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Abstract

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On the Molecular Mechanism of the Formation and Development of an Interface during Deformations of Polymeric Substances in the Highly Elastic State

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1. By the present time new concepts have been developed: mechanical properties, mechanical stretching, and rupture of macromolecules ([1]). The forces arising between macromolecules as a result of short-range interaction have been proposed to be regarded as conservative internally compensated forces ([2]). In studying phenomena caused by the manifestation of long-range interaction, transmitted along elastically stressed macromolecules under comparatively slow mechanical deformations, it has been proposed to consider the conditions of mechanical equilibrium, i.e., to apply a method based on Newton' s law of equality of action and reaction ([2-4]). The possibility of developing "macromolecular mechanics" is based on the assumption that, as a result of molecular entanglements, an elastic network is formed—a hypothetical framework ([2-4]). In the article, using rubber as an example, the possibility is discussed of studying the molecular mechanism of the formation and development of an interface during deformation.

2. A necessary condition for the formation of an interface is the rupture of all macromolecules "intersecting," at the moment of rupture of the polymer, the surface being formed. It is important to note that independent mechanical ruptures of sections of the framework cause softening of rubber, but cannot lead to the formation of an interface. Even in the presence of considerable destructive processes at elevated temperature, accompanied by substantial softening of the deformed rubber, the integrity of the specimens is preserved ([5]).

3. An interpretation of the molecular mechanism during rupture may be given on the basis of the hypothesis of the formation of a microneck. The possible structure of a microneck is shown in Fig. 1; this scheme should be regarded as a geometrical model. The central part of the microneck is a system formed by highly oriented, elastically stressed sections of macromolecules of different length and different degree of stress. The central part of the microneck may be called an "elastically stretched bundle of macromolecules" (e.s.b.). The e.s.b. must balance the oppositely directed tension of two elastically stressed bases of

Fig. 1. Geometric model of a microneck.

Figure 1: Fig. 1. Geometric model of a microneck.

the microneck. The microneck may contain a considerable number of embedded, entropically stressed sections of macromolecules.

The elastically stressed bases of the micronecks during stretching of a specimen must move as a whole by a mechanism that may be called macrovolumetric or "bundle-like." As the degree of deformation of the specimen increases and the average stress in the e.s.b. ($R_{\text{e.s.b.}}$) grows, ever larger macrovolumes must be drawn into the sphere of displacement of the bases of the microneck, which cannot but lead to mechanical rupture of the e.s.b.

The conditions of mechanical equilibrium in a microneck must be determined by the following relations

$$\bar{\sigma}_{\text{el}} = m^{-1} \sum_{1}^{m} (\sigma_1 + \sigma_2 + \sigma_3 + ... + \sigma_m) \text{ dyn}; \tag{1}$$

$$Q_M = Q'_{M'} = 10^{-6} m \bar{\sigma}_{\text{el}} = S_{M_1} R_1 = S_{M_2} R_2 = ... = S_{MR} M \text{ kg}, \tag{2}$$

where m is the number of central segments in the e. p.; $\sigma_1, \sigma_2, \sigma_3 ... \sigma_m$ is the elastic tension of the central segments in the e. p. (dyn); $\bar{\sigma}_{\text{el}}$ is the same, but the mean value (dyn); σ_z is the limiting value of the mechanical strength of a macromolecule (dyn); $S_{M_1}, S_{M_2}, S_{M_3} ... S_M$ is the total cross-sectional area of the microneck in sections $1, 2 ... M$ (cm^2); ω is a correction accounting for the fraction of stressed macromolecules in the cross section of the e. p.; $\omega = m s_0 S_{\text{el}}^{-1}$; $R_1, R_2, ..., R_M$ is the stress in the various sections of the microneck (kg/cm^2); $Q_M, Q'_{M'}$ is the total force in the stretched microneck (kg); $\bar{R}_{\text{el}} = 10^{-6} \omega \bar{\sigma}_{\text{el}} \cdot s_0^{-1}$ is the mean stress in the e. p. ($\text{kg} \cdot \text{cm}^{-2}$); s_0 is the cross-sectional area of an elastically stretched macromolecule (to a first approximation, elastic stretching is not taken into account) (cm^2); a_c is the elastic modulus in the calculation per 1 macromolecule (dyn); $\bar{\varepsilon}_{\text{el}}$ is the elastic relative elongation of macromolecules in the e. p.; the length of a fully straightened macromolecule is taken as the zero value; $R_z = 10^{-6} \sigma_z s_0^{-1}$ is the formal value of the mechanical strength of a macromolecule referred to 1 cm^2 ($\text{kg} \cdot \text{cm}^{-2}$); $\sigma_z = a_c \varepsilon_z$.

