given in Table 3.

TABLE 3. Equation of state and thermophysical property data for Sylgard and SX-358 at theoretical maximum density (TMD).

Variable (cgs units)	**Sylgard**	**SX-358 (TMD)**
θ (eV)	0.8	0.8
A (s^{-1})	5.0×10^9	5.0×10^9
C_v (erg/g-eV)	1.9×10^{11}	1.9×10^{11}
$\Gamma_s \rho_s$ (g/cm^3)	0.91	0.37
s	1.54	1.32
C_s(cm/s)	1.59×10^5	1.95×10^5

A comparison of the two-state reactive model to shock Hugoniot data [11, 16] for Sylgard is given in Figure 3.

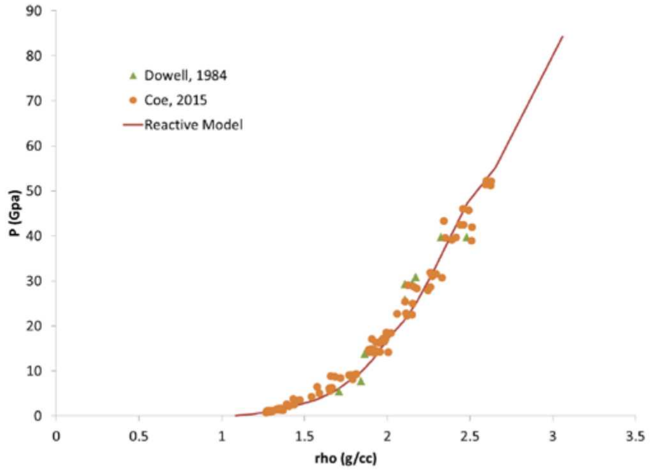

FIGURE 3. Shock Hugoniot data for Sylgard and predicted response with CTH using a reactive model that transitions from a solid to products EOS above a threshold pressure.

This method works remarkably well in reproducing the data, including multiple phase transitions in the products. The initial transition from solid to decomposition products occurs at 16 GPa. These transition points are more clearly seen in U-u_p Hugoniot data and the respective kinks predicted by the reactive model in Fig. 4. For comparison, the linear Hugoniot curve, with parameters provided by Dattelbaum *et al.* [16], is included in the plot to show where the curvature in the reactive model becomes significant at higher velocities. A high pressure linear function was used to fit the data above the break in the curve at particle velocities, u_p between 2.0 and 3.0 km/s.

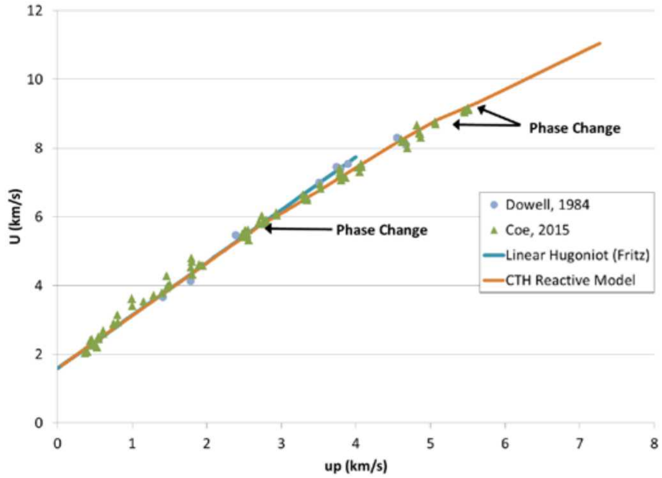

FIGURE 4. U-u_p shock Hugoniot data for Sylgard and predicted response with CTH using a reactive model that transitions from a solid to products EOS above a threshold pressure.

