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SESAME Equations of State for “Epoxy”

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I examine LANL equations of state (EOS) for Epon 828, nominally with and without addition of Jeffamine T-403 curing agent. I review the methodology used to construct the existing EOS, as well as that of a new developmental SESAME table (97605) for the decomposition products of cured epoxy. I compare shock loci extracted from all tables with data, and comment on their relative merits.

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I. INTRODUCTION

I will briefly review the status of LANL equations of state (EOS) for Epon 828 and its mixture with the curing agent Jeffamine T-403. I will also introduce a developmental EOS table for the decomposition products of the cured epoxy.

In Table I I list the numbers, authors, dates, and basic grid details of the relevant SESAME¹ tables. The density domain shrinks as one progresses through the series, and 7603 is noticeably more sparse than the previous two. The temperature domains are identical, but 7603 is the most dense by a wide margin.

The first issues to resolve (as is often the case with legacy “soft” materials) were those of composition and nomenclature. All three entries were dubbed “epoxy”. Two of those cases (7601-2) were also described as Epon 828, a liquid resin derived from bisphenol A and epichlorohydrin, while the third (7603) was based on a 70/30 wt% mixture of Epon 828 and Jeffamine T-403 curing agent. The normalized chemical composition, mean atomic weights ($\bar{A}$), mean atomic numbers ($\bar{Z}$), and reference densities (ρ_0) read from the comment tables are given in Table II. The composition underlying 7603 was actually given by wt% in its 101 subtable, so I’ve translated this to mol% in Table II. The $\bar{A}$ and $\bar{Z}$ I obtained agreed with those of the SESAME table to at least 3 significant digits, so I trust that my composition is essentially identical to that assumed previously. The compositions underlying 7601-2 and 7603 differ visibly from one another, but not dramatically so. Somewhat perplexing is the fact that 7601-2 are described simply as Epon 828, yet they contain nitrogen whereas pure Epon 828 does not. The initial densities differ by roughly 2.5%. My suspicion is that all three tables were really meant to represent the cured material (*i.e.*, that mixed with Jeffamine), but that this distinction was not appreciated when constructing the earlier tables.

II. EQUATION OF STATE METHODOLOGY

A. Inert

The only documentation for 7601-2 is found in their 102 subtables, but 7603 is thoroughly detailed in a 1994 tech report.² All three are based on the SESAME decomposition of the Helmholtz free energy^{1,3,4}

$$F(\rho, T) = \phi_0 + F_{\text{ion}} + F_{\text{elec}}. \quad (1)$$

TABLE I. Summary of new (developmental) and existing SESAME tables for epoxy. The last column indicates whether the composition is based on neat Epon 828 or its 70/30 wt% mixture with Jeffamine T-403 curing agent.

SESAME	Subtables	Grid ($n\rho \times nT$)	Domain (g/cc, K)	Author (Year)	Cured?
7601	101-2, 301-6	69 $\times$ 37	$\rho = 0 - 2.37\text{E}4$ $T = 0 - 1.16\text{E}9$	J. D. Johnson (1984)	?
7602	101-2, 301	66 $\times$ 27	$\rho = 0 - 1.32\text{E}3$ $T = 0 - 1.16\text{E}9$	J. D. Johnson (1984)	?
7603	101-2, 301-6, 401	37 $\times$ 40	$\rho = 0 - 1.16\text{E}3$ $T = 0 - 1.16\text{E}9$	J. C. Boettger (1994)	Y
97605	301	30 $\times$ 29	$\rho = 1.00975 - 3.2$ $T = 430 - 8125$	present work	Y

Here, ϕ_0 is the 0 K energy of the static lattice, F_{ion} is the contribution of the ions (including zero-point energy), and F_{elec} stems from thermal excitation of the electrons. Coupling of F_{ion} and F_{elec} is neglected. Cold curves were obtained by fitting to shock data, that for the nominally uncured being taken from the LASL Compendium⁶ and the cured from Ref. 7. Electronic contributions were in both cases based on Thomas-Fermi-Dirac theory,⁸⁻¹⁰ using either united atom (7601-2) or additive volume (7603) methodologies. The earlier EOS used a generalized Chart D model¹¹ for both Grüneisen Γ and ionic contributions, whereas 7603 used generalized Chart D for Grüneisen and JDJNuc¹² for the ionic model. In both cases, $\Gamma_0 = 0.8$. Although the 102 subtable for 7602 states that it is merely a recreation of 7601 with van der Waals loops removed, for reasons given below (Section. III) I don't think this is quite correct. See Ref. 2 for additional details on the construction of 7603.

TABLE II. Final compositions (per mol, normalized) and reference densities for the materials under survey.

Material	Composition	$\bar{A}$	$\bar{Z}$	$\rho_0(\text{g/cc})$
Epon 828 (uncured)	$\text{C}_{0.347}\text{H}_{0.577}\text{N}_{0.028}\text{O}_{0.048}$	5.9134	3.2407	1.185
Epon 828 (cured)	$\text{C}_{0.376}\text{H}_{0.534}\text{N}_{0.013}\text{O}_{0.077}$	6.46450	3.49533	1.154

B. Decomposition Products

Epoxy decomposition products were modeled under the assumption of full chemical and thermodynamic equilibrium. In keeping with the equilibrium assumption and the location of relevant states on the carbon phase diagram, solid constituents were treated as diamond. In reality, of course, the situation is far more complicated.

