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Abstract

Full Text

Physical Chemistry

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Mechanics of Stretched Polymer Systems

(Presented by Academician V. A. Kargin on 2 I 1958)

1. The principal task of molecular theory is to establish the relation between the mechanical properties of polymer molecules and the mechanical properties of a body as an aggregate of these molecules. According to the established tradition, this problem is solved by the methods of statistical thermodynamics ([1]). Substantial results have been obtained in the study of the kinetics of nonequilibrium deformation of polymers ([2]). However, up to the present time the methods of mechanics have not yet found consistent application in the development of the problem under consideration.

2. The mechanics of polymer molecules has been developed on the basis of the assumption that the act of mechanical rupture is preceded by a stage of elastic stretching of the polymer molecule ([3]). In the present article, using rubber as an example, the main questions of a "mechanical" theory of the stretching of polymer systems are discussed, based on the assumption of the determining significance of the elastic stretching of polymer molecules in the stretching of idealized rubber ([4]). The fundamental principle of mechanics is the requirement of equilibrium of forces between the stressed elements of the structure in a deformed body; therefore, the principal task in developing the theory is to study the conditions of "intracompensated" equilibrium.

3. The molecular structure of idealized rubber is usually represented in the form of "molecular segments" of equal length (a), connected at "junctions" (C–C, C–S, etc.) by strong chemical covalent bonds. The molecular "segment" is considered as the sole structural parameter ([5]). It has been proposed to introduce a second structural parameter—the length (μ) of a closed cyclic polymer contour, a polymer cycle, formed by a system of molecular segments connected with one another at junctions; the length of the shortest "polycycles" is apparently tens of times greater than the length of a segment ([6]). Stretched idealized rubber must represent a system formed by configurationally and elastically stretched segments, connected with one another not only by bonds at junctions but also through "molecular loops." Weak intermolecular local bonds, when considering the conditions of equilibrium between elastically stressed segments, should not be taken directly into account, but their indirect influence, like the

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Fig. 1. Principal scheme of HES' s. a—node A—3; b—node A—4; c—molecular loop

Figure 1: Fig. 1. Principal scheme of HES' s. a—node A—3; b—node A—4; c—molecular loop

influence of steric obstacles, is large.

4. Under conditions of sufficiently slow stretching, mutual pulling along the chains must be postulated as the principal mode of mutual equilibration of elastically stressed segments. Figure 1 gives the principal scheme of a primary stressed structural element (PSE), formed by elastically stressed segment No. 1 and by numerous other elastically stressed segments equilibrating its fluctuating tension by means of pulling along the chains. As branching proceeds, the degree of stress of the segments must decrease, in first approximation, in direct proportion to the number of these segments, while the constancy of the total stress in any section of the PSE is preserved:

$$\sigma_c = A^{k_2}\sigma_2 = A^{k_3}\sigma_3 = ... = A^{k_s}\sigma_s \text{ dyn}, \tag{1}$$

where A is the average number of branchings in a segment ($2 < A \leqslant 4$), k is the ordinal number of the segment or node, counted from node No. 1, with which segment No. 1 is connected; σ_c is the stress of the maximally elastically stretched segment No. 1, $\sigma_c = a_c\varepsilon_c \simeq 7.5 \cdot 10^{-3}\varepsilon_c$ dyn per molecule; σ_2, σ_3 are the stresses of the balancing segments No. 2, No. 3, etc.; σ_s is the mean-statistical stress of configurationally stretched segments, $\sigma_s = a_s\varepsilon_s \simeq 1 \cdot 10^{-8}\varepsilon_s$ dyn per molecule; a_c, a_s and ε_c, ε_s are, respectively, the elastic moduli and relative elongations under elastic and configurational stretching of the segments ([3]).

Fig. 1. Principal scheme of HES' s.
a—node *A*—3; *b*—node *A*—4; *c*—molecular loop

It should be pointed out that, for computational purposes, it is possible formally to apply the mathematical apparatus of the theory of chain reactions. The order of magnitude of the number of configurationally stretched segments which ultimately balance the tension of one elastically stressed segment No. 1 may be estimated as 10^4—10^5. This conclusion is a consequence of considering, by methods of mechanics, the conditions of equilibrium in the direct interaction of elastically stretched polymer molecules.

