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INVESTIGATION OF THE INTERRELATION BETWEEN MICRO- AND MACROPROPERTIES OF POLYMERS IN A BLOCK STATE

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A quantitative interrelation between the micro- and macroproperties of polymer systems is established on the basis of the interatomic interaction potential. Using the relations obtained and the structure-sensitive parameters, the rigidity coefficient of macromolecules in a block, the thermal conductivity coefficient, the destruction stress, and other characteristics of polymers are determined.

There are two aspects [1] in the establishment of interrelation between the micro- and macroproperties of a substance. The first consists in obtaining an adequate functional expression for the interatomic interactional potential [2]; the second is associated with the development of a computational procedure allowing one to establish a relation between the interatomic interaction potential and the macroproperties of the substance [3]. Previously, in [4] we showed that the interatomic interaction potential for the polymers in block state can be represented in the form

$$W(r) = A\left[\left(\frac{a}{r}\right)^{m_1} - \left(\frac{a}{r}\right)^{m_2}\right] + BE\left(\frac{a}{r}\right)^{m_3}, \tag{1}$$

where A, B, m_1, m_2, and m_3 are positive constants with $m_1 > m_2$; a is the value of the interatomic distance r at which $W(r) = 0$ when $T = 0$ K (at $T = 0$ K, $E = 0$). In this case in order to determine the specific internal energy of the system, it is necessary to summarize the potential interaction energy of all the atoms, composing a pair with the given one, and then multiply the result by the number of atoms.

In the first approximation we will present the parameter $W(r)$ (Eq. (1)) in the form of the Lennard-Jones potential [5]. Then the force acting on a given atom from the side of the remaining atoms removed from it at a distance r_i is

$$F(r) = -\frac{\partial W(r)}{\partial r} = -\frac{\partial}{\partial r}\left\{\frac{N}{2}\sum_{r_i=0}^{\infty} 4W_0\kappa\left[\left(\frac{a}{r_i}\right)^{m_1} - \left(\frac{a}{r_i}\right)^{m_2}\right]\right\}, \tag{2}$$

where $m_1 = 12$; $m_2 = 6$; W_0 is the minimum value of the interatomic interaction energy; κ is the parameter characterizing the rigidity of macromolecules; N is the number of the atoms located at the distance r_1 from the given atom.

Proceeding from the condition $\partial W(r)/\partial r = 0$, we determine the equilibrium distance r_0 between the elements of the polymer structure in block state. It turned out that $r_0 = 2^{1/2}a$, and with an increase of the distance between the kinetic elements of the polymer structure with respect to r_0 anharmonic effects begin to manifest themselves in the system [4]. In this case the interaction energy can be expanded into a Taylor series:

$$W(r) = -W_0 + \frac{1}{2}f(r - r_0)^2 - \frac{1}{3}g(r - r_0)^3 + \ldots, \tag{3}$$

where $f = [d^2W/dr^2]_{r_0}$; $g = -1/2[d^3W/dr^3]_{r_0}$. Taking account of relation (2), we have:

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$$f = \frac{36NW_0\kappa}{r_0^2}, \tag{4}$$

$$g = \frac{378NW_0\kappa}{r_0^3}, \tag{5}$$

i.e.,

$$g = \frac{21}{2}\,\frac{f}{r_0}. \tag{6}$$

Since the coefficient f is responsible for the mechanical properties and the coefficient g for the thermal properties, relation (6) indicates the existence of the interrelation between the thermophysical and deformation characteristics of polymer systems.

As a correlation parameter between f and g, we use the coefficient of volumetric thermal expansion α with account for the fact that $\alpha \approx 3\beta$. Since [6]

$$\beta = \frac{1}{r_0}\,\frac{d\bar{r}}{dT},$$

then

$$\alpha = \frac{3gk}{f^2 r_0}$$

or

$$\alpha = \frac{7}{16}\,\frac{k}{NW_0\kappa}. \tag{7}$$

Taking into consideration that cohesion determines the existence of substances in condensed state and is caused by different types of interatomic and intermolecular interactions, we define the quantity W_0 as [7]: $W_0 = E_{\mathrm{coh}}/N_a$, where E_{coh} is the cohesion energy; N_a is Avogadro's number. On the basis of this discussion, relation (7) takes the form:

$$\alpha \approx \frac{3.63}{N\kappa E_{\mathrm{coh}}}. \tag{8}$$

Expression (8) makes it possible to directly estimate the value of the rigidity parameter κ for different polymers as one of the most important characteristics of a macromolecule with which the main macroscopic thermomechanical and relaxation properties of polymer systems are associated.

