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Abstract

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On the Law of Deformation of Highly Elastic Polymeric Bodies

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When mechanical stresses act on polymeric bodies, two types of reversible deformation are observed—elastic and highly elastic (^{1,2}). Highly elastic deformation, being essentially elastic (in the broad sense of the word), differs sharply from the deformations of ordinary elastic bodies. One of its most important features is such a pronounced complex of relaxation phenomena that the application of Hooke' s law, or of any other relation between stresses and deformations that does not take into account the time regimes of mechanical interactions, proves impossible even as a rough approximation.

In the case of amorphous polymers, relaxation phenomena are associated with the slow development of processes of rearrangement of long and flexible molecules and their bundles, manifested in the lag of changes in deformation behind changes in stress (hysteresis, elastic aftereffect, stress relaxation, etc.).

The retardation in the development of deformation was associated with the presence of internal friction, and attempts were made to construct models of elastic bodies with internal friction and of viscous bodies possessing elasticity. This approach was widely developed and led to numerous analytical, mechanical, and electrical models of viscoelastic and elastoviscous bodies. However, even for a semiquantitative description of the deformation of highly elastic bodies it became necessary to construct very complex mechanical models consisting of a large number of different springs and viscous elements (dampers) (^{3,4}). Besides their complexity, such models were in almost all cases constructed without taking into account any data on the molecular structure of polymeric bodies, i.e., they were arbitrary.

However, the present state of ideas about the structure of polymers and the nature of highly elastic deformation (^{5}) opens a new path for determining the fundamental law of deformation of highly elastic bodies.

First of all, one must abandon the conception of high elasticity as the result of the summation of elasticity and internal friction. Indeed, high elasticity differs sharply from the elasticity of ordinary bodies by low values of the elastic moduli (by 2-3 orders of magnitude), by enormous magnitudes of reversible deformations (up to 1000% and more), and by opposite signs of the thermal

Fig. 1. Mechanical model of a polymer body

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effects of deformation, as well as of the temperature coefficient of the elastic modulus. All these differences are connected with the fact that highly elastic deformation is caused only by a change in the shape of the flexible long chain molecules of polymeric substances, and not by a change in the interaction energy of flexible molecules or of their mobile parts (segments). Under isothermal highly elastic deformation, the internal energy of a polymeric body does not change, and all the work of deformation is converted into heat. Therefore, the resistance of the body to its deformation is due only to a decrease in entropy ([6,7]).

Thus, high-elastic deformation should be regarded as an **independent type of reversible deformation**, and one should not attempt to decompose it into elastic and viscous component parts.

Owing to the exceptionally great length of chain molecules, simultaneous displacement of the whole molecule during deformation is impossible, since the energy required to overcome the sum of intermolecular interactions greatly exceeds the energy of chemical bonds. Therefore the motion—of large chain molecules is accomplished by means of a multitude of motions of their individual parts (segments), possible because of the flexibility of such molecules. It is clear that the smallest mobile portion of a chain molecule must still be large enough for the flexibility of the molecule, i.e., high elasticity, to manifest itself. By estimating the regularity of the motions of segments, one can understand the laws governing the displacement of chain molecules, as well as the changes in their form.

Fig. 1. Mechanical model of a polymer body

The displacement of the end of a segment u consists of three components: the irreversible displacement of the whole segment, and the elastic and high-elastic deformation of the segment (respectively $u_{\text{v}}, u_{\text{y}}, u_{\text{ve}}$):

$$u = u_{\text{v}} + u_{\text{y}} + u_{\text{ve}}. \tag{1}$$

Considering the medium surrounding the segment to be a viscous liquid, we obtain for its irreversible displacement

$$u_{\text{v}} = \frac{1}{r}\int_0^t F(\tau)\,d\tau = \frac{1}{r}D^{-1}F, \tag{2}$$

where r is the coefficient of viscous resistance; $F(t)$ is the force acting on the segment, equal to zero for $t < 0$; D is the differentiation operator. The displacement u_{y}, caused by the elastic deformation of a segment stretched by the force

$F(t)$ under the viscous resistance of the surrounding medium, can be found from the fundamental law of elasticity:

$$u_{\mathrm{y}} = \frac{1}{k}F(t) = \frac{1}{k}D^0 F, \tag{3}$$

where k is the stiffness of the segment.

