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## Changes of Activation Energy during Deformation of Rubber

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*Based on a simple molecular model, a mechanism of rubber flow characterized by a viscosity increasing with the reversible rubber-like deformation is proposed. It is associated with an activation energy of viscous flow which increases proportional to an external stress due to the entropy elasticity of macromolecules. This increase of the activation energy for jumping of molecular-kinetic units of a polymer network into vacancies during the rubber deformation process is caused by an increasing resistance of the stretching macromolecular network due to the entropy nature of macromolecule deformation.*

**Keywords** rubber deformation, polymer network, standard linear solid, Eyring's viscosity theory, activation energy, entropic elasticity

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## Introduction

The most striking peculiarity of the process of rubbers extension is the increase in the rate of increase of stress right up to breaking elongation. Calculations of the dependencies of stress on strain, constructed on the basis of the kinetic theory of rubber-like elasticity do not completely coincide with the experimental extension curves of rubber, especially with large extension<sup>[1]</sup>.

The application of Eyring's ideas regarding the influence of an outside force on the process of thermally activated flow in condensed matter<sup>[2]</sup> gives the possibility to describe, simply and fully, the stress-strain curves of rubbers on the basis of a three-element model of a standard linear solid (an SLS) as shown in Fig. 1.

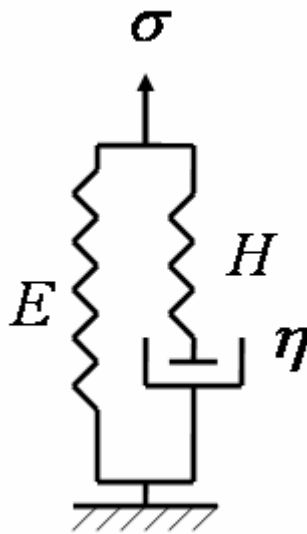


Figure 1. Model of a standard linear solid

For the model SLS  $H$  - is the elasticity modulus with extension for the spring connected with a viscous element (dashpot) of the model. This modulus represents Hookian elasticity forces.  $E$  - Is the rubber-like modulus, presented by the elastic spring parallel to the viscous element. This spring is responsible for the reversible rubber-like strain.  $\eta$  - is a viscosity factor for a viscous element,  $\sigma$  - is the stress applied to the SLS model,  $\varepsilon$  - is the resultant deformation of the model.

When phenomenologically describing the behavior of a polymer in accordance with the model SLS,  $\varepsilon$  is the total strain, to equal the rubber-like strain  $\varepsilon_{en}$ , which has an entropic character.

The spring with an elastic modulus  $E$  represents an entropic component of stress:

$$\sigma_{en} = E\varepsilon_{en} = E\varepsilon.$$

The general stress is made up of the entropic stress  $\sigma_{en}$  and the elastic stress  $\sigma_e$ , for the spring with the elastic modulus  $H$ . The elastic stress  $\sigma_e$  is equal to the stress on the dashpot  $\sigma_\eta$ . Thus the stress on the dashpot, or the elastic stress, is equal to the difference between the total stress and the entropic stress:  $\sigma_\eta = \sigma_e = \sigma - \sigma_{en} = \sigma - E\varepsilon$ .

Frenkel has suggested one can consider the flow process in a liquid as the thermally activated jumps of atoms into vacancies over an energy barrier<sup>[3]</sup>. Eyring used the theory of absolute reaction rates for describing the liquid flow process<sup>[2,4]</sup>. He also took into account the effect of an external force, decreasing the jump activation energy according to the formula:

$$\eta = Af \exp \frac{E_0 - bf}{k_B T} \quad (1)$$

Here  $A$ , the pre-exponential factor, is calculated by the theory of rate processes,  $f$  is the shear stress in the flow process,  $E_0$  the activation energy at 0°K, that is, the height of the barrier of potential energy for the jump into a vacancy of molecular-kinetic particles in the course of thermal movement of molecules in the absence of an external force,  $b$  - is a “viscosity factor” according to Eyring,  $k_B$  - is Boltzmann’s constant, and  $T$  is absolute temperature.

## Discussion

It follows from eqn. (1) that the viscosity of a liquid exponentially decreases with increasing shear stress during flow. This phenomenon is known as a “viscosity anomaly” of flow and has been experimentally confirmed, mainly, for polymer melts and solutions<sup>[5]</sup>. However, for most non-polymeric liquids, the viscosity does not depend on shear stress. This contradiction can be eliminated if one takes into account the basic feature of chain macromolecules, that is, the entropy character of their reversible rubber-like deformation. It is the tendency of macromolecules, stretched in the flowing liquid, to curl up back to the initial, most favorable, for a given temperature, conformation that causes a decrease of activation energy in flowing polymer liquids. The dependence of viscosity on the magnitude of the reversible rubber-like deformation was proposed in ref.<sup>[6]</sup>:

$$\eta = B\tau_e \exp \frac{E_0 - \delta G_e \gamma_e}{k_B T} \quad (2)$$

Here  $B$  is the pre-exponential factor,  $\tau_e$  is the shear stress,  $\delta$  is a coefficient characterizing the volume of molecular-kinetic units of the macromolecule, determined by the structure of the polymer and the flow conditions,  $E_0$  is the activation energy determined by the height of the energy barrier,  $G_e$  is the shear modulus of the macromolecular network, and  $\gamma_e$  is the reversible rubber-like shear deformation.

