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Abstract

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MOLECULAR MECHANISM IN THE DEFORMATION OF POLYMERIC SUBSTANCES

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1. Theoretical concepts of the stressed state of a deformed idealized elastic network ($^{1-4}$) and, in the study of relaxation processes of deformation of polymeric substances (^{3,5}), were developed without using concepts of the molecular mechanism. For example, in statistical theory the change in the state of polymer molecules is taken as a consequence of a change in their configuration ($^{1-4}$), without taking into account the possibility of relative displacements of macromolecules during the deformation stage of an elastic body. In relaxation theories the relative displacement of polymer molecules is considered as plastic flow (^{3,5}). Despite their great significance, relaxation theories have a fundamental shortcoming, since in them deformations of different nature are considered as independent. The molecular mechanism in deformations of polymeric substances differs substantially from the molecular mechanism in diffusion processes ($^{2,6-8}$). A difference has been established in the behavior, during deformation of polymers, of "segments" and polymer chains (^{7}). New fruitful ideas have been proposed concerning "forced elasticity" (^{6}), "chemical flow" (^{9}), and "mechanochemical effects" (^{10,11}), which manifest themselves during deformations of polymers as a result of local concentration of stresses. However, the elementary acts responsible for the manifestation of the indicated effects during deformations of polymers have not yet been clarified (^{7,9,10}). This article discusses the possibility of clarifying the molecular mechanism in the deformation of polymeric substances by interpreting the results of mechanical tests of rubber on the basis of the application of the methods of macromolecular mechanics ($^{11-13}$).

2. The process of mechanical deformation represents the relative displacement of structural elements with different accelerations. The stressed state of a polymer body must be a consequence of the preservation of the connectedness of elements of the structure that are stressed during deformation. In the deformed system, at any moment in time, internal mechanical equilibrium must be preserved among mutually connected stressed elements.

According to the structural-mechanical theory, as a result of considerable rela-

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tive displacements of a very small part of the macromolecules, during deformation of polymeric systems an elastic network must form—a hypothetical framework that takes up the main part of the external load and also equilibrates a significant part of the internal stress of the deformed elastic network penetrated by branched sections of the framework (11–13). As a means of mechanical equilibration of stresses in the framework sections, mutual pulling-over along elastically stressed chains was postulated. Then the probability of framework formation, at the corresponding temperature and rate of deformation, is determined by the contour-polycyclic structure of the network, by the formation

during deformation of molecular loops and by intermolecular interaction. The stressed state must directly be determined only by the number of framework sections formed and by the degree of their relative elastic elongation, since the determining influence of the listed factors can manifest itself only indirectly—through their influence on the structure of the elastic network being formed (12,13).

3. Important information on the molecular mechanism can be obtained by analyzing the change in the cross-sectional area (S_x) and the external surface (S_{xy}) during stretching of an elastic body that preserves a constant volume. It is known that the cross section of a cube with sides of relative length $x = y = z = 1$ decreases under uniaxial stretching according to the law $S_x = x^{-1}$. It is important to note that the area of the external surface must increase during deformation according to the law $S_{xy} = x^{0.5} = y^{-1}$. Because of the decrease in cross section, the structural elements must move toward one another in the direction of stretching and at the same time move from the periphery toward the center. In the surface layers, on the contrary, there must be a displacement of structural elements from the deeper layers into the surface layers; otherwise, during stretching, the required increase in the external surface will not be ensured. Thus, even for geometric reasons, uniaxial stretching must be regarded as three-dimensional, accompanied by complex counter and transverse displacements of structural elements.

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specimen

4. To ensure mechanical equilibrium in the surface layers, the latter must be subjected to the drawing-in action of transverse sections of the framework ([12]), which cannot fail to lead to an increased degree of deformation of the surface layers due to local motion of material from the surface layers into the inner layers. Thus, in the surface layers a contradictory—counter—motion must occur, ensuring an increased degree of deformation of the surface layers of the stretched polymer. These considerations apply equally to the internal surfaces of a separation boundary, formed, for example, when large filler particles are present in the polymer. The concepts developed provide new possibilities for understanding the mechanism of the formation and development of separation surfaces under mechanical deformations of polymeric substances.

5. At considerable elongation, the initial stage of contraction is characterized by a sharp drop in stress (Fig. 1A), which was explained by elastic contraction of the framework while the number of sections is preserved ([12,13]). In such an "elastic" state the structure of stretched rubber is characterized by greater stability. For example, with repeated alternation of small contractions and elongations carried out after slight contraction of a highly stretched specimen, rubbers based on natural (NR), isoprene, sodium-butadiene (SKB), divinylstyrene (BSK), polychloroprene rubber, and butyl rubber almost do not change their elastic properties (E_φ = const.), while rubbers based on divinylnitrile and divinylstyrene "carboxylate" rubber change their elastic properties only slightly. With complete contraction, "structural" hysteresis is observed (shown by hatching in Fig. 1), and with repeated stretching of the polymer thixotropic softening appears (Fig. 1B), reflecting a significant change in structure. It is essential to note that this change ("fi-

