Experimental investigation of phenylene and polystyrene under conditions of shock loading and isentropic expansion. Equations of state of plastics at high energy densities

A. V. Bushman, I. V. Lomonosov, V. E. Fortov, and K. V. Khishchenko

Center for Scientific Research on the Thermal Physics of Pulsed Excitations, Russian Academy of Sciences, 127412 Moscow, Russia

M. V. Zhernokletov and Yu. N. Sutulov

All-Russia Scientific Research Institute for Experimental Physics, 607200 Sarov, Nizhniĭ Novgorod Region, Russia

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We have experimentally investigated the shock adiabats of phenylene up to pressures $p \approx 600$ kbar and the dynamic compressibilities of phenylene and polystyrene subjected to reflected shock waves at $p \approx 1.25$ and 1.3 Mbar respectively. We also have obtained plots of the expansion isentropes of these materials up to $p \approx 2$ kbar. We used the totality of of our experimental data to formulate a semiempirical equation of state for these plastics over a wide range of high-energy states. © *1996 American Institute of Physics.* [S1063-7761(96)01205-X]

1. INTRODUCTION

A topic of considerable interest to researchers in the physics of materials at high energy densities[1] is the thermodynamic properties of these materials under conditions of high-energy loading. Such loading regimes are realized when concentrated energy fluxes, e.g., laser light or x-rays, ion or relativistic electron beams, or high-power shock waves, act on condensed phases of matter. The use of traditional methods to investigate these thermodynamic properties at high-energy densities,[2,3] i.e., shock compression of solid[4–6] and porous[7–9] samples with subsequent isentropic expansion,[10,11] has made it possible to construct equations of state for many metals, equations that are used in a wide range of phase diagrams (see Ref. 12 and the citations contained therein).

The unique physical properties of polymer materials, typical representatives of which are phenylene and polystyrene, have been much less studied. These materials are characterized by low density, small values of electronic and thermal conductivity, high radiation resistance, plasticity, and wear resistance, which lead to their widespread use as structural elements that are subject to intense force and thermal loading. For example, phenylene is used to make various strength-bearing parts in aerospace technologies, while polystyrene is used to simulate layered thermonuclear targets. The numerical solution of many problems in high energy density physics calls for the equations of state of these plastics over a wide range of densities and pressures.[13] The expressions for the structures of phenylene and polystyrene are complicated and in practice exclude the possibility of even qualitative calculation of their thermodynamic properties by the methods of quantum mechanics. In this situation, the construction of equations of state for plastics becomes possible only within the framework of a semi-emperical model, for which theoretical representations are enlisted to establish the general form of the functional dependences of the potential, while the aggregate of experimental data is used to determine the numerical coefficients in these dependences.

Experimental studies of phenylene using high-power shock waves have not been carried out up to now, and available papers on polystyrene at high pressures[6,14–16] contain only disconnected data on the dynamic compressibility of samples with various initial densities. To a considerable degree, this was the stimulus that led us to make experimental measurements of the characteristics of plastics at high energy densities and to construct semiempirical equations of state based on the aggregate of available and newly obtained data. We have implemented similar programs in the past to obtain the equations of state of plexiglass and Teflon[17] and of polyimide.[18] In this paper, we obtain data on the compressibility of phenylene subjected to shock waves with intensities up to $p \approx 600$ kbar, and present data on the states of phenylene and polystyrene under repeated dynamic loading up to $p \approx 1.25$ and 1.3 Mbar respectively, and in isentropic unloading waves up to $p \approx 2$ kbar. The available and newly acquired experimental data are incorporated together in wide-range equations of state.

2. EXPERIMENTAL METHODS AND RESULTS OF STUDY

The samples we investigated experimentally consisted of phenylene and polystyrene with initial densities $\rho_0 = 1.33$ and $1.05\ \mathrm{g/cm^3}$ respectively. Shock waves were generated in the samples through copper, aluminum, or iron plates by steel projectiles accelerated by the detonation products of condensed explosive materials up to velocities of 5.0 and 6.1 km/s. By recording the velocity of the initial shock front D (with an error of $\approx 1.5\%$) in the samples, we were able to compute the bulk velocity u and pressure p[2] based on the known shock adiabatics of the plates and the preset parameters of the shock waves generated in them (i.e., the mass velocity u_*). Table I contains the characteristics of the projectile systems and the data averaged over six to eight recordings, obtained in trials where we measured the dynamic compressibility of phenylene; the corresponding experimental points are plotted in $D-u$ coordinates in Fig. 1.