In the absence of deformations and stresses in a solid substance the spontaneous transfer of atoms and groups through the vacancy in the whole volume of the material doesn't occur. However, the transfer into vacancy and back is possible in the course of oscillatory movements of atoms owing to fluctuations of thermal energy. Thereby the rate of direct and return transfer is equal<sup>[7]</sup>. In the event of extension of an elastomer with constant rate of strain at the expense of elastic extension of the covalent backbone bonds and the subsequent thermally activated jump of the molecular-kinetic units of macromolecules in the vacancy, there begins a migration of these units in the direction of an outside force. When this occurs, there is a change in the relative rearrangement of the units to each other; which is, in effect a manifestation of material flow.

An attempt to describe the deformation process of solids, including polymers, with the help of the theory of rate processes was made by Eyring and co-authors using Maxwell's and SLS models<sup>[4,8,9]</sup>. However, these descriptions lead to stress-strain curves with monotonic decreasing rate of the stress growth in constant strain-rate tests. Then the stress, with time, passes either to the constant stress - yield stress, described in Maxwell's model or the constant speed of stress-increase described in the SLS model<sup>[10]</sup>. In all cases, the description of the deformation of materials was made according to eqn. (1).

However, this approach contradicts the fact that the rate of the stress increase in an elastomer increases with deformation. In our view, this fact can be explained by the influence of a reversible rubber-like deformation on the activation energy in the rubber deformation process. This influence is based on the entropy character of chain deformation in a polymer network.

### **Mechanism of Extension of Rubber**

It is possible to represent this peculiarity of polymer networks having an effect on the process of their deformation by using the molecular model of the deformation of a polymer schematically illustrated in Fig. 2.

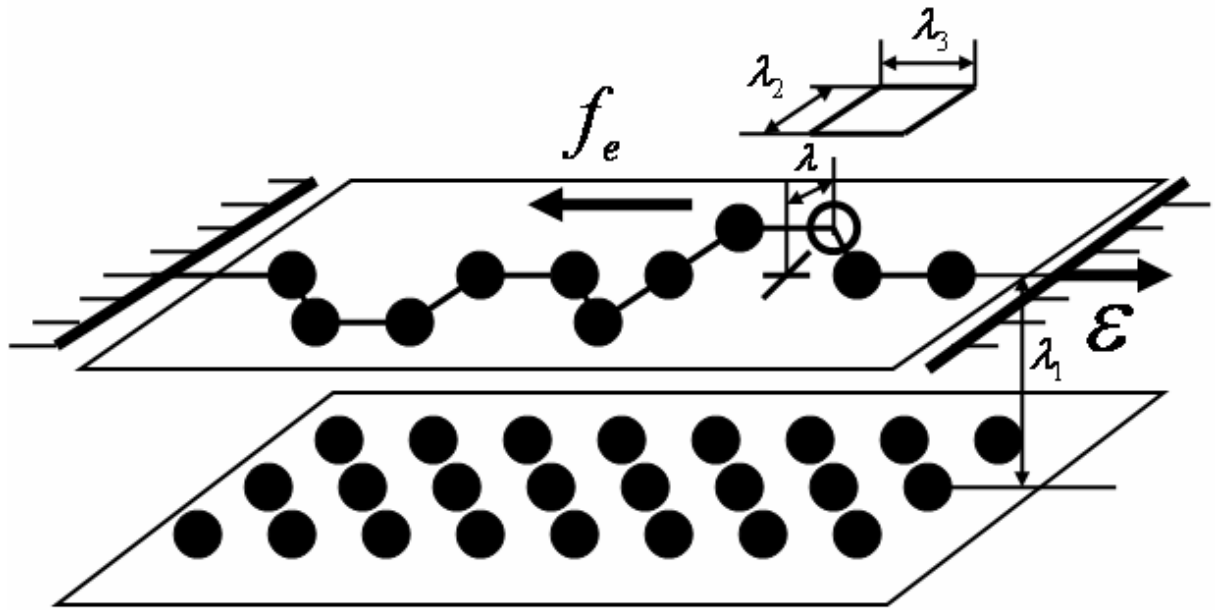


Figure 2. Diagram illustrating the transfer of molecular-kinetic units of a chain of an elongated polymer network to a vacancy in the event of unidirectional elongation

First, let us consider a simplified scheme of stretching a fragment of a polymer chain, such as stretching a chain between crosslinks of the polymer network. The ends of this chain are fixed in the grip of the tension testing machine (Fig. 2). The stationary grip is depicted in the figure to the left of the hatched border. On the movable grip to the right of the arrow, the elongation direction is shown. During deformation there is the extension of the polymeric chain with the change of its conformation with preservation of covalent backbone bonds. The applied external force helps overcome the intermolecular interaction forces as well as forces preventing the turning of backbone units with respect to each other. The process of a stretching of a chain is realized by the jump of a molecular-kinetic unit of a chain to a vacancy during fluctuations of thermal oscillations of atoms<sup>[3]</sup>. Thus the external force, transferring elastic energy of the extension through covalent backbone bonds, helps to break a potential barrier for the transition of a kinetic unit from one position of equilibrium to another, in the vacancy<sup>[4]</sup>.

To simplify consideration of the flow process we will assume that molecular-kinetic unit of the stretching chain (the chain of the black circles, Fig. 2) is situated in one upper plane and moves under the influence of external stress relative to neighboring atoms of other macromolecules situated in the lower plane. Neighboring atoms or molecular-kinetic units are depicted as black circles.