POROUS EOS MODELING

As shown in the previous section, both solid PU and SX-358 at TMD (and Sylgard) decompose at high pressures, a characteristic typical of polymers [4]. Additionally, Dattelbaum *et al.* [3] demonstrated that foam with a polymer matrix exhibits a similar characteristic, except the decomposition occurs at lower pressures, and the products transition to a lower density during compaction instead of a larger one, and oddity of polymer-based foams. The researchers also showed that for PMDI foam, the transition pressure monotonically decreased from 4.6 GPa at 0.868 g/cc to 1.2 GPa at 0.329 g/cc. This transition was accompanied with an abrupt expansion to a multiphase gaseous products mixture. Similar to their treatment of PU, separate models for the inert foam and products EOS were developed. In this work, we present new EOS data for PMDI foam at a very low density of 0.087 g/cc. Furthermore, high strain rate data will also be presented for SX-358. Based upon the aforementioned studies, it is expected that these materials will also decompose at low transition pressures.

Herein, we seek to apply the same two-state modeling approach presented for polymers to polymer foams, with a few notable modifications. For porous materials, a common method for representing the inert phase is to account for the porosity by treating it as a state variable dependent upon pressure and internal energy. The energy dependence is often ignored explicitly due to a lack of data, and treated implicitly through the Hugoniot reference curve, reducing the distension parameter to a function of pressure only. This explicit pressure dependence is treated with a compaction relationship [12]. Herrmann was the first to formulate an equation of state in terms of a distension parameter, using the method to predict the compaction of aluminum and iron honeycomb foam [17]. In CTH, a version of this model is available with the Mie-Grüneisen and SESAME equations of state, activated by the user when the porous initial density is below the initial density of the solid matrix [6, 10]. A major assumption is that the P-α model, which was originally implemented for a metal foam, can be applied to polymer foams. The validity of this assumption will be examined by comparing the model to compaction data for foams with initial porosities ranging from 30 to 93%. Another key modification to the model is the revision of the Arrhenius Reactive Burn EOS to include distributed activation energies following the work of Hobbs and Lemmon [9] for polyurethane foams under extreme thermal environments.

Compaction wave end states for steady, nonreactive stress waves are calculated from bulk foam interface conditions measured experimentally. The algebraic Rankine-Hugoniot jump conditions across the porous foam samples are given by

$$\rho\left(U_c - u_p\right) = \rho_0 U_c\,, \tag{2}$$

$$P = \rho_0 u_p U_c\,, \tag{3}$$

$$E = \frac{P}{2}\left(\frac{1}{\rho_0} - \frac{1}{\rho}\right), \tag{4}$$

The values of density, pressure, and energy in the solid are given by

$$\rho_S = \frac{\rho}{\phi_S}\,,\; p_S = \frac{P}{\phi_S}\,,\; E_s = E\,. \tag{5}$$

The compression of the solid, computed from conservation relationships and the U-u_p Hugoniot (Eqn. 1) is given by the Mie-Grüneisen equation of state for the solid

$$p_s = P_{ref}\left(\rho_s\right) + \Gamma_s \rho_s \left[E - E_{ref}\left(\rho_s\right)\right], \tag{6}$$

where the Grüneisen coefficient Γ_s of the solid is inversely proportional to the solid density ρ_S defined by the relationship

$$\Gamma_s \rho_s = \Gamma_{s0} \rho_{s0}\,. \tag{7}$$

The reference line is taken to be the normal Hugoniot of the solid from the initial state at ambient density, pressure, and energy such that $p_{ref} = p_H$, $E_{ref} = E_H$. These expressions for the Hugoniot end states are given by the following equations.

$$p_H = \rho_{s0}\left(\frac{C_s}{1 - s\varepsilon}\right)^2 \varepsilon,\;\; \varepsilon = 1 - \rho_{s0}/\rho_s\,. \tag{8}$$

$$E_H = \frac{\varepsilon}{2\rho_{s0}} P_H\,. \tag{9}$$

Equations (2-9) are solved algebraically for the following unknown variables: p_s, ρ_s, ϕ_s, U_c, and ρ. Input equilibrium values from the experiments are C_s, s, u_p, P, ρ_{s0}, and ϕ_{s0}. These computed quantities are used to fit the P-α compaction relationship for inert response of the foam samples from shock loading. Reference gas gun data were acquired as part of this study by Alexander and Reinhart [18], recently reported data by Dattelbaum et al. [3], historical data from Marsh [2] for PMDI foam, and data from LANL by Coe [11] for the SX-358 foam. The distension parameter, α is defined by

$$\alpha = \frac{1}{\phi_s}\,. \tag{10}$$

The process of void removal is computed analytically with this model, where the distension α is given as a function of bulk pressure P for pressures below a 'crush' pressure, P_c as

$$\alpha = 1 + \left(\alpha_0 - 1\right)\cdot\left[\frac{P_c - P}{P_c}\right]^n. \tag{11}$$