In experiments where we studied reflected shock waves and isentropic expansion waves, the measured quantity was

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TABLE I. Experimental data on shock compression of phenylene.

Plate material	u_*, km/s	u, km/s	D, km/s	p, kbar
copper	0.22	0.39	3.22	17
copper	0.48	0.83	3.85	43
aluminum	0.91	1.32	4.61	81
aluminum	1.16	1.65	5.19	114
aluminum	1.45	2.02	5.78	155
aluminum	1.72	2.38	6.10	193
copper	1.55	2.59	6.23	215
aluminum	2.07	2.86	6.46	246
copper	1.75	2.91	6.46	250
aluminum	2.25	3.11	6.47	268
aluminum	2.70	3.70	7.14	351
iron	2.48	4.00	7.64	406
aluminum	3.29	4.42	8.22	483
iron	2.81	4.49	8.34	498
aluminum	3.71	4.92	9.05	592

the shock-wave velocity D_* in obstacles with various dynamic impedances placed after the samples, allowing us to determine the parameters of the final states analogously. A number of points on the repeated shock adiabatics were obtained by reflection from obstacles that were more rigid than the plastics under study, and with known dynamic adiabatic curves (copper, aluminum, Teflon). The region of decreased pressure and significant rarefaction was studied using soft dynamic obstacles (polyethylene, foam plastics of various densities, and a heavy inert gas—argon—at various pressures), the shock adiabatics of which are also known (see, e.g., Ref. 10).

In order to monitor the parameters of the original states, in the majority of trials on samples with diameter 38 and thicknesses 2 mm we used both preforms made of obstacle materials with dimensions 12 and 3 mm respectively and preforms made from the materials under study themselves. We measured the parameters of the initial and final states in the condensed media by the method of reflection, using an electrical-contact detector to record the shock-wave velocity. For the case of argon, we used an optical method, recording light from the front of the shock wave. A detailed description of the methods and components used to perform the experiments is contained in a paper on isentropic expansion of shock-compressed metals.[10] Table II contains a summary of our trial data for repeated shock compression and isentropic expansion of phenylene and polystyrene; the experimental points, each of which is an average of six to eight independent recordings, are plotted on the $p-u$ diagram of Fig. 2.

3. MODEL OF THE EQUATION OF STATE

The newly-obtained shock wave data for phenylene fix only the course of a continuous adiabat on the energy surface of these plastics in pressure–volume–energy space. Likewise, the available data from previous dynamic testing of polystyrene[6,14–16] determine the parameters of compressed states of this material for only a few shock adiabats. The experimental data on repeated shock compression and isentropic expansion presented in the present paper constitute an important source of information about the behavior of phenylene and polystyrene at high energy densities. We carried out similar experiments previously in constructing the equations of state of a number of metals,[10] plexiglass and Teflon,[17] thereby determining the accuracy of a thermodynamic description of these materials over a new range of densities and pressures that had not been studied by other experimental methods. Nevertheless, the relatively small amount of experimental data and the uncertainties of theoretical representations of the behavior of polymers at high energy densities impose considerable restrictions on the form of the semiempirical potential, making it necessary to use simplified models for the equation of state with a small number of fitting parameters.