Analogous to Eyring's conclusion regarding the process of liquid flow from the position of the theory of rate processes<sup>[4]</sup> let us assume that for the model in Fig. 2 the difference in rate of shift of molecular-kinetic units of the extended chain in the upper plane relative to the neighboring units in the lower plane is equal to  $\Delta u$ , the distance between the planes is  $\lambda_1$ , the distance between the neighboring molecular-kinetic units in one plane is  $\lambda_2$  and  $\lambda_3$ , and the distance between the two positions of equilibrium is  $\lambda$ .

The straightening and shift of the macromolecule fragments in the volume of the polymer, induced by an external stress, leads to a spatial redistribution of their molecular-kinetic units, i.e. to a flow. The motion of molecular-kinetic units is achieved via turning of backbone units. The shifting unit depicted in Fig. 2 as a white circle in the upper flat area under the influence of the external force jumps to a new position of equilibrium, into a vacancy, depicted as a cross, in the during of fluctuations in their thermal oscillations.

Let us consider the distribution of forces on a moving unit of flow in some intervals of time after the jumping into the vacancy and the establishment of equilibrium of forces taking place after this. From the right side this unit is subjected to the external force. From the left side (the side of the stationary grip) it is subjected to the force resisting the deformation,  $f_e$ , which is opposite in direction to the external force.

Both these forces impede the transfer of kinetic units into the vacancy since the fluctuation of thermal energy must also overcome these forces of elastic energy.

Further growth of extension causes an increase in entropic elasticity forces of the stretched chains  $\sigma_{en} = E\varepsilon$ , where  $E$  is the rubber-like elasticity modulus (see Fig. 1), and  $\varepsilon$  is the rubber-like deformation equal to the general deformation of the sample for the SLS model. It leads to an increase of resistance of kinetic units to a flow; i.e. to growth of a potential barrier of a jump into the vacancy. For the realization of the process of kinetic units jumping, an increase in external force,  $\sigma$ , of some size exceeding the growing size of the force of jumping resistance, i.e. the forces of entropic elasticity,  $E\varepsilon$ , is required. This gain of external force of size  $(\sigma - E\varepsilon)$  during straining of the rubber provides the necessary energy for overcoming the growing potential barrier of the jumping of kinetic units of a stretched polymer rubber network, i.e. results in the flow of the material during the strain.

Taking into account that the gradient of flow between the two layers of the molecular model in Fig. 2 is equal to  $\frac{\Delta u}{\lambda_1}$ , and the force resulting in flow, i.e. in the movement of the upper layer, is equal to  $(\sigma - E\varepsilon)$ , we obtain a coefficient of viscosity  $\eta$  when flowing equal to :

$$\eta = \frac{(\sigma - E\varepsilon)\lambda_1}{\Delta u} \quad (3)$$

As applied to the diagram in Fig. 2, the force applied to the shifting kinetic unit in the direction of movement is equal  $(\sigma - E\varepsilon)\lambda_2\lambda_3$ , since  $\lambda_2\lambda_3$  is an effective site size corresponding to one molecular-kinetic unit of flow (Fig. 2). This force enables a shift of the kinetic unit into the vacancy. By this motion the valence bonds of a macromolecule are not broken, and resistance to motion of the kinetic unit in to the vacancy increases.

Consequently, the additional energy which the kinetic unit needs to acquire to reach the peak of the energy barrier at a distance of  $\frac{1}{2}\lambda$  and overcome the potential barrier with activation energy of  $E_0$ , is equal to the quantity  $(\sigma - E\varepsilon)\lambda_2\lambda_3\frac{1}{2}\lambda = \frac{1}{2}(\sigma - E\varepsilon)\lambda_2\lambda_3\lambda$ . The activation energy increases to this quantity at the time of the jumping of a kinetic unit into a vacancy. According to the theory of rate processes<sup>[4]</sup> the specific rate of flow in the direction of force  $k_\sigma$  (the number of transitions of a kinetic unit through a barrier in one second) will be given by:

$$k_\sigma = \frac{k_b T}{h} \cdot \frac{F_a}{F} \exp\left(-\frac{E_0 + \frac{1}{2}(\sigma - E\varepsilon)\lambda_2\lambda_3\lambda}{k_b T}\right) \quad (4)$$

Here  $F$  and  $F_a$  are the partition functions<sup>[2]</sup> of a unit volume of kinetic units in their initial and activated state,  $h$  - Planck's constant. Because of the forced character of deformation of a solid body, when the direction of action of the external force is continuously directed to the moving grip, it is possible to disregard the rate of jumps of the kinetic units in the direction opposite to the external force. As the kinetic unit moves the distance  $\lambda$  in one jump, so the rate of movement  $\Delta u$  of a layer with a macromolecule under strain relative to the lower layer will be equal to  $\Delta u = k_\sigma\lambda$ , and the coefficient of viscosity due to the strain will be equal to:

$$\eta = \frac{(\sigma - E\varepsilon)\lambda_1}{k_\sigma\lambda} = \frac{(\sigma - E\varepsilon)\lambda_1}{\lambda \frac{k_b T}{h} \cdot \frac{F_a}{F} \exp\left(-\frac{E_0 + \frac{1}{2}\lambda_2\lambda_3\lambda(\sigma - E\varepsilon)}{k_b T}\right)} \quad (5)$$