It should be noted that the value P_c is a fitting parameter, and does not represent the pressure where the void is completely removed in a dynamic process. For these polymer based foams, the strain rates are sufficiently large that the material decomposes before the pressures (or densities) approach the compression curve for the matrix material initially at TMD. Given α, P pairs at an initial distension $\alpha_0 = 1/\phi_{s0}$ from porous Hugoniot experimental data, the parameters and P_c and n are determined to be 2.28 GPa and 7.3, respectively, for PMDI foam and 3.5 GPa and 1.7, respectively, for SX-358.

REACTIVE EOS MODELING

As a shock wave passes across the foam, the energy across the shock can be partitioned into compaction and compression. As void is removed in the compaction process, the shock wave is dispersed over the foam matrix. Furthermore, stress localization at the contact points within the pore structure, stress bridging, fracture and rearrangement, and other localization processes as the shock passes over the foam matrix lead to time-dependent compaction behavior. Compaction-induced heating, and hot-spot formation from shock localization are key mechanisms that contribute to the matrix material decomposing at elevated stress states. Dattelbaum *et al.* [3] predicted shock temperatures in excess of 3000K, consistent with the values reported herein.

The Arrhenius Reactive Burn (ARB) model was used to predict transition from the inert to the decomposed products phase. Details of the model are included in the CTH reference manuals [6]. To better represent the complex reaction mechanisms in foam and to improve agreement with experimental data, the traditional ARB model was updated to include an extra parameter for distributed activation energy (DAE), as shown in the following development [9]. In CTH, the extent of reaction λ varies from 0 to 1 as the material transitions from an unreacted to a reacted state. The rate law describing the extent of reaction based upon single-step Arrhenius kinetics with DAE is given in Eqn. (9).

$$\frac{d\lambda}{dt} = (A + z\sigma)\cdot(1-\lambda)e^{-\theta/T}\,. \tag{9}$$

The user specifies three independent constants, A, θ, and σ, and z is computed as the ordinate of the cumulative distribution function, as described in Ref. 9. The DAE model tends to smooth reaction rates and permits a more gradual change in the extent of reaction, reducing the abrupt transitions in the solution of Eqn. (9). For a value of $\sigma = 0.1$ (s^{-1}), and kinetic parameters given in Table 1, the extent of reaction is plotted in Fig. 5.

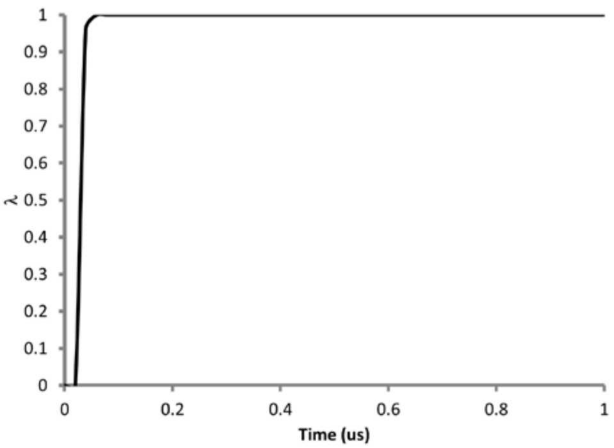

FIGURE 5. Extent of reaction progress variable for PMDI foam under shock loading.

Hence, a two-state reactive model that transitions from the porous inert state to the products state using Arrhenius kinetics with DAE was developed with the aforementioned models for polymer-based foams, PMDI and SX-358. The same products EOS, which was converted into a tabular SESAME table, for the inert material was used for the distended material, since the composition of the foam matrix was the same as the polymer at TMD.

