Thermodynamic Properties of Polymer Materials at High Temperature and Pressure[1]

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ABSTRACT

The semiempirical model of condensed-phase equations of state for polymer materials in a wide range of thermodynamic parameters is proposed. Equations of state for polyethylene, polystyrene, and polymethylmethacrylate are constructed on the base of model developed, and the critical analysis of calculated results with the complex of available at high temperatures and pressures experimental data is made.

KEY WORDS: equation of state; phase diagram; polyethylene; polymethylmethacrylate; polystyrene; shock Hugoniot.

1. INTRODUCTION

The analysis of the thermodynamic properties of various substances over a wide region of phase diagram is of fundamental as well as practial interest. Structural material thermodynaics under conditions of high temperatures and pressures are a necessary part for carrying out the computer simulation of nonsteady hydrodynamic processes, generated by the influence of intense pulse energy fluxes on condensed media [1].

The base of difficulty confronting a systematic theoretical calculations of the equation of state (EOS) under high energy processes conditions is the need to incorporate correctly the structurally complicated interparticle interaction. The introduction of model simplifications is possible in a limited range of application [2], this possibility being considerably decrease for chemical compounds. Therefore for common description of matter properties in a wide range of thermodynamic parameters on phase diagram it is traditionally to apply semiempirical models in which different experimental data are used to determine the numerical coefficients of general functional dependences found from theoretical considerations.

In this report we describe the semiempirical model of wide-range EOS for polymer materials in the condensed phase. It takes into account depositions of the elastic lattice component, acoustic and optical modes of thermal vibrations of nuclei with anharmonic effects at high temperatures, thermally exited electrons. EOS for polyethylene (PE), polystyrene (PS), and polymethylmethacrylate (PMMA) are constructed on the base of model developed, and phase diagrams of investigated plastics are constructed with calculations of shock Hugoniots, isotherms, and isentropes. The critical analysis of calculated results with the complex of available at high energy densities experimental data is made.

2. EOS MODEL

A thermodynamically complete EOS for condensed phase of substance is defined by the free energy F preassigned as a sum of three components

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T),$$

describing the elastic part of interaction at $T = 0$ K (F_c) and the thermal contribution by atoms (F_a) and electrons (F_e).

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

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

where $\sigma_c = V_{0c}/V$, V_{0c} is the specific volume at $P = 0$ and $T = 0$ K, B_{0c} is the bulk modulus $B_c = -VdP_c/dV$ ($P_c = -dF_c/dV$) at $\sigma_c = 1$, E_{coh} is the cohesive energy. The normalization condition $E_c(V_{0c}) = 0$ gives $E_{coh} = B_{0c}V_{0c}/mn$. The derivative of the elastic bulk modulus with respect to pressure $B_c' = dB_c/dP_c$ at $\sigma_c = 1$ determines the relation between parameters m and n in the form $n = B_{0c}' - m - 2$. The values of parameters V_{0c}, B_{0c} and B_{0c}' for each substances are chosen by iterations so that the tabulated 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 undetermined parameter m in equation for elastic compression energy F_c can be found from the conditions of the best description of the experimental data on the dynamic compressibility of plastics in forward and reflected shock waves.

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

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

$$F_a^{acst}(V,T)=\frac{RT}{\nu}\left\{3\ln\left(1-\exp\left(-\sqrt{\theta_{acst}^2(V)+\sigma^{2/3}TT_a}\,/T\right)\right)-D(\theta_{acst}(V)/T)\right\},$$

$$F_{a\alpha}^{opt}(V,T)=\frac{RT}{\nu}\ln\left(1-\exp\left(-\sqrt{\theta_{opt\alpha}^2(V)+\sigma^{2/3}TT_a}\,/T\right)\right),$$