Let us present this expression thus:

$$\eta = A_i(\sigma - E\varepsilon) \exp\left(\frac{E_0 + b_i(\sigma - E\varepsilon)}{k_B T}\right) \quad (6)$$

where  $A_i = \frac{\lambda_1 h}{\lambda k_B T} \cdot \frac{F}{F_a}$  - is the pre-exponential factor in the expression for viscosity of flow under stress during strain of the rubber, and  $b_i = \frac{1}{2} \lambda_2 \lambda_3 \lambda$  - is the volume coefficient characterizing the structure of the molecular-kinetic units taking part in the jumping in to the vacancy, that is to say in flow. Let us assign to coefficients  $A_i$  and  $b_i$  the index  $i$  (*increment*) to indicate the growth of activation energy and viscosity for the given dependence. In this way, during the extension of the polymer network of the rubbers with a constant strain-rate  $\dot{\varepsilon}$  according to the increase of deformation, there takes place an accelerant growth of viscosity and stress in accord with Newton's law of flow:  $\sigma = \eta \dot{\varepsilon}$ , where the coefficient of viscosity  $\eta$  is determined by eq. (6).

However for the initial section of the stress-strain curves of rubbers, after a small section of Hookian elastic strain, the rate of stress growth decreases with the increase of strain to certain limits, after which there begins an increase in the rate of stress growth (see Figs. 3 and 4). It is possible to presume that in the first section inelastic deformation comes about with the jumps of molecular-kinetic units into the vacancies owing to the transfer of external stress through elastic intermolecular and interatomic bonds of the macromolecules, with the destruction of old intermolecular bonds and the generation of new bonds after the jumps of kinetic units. This process is similar to the process of inelastic deformation of non-polymeric solid bodies. This process can be described by the mechanism of flow with a decrease of activation energy according to Eyring and according to equation. (1). But, for polymer networks, deforming in accordance with the model SLS, the force resulting in flow is the difference between stress and the force of entropic elasticity  $(\sigma - E\varepsilon)$ , connected with the elastic element (spring) with the modulus  $H$ , which reflects the action of elastic forces on the flow in the dashpot. It is probable that, with small deformations, there takes place not so much strain of the total polymer network for the whole specimen, as a break-down of the amorphous globular structure of the aggregates united by intermolecular bonds. In this process, the jumping of the molecular-kinetic units is facilitated by elastic forces, conveyed through the total bonds of the aggregates of primary structure of the polymer. Thus, the failure of a part of such bonds and jumping of kinetic elements into vacancies in the direction of the applied force is facilitated at the expense of this



force. That leads to a reduction of the energy barrier to movement in the force direction by a quantity proportional to the force  $(\sigma - E\varepsilon)$ , in conformity with the SLS model. Then the viscosity of flow during strain of the rubber can be described by the equation (7) derived from the position of Eyring's theory, analogous to the inference of equation (6):

$$\eta = A_d(\sigma - E\varepsilon) \exp\left(\frac{E_0 - b_d(\sigma - E\varepsilon)}{k_B T}\right) \quad (7)$$

Here the index  $d$  (*decrement*) with the coefficients  $A_d$  and  $b_d$  shows that the given dependence describes the processes of deformation with a reduction of viscosity and of activation energy. This view of the dependence of viscosity on stress for the SLS model is connected with the fact that the reduction of activation energy is basically assumed, as mentioned above, due to of the action of elastic bonds on the break-down and subsequent restoration of intermolecular bonds with flow in the process of jumps of the kinetic units into vacancies. With this, it is possible to disregard deceleration of the jump kinetic units by the force of entropic elasticity of unwrapped chains in comparison to the action of an external force on the reduction of the potential barrier for this jumping, at least up to the moment when the accelerating growth of stress begins on the stress-strain curves of rubber.

After that moment the growth of resistance to the strain of the chain between crosslinks brings about the growth of the activation energy of flow in accordance with equation (6) and, by the same token, to an exponential increase in viscosity. This becomes apparent in the acceleration of the increase in stress at a constant strain-rate in the second section of the extension curve of an elastomer.

It is well known that the viscosity  $\eta$  and the relaxation time  $\tau_r$ , when considering the mechanical behavior of materials using Maxwell's and Voight-Kelvin models together, are related by<sup>[11]</sup>:

$$\tau_r = \frac{\eta}{H} \quad (8)$$

where  $H$  - is the elasticity modulus. Then, for the process of inelastic deformation with decreasing rate of stress increase according to the equation (7), it is possible to state:

$$\tau_r = C_d(\sigma - E\varepsilon) \exp\left(\frac{E_0 - b_d(\sigma - E\varepsilon)}{k_B T}\right) \quad (9)$$

Here the pre-exponential factor  $C_d$  is equal to  $\frac{A_d}{H}$ .

For the second section of inelastic deformation, with accelerating rate of stress increase, the relaxation time in accordance with the equation (10) grows exponentially with stress increase:

$$\tau_r = C_i(\sigma - E\varepsilon) \exp\left(\frac{E_0 + (\sigma - E\varepsilon)}{k_B T}\right) \quad (10)$$

where  $C_i = \frac{A_i}{H}$ . From this it follows that the relaxation time in phenomenological models, describing the deformation of polymers using elements of Maxwell and Voight-Kelvin are not constant but a variable parameter, depending on stress and reversible rubber-like deformation, i.e., on the fundamental peculiarity of a polymer body - of entropic character of deformation of chain macromolecules.