The caloric model, which can be used to describe the thermodynamic properties of polymers, implies the following general form for the equation of state:

$$p(V,E)=p_c(V)+\frac{\Gamma(V,E)}{V}[E-E_c(V)], \qquad (1)$$

where $E_c(V)$ and $p_c(V)=-dE_c/dV$ are the elastic compo-

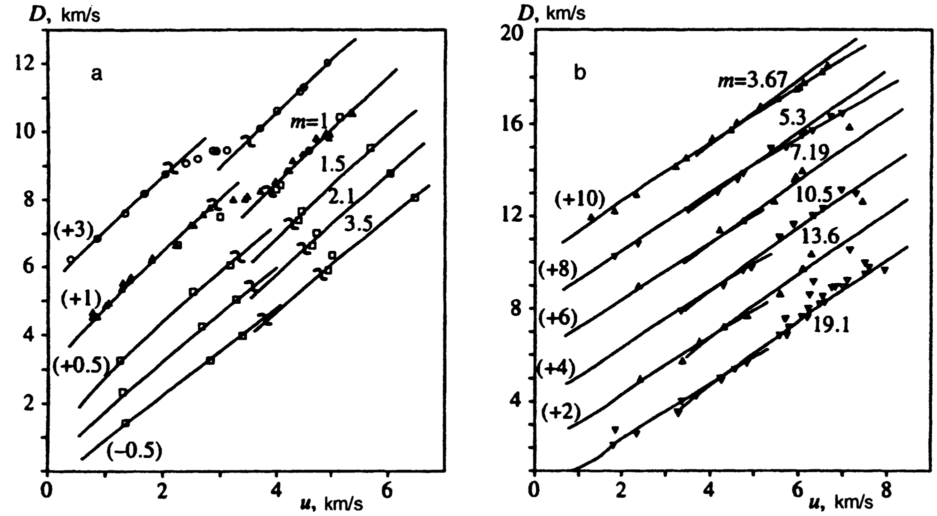

FIG. 1. Shock adiabatics of phenylene (a, upper curve) and polystyrene (a, b); $m=\rho_0/\rho_{00}$ is the value of the initial porosity of the polystyrene samples, and the numbers in parentheses denote the shift of the curves along the ordinate axis. The wavy lines denote the position of boundaries where the region of physical-chemical conversion of the shock-compressed plastics takes place. Experiment: ○, ●—this work, △, ▽—Ref. 6, □—Ref. 15.

TABLE II. Experimental data on repeated shock compression and isentropic expansion of phenylene and polystyrene.

	Phenylene			Polystyrene		
Obstacle material	D_*, km/s	u, km/s	p, kbar	D_*, km/s	u, km/s	p, kbar
copper	6.93	2.02	1250	7.04	2.07	1301
aluminum	9.70	3.22	846	9.64	3.18	831
Teflon	8.19	3.73	669	8.20	3.74	672
phenylene	8.12	4.33	468	-	-	-
polystyrene	-	-	-	8.46	4.58	407
polyethylene	9.59	4.56	402	9.62	4.58	405
foam plastic 0.71	8.29	5.26	309	7.95	5.01	283
foam platic 0.53	8.04	5.51	235	-	-	-
foam plastic 0.51	-	-	-	7.94	5.53	224
foam plastic 0.34	8.02	6.00	164	8.14	6.01	166
argon 20	-	-	-	-	7.88	25
argon 16	9.35	8.21	24	-	-	-
argon 15	-	-	-	-	8.36	20
argon 11	9.68	8.53	17	-	-	-
argon 10	-	-	-	-	8.59	14
argon 6	9.91	8.75	9	-	-	-
argon 1	11.02	10.09	2	-	10.04	2

Note. The numbers after the foam plastic obstacles correspond to the plastic density (g/cm^3), those next to the argon gas the argon pressure (in bar).

nents of the energy and pressure at $T=0$ K; the coefficient $\Gamma(V,E)$ determines the contribution of thermal components to the equation of state.