5. Quantitative relations can be derived if the "framework" hypothesis ([4]) is adopted. According to this hypothesis, when a rubber specimen is stretched, there arises—and, as the specimen is stretched further, there grows—a continuous equilibrated system of elastically stretched segments, called the framework ("elastic network"), which takes up the main share of the external load, as well as that part of the stress of the internal force field

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("elastic network") which cannot be balanced by the action of external forces. Thus it is assumed that the stress of a stretched specimen is determined by the potential energy of elastically stretched polymer molecules. The ideas being developed may be reconciled with notions of "forced elasticity" ([7]); however, in contrast to the generally accepted views ([1],[2],[5],[8]), no direct links can be established between the parameters of the mechanical properties and the thermodynamic parameters, although in some cases the manifestation of correlation links may be expected. It is essential to note that, according to the framework hypothesis, entropic deformations of segments must be compensated predominantly within the specimen, without being reflected in the external stress of the specimen. Thermodynamic theories remain valid with respect to thermal effects; however, corrections are required to take account of the role of elastic stretching of the segments. The sections of the framework must penetrate the elastic medium; therefore the mechanism of deformation of the specimen may be microvolumetric rather than molecular. Such concepts are consistent with the notions of a special "chemical flow" under mechanical deformation of polymers ([9]). Relations between the stress of the specimen (f), the stress of the maximally elastically stretched segment No. 1, and the number of such segments (n) in the cross section of the specimen can be established if it is assumed that the number of continuous longitudinal "sections" of the framework corresponds to the average number of individual HES' s in the cross section of the specimen. This assumption is quite justified, since according to (1) the stress in any section of an HES remains constant and equal to σ_c. Then the condition of longitudinal equilibrium will be described by the equation:

$$f = 10^{-6}\sigma_c \sum_{1}^{x}(n_1 + n_2 + n_3 + ... + n_x)$$

or

$$f = 10^{-6}\sigma_c n \text{ kg/cm}^2, \tag{2}$$

where $\sigma_c = a_c\varepsilon_c$; $n_1, n_2, n_3 ... n_x$ is the number of sections formed at the corresponding elongations of the specimen, and n is the total average number of sections in the cross section of the stretched specimen.

The limiting number of independent, noninteracting NES' s in the cross section of a stretched specimen, n', can be estimated if the value of σ_c is specified. For $\sigma_c = 1 \cdot 10^{-4}$—$1 \cdot 10^{-3}$ dyn per molecule and for $f = 1$ kg/cm^2, the order of the number is $n' = 1 \cdot 10^{10}$—$1 \cdot 10^{9}$ cm^{-2} per 1 kg of stress in the stretched specimen; in this case the total area of the maximally stressed regions in the cross section of the stretched specimen is of the order of only $1 \cdot 10^{-5}$—$1 \cdot 10^{-6}$ of the total cross section of the specimen. According to the concepts being

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developed, the experimentally determined "load—elongation" curve should reflect the probability of an increase in the number of framework sections (n) upon stretching of the specimen; this also accounts for the great importance of tensile testing of polymeric substances—a method widely used in practice.

6. In studying the conditions of framework formation, it is advisable to consider three stages. The first stage is the formation of individual NES' s; the second is the interaction of NES' s and the appearance of internal force fields equilibrated by individual portions of the framework; the third stage is the formation of continuous "longitudinal" (x) and "transverse" (y, z) sections of the framework. With an increase in concentration, the NES' s must interact, joining one another. In the case of consecutive—longitudinal interaction, rigid, slightly extensible framework sections must be formed; the relative elongation of these sections must coincide in magnitude with the relative elongation of the specimen, if the elongation at which the given section was formed is taken as the initial length. If the NES' s first interact in parallel and then consecutively, then as a result of secondary interaction of transversely and longitudinally equilibrated elastically stretched structures, elastically stressed contours must be formed, whose subsequent interaction must lead to the formation of three-dimensionally equilibrated branched sections of the framework.