To shift from a linear to a volumetric model of structural interaction, we shall use the compression coefficient of the system K and the true value of its heat capacity C_p. For this purpose, the most appropriate is the Grüneisen relation [6]:

$$\gamma_{\mathrm{G}} = \frac{\alpha K}{\rho C_p}, \tag{9}$$

where ρ is the polymer density; γ_{G} is the Grüneisen parameter. With account for the fact that [7]: $KV/E_{\mathrm{coh}} \approx \mathrm{const}$, where V is the mole volume, and for relation (8) we will have

$$\alpha K = \frac{\mathrm{const}}{\kappa V}. \tag{10}$$

TABLE 1. Thermophysical and Structural Mechanical Characteristics of Polymers ($T = 280$ K)

Polymer	$\alpha\cdot 10^4$, K^{-1} [7]	E_{coh}, kJ/mole [7]	κ	$M\cdot 10^3$, kg/mole	C_p, kJ/(kg· K) [7]	κMC_p, J/(mole· K)
Polyvinylchloride	1.932	17.598	1.069	62.5	0.886	59.12
Polystyrene	1.802	41.062	0.490	104.1	1.134	57.91
Polyvinylacetate	2.140	31.697	0.535	86.1	1.280	58.98
Polymethylacrylate	2.196	31.760	0.520	86.1	1.320	59.15
Polyethylacrylate	3.136	35.950	0.322	100.1	1.752	56.47
Polyethylmethacrylate	3.136	31.880	0.363	114.1	1.390	57.58
Polymethylmethacrylate	2.691	30.000	0.450	100.1	1.298	58.42
Polyethylene (low density)	3.358	9.596	1.127	28	1.852	58.42
Polychlortrifluorethylene	3.045	19.860	0.600	116.5	0.830	58.04

Comparing Eqs. (9) and (10) and taking into consideration that the Grüneisen parameter changes insignificantly in the shift from one type of a polymer to another [8], we obtain

$$\kappa MC_p \approx \text{const}\,, \tag{11}$$

where $M = \rho V$ is the molar mass of the polymer. As seen from the results given in Table 1, relation (11) is valid for various polymers, and the value of const lies within the range 58–59.

To determine the interrelation between the force $F(r)$, acting between the structural elements, and the macroscopic properties of polymers in block state, we will consider the systems in the form of the Kirkwood–Raizman model [9]. From the extremum condition $\partial F(r)/\partial r = 0$ it follows that in a system undergoing deformation the maximum force of the interaction between the atoms is equal to:

$$F_{\max} = \frac{12NW_0\kappa}{b^7 a}\left(\frac{2}{b^6} - 1\right), \tag{12}$$

where $b = r_{\max}/\alpha$; $r_{\max}$ is the maximum distance between the atoms of the polymer at $F(r) = F_{\max}$. Calculations show that $b = 1.245$ and then $(2/b^6 - 1) < 0$, i.e., $F_{\max}$ represents the attractive force, and the disruptive force is equal to

$$F_{\text{br}} = \frac{12NW_0\kappa}{b^7 a}\left(1 - \frac{2}{b^6}\right). \tag{13}$$

Consequently, once the value of the external (or internal) force action on the system has become equal to the value of F_{br} or exceeded it, the material disintegrates.

Let us analyze the process of its disintegration on exposure to a temperature field. As the temperature rises, the amplitude of atomic oscillations, whose value is proportional to r, increases. Taking into account the fact that the equilibrium distance between the atoms of the proposed model is equal to r_0, we shall determine the coefficient of overlapping (μ_i) between the surfaces of the oscillating atoms. Its calculation will be based on the concepts suggested in [10] according to which the volume of an atom is described by a sphere with the intermolecular radius R. If this atom is chemically bonded to other atoms, then these adjacent atoms cut off a portion of the sphere from it, since the sum of the intermolecular radii of bivalent-bound atoms is always larger than the bond length d_i. Then the coefficient μ_i will be determined as

$$\mu_i = 1 - \frac{\Delta S}{S_\alpha + S_\beta}, \tag{14}$$

where $S_\alpha = 4\pi R_\alpha^2$; $S_\beta = 4\pi R_\beta^2$; $\Delta S = 2\pi Rh$; $h = R - (R^2 + d^2 - R_i^2)/2d_i$; R_i are the intermolecular radii of the adjacent valence atoms; h is the segment height.

Analysis of relation (14) shows that when $0 < \mu_i \leq 1$, energy transfer processes are possible in the polymer in block state. As soon as the maximum amplitude of the oscillations of atoms reaches the value of $(R_\alpha^2 + R_\beta^2)/R$, the process of thermal disintegration of the polymer in block state will take place.

