International Journal of Thermophysics, Vol. 23, No. 1, January 2002 (© 2002)

Thermodynamic Properties and Physical–Chemical Transformations of Polymer Materials at High Temperatures and Pressures[1]

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A semiempirical equation-of-state model for polymer materials over a wide range of thermodynamic parameters is proposed, allowing for the transformation of compounds at high dynamic pressures. Equations of state for polystyrene, polyimide, and poly(*m*-phenylene isophthalamide) are developed, and a critical analysis of calculated results in comparison with the set of available high-energy density experimental data is made.

KEY WORDS: equation of state; phase diagram; polystyrene; polyimide; poly(*m*-phenylene isophthalamide); shock Hugoniot.

1. INTRODUCTION

A description of the thermodynamic properties of various substances over a wide region of the phase diagram is of fundamental as well as practical interest. Structural material thermodynamics under conditions of high temperatures and pressures is necessary for carrying out the computer simulation of non-steady-state hydrodynamic processes, generated by the influence of intense pulse energy fluxes on condensed matter [1–3]. In view of the significant difficulties arising in the calculation of the complex collective interactions between particles in a heated multicomponent disordered medium [4], the thermodynamics of such states is usually constructed in

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25–30, 2000, Boulder, Colorado, U.S.A.

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terms of semiempirical models. For these, the general form of functional dependences of the potential is motivated using theoretical concepts, whereas available experimental data are used to determine the numerical values of free parameters in relevant relationships [1].

Polymer materials represent an important class of substances that are used as structural elements subjected to intense mechanical and thermal loads. Using traditional methods of investigating thermodynamic properties under the shock compression of solid and porous samples with subsequent adiabatic expansion makes it possible to obtain wide-range equations of state (EOSs) in the caloric form $E(P, V)$ for a number of polymers, for example, polymethylmethacrylate and polytetrafluoroethylene [5], polyimide (PI) [6], poly(*m*-phenylene isophthalamide) (PA), and polystyrene (PS) [7]. However, the determination of the dependence of the internal energy on pressure and volume [7, 8] does not yield thermodynamically complete information on the state of matter and, in particular, on its temperature and the Gibbs free energy.

An analysis of the shock wave data for organic compounds [6, 7, 9–12] indicates that these substances undergo physical–chemical transformations under the action of intense dynamic loading, resulting in properties of a denser state that differ appreciably from these observed under normal conditions. Traditionally, this is explained by breaking of chemical bonds of the original compound and the formation of a low-compressibility mixture of a diamond-like phase of carbon and various low molecular weight components [13, 14]. It is characteristic for aromatic compounds that the transformation on the shock Hugoniots involves a significant change in the density (by $\sim 20\%$) and compressibility of the medium.

We propose a thermodynamically complete semiempirical EOS model for polymer materials, which enables one to take into account the transformation of compounds at high dynamic pressures. EOSs for three aromatic polymers, namely, PS, PI, and PA, are constructed on the basis of the model developed, and the critical analysis of calculated results in comparison with a set of available high-energy density experimental data is made. The typical form of the phase diagram for aromatic substances at high temperatures and high pressures is discussed.

2. EOS MODEL

According to the EOS model, the Helmholtz free energies for polymers, F, and the products of its transformation, F^*, are preassigned as the sum of two components,

$$F(V, T) = F_{\mathrm{c}}(V) + F_{\mathrm{a}}(V, T)$$

describing the elastic part of the interaction at $T = 0$ K (F_c) and the thermal contribution by atoms (F_a). The contribution by thermal excitation of electrons is negligible in the case of polymer materials (that are originally dielectrics) at temperatures $T \ll \Delta_0/2k$, where k is the Boltzman constant and Δ_0 is the energy gap between the valence band and the conduction band under normal conditions (the effective value $\Delta_0 \simeq 2$ eV) [15, 16].