At least three causes must give rise to a substantial difference between the elongation of the sections of the extensible framework and that of the specimen: the different initial absolute length of the specimen and of the section; the three-dimensionality of the contour structure and the curvature of the sections; the mismatch of macro- and microextensions, especially significant for rubbers filled with fillers [10]. The scale correction (λ) takes into account the ratio of the relative length of the section formed (x_n) to the relative length of the specimen (x) at which this section was formed,

$$\lambda = \frac{x_n}{x},$$

where $x_n < x$. The correction π takes into account the peculiar feature of the framework structure—its three-dimensional construction (x, y, z), the longitudinal distance (e) between NES' s in a section, the transverse distance between sections of one and the same contour (i_y, i_z), and the curvature of the longitudinal (j_x) and transverse (j_y, j_z) contour-connected sections:

$$\pi = j_x + 2\frac{i}{e}j_y.$$

Since $j_x > 1$, $j_y, j_z < 1$, $i > e$, then π must also be greater than 1.

The third scale correction φ takes into account the increased elongation of the microvolumes of the vulcanizate located between filler particles:

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$$\varphi = \frac{x'}{x},$$

where x' is the average relative length of the microvolume at the relative length of the specimen x. Owing to the decrease in cross section when the specimen is stretched, longitudinal sections must elongate at the expense of transverse ones while the stress of the contour and of the framework sections remains constant. Thanks to internal displacements of the "elastic medium," the stress of the sections must decrease; this explains certain relaxation processes and the growth of residual elongations. For equilibration of the transverse sections of the framework, the degree of stretching of the surface layers must be

substantially greater than in the deep layers, except for the internal surfaces of the section, where the stresses must also be considerable.

7. Without additional assumptions one can establish relations between the parameters characterizing the elastic stretching of polymer molecules and the parameters of the mechanical properties of rubber stretched sufficiently slowly. If one estimates the total length of the sections, calculates the work for the elastic stretching of the portions, and takes scale corrections into account, the following formula can be derived:

$$\beta_1 = \pi\varphi\varepsilon_c = \frac{2(A_p - a)}{fx}, \tag{3}$$

where A_p is the work of stretching, determined by graphical integration of the experimental load–elongation curve, in kg · cm/cm^3; a is the correction for the work directly expended on the entropy deformation of the polymer molecules. The work expended on the entropy deformation of the main part of the molecules cannot be determined in tensile tests, since it is additionally transmitted through the framework; such is the prediction of the mechanical theory. The degree of stress drop at the very beginning of contraction of a strongly stretched specimen can be determined if, using formula (2), the number of sections is estimated and scale corrections are introduced:

$$\beta_2 = \pi \cdot \varphi \cdot \bar{\varepsilon}_c = -\frac{f}{xE_\beta}, \tag{4}$$

where E_β is the nonequilibrium modulus of elasticity, determined from the slope of the contraction curve in kg/cm^2; the value of E_β is numerically equal to the stress drop upon a conditional contraction of the specimen by 100%. Despite the rough assumptions made in deriving formulas (2), (3), and (4), the experimental results obtained in testing a wide set of rubbers of different structural types, including filled rubbers, agree quite well with the predictions of the mechanical theory of stretching of polymer systems.

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8. The relative fraction (η) of elastically stretched portions can be estimated from the formula: $\eta \approx \dfrac{Fs_0}{10^{-6}\sigma_c}$, where $F = fx$, s_0 is the effective cross-sectional area of a natural-rubber molecule, $s_0 = 25 \cdot 10^{-16}$ cm^2 at $F = 1 \cdot 10^3$ kg/cm^2 and $\sigma_c = 0.25 \cdot 10^{-3}$ dyn; the "coefficient of nonuniformity" is $\eta \approx 1\%$.

It is essential to note that the framework hypothesis is based on the assumption of a very high strength of polymer molecules ([3]). The ideas developed may be used in formulating a program of work in the field of polymers and certain solid bodies.

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