Let us note that (2) and (3) can be written in the general form:

$$u(\alpha) = \frac{1}{\chi(\alpha)} D^{-\alpha} F \qquad (\alpha = 0,\, 1), \tag{4}$$

where $\chi(\alpha)$ is a constant quantity for each value of α.

Since high-elastic deformation combines many features of elastic and plastic deformation, but is not their combination, the natural idea arises that the simplest high-elastic deformation, i.e., deformation of a segment, obeys the generalized law (4)

$$u_{\mathrm{ve}} = \frac{1}{\chi} D^{-\alpha} F \qquad (0 < \alpha < 1; \quad \chi = \mathrm{const}). \tag{5}$$

Having made this assumption, it is necessary to reveal the meaning of the operator $D^{-\alpha}$. The operation of fractional integration (as well as fractional differentiation)

has long been known (see, for example, (^{8,9})) and is defined as follows:

$$D^{-\alpha} f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t f(\tau)(t-\tau)^{\alpha-1} d\tau = \frac{1}{(\alpha-1)!} \int_0^t f(\tau)(t-\tau)^{\alpha-1} d\tau, \tag{6}$$

where $(\alpha - 1)! \equiv \Gamma(\alpha)$ is the gamma function.

Let us now consider the consequences following from (5). First of all, we note that (5) describes a reversible deformation. Indeed, if $F(t) \neq 0$ only for $0 < t < t_0$, then from (5) and (6) it follows, for $t > t_0$ ($F_M = \max |F(t)|$):

$$|u_{\mathrm{ve}}| = \frac{1}{\chi} \frac{1}{(\alpha-1)!} \left| \int_0^{t_0} F(\tau)(t-\tau)^{\alpha-1} d\tau \right| < \frac{1}{\chi} \frac{1}{\alpha!} F_M \left[t^\alpha - (t-t_0)^\alpha \right]. \tag{7}$$

Thus, after the action of the force ceases, $\lim_{t\to\infty} u_{\mathrm{ve}} = 0$, i.e., ultimately no residual displacements are retained. It is also easy to verify that, under the action of a periodic force $F(t) = F_0 \exp i\omega t$, equation (5) gives

$$u_{\text{ve}} = \frac{1}{\chi}\frac{1}{(\alpha-1)!}\int_0^t F_0 e^{i\omega\tau}(t-\tau)^{\alpha-1}d\tau = u_{\text{ve}}(\omega,t)e^{i\omega t},$$

i.e., the law of establishment of stationary oscillations u_{ve} with the frequency of the driving force and with a phase lag behind it. Hence it follows that, for established oscillations, the lag of displacement behind the force is given by the phase-shift angle $\varphi = \alpha\pi/2$ $(0 < \alpha < 1)$.

Thus the delay in the development of high-elastic deformation, characteristic of it and lying at the basis of mechanical relaxation phenomena in the deformation of amorphous polymers, is conveyed by equation (5).

From (5) it is easy to obtain the characteristic features of various relaxation processes (elastic aftereffect, hysteresis, etc.). For example, if for $t > 0$, $u_{\text{ve}}(t) = \text{const} = (u_{\text{ve}})_0$, then, writing (5) in differential form,

$$F(t) = \chi D^{\alpha}u_{\text{ve}} = \chi D\cdot D^{-(1-\alpha)}u_{\text{ve}} = \frac{\chi}{(-\alpha)!}\frac{d}{dt}\int_0^t u_{\text{ve}}(\tau)(t-\tau)^{-\alpha}d\tau$$

$$(0<\alpha<1), \quad \text{we have} \quad F(t) = \frac{\chi}{(-\alpha)!}(u_{\text{ve}})_0\frac{d}{dt}\int_0^t (t-\tau)^{-\alpha}d\tau = \frac{\chi}{(-\alpha)!}(u_{\text{ve}})_0 t^{-\alpha},$$

whence follows the relaxation of the force at a constant value of the displacement of the end of the segment.