Fig. 1. Geometric model of a microneck. A, B are the elastically stressed bases of the microneck; C is the central part of the microneck– "elastic bundle," circles are chemical bonds; $K = mK'$. Elastically unstressed segments are not shown in the diagram.

The increase in the elastic tension of macromolecules upon stretching of the e. p. can be approximated by Hooke' s law; then

$$\bar{\sigma}_{\text{el}} = a_c \bar{\varepsilon}_{\text{el}} \text{ dyn}; \tag{3}$$

$$Q_M = 10^{-6} m a_c \bar{\varepsilon}_{\text{el}} \text{ kg}; \tag{4}$$

$$\eta_1 = \bar{\sigma}_{\text{el}} : \sigma_z = \bar{\varepsilon}_{\text{el}} : \varepsilon_z; \tag{5}$$

$$\eta_2 = \bar{F}_S : R_{\text{el}} \simeq m s_0 : S_M. \tag{6}$$

4. Taking into account the effect of overstressing of the surface layers and accepting the hypothesis of microneck formation, one can establish a quantitative relation (η_z) between the maximum experimental value of the strength of rubber (F_z) and the strength of a macromolecule (R_z) by the following formula:

$$\eta_z = \eta_1 \eta_2 \eta_3 \eta_4 = \frac{F_z}{R_z}, \tag{7}$$

where

$$\eta_3 = F_{\max} : \bar{F}_S = 1 : x^{0.5} \varphi_S, \tag{8}$$

$$\eta_4 = F_z : F_{\max} = 1 : \varphi_{\max}; \tag{9}$$

$\bar{F}_S$ is the mean stress in the surface layers over the actual cross section ($\text{kg} \cdot \text{cm}^{-2}$); $F_{\max}$ is the maximum local stress in the specimen ($\text{kg} \cdot \text{cm}^{-2}$).

As is known, in the first approximation $F = fx$, where f is the stress in $\text{kg} \cdot \text{cm}^{-2}$, referred to the initial cross section, and x is the relative length. The remaining conventional notation is given in item 3 and in previously published papers ([1–4]). According to ([2]), the ratio $\bar{F} : F_{\max} = \varphi$; however, in studying the stretching of rubber the mean value of φ is determined, whereas in estimating the value of the coefficient η_4 it is necessary to estimate the quantity $\varphi_{\max}$. Therefore it is necessary to study the distribution of φ by magnitude. According to ([4]), from geometrical considerations the overstress in the surface layers is directly proportional to the quantity $x^{0.5}$. In addition, according to ([2]), it is necessary to take into account the overstress caused by the action in the surface layers of the transverse sections of the framework; this effect can be taken into account by introducing the coefficient φ_S. Then the total magnitude of the overstress will be expressed by the product of the indicated quantities and the coefficient $\eta_3 = 1 : x^{0.5} \varphi_S$.