In view of the deduced mechanisms it is possible to quantitatively describe the stress-strain curve of a rubber using basic models of viscoelastic behavior. For a polymer network with reversible rubber-like deformation we use the three-element model of a standard linear solid (SLS), illustrated in Fig. 1. It is possible to state the connection between the two elastic and the viscous elements in this model in the form of the differential equation<sup>[11]</sup>:

$$\tau_r(H + E)\dot{\varepsilon} + E\varepsilon = \tau_r\dot{\sigma} + \sigma \quad (11)$$

or in the form of the differential equation:

$$\eta(H + E)\dot{\varepsilon} + HE\varepsilon = \eta\dot{\sigma} + H\sigma \quad (12)$$

where  $\dot{\varepsilon}$  is the strain-rate,  $\dot{\sigma}$  - the rate of the stress change in the time of deformation.

From equation (12) we obtain the coefficient of viscosity in the SLS model:

$$\eta = \frac{H(\sigma - E\varepsilon)}{(H + E)\dot{\varepsilon} - \dot{\sigma}} \quad (13)$$

For a description of the deformation process of a networked polymer with the help of equation (13) we use equations (6) and (7). For the section with an increasing rate of stress growth, we use equation (6). Equating of the equations on the right of equations (6) and (13), we obtain:

$$\frac{H(\sigma - E\varepsilon)}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = A_i(\sigma - E\varepsilon) \exp\left(\frac{E_0 + b_i(\sigma - E\varepsilon)}{k_B T}\right) \quad (14)$$

Here it means that the coefficient of viscosity  $\eta$  reflects the mechanism of flow in relation to the molecular model shown in Fig. 2 and is referring to the whole material sample that can be stretched. Taking into account that  $C_i = \frac{A_i}{H}$ , from equation (14), after the cancellation shortening of the factor  $H(\sigma - E\varepsilon)$ , we obtain equation:

$$\frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = C_i \exp\left(\frac{E_0 + b_i(\sigma - E\varepsilon)}{k_B T}\right) \quad (15)$$

Logarithmically equation (15) can be expressed as follows:

$$\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = (\ln C_i + \frac{E_0}{k_B T}) + \frac{b_i}{k_B T} (\sigma - E\varepsilon) \quad (16)$$

If the experimental data on the deformation of polymers show an observance of a linear dependence  $y$  to  $x$  where:

$$y = \ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} \quad \text{and} \quad x = \sigma - E\varepsilon \quad (17)$$

then this will justify considering as correct the proposed molecular model of strain of the macromolecular network (Fig. 2) with an increase in activation energy of viscous flow according to the growth of stress and forces of entropic elasticity. The combination of this model with standard models of viscoelasticity allows us to describe quantitatively the stress-strain curve of a rubber and to give their extrapolative prognosis.

Analogous calculations can be carried out for the first section of the inelastic deformation of rubbers, when the rate of stress increase decreased with strain. Equating the right-hand parts of equations (7) and (13) we obtain, as a result, the following equation:

$$\frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = C_d \exp\left(\frac{E_0 - b_d(\sigma - E\varepsilon)}{k_B T}\right) \quad (18)$$

After taking the logarithm of this equation we obtain:

$$\ln \frac{1}{(H + E)\dot{\varepsilon} - \dot{\sigma}} = (\ln C_d + \frac{E_0}{k_B T}) - \frac{b_d}{k_B T}(\sigma - E\varepsilon) \quad (19)$$

From the angle of slope of linear relationships (16) and (19) it is possible to calculate the quantities  $b$  as coefficients with the argument  $(\sigma - E\varepsilon)$ . These coefficients determine the dimensions of the volume of material  $b$ , in all probability depending on the number and structure of the molecular-kinetic units participating in the process of flow and change of chain conformation. That is to say, they are volume-kinetic parameters reflecting both the dimensions and the structure of kinetic units of the macromolecules taking part in the relaxing process and the given conditions of loading (form and rate of deformation) for the mechanical test that is being carried out.

The section  $(\ln C_i + \frac{E_0}{k_B T})$ , cut off by the linear relationship (16) on the axis of the ordinate, enables us to calculate the quantity  $C_i$ , if the quantity  $E_0$  is known. It is possible to determine the quantities  $E_0$  if a series of experiments on deformation are carried out at different temperatures. In a series of cases it is possible, proceeding from the chemical and physical structure of the polymer, to make an assumption about the quantities  $E_0$ , determined by different methods. For example, it is known that the potential barrier for the change of chain conformation is determined by the inhibition of internal rotation of the monomeric units of the polymer around the C-C bonds and can be about 13.8 kJ/mol (3.3 kcal/mol)<sup>[12]</sup>.

The energy of intermolecular interaction for organic polymers can be about 4.18 – 29.27 kJ/mol (1 - 7 kcal/mol). Taking as a first approximation  $E_0 = 20.93$  kJ/mol (5 kcal/mol), it is possible to calculate the quantities  $C$  from equations (16) and (19).

## Comparison with Experimental Results

To check the validity of the proposed dependence as indicated in equations (6), (7), (16) and (19), experiments were carried out to compare them with the predictions.

A specimen of rubber was stretched on a “Frank” testing machine at a rate of 200 mm/min, at a temperature of 23<sup>0</sup>C. The calculation of the extension curves was carried out to determine the relationship of true stress  $\sigma$  with the relative deformation  $\epsilon$  with regard to the decrease in area of the cross-section of the specimen in accordance with its stretching with a Poisson coefficient equal to 0.5.

In Fig. 3 we give the extension curves of the rubber specimen for both true stresses and for comparison, for nominal or conventional stress, calculated on the basis of the initial cross-section of the specimen, while being stretched at a rate of 0. 1667 s<sup>-1</sup>.