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

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

is Debye function [3], $\sigma=V_0/V$, θ_{acst} and $\theta_{opt\alpha}$ are the characteristic temperatures of acoustic and optical modes of phonon spectrum, T_a is empirical parameter, which enables best to describe data of dynamic experiments at high pressure. The volume dependences of θ_{acst} and $\theta_{opt\alpha}$ are determined by the interpolational formula

$$\theta_{acst}(V)/\theta_{0acst}=\theta_{opt\alpha}(V)/\theta_{0opt\alpha}=$$

$$=\sigma^{2/3}\exp\left\{(\gamma_0-2/3)\frac{\sigma_n^2+\ln^2\sigma_m}{\sigma_n}\mathrm{arctg}\left(\frac{\sigma_n\ln\sigma}{\sigma_n^2-\ln(\sigma/\sigma_m)\ln\sigma_m}\right)\right\},$$

where γ_0 is the value of Gruneisen gamma under normal conditions, σ_m and σ_n are free parameters, chosen from the requirement of the optimal description of experimental data on measurements of dynamic compressibility of porous specimens of researched substances. The values of coefficients θ_{0acst} and $\theta_{0opt\alpha}$ are defined from tabular values for specific heat capacity $C_P=T(\partial S/\partial T)_P$ at normal pressure and various temperature [4]. For model simplification the spectrum of optical vibrations is represented by three degenerate frequencies with corresponding degeneration factors α_1, α_2, and α_3, its sum being $\alpha_1+\alpha_2+\alpha_3=3(\nu-1)$. The quality of the proposed form of contribution of thermal vibrations of atoms to the thermodynamic potential is examplified by the EOS calculations for PE, PS, and PMMA as compared with the experimental data [4] for specific heat capacities in Fig. 1.