"fixation" of the structure at room temperature occurs only at the stage of complete contraction of substantially stretched rubber and is not observed upon partial contraction of stretched rubber (Fig. 1A). It is known that, in the stretching of polymers, orientation processes are observed, caused by changes in the structure of the elastic network; the orientation effects are completely eliminated when the polymer is contracted at a temperature above the glass-transition temperature. In our work it has been established that, along with restoration of the structure during contraction, a further irreversible change in the structure occurs simultaneously. Holding rubber at room temperature in the stretched state leads to a substantial increase in residual deformations, but has almost no effect on the magnitude of the hysteresis and thixotropic changes in structure. Thus, residual elongations must be associated with displacements of elements of the elastic network in the stretched specimen, whereas "structural effects" —hysteresis, thixotropic changes, etc.—must be due to changes in the elastic network occurring during the contraction stage. At elevated temperature (above 100–120° C), the structural effects caused by changes occurring

Fig. 2. Thixotropic softening of rubber from NK. 1— “unloaded” ; 2—channel black (10-30 cm^3); 3—mineral fillers: kaolin, zinc oxide, chalk, mica (10-20 cm^3)

Figure 2: Fig. 2. Thixotropic softening of rubber from NK. 1— “unloaded” ; 2 —channel black (10-30 cm^3); 3—mineral fillers: kaolin, zinc oxide, chalk, mica (10-20 cm^3)

Fig. 3. Structural hysteresis (in $\text{kgf} \cdot \text{m} \cdot \text{cm}^{-3}$). Rubbers with channel black (20-25 cm^3): 1—NK; 2—SKB; 3—BSK

Figure 3: Fig. 3. Structural hysteresis (in $\text{kgf} \cdot \text{m} \cdot \text{cm}^{-3}$). Rubbers with channel black (20-25 cm^3): 1—NK; 2—SKB; 3—BSK

during the contraction stage are hardly manifested in rubber deformations.

Fig. 2. Thixotropic softening of rubber from NK.
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6. It has been established experimentally* that thixotropic changes in structure are always irreversible if the stress (f) exceeds the critical value (f_k). For the most stable—unloaded—rubbers from NK,

$$f_k = 20\text{-}50\ \text{kgf} \cdot \text{cm}^{-2}.$$

“Carbon-black” rubbers from NK are likewise distinguished by great stability of mechanical properties; conversely, rubbers with mineral fillers are characterized by very considerable irreversible thixotropic changes. In Fig. 2 the irreversible thixotropic changes are evaluated by the magnitude of the maximum relative decrease in the conditional moduli $\mu_n = f : f_0$ (^{14}). The “reversible” part of the thixotropic changes was eliminated by heating the specimens in glycerine at a temperature of 100-120° C.

Fig. 3. Structural hysteresis (in $\text{kgf} \cdot \text{m} \cdot \text{cm}^{-3}$). Rubbers with channel black (20-25 cm^3): 1 —NK; 2 —SKB; 3 —BSK

7. The nature of structural hysteresis at substantial deformations may be interpreted as a consequence of elastic contraction of sections of the framework and the impossibility of spontaneous displacement of these sections. The nature of structural hysteresis should be common to all polymers in the elastic state; therefore the linear dependence of hysteresis losses (Γ) on the work of stretching (A), first established as early as 1931 in the study of rubbers from NK (^{15}), becomes understandable. G. A. Patrikeev and V. M. Fedorov, in processing the indicated (^{15}) and their own results, proposed the empirical equation

$$\Gamma = k \cdot (A - e) \text{ kgf} \cdot \text{cm} \cdot \text{cm}^{-3} \quad \text{or} \quad \eta = \Gamma : A = k \cdot (1 - e \cdot A^{-1}),$$

valid for

$$A \geq 50\text{–}70 \text{ kgf} \cdot \text{cm} \cdot \text{cm}^{-3},$$

where k and e are constants determined graphically (see Fig. 3). To a first approximation, the magnitude of structural hysteresis at considerable extensions, in contrast to hysteresis losses at small deformations, depends little on the type of rubber, the type and of the filler content and the degree of vulcanization (at $A \geq 200$ kg $\cdot$ cm $\cdot$ cm^{-3}, $\eta = 0.60\text{–}0.85$).

8. When the elastic network is eliminated, the action of the external force field must be directly balanced by the deformed elastic network. Therefore, after the completion of the elastic contraction of the framework, the nature of the stressed state and the molecular mechanism of contraction must change fundamentally. It is known that at this stage of deformation the elastic modulus becomes smaller than the “conditionally equilibrium” modulus. This can be explained by the opposition to deformation of the elastic network exerted by the “relaxed” sections of the framework. Therefore, upon complete contraction, one should expect not only displacement of the elastic network relative to the sections of the framework, but also the emergence of internal stresses.

9. The molecular mechanism of deformation of the elastic network in the stretching stage cannot be clarified on the basis of the concepts developed ([12]). During the stretching of rubber one may expect the manifestation of a “rigid” displacement of microvolumes, carried along by the penetrating and enclosing sections of the framework. Subsequently, the rigidly displaced microvolumes of the elastic network may be deformed according to the molecular– “segmental” –mechanism. The boundary layers between rigidly displaced microvolumes must be deformed very strongly; however, in the absence of mechanical ruptures, owing to intermolecular interaction, a “healing” effect should take place, and therefore the formation of separation surfaces should not be expected.

10. The method of large elongations is widely used for evaluating the mechanical properties of polymer substances. This type of testing may be used as an indirect method for studying the structure of polymer substances, the molecular mechanism of deformation of polymers, and the mechanical properties of polymer molecules. It is therefore necessary to improve the

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* Jointly with E. A. Abramova and T. S. Dvorkina.

apparatus for mechanical testing of polymers and to continue the development of macromolecular mechanics. Experimental proof of the formation of an elastic network during deformation of polymers is also of substantial interest.

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