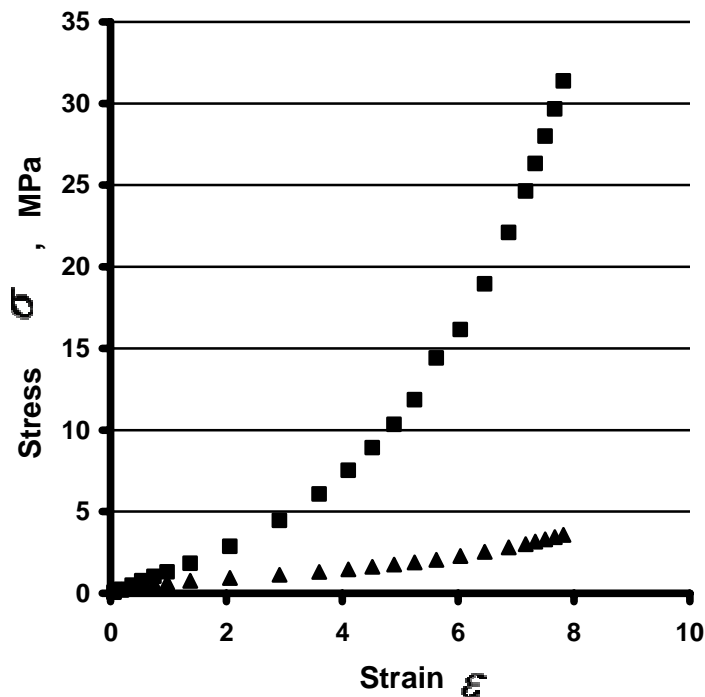


Figure 3. The dependence of true stress (squares) and nominal stress (triangles) during the elongation of rubber with stretching of the specimen at a rate of 0. 1667 s<sup>-1</sup>

Shown in Fig. 4 is a plot of the stress - strain curve of rubber, with nominal stress, on an enlarged scale to show more clearly the two sections of the extension curve.

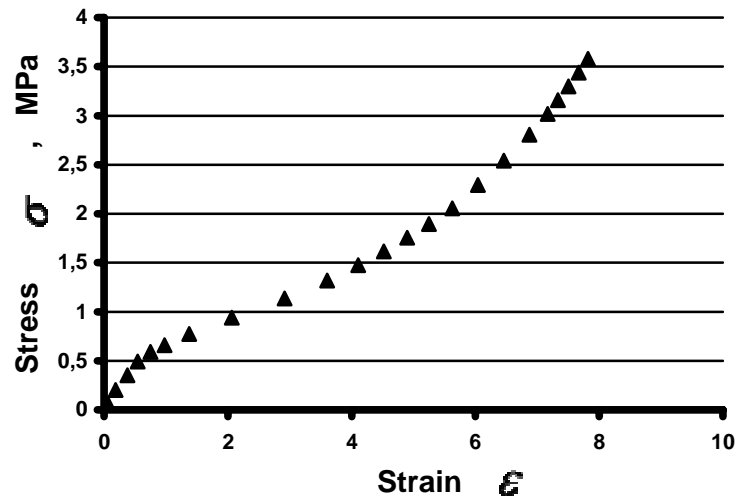


Figure 4. The dependence of nominal stress during the elongation of rubber with stretching of the specimen at a rate of  $0.1667 \text{ s}^{-1}$

The extension curves shown in Figs. 3 and 4 are characteristic for rubbers and can be explained in such a way as was already assumed above; in the first stage of rubber stretching, after a small section of the Hookian elastic deformation, there begins the processes of inelastic tension according to the mechanism of Eyring with a non-linear reduction of viscosity in conformity with equation (7). In the second stage there is an increase in the contribution of tension of the macromolecular network; this resistance to flow is connected with the increase of the force of entropic elasticity of the chain between crosslinks. This brings about an increase in the rate of stress growth with further strain.

Therefore it is necessary to describe the stress-strain curves of rubbers in terms of the two equations: in the first section of the stress-strain curve with lowering rate of stress increase – equation (19), and in the second section of the stress-strain curve with increasing rate of stress growth – equation (16). Both equations are based on the SLS model using the proposed dependence of viscosity on stress in terms of equations (6) and (7).

Figure 5 shows the dependence of  $\gamma$  on  $x$  for rubber, calculated in accordance with equation (17). When constructing this plot we used the values of relative deformation  $\epsilon$ , and stress  $\sigma$ , and also the rate of strain  $\dot{\epsilon}$  and the rate of increase of stress  $\dot{\sigma}$ , obtained from the experimental data of the “true stress-strain curve” of rubber. The values of elasticity modulus  $H$ , and rubber-like elasticity modulus  $E$ , were taken based on theoretical estimations shown in ref. <sup>[12]</sup>; i.e.  $H = 2000 \text{ MPa}$ ,  $E = 0.5 \text{ MPa}$ .