PMDI Two-state Reactive EOS

To gain confidence in the use of this approach for porous materials, historical gas gun data from the Marsh compendium and more recent data on PMDI foam from Dattelbaum et al. were used for validation [2, 3]. An example of this approach is shown in Fig. 7 where the model was compared to high strain rate data at the initial densities of 0.348 g/cc and 0.868 g/cc. Here, the material does not fully compact before abruptly expanding at the transition pressure to decomposition products. Then, these products are compressed at higher pressures. The reduction in transition pressure predicted by the model is consistent with previously reported data, lending validity to this modeling approach as a means of predicting the complex response of reactive, non-energetic foam to shock loading.

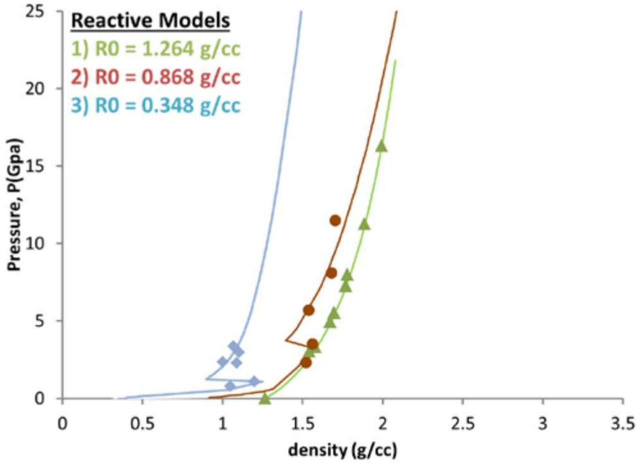

FIGURE 6. Comparsion of two-state reactive model to high-strain rate shock data for PMDI foam [2, 3].

Given the success in using this approach at foam densities to 0.348 g/cc, the same was applied to a lower density of 0.087 g/cc. In the Marsh compendium [2], data are reported at 0.096 g/cc up to 1 GPa, below the threshold for reaction. To fill this gap at higher pressures, and to verify the conjecture that decomposition would occur, data were acquired at the STAR facility at Sandia National Laboratories [18]. Results are given in Fig. 7.

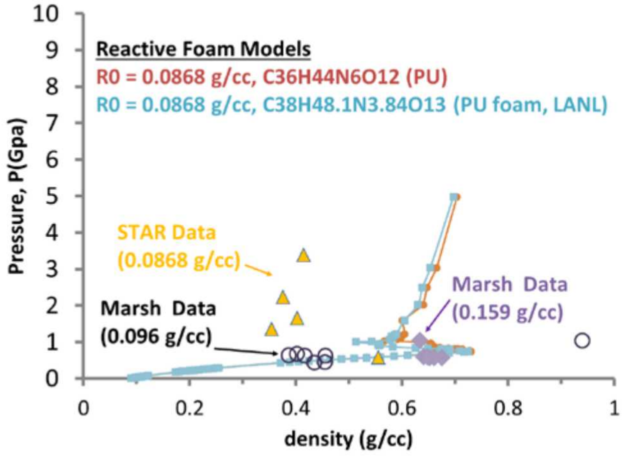

FIGURE 7. Comparsion of two-state reactive model to high-strain rate shock data for PMDI foam at 0.087 and 0.096 g/cc [2, 3, 11].

New data acquired as part of this work clearly demonstrates that decomposition occurs at Hugoniot pressures above 1 GPa [18]. One data point at approximately 0.55 g/cc is for an unreacted state, and lies in between legacy data from Marsh at 0.096 g/cc. This datum is included in the calculation of the distension parameter α; more inert data are needed to assess the extent of the compaction region since the material decomposes before reaching full compaction, experiencing a nearly three-fold decrease in density. Other data from Marsh at a higher density 0.159 g/cc are included, indicating inert or partially reacted states.

