Shock compressibility and equation of state of a polyimide

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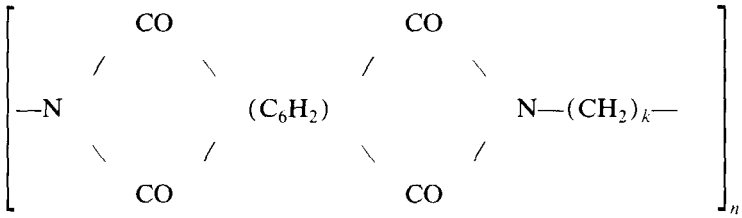
The compressibility of polyimide foam plastics of four initial densities has been studied experimentally in shock waves at pressures up to ≈ 700 kbar. The data are used to construct a semiempirical equation of state for the polyimide for a wide region of high-energy states.

Topics attracting much interest in the physics of high energy densities are the equations of state of substances being bombarded by intense pulsed ion or relativistic electron beams, laser beams, and x radiation.[1] Experimental results on the thermodynamic properties of substances during dynamic compression of nonporous samples yield the equation of state near the shock adiabat.[2] The region of the state diagram which is accessible to measurements can be enlarged considerably by using porous samples in shock wave experiments.[3] Semiempirical equations of state have been constructed for a large number of metals on the basis of dynamic data on the shock compressibility of porous and nonporous samples for a broad region of the phase diagram (see Ref. 4 and the papers cited there).

When we turn to the thermodynamics of plastics, with their unique physical properties, we find a completely different situation. Plastics are characterized by a low density, extremely low electrical and thermal conductivities, a high radiation stability, a high plasticity, and a high wear resistance. Plastics are promising new materials, used widely in structures which carry heavy loads and which are subjected to intense heat loading. The equations of state of plastics over a wide range of densities and pressures are necessary for solving many problems in the physics of high energy densities, e.g., in the numerical simulation of high-velocity penetration of protective shields of spacecraft[5] and the effect of relativistic electron beams on plastic targets.[6] However, there have been exceedingly few experimental studies of the shock compressibility of porous and nonporous plastics.[7–9] So far, we do not have equations of state for them. This situation has stimulated experimental research on the characteristics of plastics at high energy densities and the construction of equations of state on the basis of the data which are available from current and earlier research. We have previously found[10] the equations of state of polystyrene, polymethyl methacrylate, and a Teflon-like material.[11] In the present letter we are reporting the first measurements of the dynamic compressibility of porous samples of a polyimide. We construct an equation of state for this material on the basis of the results.

The polyimides are typical complex high-molecular polymers with the characteristic physical properties listed above. They are accordingly widely used along with composites based on polyimide fibers in the manufacture of parts for aerospace technology. The structural formula of a polyimide,



is rather complex. It essentially rules out a calculation of the thermodynamic properties by the methods of quantum mechanics. Accordingly, an equation of state of polyimides has been constructed on the basis of a semiempirical model, in which the general functional relationships for the thermodynamic potential are established with the help of theoretical ideas, and the experimental data available are used to determine the numerical coefficients in these relationships. In the present study we have obtained data on the shock compressibility of polyimide foam plastics of four initial densities. We generalize the existing experimental results in the form of a wide-range equation of state.

The porous samples (cylindrical tablets 12 mm in diameter and 3 mm thick) were made from intermediate products prepared by foaming powders prepared from a polyimide resin, followed by a solidification of the foam plastic that formed. The density of the nonporous samples of a platelet which we studied was $\rho_0 = 1.41$ g/cm^3. In the experiments we used polyimide tablets with initial densities $\rho_{00} = 1.33$, 0.68, 0.48, and 0.32 g/cm^3. Shock waves were excited in the samples through aluminum screens by steel strikers of various thicknesses, accelerated by detonation products of condensed explosives. The velocity of the strikers ranged up to ≈ 5.6 km/s. At fixed amplitudes of the shock waves in the screens, the measurements of the wave velocity in the samples, D (within an error $\approx 1.5\%$), make it possible to work from the known dynamic adiabat of the screen to determine the mass velocity u and the pressure p by the reflection method.[2] Measurements were taken by an electric-contact basis method; the signals from the detectors were displayed on a fast oscilloscope. The experimental data are summarized in Table I. Figure 1 is a D–u diagram of the results; each point here is an average over six to eight independent measurements. The experimental data obtained from the samples of the lowest porosity, $m = 1.06$, agree satisfactorily with the results of previous studies of the shock compression of nonporous polyimide samples.[9]

On the pressure–volume–energy surface for the plastic studied, the shock-wave measurements reveal only one shock adiabat, corresponding to the compressed state of the nonporous material. The experimental data obtained here on the dynamic compression of porous samples provide more important information on the behavior of the polyimide at high energy densities. To describe the results of the measurements and the results of previous studies,[9] we used a simplified model of the equation of state, with a small number of adjustable parameters.