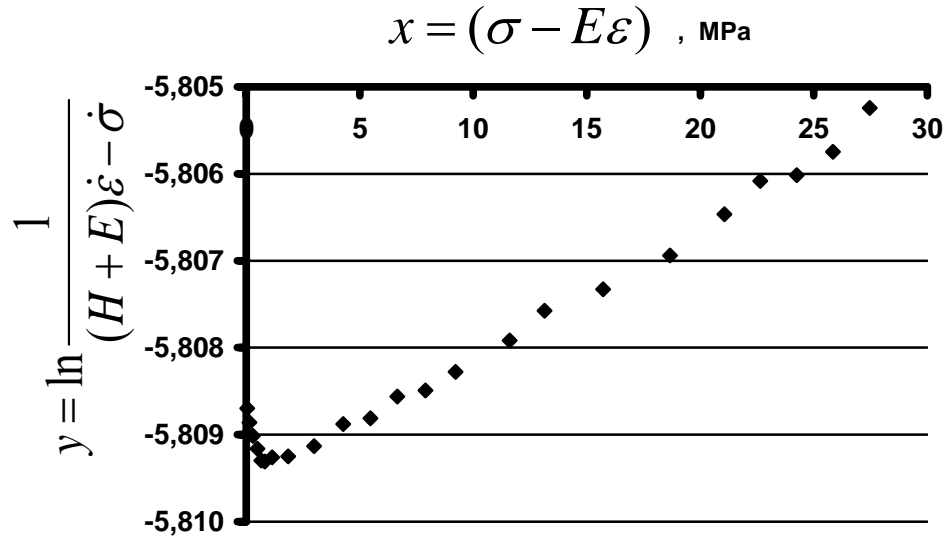


Figure 5. Plot of  $y$  against  $x$  as given in equation (17)

In accordance with the graph in Fig. 5, the two stages of inelastic deformation are reflected with negative and positive slopes of the dependence of the left parts of the equations (19) and (16) on the stress  $(\sigma - E\varepsilon)$  on the dashpot in the SLS model.

The linearization of the two parts of the stress-strain curve of rubber with a negative and positive slope of the logarithmic dependence shown above for the proposed model of deformation of a polymer network gives grounds for the confirmation of the assumptions above regarding the mechanism of rubber deformation.

In Fig. 6 is shown the relation of  $y$  against  $x$  according to equation (17) for the first section of the stress-strain curve of rubber, where processes of flow of the molecular-kinetic units are predominant, there being a decrease of the activation energy at rather small sizes of reversible deformation which are not exceeding 100-200 %. It is reflected in the negative slope for the linear dependence of equation (19). For the first five points, taking into account the difficulties of graphic differentiation on the initial section of the stress-strain curve of rubber, the coefficient of correlation of a linear relationship equal to 0.9851 can be considered as a satisfactory confirmation of the relations in equation (19) having a minus sign for the argument  $(\sigma - E\varepsilon)$ .

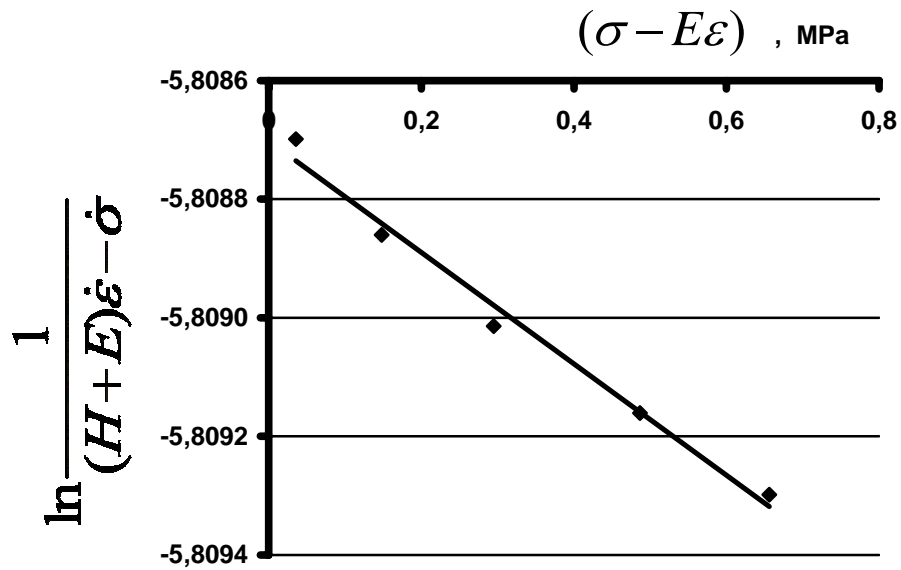


Figure 6. Plot of  $y$  against  $x$  as given in equation (19) for the initial section of the stress – strain curve of rubber

Shown in Fig. 7 is the plot of  $y$  against  $x$  for the second, basic section of the stress-strain curve of rubber (based on equation (16)) for which there is a large reversible deformation. In this section, where the changes in conformations of the stretched chains are large, there is a predominance of the process of growth of the entropic resistance to the deformation of the specimen with an increase in activation energy. This is reflected in the positive slope for the linear dependence of equation (16). The coefficient of correlation of linear dependence for the graph in Fig. 7 is equal to 0.9944 which is indicative of a good implementation of the dependence given in equations (16) and (6)