The bulk free energy of fluid components was calculated with Ross perturbation theory¹³ based on an EXP6 potential.¹⁴ The latter has the form

$$\phi(r) = \frac{\epsilon}{\alpha - 6} \left[6e^{-\alpha\left(\frac{r}{r_0}-1\right)} - \alpha \left(\frac{r_0}{r}\right)^6 \right], \quad (2)$$

where α sets the steepness of the repulsive wall, ϵ represents the energetic well depth, and r_0 gives the separation at which the intermolecular potential is minimized. EXP6 parameters for each species were calibrated to shock data on the pure fluid,¹⁵ and are listed in Table III. While I started with the full list shown there, I progressively pruned constituents whose mol number was everywhere two orders of magnitude down from the rest in order to facilitate numerical robustness. This yielded a fairly simple material comprising only the bold species in Table III. Fluids were combined in the form of an ideal mixture.¹⁶

The EOS for bulk diamond ($\rho_0=3.51$ g/cm³) was of Mie-Grüneisen form¹⁷ ($\Gamma = 0.88$)¹⁸ built from a Murnaghan¹⁹ cold curve ($B_0 = 440$ GPa, $N = 3.65$)²⁰ and a Debye thermal ionic contribution²¹ ($\theta_D = 1850$ K)¹⁸; thermal electronic contributions to the free energy are negligible over the relevant domain and therefore were neglected. In keeping with fairly standard practice,²² Γ/V was assumed constant. The free energy of the complete mixture (fluids+solid) was minimized as a function of chemical composition subject to conservation and non-negativity of elemental mass fractions. I have no real data on epoxy heat of formation, so it was simply set to zero.

III. HUGONIOTS

In Figures 1-2, I compare Hugoniot interpolated from the relevant SESAME tables with shock data^{6,7} in the $U_s - u_p$ and $P - V$ planes. In all plots I have added considerably to the grid for the sake of obtaining smooth curves. Ambient sound speeds read from 7601-3 are roughly 20%, 5%, and 2% (respectively) higher than the experimental value of 2.265 km/s.⁶

TABLE III. EXP6 parameters (see eqn. 2) of fluids comprising the decomposition products mixture for epoxy.¹⁵ All constituents were included initially, but only those in bold were retained for construction of the final table. Pair potentials were translated to bulk free energies using thermodynamic perturbation theory.¹³

Component	$r_0/\text{\AA}$	$(\epsilon/k_B)/\text{K}$	α
N ₂	4.0876	128.24	12.936
NO	3.995	117.1	12.08
O ₂	4.11	75.0	13.117
CO ₂	4.096	335.0	13.781
H₂O	3.5	424.0	10.0
CO	4.0876	128.24	12.936
CH ₄	4.22	154.1	12.5
H₂	3.43	36.4	11.1
HCO ₂ H	4.096	335.0	13.781
NH₃	3.3	424.0	12.0
N ₂ O	4.096	335.0	13.781
C ₂ N ₂	4.9	330.0	13.0

Concavity at low particle velocity is a common Hugoniot feature of soft materials such as epoxy.¹⁷ All four tables do a reasonable job with the data at high particle velocity.

Both data sets display a discontinuity beginning around $u_p \approx 3$ km/s. While 7602 transitions smoothly from reactant to products, 7601 and 7603 preserve the cusp. They achieve this, however, through adjustment of the cold curve (which was explicitly constructed to recover the Hugoniot, see Section II A), as shown in Figure 3. This highlights one of the pathologies of using a single table to describe both an organic solid and its decomposition products: the transition from one to the other is completely independent of temperature, and persists even at 0 K. SESAME 7602 lacks a 306 subtable, but its smoothness over the corresponding stretch of particle velocities belies its being merely a “Maxwellized” version of 7601.

FIG. 1. Hugoniot in the $U_s - u_p$ plane, as read from SESAME tables for epoxy. Results are compared with shock data taken from Refs. 6 and 7.

FIG. 2. Hugoniot in the $P - V$ plane, as read from SESAME tables for epoxy. Results are compared with shock data taken from Refs. 6 and 7.

FIG. 3. Cold curves read from SESEAME 7601 and 7603, as compared with shock data taken from Refs. 6 and 7.

IV. SUMMARY

I have generated a developmental SESAME table (97605) for epoxy decomposition products, and reviewed the origin and quality of epoxy tables (7601-3) already in the official repository. Here are some conclusions:

- The experimental basis for all these tables is extremely thin, and appears to consist entirely of shock and sound speed data.
- Of the existing tables 7601-3, only 7603 is based on the correct chemical composition. Proper adjustment would most likely constitute a small correction to 7601-2. The composition underlying 97605 is the same as that used to construct 7603.
- Of the existing tables 7601-3, 7603 does the best job of reproducing the ambient sound speed.
- Of the existing tables 7601-3, only 7602-3 attempt to recover the Hugoniot discontinuity believed due to decomposition. However, their means of doing so is physically unjustifiable.

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