Our team has shown that the matrix may actually include other constituents that did not fully react during the foam synthesis. Additionally, no single foam is alike, and may have a slightly different composition with minimal effect on the computed shock Hugoniot. Reactive models for PMDI foam using two slightly different molecules (additionally $C_{38}H_{48.1}N_{3.84}O_{13}$ from Ref. 2) followed the same trends as the data, having a compaction zone and a transition pressure at 1 GPa. However, the models predicted a decomposition products region beginning at a higher density than measured. For these highly distended foams with over 90% void volume, the reactive models developed herein are unable to capture the range of densities in compaction or the large volume expansion in decomposition. According to Baer [19], who developed a multiphase model for a rigid PU foam at an initial density of 0.038 g/cc subjected to normal shock impingement in air at $M = 1.4$, a single-phase treatment of these low density materials was not adequate for capturing the wave interactions during compaction. With a solid volume fraction of only three percent, compaction waves propagated at vastly different speeds in the solid and in the air. How this treatment might be extended to foams which react at higher pressures is a subject currently under research.

SX-358 Two-state Reactive EOS

Given the apparent success in representing PMDI foam at initial densities above 0. 348 g/cc as shown in the previous section, the two-state reactive modeling approach is applied to SX-358 foam at 0.41 g/cc. To support the model validation effort, gas gun data were acquired as part of this work at pressures in excess of 14 GPa [18]. A comparison between the response using CTH with the reactive model and the collected experimental data is shown in Fig. 8.

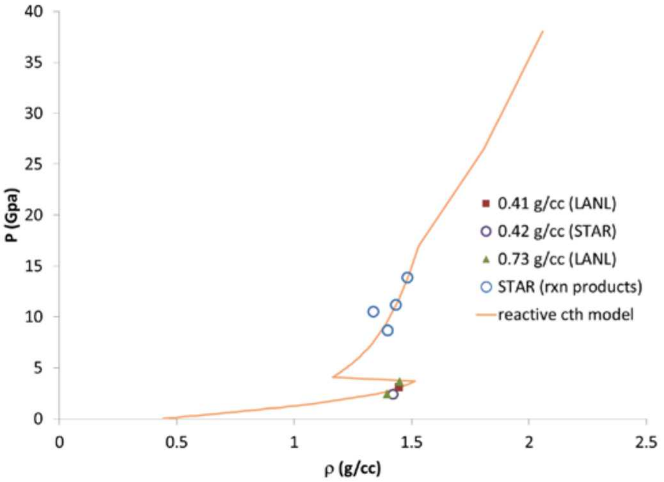

FIGURE 8. Comparison of two-state reactive model to high-strain rate shock data for SX-358 foam at 0.42 g/cc [11,18].

Here, the model predicts the limited set of compaction data and the response of the material at pressures above the 3.7 GPa threshold. Additionally, kinks in the response at pressures above 15 GPa are indicative of phase change within the product species. The composition of the decomposition product species includes solid, liquid, and gaseous phases, as shown at point near the Hugoniot ($P = 14.2$ GPa, $T = 5865$ K, $\rho = 1.49$ g/cc) in Table 4.

TABLE 4. Equilibrium products composition of SX-358 predicted by JCZS EOS in TIGER.

Species	Mole (%)
H_2	35.4
SiC (l)	21.7
CO	13.2
H_2O	10.3
SiO	4.4
C_2H_6	3.5
CH_4	3.4
H	2.3
SiO_2 (s)	0.9

SUMMARY AND CONCLUSIONS

A two-state reactive model for polymer-based foams was developed to predict the response of non-energetic materials that decompose under shock loading at elevated pressures. These materials experience an anomalous compaction behavior where the density abruptly decreases at low threshold pressures, well below the transition point for the polymer matrix. A reactive burn model with single step Arrhenius kinetics, including a normal distribution of states via a distributed activation energy term, was used to transition from an inert compacted state to a products state. Compaction was modeled with a Mie-Grüneisen EOS for the solid coupled with P-α distension relationship for the porous material, whereas a tabular EOS in a SESAME format was used to specify the decomposition products for both PMDI and SX-358. For polyurethane foam above 0.348 g/cc and the SX-358 at a nominal density of 0.42 g/cc, predicted shock Hugoniot end states compared reasonably well to available high strain rate data. However, for highly distended PMDI foam below 0.096 g/cc, this approach had limited utility, challenging the assumption of a single phase material at a given state. Nonetheless, a novel approach was used to develop a single model to capture the response of polymer-based foams over a wide range of shock pressures. This method was also used to accurately predict Hugoniot states within the polymer to pressures beyond 50 GPa.