The volume dependence of the elastic component of energy is expressed as follows:

$$F_c(V) = F_{0c} + \frac{B_{0c}V_{0c}}{m-n}\,[(\sigma_c^m/m) - (\sigma_c^n/n)] + E_{coh}$$

where $\sigma_c = V_{0c}/V$, V_{0c} is the specific volume at $P = 0$ and $T = 0$ K, and B_{0c} is the bulk modulus,

$$B_c = -V(dP_c/dV) \qquad (P_c = -dF_c/dV)$$

at $\sigma_c = 1$. The value of E_{coh}, the cohesive energy, is determined from the normalization condition, $F_c(V_{0c}) = F_{0c}$, which gives $E_{coh} = B_{0c}V_{0c}/(mn)$. The values of the parameters n, V_{0c}, and B_{0c} for each substance are chosen by means of iterations so that the value of the specific volume, $V = V_0$, and the isentropic bulk modulus,

$$B_S = -V(\partial P/\partial V)_S = B_{S0}$$

and its derivative with respect to pressure,

$$B'_S = (\partial B_S/\partial P)_S = B'_{S0}$$

determined from the results of dynamic measurements would be satisfied under normal conditions, $P = 0.1$ MPa and $T = 298$ K. The remaining free parameter m in the equation for elastic compression energy, F_c, can be found from the best fit to experimental data on the dynamic compressibility of plastics in direct and reflected shock waves. The difference $F^*_{0c} - F_{0c}$ of energies for the products of transformation and the original polymer at zero pressure and zero temperature is determined from the condition in accordance with the calculated pressure value for the transformation beginning point on the principal Hugoniot with the experimental evaluation.

The thermal component of free energy is defined by excitation of acoustic and optical modes of thermal vibrations of atoms:

$$F_{\mathrm{a}}(V,T)=F_{\mathrm{a}}^{\mathrm{acst}}(V,T)+\sum_{\alpha=1}^{3(v-1)}F_{\mathrm{a}\alpha}^{\mathrm{opt}}(V,T)$$

$$F_{\mathrm{a}}^{\mathrm{acst}}(V,T)=\frac{RT}{v}\left[3\ln(1-e^{-\theta^{\mathrm{acst}}/T})-D(\theta^{\mathrm{acst}}/T)\right]$$

$$F_{\mathrm{a}\alpha}^{\mathrm{opt}}(V,T)=\frac{RT}{v}\ln(1-e^{-\theta_{\alpha}^{\mathrm{opt}}/T})$$

where R is the gas constant, v is the number of atoms in the repeating cell of the polymer chain, and

$$D(x)=\frac{3}{x^3}\int_0^x\frac{t^3\,dt}{e^t-1}$$

where D is the Debye function [17], $\sigma=V_0/V$, and θ^{acst} and $\theta_{\alpha}^{\mathrm{opt}}$ are the characteristic temperatures of the acoustic and optical modes of the phonon spectrum. The volume dependences of θ^{acst} and $\theta_{\alpha}^{\mathrm{opt}}$ are determined by the formula

$$\begin{aligned}&\theta^{\mathrm{acst}}(V)/\theta_0^{\mathrm{acst}}\\&\quad=\theta_{\alpha}^{\mathrm{opt}}(V)/\theta_{0\alpha}^{\mathrm{opt}}\\&\quad=\sigma^{2/3}\exp\left\{(\gamma_0-2/3)\frac{\sigma_{\mathrm{n}}^2+\ln^2\sigma_{\mathrm{m}}}{\sigma_{\mathrm{n}}}\operatorname{arctg}\left[\frac{\sigma_{\mathrm{n}}\ln\sigma}{\sigma_{\mathrm{n}}^2-\ln(\sigma/\sigma_{\mathrm{m}})\ln\sigma_{\mathrm{m}}}\right]\right\}\end{aligned}$$

where γ_0 is the value of the Gruneisen parameter under normal conditions, and σ_{m} and σ_{n} are free parameters, chosen from the requirement of the optimum description of experimental data on measurements of the dynamic compressibility of porous specimens of studied substances. The values of the coefficients θ_0^{acst} and $\theta_{0\alpha}^{\mathrm{opt}}$ for polymers are defined from measured values of the isobaric heat capacity C_{P} at normal pressure and various temperatures [18]. The quality of the proposed form for the contribution of thermal vibrations of atoms to the thermodynamic potential is illustrated in Fig. 1.

In the case of products of the materials transformation, we have used data from shock wave experiments with solid and porous samples under pressures above the region of transformation to determine the characteristics of the products that are important in constructing the EOS, e.g., V_0^*, B_{S0}^*, $B_{S0}'^*$, $\theta_0^{\mathrm{acst}*}$, and $\theta_{0\alpha}^{\mathrm{opt}*}$.

