THEORETICAL STRENGTH OF POLYMERS
IN A COMPLETELY ORIENTED STATE

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A solution is presented of the problem on the theoretical strength of a completely oriented polymer by accounting for the intermolecular interaction and finiteness in the length of polymer chains.

Theoretical strength is the maximum possible strength of the given material. Conditions at which theoretical strength may be realized are: low temperature, ideal defectless structure, and quasistatic application of an external force [1]. Such conditions cannot be fulfilled in practice; therefore, the strength of the material is always less than the theoretical strength. However, the knowledge of theoretical strength is necessary in order to evaluate the maximum strength reserve of the given material, that natural "ceiling" above which no increase in strength be attained. Attempts to calculate the theoretical strength of polymers have been made earlier by different authors [2-4]. However, in these studies the intermolecular interaction was either completely unaccounted for [2], or accounted for with insufficient accuracy [3, 4]. In [5] a study of the temporal dependence of strength was made of a completely oriented polycaprolactam by accounting for intermolecular interaction; however, the ultimate length of the polymer chains had not been considered. In the present study, calculation was made of the theoretical strength of polymers in a completely oriented state with accounting for the intermolecular interaction and molecular weight of macromolecules. A model of a fully oriented polymer is that ideal to which the technologists are striving for in attempts to obtain fibers with the higher possible strength. The closest to this model are polymer single crystals, obtained by polymerization in a monomer solid phase [6].

We shall use a model described by us in [7] (Fig. 1). In a uniaxially fully oriented solid polymer completely stretched macromolecules are arranged in one direction parallel to each other. Each macromolecule is illustrated by a model as a continuous elastic thread with a modulus \( k_t \) and strength \( T_1 \). Intermolecular, dispersion bonds, designated in Fig. 1 by springs of length \( h \), modulus \( k_0 \), and strength \( T_0 \), are active between the ends of macromolecules. These parameters correspond to the equilibrium length, modulus, and strength of dispersion bonds.

The macromolecules and the dispersion bonds joining their ends form some complex one-dimensional chain. The whole sample can be regarded as a set of such chains displaced with respect to each other and interacted with each other.

We shall examine a macromolecule with having been completely stretched represents a plane zigzag (polyethylene, polyvinyl alcohol, Kapron, etc.) (Fig. 2a). If such a macromolecule is stretched along its axis by forces \( F \), the chemical bonds between the neighboring atoms (for example, between atoms 1-2 or 2-3) and valence angles (for example, 1-2-3) are deformed. The deformation of the angles considerably exceeds the deformation of the bonds; therefore, the deformation of the whole macromolecule is determined by the deformation of valence angles. However, the rupture of the macromolecule occurs along the chemical bonds.
Fig. 1. A model of a completely oriented polymer.

Fig. 2. Stretching a zigzag macromolecule.

We shall isolate one link (Fig. 2b), formed by atoms 1-2-3 and chemical bonds between them. The force \( F \) applied to atoms 1 and 3 can be resolved into two components, normal \( F_n \) and tangential \( F_t \). The normal component deforms the valence angle, while the tangential component deforms the chemical bond. If the energy of chemical interaction of atoms 2-3 is equal to \( U(r) \) the tangential force component \( F_t = \frac{dU}{dr} \). By using the expression for the interaction energy, for example, as a Morse potential, we find the obvious expression for the tangential component:

\[
U(r) = D \left( e^{-\frac{2(r-r_0)}{a}} - 2e^{-\frac{1}{a}(r-r_0)} \right); \quad (1a)
\]

\[
F_t = \frac{\partial U}{\partial r} = \frac{2D}{a} \left( e^{-\frac{1}{a}(r-r_0)} - e^{-\frac{2}{a}(r-r_0)} \right). \quad (1b)
\]

The maximum value of the tangential component, equal to \( F_{t\text{max}} = D/2a \), is the strength of the chemical bond. The external force at the moment of the chemical bond rupture, i.e., the strength of the link 1-2-3 is equal to

\[
F_{\text{max}} = \frac{F_{t\text{max}}}{\sin q} = \frac{D}{2a \sin q},
\]

where \( q \) is the magnitude of the valence angle at the moment of rupture of chemical bond, larger than the equilibrium value of the valence angle \( \phi_0 \). In polyethylene macromolecule, for example, all links are the same and represent single C–C bonds, therefore its rupture occurs at once along all links. In a Kapron macromolecule alongside with C–C bonds weaker C–N bonds are present. The macromolecule rupture proceeds along these bonds, therefore the strength of Kapron macromolecule is smaller than the strength of polyethylene macromolecule. The strength of polyethylene macromolecule, calculated from Eq. (2) is \( 6 \cdot 10^4 \) dynes, of Kapron it is \( 5.2 \times 10^{-4} \) dynes.

We shall examine a system of complex one-dimensional chains arranged in parallel. The position of each point of any chain, prior to applying external load, is determined by coordinate \( x \). After applying the load, the coordinate of the same point becomes equal to \( x' = x + u(x) \), where \( u \) is the displacement of the point \( x \) from the original position. The deformed state of each chain is completely determined by the function \( u(x) \). For noninteracting chains the functions \( u(x) \) are independent; the displacement of the points of one chain is independent of the displacement of the points of neighboring chains. If the chains interact, it means that some forces interact between them. These are intermolecular forces — van der Waals forces or hydrogen bonds. As in [7], we shall consider intermolecular interaction continuously distributed along the macromolecule length at some density. In [7] an expression is derived for the density of forces in intermolecular interaction.

As in [7], we shall isolate in the model in Fig. 1a structural element AA'B'CA'A, a kind of an "elementary cell". All "elementary cells" are in the same conditions; therefore, if we elucidate the state of one of them, we shall know the state of any other. Elastic equilibrium of an "elementary cell" was considered by us in the calculation of the modulus of elasticity [7]. At present we would like to determine the maximum state of the cell.

It was shown in [7] that elastic equilibrium of an "elementary cell" (Fig. 3) is described by the following system of differential equations:

\[
\begin{align*}
&u'' - \frac{\alpha}{k_1} (u-v) = 0; & x_1 \leq x \leq x_2 \\
&v'' + \frac{\alpha}{k_1} (u-v) = 0; & x_3 \leq x \leq x_4.
\end{align*}
\]

(3)