TABLE I. Experimental data on the shock compressibility of a polyimide foam plastic.

u, km/s	D, km/s	p, kbar
	$\rho_{00}=1.33,\ m=1.06$	
0.62	3.27	27
1.13	4.24	64
1.45	4.66	90
1.63	4.93	107
2.06	5.64	155
2.16	5.53	159
2.61	5.82	202
2.80	6.19	231
2.94	6.09	238
3.35	6.52	291
3.72	7.00	346
4.00	7.63	406
4.85	8.99	580
5.33	9.63	683
	$\rho_{00}=0.68,\ m=2.08$	
1.38	2.31	22
2.50	4.12	70
3.22	4.95	108
3.34	5.13	117
3.94	5.82	156
4.38	6.27	187
5.22	7.42	264
5.39	7.64	280
6.29	8.95	383
	$\rho_{00}=0.48,\ m=2.95$	
1.43	2.12	15
2.61	3.92	49
3.31	4.55	72
3.50	5.04	85
4.16	5.63	112
4.61	6.17	137
5.51	7.41	196
5.56	7.48	200
6.65	9.02	288
	$\rho_{00}=0.32,\ m=4.42$	
1.47	1.89	9
2.72	3.61	31
3.37	4.37	47
3.67	4.69	55
4.35	5.51	77
4.82	6.18	95
5.72	7.25	133
5.78	7.48	138
7.00	9.02	202

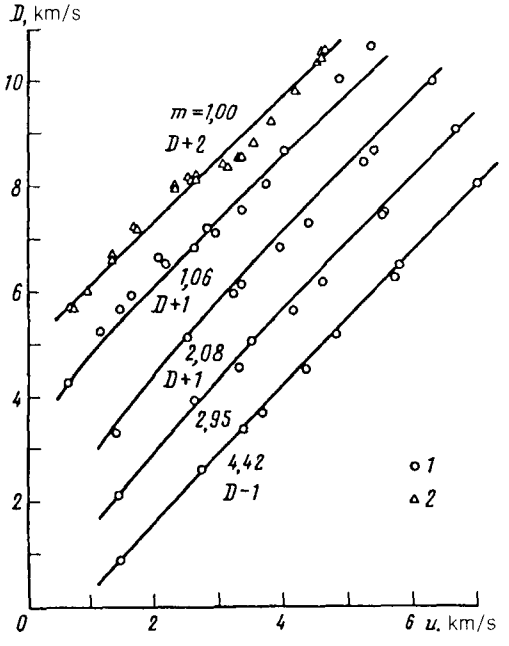


FIG. 1. Shock adiabats of polyimide samples of various porosities ($m=\rho_0/\rho_{00}$). 1–Experimental data of the present study; 2–of Ref. 9.

A caloric model of the wide-range equation of state adopted for the thermodynamic description of the properties of the polyimide is specified in a generalized Mie–Grüneisen form:

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

where $E_c(V)$ and $p_c(V)=-dE_c/dV$ are the elastic components of the energy and the pressure at $T=0$ K. The Grüneisen coefficient, which depends on the volume and the energy, is given by

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

where $\sigma_c=V_{0c}/V$, V_{0c} is the specific volume at $p=0$ and $T=0$ K, the expression for $\gamma_c(V)$ corresponds to the case of low thermal energies, and γ_i characterizes the region of a highly heated condensed substance. The anharmonicity energy E_a determines the thermal energy of the transition from one limiting case to the other. It is found from data of shock wave experiments at high pressures. A detailed description of the model is given in Refs. 10 and 11, along with a description of the procedure for finding the coefficients of the equation of state from the results of dynamic measurements.

Analysis of the data obtained from the present study and the data in the compendium of Ref. 9 indicates that there is a physicochemical conversion of the substance at the shock front. On the shock adiabat of the nonporous substance, this conversion begins at pressures $p\approx 200$ kbar. It involves a significant change in the

density and compressibility of the medium. On the porous adiabats, the effect is smoothed out considerably because of the high temperatures that arise. This result is usually attributed to destruction of the polymer caused by the rupture of C–H bonds, resulting in the formation of a slightly compressible, high-pressure, diamond-like phase of carbon and a corresponding amount of molecular hydrogen, along with other low-molecular components.[12] For convenience in practical applications, we have constructed a generalized equation of state for the polyimide, which gives a unified description of the low- and high-pressure phase modifications. This simplification is valid in practical numerical calculations on time-varying gasdynamic processes, since the integrated picture of the flow depends only weakly on the local features of the thermodynamic description of the properties of the medium. As can be seen from Fig. 1, the equation of state constructed for the polyimide gives a satisfactory description of the measurements of the shock compressibility of porous and nonporous samples over the entire range of kinematic characteristics realized.

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