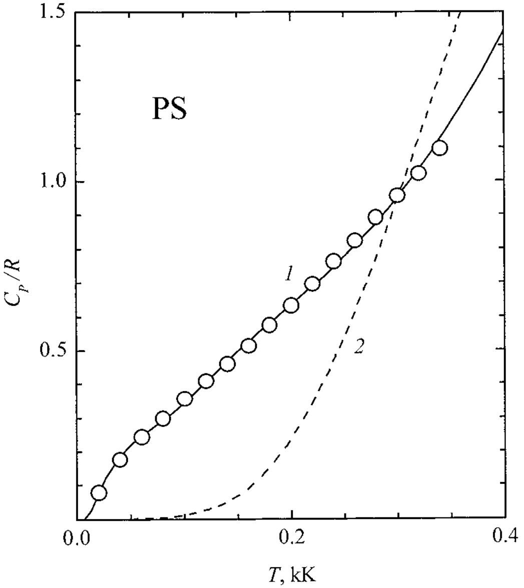


Fig. 1. Specific heat capacity of PS ($R = 1.277$ $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$) under normal pressure: (1) this EOS model; (2) the Debye model [17]. Experimental data from Ref. 18.

3. THERMODYNAMIC PROPERTIES OF PS, PI, AND PA

The shock compressibility of PS, PI, and PA samples with different initial porosities, $m = \rho_0/\rho_{00}$ (where $\rho_0 = 1.05$, 1.41, and 1.33 $\mathrm{g \cdot cm^{-3}}$ are normal densities of the three plastics, respectively, and ρ_{00} is the initial density of samples), was investigated experimentally using the traditional explosive propellant systems at pressures of up to $P = 70$ GPa [6, 7, 9, 10, 19]. The dynamic compressibility of PS and PA under reflected shock wave loading was studied up to $P = 130$ GPa [7]. On the principal Hugoniots of PS, PI, and PA, the physical–chemical transformations take place in the ranges of pressures $P = 20$–33, 16–30 ($m = 1.06$), and 18–31 GPa, respectively, and terminate with considerable changes in the density (by $\sim 20\%$) and compressibility of the medium.

The resulting EOSs for PS, PI, and PA adequately describe the experimental data for the shock compressibility of solid and porous (PS, PI) specimens of these plastics [6, 7, 10, 19] over entire ranges of kinematic and dynamic characteristics realized, as can be seen from Figs. 2–4. It is important that we have assumed that the physical–chemical transformations

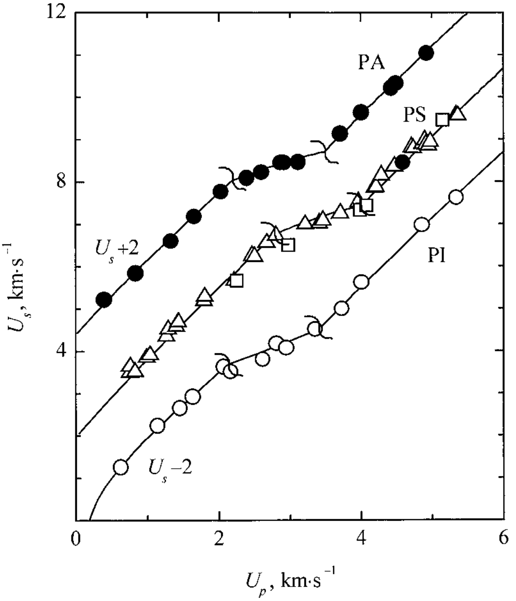
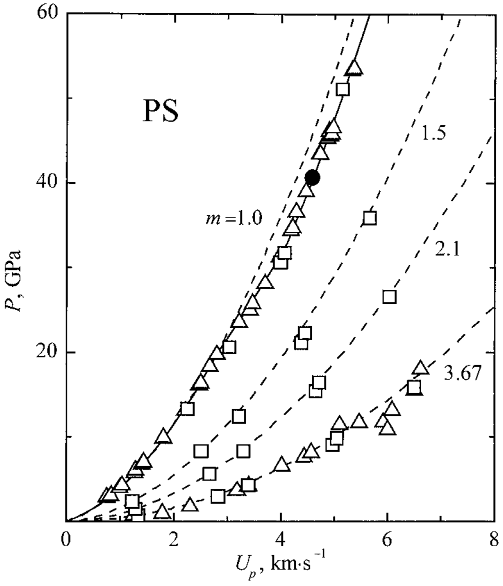


Fig. 2. Shock Hugoniots of PA, PS, and PI: U_s and U_p, shock and particle velocities. The wavy lines denote the positions of boundaries where the region of physical–chemical transformations of the shocked plastics occurs. Experimental data: □ [19]; △ [10]; ○ [6]; ● [7].

of the shocked aromatic compounds are endothermic. This assumption only results in adequate description of shock wave data for the three plastics. For the first time, Krupnikov and Krupnikova [20] have made an analogous conclusion for another aromatic polymer material, namely, epoxy resin, on the basis of their experimental data for compressibility under first and second shock waves, measurements of sound speed behind the shock front, and semiempirical EOS calculations.