For the volume dependence of the elastic energy of compression we will use the potential

$$E_c(V)=\frac{V_{0c}B_{0c}}{m-n}\left(\frac{\sigma_c^m}{m}-\frac{\sigma_c^n}{n}\right)+E_d, \qquad (2)$$

in which $\sigma_c=V_{0c}/V$, V_{0c} is the specific volume at $p=0$, $T=0$ K, and B_{0c} is the modulus of elastic compression $B_c=-V dp_c/dV$ evaluated at $\sigma_c=1$. The quantity E_d, which has the sense of a characteristic energy for destruction, is defined from the normalization condition $E_c(V_{0c})=0$, which leads to the relation $E_d=B_{0c}V_{0c}/mn$. A relation can be derived between the coefficients m and n in the form $n=B'_{0p}-m-2$ in terms of the derivative of the modulus of elastic compression with respect to pressure $B'_{0p}=dB_c/dp_c$ evaluated at $\sigma_c=1$. The parameters V_{0c}, B_{0c} and B'_{0p} are chosen for each material by iteration so that they match tabulated values of the specific volume $V=V_0$, the adiabatic velocity of sound $c_S=c_{S0}$, and the derivative of the isentropic modulus of compression $B_S=-V(\partial p/\partial V)_S$ with respect to pressure $B'_S=B'_{S0}$ under normal conditions, as determined from dynamic measurement data. The remaining free exponent m in Eq. (2) is found from the best fit to experimental data obtained in direct and reflected shock waves.

The dependence of the coefficient Γ on volume and energy is defined as follows:

$$\Gamma(V,E)=\gamma_i+\frac{\gamma_c(V)-\gamma_i}{1+\sigma_c^{-2/3}[E-E_c(V)]/E_a}. \qquad (3)$$

Here the expression for $\gamma_c(V)$ corresponds to the case of low thermal energy, while the quantity γ_i characterizes the region of strongly heated condensed matter. The anharmonic

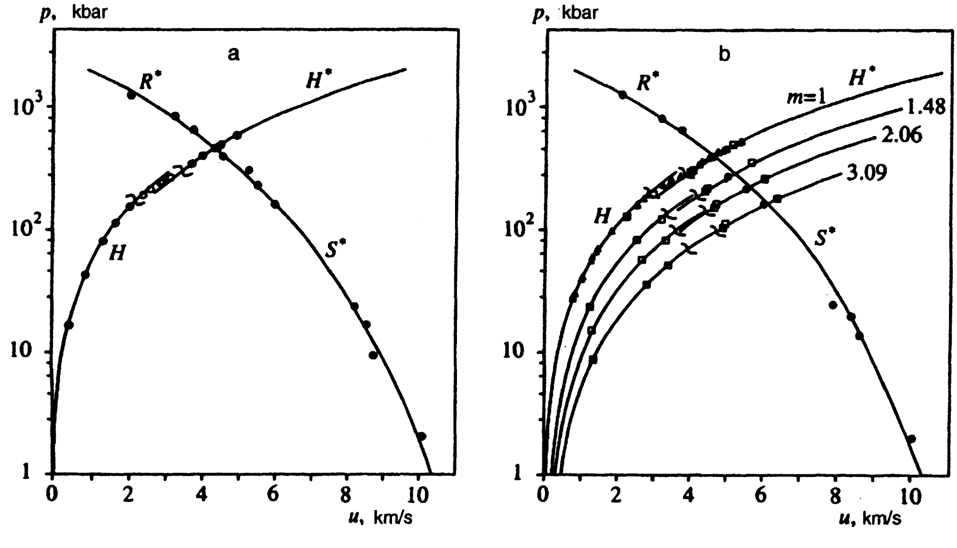

FIG. 2. Experimental (points) and computed (solid curves) shock adiabatics (H), curves of repeated compression (R) and expansion isentropes (S) for phenylene (a) and polystyrene (b). The stars denote curves that correspond to conversion products. For the remaining notations, see the inset to Fig. 1.

energy E_a specifies the thermal energy required for the transition from one limiting case to the other, and is found by fitting data from dynamic experiments at high pressures. The volume dependence of the elastic component of the coefficient Γ is given by expression

$$\gamma_c(V)=\frac{2}{3}+\left(\gamma_{0c}-\frac{2}{3}\right)\frac{\sigma_n^2+\ln^2\sigma_m}{\sigma_n^2+\ln^2(\sigma/\sigma_m)}, \tag{4}$$

where $\sigma=V_0/V$,

$$\gamma_{0c}=\gamma_i+(\gamma_0-\gamma_i)\left[1+\left(\frac{V_0}{V_{0c}}\right)^{2/3}\frac{E_0-E_c(V_0)}{E_a}\right]^2,$$