Using relation (13), we determine internal stresses arising in the system:

$$\sigma_{\text{br}} = \frac{E_{\max}}{a^2} = \frac{12NW_0\kappa}{b^7 a^3}\left(1 - \frac{2}{b^6}\right). \tag{15}$$

The results of calculations for polyvinylchloride (PVCh) show that the maximum internal stress for the C–C-bond along a chain of main valences is $2.76 \cdot 10^{11}$ N/m^2, whereas in the case of the interaction between side groups for a forming H–Cl-bond it is $1.49 \cdot 10^{10}$ N/m^2, and for a forming H–H-bond it is $5.25 \cdot 10^{10}$ N/m^2. Consequently, energy exchange processes are more intense along the chain of the main valences of linear amorphous polymers. Energy exchange between the atoms or groups of atoms of the side branches are less intense. This allows us to claim that there should exist a quantitative interrelation between the strength properties of the material and heat transfer. Taking into account the fact that the mean statistical dimensions of the structural element participating in heat exchange are defined as [6]

$$\bar{L} = \text{const}\, r_0 \frac{f^3}{g^2 kT} = \text{const}\, \frac{r_0}{\alpha T},$$

and the propagation velocity of acoustic oscillations is

$$\bar{v} \sim \sqrt{\left(\frac{K}{\rho}\right)} = \text{const}\sqrt{\left(\frac{E_{\text{coh}}}{M}\right)},$$

then proceeding from the Debye equation, we obtain

$$\lambda = \text{const}\, \rho C_v \frac{r_0}{\alpha T}\sqrt{\left(\frac{E_{\text{coh}}}{M}\right)}.$$

Since in the given temperature range ($T = 280$ K) $C_p \approx C_v$, then using relation (11), we obtain:

$$\lambda = \text{const}\, \frac{r_0 E_{\text{coh}}^{3/2}}{VTM^{1/2}}. \tag{16}$$

The check of relation (16) for various polymers gives a satisfactory agreement between the calculated and experimental results (Table 2) for const ≈ 0.5.

If we consider the phonon heat conduction theory, then its analysis gives that $\lambda = 1/3 C_v \rho (1/\gamma)$, where γ is the scattering coefficient of phonons. It is found [8] that between the coefficients γ and g^2 there exists a directly proportional dependence, which makes it possible to obtain the following expression for the thermal conductivity coefficient:

$$\lambda = \frac{BC_v v\rho}{g^2}.$$

Then the total breaking stress of the material (Eq. (15)) will be expressed as:

$$\sigma_{\text{br}} = k\sqrt{\left(\frac{C_v v\rho}{\lambda}\right)}, \tag{17}$$

TABLE 2. Molecular Parameters and the Thermal Conductivity Coefficient of Polymers ($T = 280$ K)

Polymer	r_0, Å	$V\cdot10^6$, m^3/mole	λ, W/(m·K)	
			Eq. (16)	[7]
Polyvinylchloride	4.496	45.1	0.166	0.168
Polyethylmethacrylate	5.948	102	0.175	0.186
Polychlortrifluorethylene	4.711	60.7	0.147	0.143
Polymethylmethacrylate	5.625	85.6	0.193	0.198

where $k = \sqrt{B}/b^7[1 - 2/b^6]$, i.e., really the strength properties of the material and its thermal conductivity coefficient are interrelated as $\sigma_{br} \sim \lambda^{1/2}$. Consequently, the prediction of the limit of the strength properties of materials can be made if their thermophysical properties are known and conversely.

From relations (15) and (16) it follows that

$$\frac{\sigma_{br}}{NW_0\kappa\lambda T} = \frac{24\sqrt{2}\,(1 - 2/b^6)\,VM^{1/2}}{b^7 r_0^4 E_{coh}^{3/2}}. \tag{18}$$

The right-hand side of relation (18) represents a constant value. Actually, calculations show that in the case of the C–C-bond ($r_0 = 1.54$ Å) its value is $2.91\cdot10^{28}$ for (PVCh), $3.14\cdot10^{28}$ for (PMMA), and $3.65\cdot10^{28}$ for (PEMA).

It is evident from theoretical investigations [8] and experimental results that in the general case the temperature dependence λ of polymers has a maximum observable in a wide temperature range. This should be taken into account in calculating the value of λ in Eq. (18) at a certain temperature.

Apart from the possible prediction of the mechanical properties of polymer systems on the basis of the results of investigation of their thermophysical properties and conversely, the relations established can be also useful for a further development of the theory of disruptive strength and (or) of the melting of polymer materials.

NOTATION

E_{coh}, cohesion energy; ρ, density; K, bulk modulus of elasticity; C_p, heat capacity at constant pressure; f, coefficient of quasi-elastic force; g, anharmonicity coefficient; M, molar mass; V, mole volume; σ_{br}, breaking stress; λ, thermal conductivity coefficient; α, coefficient of the volumetric thermal expansion.

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