On the basis of the foregoing we obtain the following desired relation

Fig. 2

Figure 2: Fig. 2

$$\eta_2 = \frac{F_z}{R_z} = -\frac{\bar{\varepsilon}}{\varepsilon_z}\frac{ms_0}{S_M}\frac{1}{x^{0.5}\varphi_S}\frac{1}{\varphi_{\max}}. \tag{10}$$

Let us note that we obtained indirect experimental proof of deformation of the surface layers of rubber at a rate greater than the average ([6]). The formation of "filaments," observed at the mouths of growing cracks ([7]), indirectly confirms the validity of accepting the hypothesis of micro-neck formation. The ideas being developed can be reconciled with concepts of the "bundle" structure of crystalline polymers ([8]), as well as with concepts of the "long-term" strength of polymers ([9]).

Fig. 2. Effect of the decrease in resistance to rupture when standard specimens are weakened by cuts. 1 —rubber based on natural rubber; 2 —rubber based on divinylnitrile rubber; f_{50}, f_{100} —resistance to rupture of specimens with cuts of depth 50 and 100 μ, respectively; n_z — "effective" magnitude of the hidden defect.

It is natural to expect that the formation of micro-necks will take place in the surface layers as a result of displacement of structural elements in opposite directions according to the macrovolume mechanism ([4]).

5. The energy density during elastic stretching of macromolecules is of the order of 10^3 cal$\cdot$cm^{-3} ([1]); therefore the central part of a micro-neck must exhibit very high chemical activity. Mechanical rupture of the u.p., including during chemical dissociation, must be accompanied by dissipative processes of an explosive character ([1]) and may be regarded as a local explosion. The efficiency coefficient in the conversion of mechanical energy into other forms of energy, if one does not take into account the chemical excitation of the ruptured parts of the macromolecules, is very high, since $\eta = 1 - m/K = 1 - 1/K'$, where K is the number of "segments" forming the u.p. ([1]). When ozone acts on stretched rubber, microcracks are formed intensively; this finds a simple interpretation on the basis of the hypothesis of formation of micro-necks in the surface layers. It may be supposed that the primary centers of failure under repeated deformations are likewise micro-necks. The ideas being developed make it possible to refine the hypotheses stated earlier ([1]).

6. Mechanical rupture of the u.p., apparently occurring by a chain mechanism, should be regarded as the primary elementary act in the formation of microcracks. The initial stage of development of the surface—

the surface of separation must take place by an alternation of the formation of micro-necks at the mouths of primary microcracks and the subsequent rupture of

the u. p. During rupture of the u. p., owing to dissipative processes, secondary effects must appear, for example chemical and thermal destruction and even "melting" of the surface being formed. Together with V. K. Antchak, B. G. Gusarov, V. D. Vorzhev, and M. D. Kaplan it has been established that, in the presence of an artificial notch, during stretching of rubber there is first observed an increase of the notch at its mouth, and when the critical stress value is reached (see Fig. 2) instantaneous rupture of the standard specimen occurs [10]. This method is applicable to the study of the structural strength of polymers and to the evaluation of the dependence of strength on the magnitude of "hidden" defects.

Table 1

Rubber	Filler	$\bar{f}_z$, kg · cm^{-2}	f_{max}, kg · cm^{-2}	f_{min}, kg · cm^{-2}	f_{50}, kg · cm^{-2}	n_z, μ
NK	Zinc oxide, litho-pone	265	303	221	214	37 (42)
SKS-30A	Gas black	255	305	205	202	45 (51)
SKI	White black	275	319	231	222	39 (43)
Butyl rubber	White black	246	298	194	180	34 (–)
SKN-40	White black	150	174	124	75	15 (20)

Note. The figures in parentheses denote indices determined at a stretching rate of 3.6 m · sec^{-1}.

Table 1 gives data, obtained jointly with B. G. Gusarov and V. D. Vorzhev, characterizing the strength of rubbers according to the ordinary (GOST 270–53) and the new indices.

The concepts developed in the article are recommended for use in studying a wide range of phenomena in the field of polymers.

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