Let us now use (5) to derive the fundamental law of deformation of high-elastic bodies. From (1)–(6), for the deformation of a segment we obtain:

$$u(t) = \frac{1}{r}\int_0^t F(\tau)\,d\tau + \frac{F(t)}{k} + \frac{1}{\chi}\frac{1}{(\alpha-1)!}\int_0^t F(\tau)(t-\tau)^{\alpha-1}d\tau. \tag{8}$$

To pass from the deformation of a segment to the deformation of an entire chain molecule located in a polymer body, one should recall that such a molecule is a chain of sequentially connected identical segments surrounded by other chain molecules, which form a viscous medium.* Representing the simplest elements of viscous resistance, elasticity, and high elasticity, which obey equations (2), (3), and (5), respectively, by a sphere, a spring, and a rectangle (inside which a flexible chain molecule is symbolically denoted), we obtain a mechanical model (see Fig. 1) describing the deformation of a polymer, whose molecules

* More strictly, the medium should be regarded not as viscous but as highly elastic, which can be taken into account in the second approximation of the calculation.

are linear chains*. The equations of motion of this model, giving the displacements u_l of its l-th points, can be obtained easily (see the analogous derivation in ([10,11])):

$$\left(\frac{rD}{\chi}+1\right)u_1-u_2=0;$$

$$-u_{l-1}+\left(\frac{rD}{\chi}+2\right)u_l-u_{l+1}=0 \qquad (l=2,3,\ldots,n-1);$$

$$-u_{n-1}+\left(\frac{rD}{\chi}+1\right)u_n=\frac{1}{\chi}F(t); \qquad u_{n+1}-u_n=\frac{1}{\chi}F(t), \tag{9}$$

where the operator $1/\chi$ has the form

$$1/\chi=1/k+D^{-\alpha}/\varkappa.$$

The solution of system (9), which for brevity is not given here, yields relations in complete agreement with the Boltzmann and Volterra equations derived by them for describing mechanical relaxation processes on the basis of the most general considerations, without taking into account the molecular structure of bodies ([12–14]). In contrast to them, the solution of system (9) gives a concrete expression for the kernel of the Boltzmann-Volterra integral equation. A feature of this solution is the dependence of the above-mentioned kernel on fractional powers of time, since it can be represented as a function of series with terms of the type $A_m t^{\beta m+n}$, where m and n are integers and β is a proper fraction. This circumstance is of special interest, since it makes it possible theoretically to substantiate, from a unified point of view, analogous particular empirical relations that excellently describe the experimental data ([15]).

Thus, assumption (5) has led to a theory of deformation of polymer bodies that takes into account the principal features of their mechanical properties (with the exception, of course, of strength), is in good agreement with previously established empirical dependences and phenomenological theories. In addition, the proposed model takes into account modern ideas concerning the molecular structure of polymer bodies and opens up the possibility of expressing the principal constants r, k, $\varkappa$, and α through molecular characteristics.

In conclusion it should be noted that the possibility of a theoretical derivation of the concrete form of the kernel of the Boltzmann-Volterra equation from the solution of system (9) provides ways for calculating complex stressed states of polymer bodies by means of the Boltzmann-Volterra theory in tensor form, taking into account the results of the solution of system (9). The significance of this for the development of a technical theory of the mechanical properties of polymer materials is obvious.

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* In the case of spatially structured polymers, when all molecules are connected into a single network and viscous flow is impossible, the corresponding model

differs only in the rigid attachment of one end of the chain to the shell of the model (see (10)). The corresponding equations of motion are easily derived from the system of equations (9).

Note: Figure translations are in progress. See original paper for figures.

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