The diagram of states for PA shown in Fig. 4 contains the dynamic experimental data from Ref. 7; also plotted are the calculated principal Hugoniot, curves of second-shock compression, zero isotherm, and boundaries of the region of physical–chemical transformation of the shocked plastic. Comparison of the calculated results with experimental points identified in direct (open circles) and reflected (filled circles) shock waves shows that the EOS we developed provides an accurate description of the material properties for the entire range of densities and pressures investigated under compression.



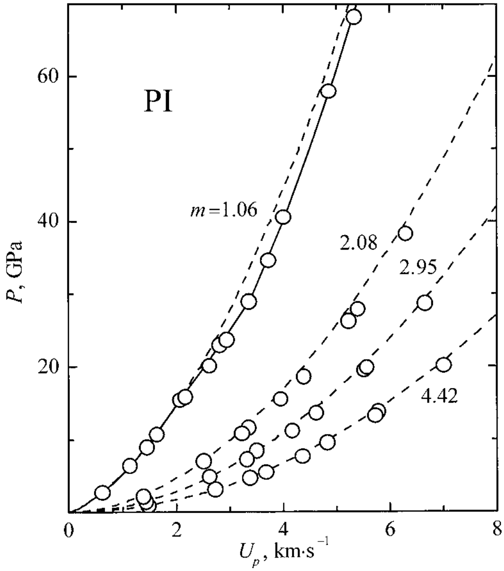


Fig. 3. Shock Hugoniots for PS and PI: *m*, initial porosity of samples. Dashed lines correspond to results of calculations without taking into account the physical–chemical transformation of plastics. Experimental data: □ [19]; △ [10]; ○ [6]; ● [7].

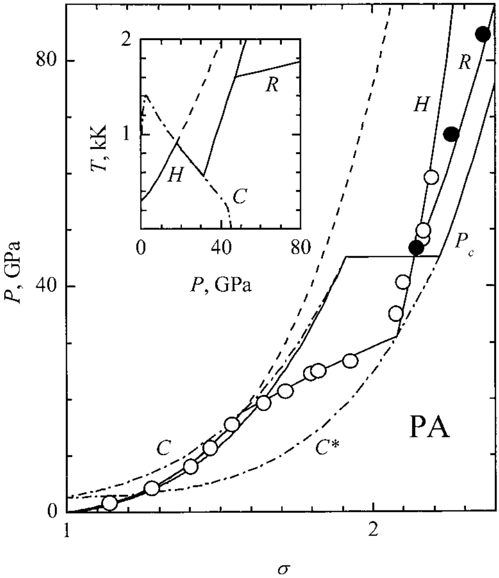


Fig. 4. Diagram of states for PA: $\sigma = V_0/V$; H, principal Hugoniot; R, curve of second-shock compression; P_c, elastic compression curve at zero temperature; C and C^*, boundaries of the region of physical–chemical transformation of the shocked plastic (C^* denotes the curve that corresponds to conversion products). The dashed line shows the metastable shock Hugoniot of supercompressed plastic under pressures above the transformation beginning point. Experimental data from Ref. 7. Inset: PA temperature versus pressure for the relevant curves.

The inset in Fig. 4 illustrates the PA temperature values as a function of pressure on the transformation curve and shock Hugoniots. The curve of shocked plastic transformation has a negative slope dT/dP in the range of pressures realized on the principal Hugoniot. The calculated temperature of converting PA is maximum at a pressure of about $P_m \simeq 2.5$ GPa. The slope of the transformation curve dT/dP is positive at lower pressures. We suggest that such a shape of the transformation curve is a typical feature of the phase diagram for aromatic substances at high temperatures and high pressures.

4. CONCLUSION

Calculations by means of the EOS model presented demonstrate that thermodynamic characteristics of polymer materials are described by unified analytical formulas in the range from normal conditions to the highest temperatures and pressures attained in experiments. The resulting wide-range EOSs for PS, PI, and PA describe consistently all of the available static and dynamic experimental data, and they can be employed effectively in numerical modeling of hydrodynamic processes in materials under extreme conditions of high energy density.

ACKNOWLEDGMENT

The work was carried out under the financial support of the Russian Foundation for Basic Research, Grant 00-02-16324.

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