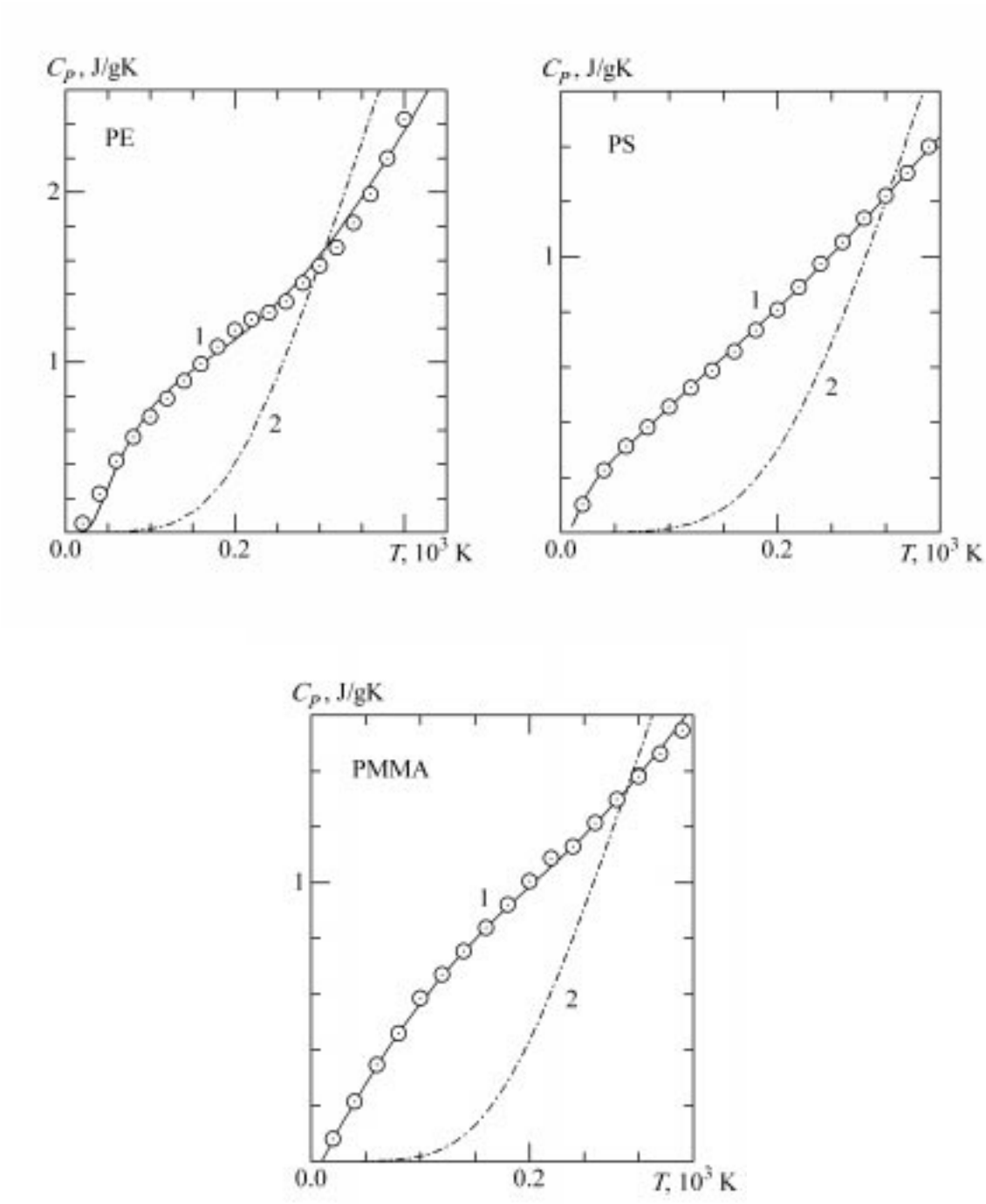

Fig. 1. Specific heat capacity of PE, PS, and PMMA at normal pressure, 1 — this EOS model, 2 — the Debye model [3]. Experiment [4].

The electron component of free energy is included in the form:

$$F_e(V,T) = -RZ_e T \exp(-T_s(V)/T) \ln\left\{1 + AV_0 T^{3/2} \sigma^{-\gamma_e(T)} / RZ_e\right\},$$

where $A = 4k\left(2\pi m_e k / h^2\right)^{3/2}$, k and h are the Boltzman and Plank constants, m_e is electron mass,

$$T_s(V) = \Delta_0 \exp((1-\sigma)/\sigma_s)/2k,$$

Δ_0 is the energy gap between the valence band and the conduction band at normal condition, parameter σ_s defines the rate at which the gap is narrowed,

$$\gamma_e(T) = 1 + (\gamma_{e0} - 1)\exp\left(-T/T_g\right)$$

is analogues of the electronic Gruneisen coefficient. Such form of F_e in constructing of EOS for dielectrics takes into account the thermal exitation of electrons into the conduction band which occurs when a substance is heated [5, 6]. Also chosen F_e—T-dependence describes the transition to plasma with average ion charge Z_e at temperature limit $T \to \infty$.

3. THERMODYNAMIC PROPERTIES OF PE, PS, AND PMMA

The resulting EOS for PE, PS, and PMMA adequately describe the experimental data on the shock compressibility of solid and porous (PS) specimen of these plastics [7-12] over the entire range of kinematic (U_s, U_p — shock-wave and particle velocities) and dynamic characteristic realized, as can be seen from Fig. 2-4. A comparison of the calculated temperature values for the shocked PMMA with the results of measurements at the ultrahigh pressure range [11, 13] presented in Fig. 5 shows their good correlation too.

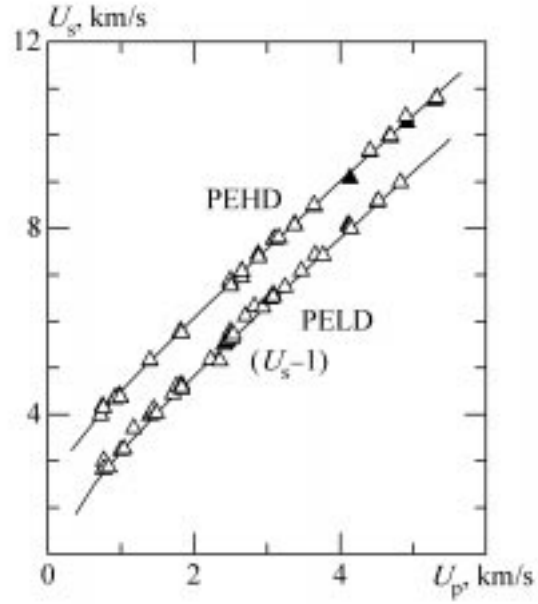

Fig. 2. Shock Hugoniots of high and low density PE (HD and LD). Experiment [7].