E_0 and γ_0 are the specific internal energy and the Grüneisen constant, i.e., $\gamma=V(\partial p/\partial E)_V$, under normal conditions. It is not difficult to see that the form of the function $\gamma_c(V)$ we have chosen ensures that the condition $\gamma(V_0,E_0)=\gamma_0$ is satisfied, as well as the asymptotic value $\gamma_c=2/3$ in the limiting cases of small and large degrees of compression. The fitting parameters σ_n and σ_m in Eq. (4) are determined by requiring an optimal description of the experimental data from measurements of the dynamic compressibility of porous samples and the shapes of isentropes for unloading of the materials under discussion.

4. RESULTS OF CALCULATIONS

Analysis of the experimental data obtained in this paper and previously[6,14–16] indicates that the materials under study undergo a number of physical–chemical transformations as the pressure at the shock front increases, resulting in properties of the denser state that differ appreciably from these observed under normal conditions. On the shock adiabatics of phenylene and polystyrene these transformation begin in the range of pressures $p\approx 180$ and 200 kbar, respectively, and terminate with considerable changes in the density (by $\approx 20\%$) and compressibility of the medium. Traditionally this is explained by breaking of chemical bonds of the original compound under the action of the intense dynamic loading, and the formation of a low-compressibility mixture of a diamondlike phase of carbon and various low-molecular weight components.[19] In this paper we construct equations of state for phenylene and polystyrene based on the caloric model[1–4] for the materials before and after the transformation separately. In this case, we use data from shock wave experiments with continuous and porous samples under pressures above the region of transformation to determine the characteristics of the products of the transformation of these materials that are important in constructing the equation of state, e.g., the density and bulk compressibility modulus under normal conditions. Table III lists the coefficients we have found for wide-range equations of state for phenylene and polystyrene that optimally generalize the available thermodynamic information.

TABLE III. Coefficients of the equations of state for phenylene and polystyrene.

	Phenylene		Polystyrene	
V_0	0.752	0.47*	0.956	0.53*
V_{0c}	0.744	0.464	0.923	0.523
B_{0c}	8.075	23.53	4.856	35.37
m	3.3	5.6	2.9	7.65
n	1.35	0.9	2.85	0.65
σ_m	0.95	0.95	0.95	0.98
σ_n	1	1	1	0.28
γ_{0c}	0.7	1.05	0.8	1.3
γ_i	0.35	0.4	0.3	0.55
E_a	20	60	10	70

Note. The coefficients in the columns marked with the sign $*$ refer to the products of physical–chemical conversion of phenylene and polystyrene during shock-wave loading. The units of measurement for the coefficients correspond to the original units: $p=10$ kbar, $V=1$ cm^3/g, $E=1$ kJ/g.

Our equations of state for phenylene and polystyrene adequately describe the results of measurements of the shock compressibility of continuous and porous (polystyrene) samples of these plastics over the entire interval of kinematic characteristics that we generated; this is clear from Fig. 1. In calculating the parameters of the shock adiabats corresponding to the post-transformation materials, we took into account the presence of an effective initial porosity of the plastics relative to the normal density of the transformation products. It should be noted that a combined analysis of the computed adiabats and the experimental data on the compressibility of porous samples of polystyrene[15] made it possible for us to determine the state parameters of the products of the transformation under normal conditions with a high degree of reliability. Interpretation of the results of experiments on dynamic loading of highly porous foamed polystyrene[6,16] in constructing the equation of state was to a considerable degree hindered by the large random scatter of the data, caused by the lack of uniformity of the process of pore collapse in the shock wave. We could only identify the presence of two parts of the corresponding adiabats with differing slopes—before and after the conversion (see Fig. 1b). An exception was the data on the compression of polystyrene with an initial porosity $m=3.67$.[6] We also identified states of the shock-compressed material in which no transformation occurred over the entire range of intensities investigated in these experiments.[6] This was probably due to the relatively large value of the characteristic transformation time behind the wave front for the rather thick samples we used, obtained by compressing blanks made of foamed polystyrene with $\rho_{00}=0.055$ g/cm^3.