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REFERENCES

[1] Gibson, L. J., and Ashby, M. F., 1997, *Cellular Solids: Structure and Properties*, 2nd ed, Cambridge University Press, Cambridge, UK..

[2] Marsh, S. P. (ed.), 1980, *LASL Shock Hugoniot Data*, University of California Press, Berkeley, CA.

[3] Dattelbaum, D. M., Coe, J. D., Kiyanda, C. B., Gustavsen, R. L., and Patterson, B. M., 2014, "Reactive, Anomalous Compression in Shocked Polyurethane Foams," *J. Appl. Phys.*, **115**, 174908.

[4] Carter, W. J., and Marsh, S. P., 1995, "Hugoniot Equation of State of Polymers," Technical Report LA-13006-MS, Los Alamos National Laboratory.

[5] van Thiel, M. (ed.), 1977, *Compendium of Shock Wave Data*, Lawrence Livermore Laboratory Report UCRL-50108, 603.

[6] Hertel, E. S., Jr., and Kerley, G. I., "CTH Reference Manual: The Equation of State Package," Sandia National Laboratories Report, SAND98-0947, 1998.

[7] Hobbs, M .L., Brundage, A. L., and Yarrington, C. D., "JCZS2i: An Improved JCZ Database for EOS Calculations at High Temperature and Pressure," paper presented at 15th International Detonation Symposium, San Francisco, CA, July 13-18, 2014.

[8] Hobbs, M. L., Baer, M. R., and McGore, B. C., 1999, "JCZS: An Intermolecular Potential Database for Performing Accurate Detonation and Expansion Calculations," Propellants, Explosives, Pyrotechnics 24, pp. 269-279.

[9] Hobbs, M. L., and Lemmon, G.. H., 2003, "Polyurethane Response to Fire in Practical Geometries" *Polymer Degradation and Stability* **84**, pp. 183-197.

[10] McGlaun, J. M., Thompson, S. L., and Elrick, M. G., "CTH: A three-dimensional shock wave physics code," *Int. J. Impact Engng.* **10**, 1990.

[11] Coe, J. D., 2015, "SESAME Equations of State for Stress Cushion and Related Materials," Technical Report LA-UR-15-21390, Los Alamos National Laboratory.

[12] Grady, D., "Analytic Solutions and Constitutive Relations for Shock Propagation in Porous Media," *Shock Compression of Condensed Matter*, eds. M. D. Furnish, Y. M. Gupta, and J. W. Forbes, pp. 205-208, 2003.

[13] Kipp, M. E. and Setchell, R. E., "A Shock Initiation Model for Fine-Grained Hexanitrostilbene," *Ninth Symposium*

(International) on Detonation, OCNR 113291-7, pp. 209-218, 1989.

[14] Brundage, A. L., and Gump, J. C., 2012, “Modeling Compressive Reaction and Estimating Model Uncertainty in Shock Loaded Porous Samples of Hexantitrostilbene (HNS),” *AIP Conf. Proc*. **1426**, 529.

[15] Dattelbaum D. M., Jensen, J. D., Schwendt, A. M., Kober, E. M., Lewis, M. W., Menikoff, R., 2005, “ A Novel method for Static Equation-of-state-development: Equation of State of a Cross-linked Poly(dimethylsiloxane) (PMDS) Network to 10 GPa,” *J. Chem. Phys.* **112**, 144903.

[16] Dowell, F., 1984, “A Simple EOS for the Silicone Rubber Sylgard 184,” Technical Report LA-10164-MS, Los Alamos National Laboratory.

[17] Herrmann, W., 1969, “Constitutive Equation for the Dynamic Compaction of Ductile Porous Materials,” *J. Appl. Phys.* **40**, 2490.

[18] Alexander, C. S., and Reinhart, W. D., 2016, Personal Communication, Sandia National Laboratories.

[19] Baer, M. R., 1992, “A Numerical Study of Shock Wave Reflections on Low Density Foam,” *“Shock Waves* **2**, pp.121-124.