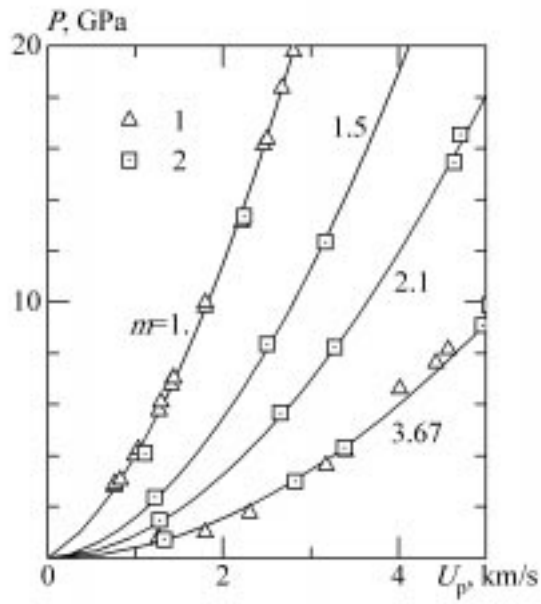

Fig. 3. Shock Hugoniots of PS, $m = \rho_0 / \rho_{00}$ — initial porosity. Experiment: 1 — [7], 2 — [8].

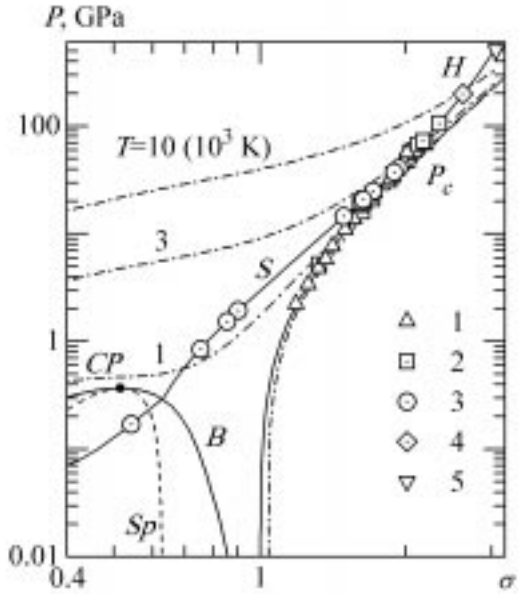

Fig. 4. Diagram of states for the condensed phase of PMMA, H — principal Hugoniot, S — isentrope, P_c — elastic compression curve at $T = 0$ K, T — isotherms, B — condensed phase—vapour equilibrium curve with critical point (CP), Sp — spinodal. Experiment: 1 — [7], 2 — [9], 3 — [10], 4 — [11], 5 — [12].

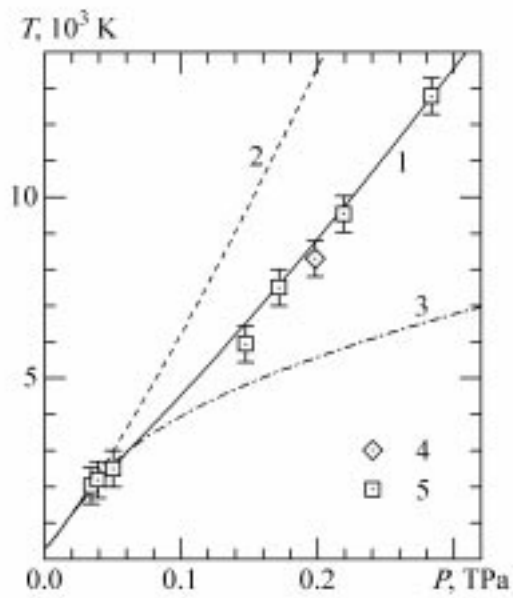

Fig. 5. Temperature vs pressure for shocked PMMA, 1 and 2 — this EOS model with and without electron component, 3 — with electron component by model [6]. Experiment: 1 — [11], 2 — [13].

Analysis of the data [7, 8, 14] for PS indicates that there is a physicochemical conversion of the substance at the shock front. On the principal Hugoniot this conversion begins at pressures $P \approx 20$ GPa. It involves a significant change in the density (by ~20%) and compressibility of the medium. This result is usually attributed to destruction of the polymer caused by the rupture of chemical bonds, resulting in the formation of a slightly compressible mixture of a diamondlike phase of carbon and various low-molecular weight components [15]. In this paper we construct EOS for PS before transformation. The model evaluation for temperature of conversion beginning on the principal Hugoniot is $T \approx 1500$ K.