Figure 2 shows the calculated shock adiabats for phenylene and polystyrene, and also curves for repeated loading and expansion isentropes of the products of the transformation. Comparison of the calculated results with the experimental data obtained in this work shows that the equation of state we developed provides an accurate description of the material parameters in regions of compression above the shock adiabatic and of rarefaction states. An analogous conclusion follows for the entire range of densities and pressures investigated under compression, as shown by Fig. 3, where the calculated adiabats are compared with experimental points identified in direct and reflected shock waves.

The $p-\rho$ diagrams for phenylene and polystyrene shown in Fig. 3 reveal a region of states realized in the reflected waves whose energies are high compared to the measured parameters of the shock-wave adiabat. The region

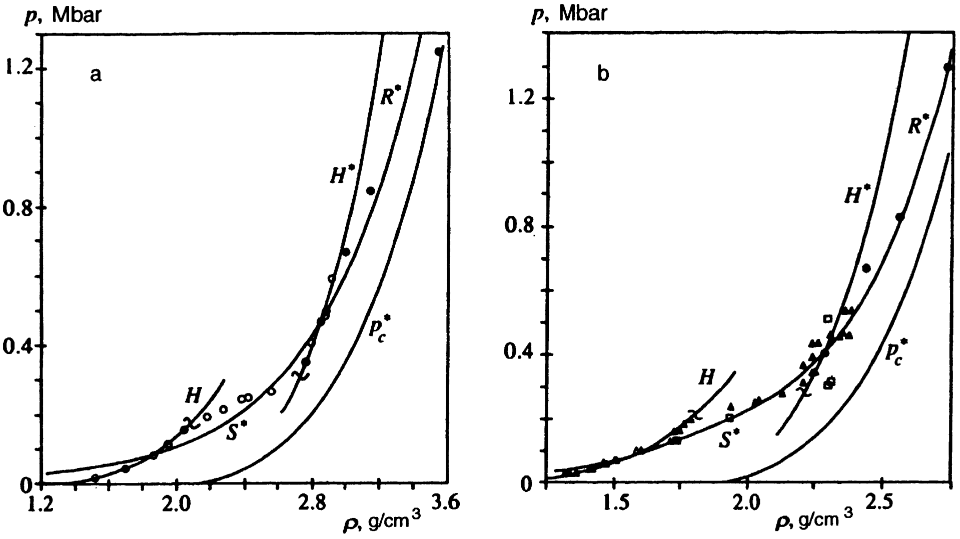

FIG. 3. State diagrams for phenylene (a) and polystyrene (b) at high densities and pressures. The notation is analogous to Fig. 2; p_c is the curve for elastic compression at $T=0$ K.

under study was extended both toward the elastic curve p_c (repeated adiabats R) and toward the region of the rarefied-gas phase (isentropes S). Note that the unloading isentropes begin with states that contain dissociative and weakly ionized material generated by the action of the intense dynamic loading of the samples, and continue up to rarefied-gas gas states with pressures $p \approx 2$ kbar and densities $\rho \approx 0.3\rho_0$. In this case, experiments show no significant jumps in the thermodynamic functions or hydrodynamic anomalies (see Fig. 2) that could be connected with phase changes of the transformation products for phenylene and polystyrene in this region of parameters of the unloading wave. It should also be noted that the computed value $\Delta = (u - 2u_0)/u_0$ of the deviation from the well-known rule that the velocity doubles when shock-compressed material expands in air[3] came to $\approx 35\%$ for phenylene and $\approx 21\%$ for polystyrene for the isentropes we investigated.

Thus, our experimental results of this paper encompass a previously unstudied range of densities and pressures. The equations of state we have derived for polymers describe the complex of data available for phenylene and polystyrene at high energy densities with a high degree of reliability. This allows us to use the wide-range equations of state we have constructed effectively in the numerical simulation of processes by which intense energy fluxes act on polymer materials.

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