The diagram of states for the condensed phase of PMMA plotted in Fig. 4 contains the dynamic experimental data; also plotted are calculated principal Hugoniot, curve of isentropic expansion, isotherms, condensed phase—vapour equilibrium curve and spinodal. Note that the experimental release isentrope [10] begins with state of highly heated shocked condensed matter and continues up to rarefied-gas states. The isentropic expansion technique [10] has enabled to record the point of boiling of substanse. In this case, kink in the calculated curve at the onset of evaporation corresponds to the experimentally observed additional increase of the expansion rate within the two-phase liquid—vapour region. The obtained value of equilibrium evaporation temperature at normal pressure $T_{v0} = 473$ K practically coincides with the tabular one for PMMA depolymerisation (methylmethacrylate is gas at such temperature). Calculation of temperature on condensed-phase spinodal $(\partial P/\partial V)_T = 0$ at normal pressure gives $T_{sp0} = 790$ K, that is close to experimental value of limiting temperature of attainable overheating $T_l = 788$ K [6]. The parameters of the critical point for PMMA were evaluated on the base of proposed EOS model, these are $P_{cr} = 0.37$ GPa, $T_{cr} = 953$ K, $V_{cr} = 1.64$ cc/g, $S_{cr} = 6.09$ J/gK.

4. CONCLUSION

Calculations by presented EOS model demonstrate that thermodynamic characteristics of condensed phase of plastics are descrepted by analytical formulas which are the same both at the normal conditions and at the highest temperatures and pressures attained in experiments. The resulting wide-range EOS for PE, PS, and PMMA describe consistently all of the available static and dynamic experimental data, and they can be employed effectively in numerical modelling of nonsteady gasdynamic processes at high energy density.

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REFERENCES

1. A. V. Bushman, V. E. Fortov, G. I. Kanel', A. L. Ni, Intense Dynamic Loading of Condensed Matter (Taylor & Francis, Washington, 1993).
2. A. V. Bushman, V. E. Fortov, *Sov. Phys. Usp.* **26:**465 (1983).
3. L. D. Landau, E. M. Lifshits, Statistical Physics (Pergamon Press, Oxford, 1980)
4. B. Wunderlich, H. Baur, *Forschritte der Hochpolym. Forshung* **7:**151 (1970).
5. A. F. Ioffe, Fizika Poluprovodnikov (Physics of Semiconductors) (Izdat. Akad. Nauk SSSR, Moscow, 1957).
6. K. V. Khishchenko, I. V. Lomonosov, V. E. Fortov, O. F. Shlensky, *Dokl. Akad. Nauk* **349:**322 (1996).
7. S. P. Marsh (Ed.), LASL Shock Hugoniot Data (Univ. California Press, Berkeley, 1980).
8. I. M. Dudoladov, V. I. Rakitin, Yu. N. Sutulov, G. S. Telegin, *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 4, 148 (1969).
9. A. A. Bakanova, I. P. Dudoladov, R. F. Trunin, *Sov. Phys. Solid State* **7:**1307 (1965).
10. A. V. Bushman, M. V. Zhernokletov, I. V. Lomonosov, Yu. N. Sutulov, V. E. Fortov, K. V. Khishchenko, *Phys. Dokl.* **38:**165 (1993).
11. Ya. B. Zel'dovich, S. B. Kormer, M. B. Sinitsyn, A. I. Kurekin, *Sov. Phys. Dokl.* **3:**938 (1958).
12. R. F. Trunin, *Usp. Fiz. Nauk* **164:**1215 (1994).
13. S. B. Kormer, *Usp. Fiz. Nauk* **94:**641 (1968).
14. A. V. Bushman, I. V. Lomonosov, V. E. Fortov, K. V. Khishchenko, M. V. Zhernokletov, Yu. N. Sutulov, *JETP* **82:**895 (1996).
15. F. H. Ree, *J. Chem. Phys.* **70:**974 (1979).