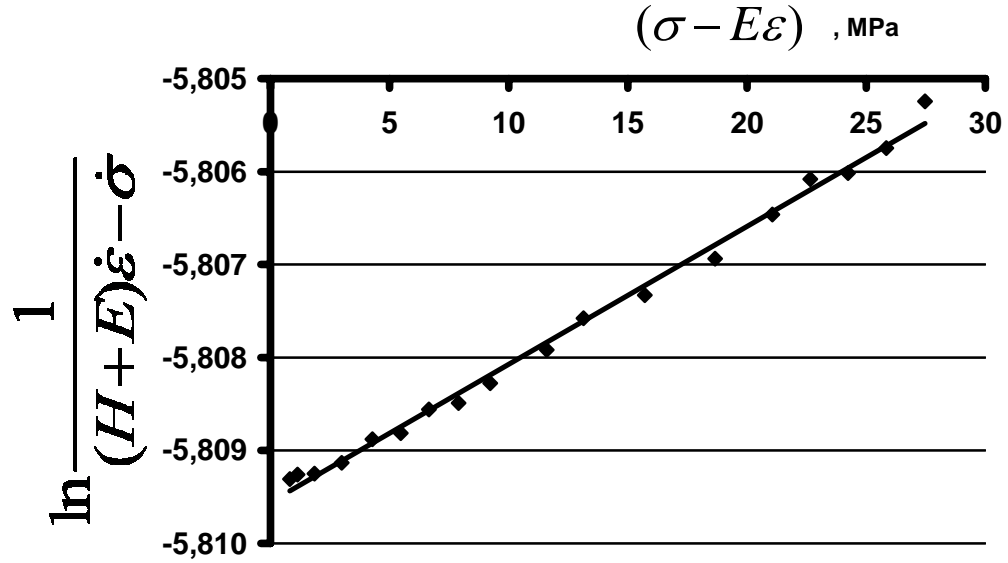


Figure 7. Plot of  $y$  against  $x$  as given in equation (16) for the second section of the stress-strain curve of rubber

From the inclination angles of the linear relationship corresponding to equations (16) and (19) and the sections cut by them on the ordinates axis, it is possible to find the values of the coefficients  $b_i$  and  $b_d$ , and the quantities  $\left( \ln C_i + \frac{E_0}{k_B T} \right)$  and  $\left( \ln C_d + \frac{E_0}{k_B T} \right)$ .

For the initial section of the stress-strain curve of rubber, in accord with equation (19), the quantity  $\frac{b_d}{k_B T}$  is  $-0.0009 \text{ MPa}^{-1}$ , and the volume coefficient  $b_d = 3.68 \cdot 10^{-24} \text{ cm}^3$ . The quantity  $\left( \ln C_d + \frac{E_0}{k_B T} \right)$  for the first section of the stress-strain curve of rubber is equal to  $-5.8087$ .

Assuming that  $E_0 \cong 20.93 \text{ kJ/mol}$  ( $5 \text{ kcal/mol}$ ), which is characteristic for the activation energy of intermolecular interaction, then the value  $C_d = 6.137 \cdot 10^{-7} \text{ s/MPa}$  and  $A_D = C_d H = 1.227 \cdot 10^{-3} \text{ s}$ .

For the second, major section of the stress-strain curve of rubber, the value of the volume coefficient is  $b_i = 0.6 \cdot 10^{-24} \text{ cm}^3$ . Lower values of the volume coefficient for equation (16) can signify the participation of a larger number of kinetic units in the process of deformation of the specimen in the major process of its tensile deformation.

For the same second section of the stress-strain curve of rubber where, with the growth of deformation, the stress increases exponentially, the value  $(\ln C_i + \frac{E_0}{k_B T})$  is -5.8096,  $C_i = 6.132 \cdot 10^{-7} \text{ s/MPa}$  and  $A_i = C_i H = 1.226 \cdot 10^{-3} \text{ s}$ .

For a comparison it is possible to refer to the values of relaxation time  $\tau_r$  and viscosity  $\eta$  with deformations and stresses at the beginning and at the end of the stress-strain curve of rubber shown in Fig. 3. For a strain of 0.187 and stress 0.242 MPa, the relaxation time  $\tau_r = 2.22 \cdot 10^{-4} \text{ s}$  and the viscosity is  $\eta = 4.439 \cdot 10^2 \text{ Pa} \cdot \text{s}$ . For a strain of 7.666 and stress 29.671 MPa, the value of the relaxation time is  $\tau_r = 3.88 \cdot 10^{-2} \text{ s}$  and the value of viscosity is  $\eta = 776.8 \cdot 10^2 \text{ Pa} \cdot \text{s}$ . These figures illustrate that, with given set values of activation energy  $E_0$ , elasticity modulus  $H$  and rubber-like elasticity modulus  $E$ , the viscosity of the rubber at the beginning of the process of deformation is small. This is evidence of weak forces of intermolecular interaction. With deformations near to the breaking-point and stresses about 30 MPa, the viscosity grows under tension by two or three orders of magnitude.

## Conclusions

Although the model and the mechanism of deformation presented in this article were considered for rubbers, i.e. for polymers in a rubber-like state in the absence of residual deformation, there is no reason to suppose that conformity to the natural laws that were found is not applicable to all polymers. But here it is necessary to bear in mind that the calculation according to equations (6), (7), (16) and (19) are correct provided that during the course of the experiment the specimen is deformed uniformly without necking or the destruction of the specimen. If necking occurs it is necessary to find means of determining the cross section and the true stress of the specimen. In addition, an appraisal of possible irreversibility of material flow is necessary. For specimens of polymers of different sizes and form, with different preparations when molded and with different chemical and super-molecular structure, there is a large variety of mechanical behavior possible. For example, the appearance at the beginning of deformation of a narrow neck which then spreads over the whole specimen, reaching large degrees of elongation<sup>[13]</sup>. This condition will call for further elaboration of the model, for example examination of the local areas of flow of the material under the action of tangent shear stresses.

Features of the structure connected with different levels of crystallinity, with different density of crosslinks for networks polymers, with temperatures ensuring glass-forming, rubber-like or

viscous-flow condition of the thermoplastics – all these leave their mark on the deformational behavior of the polymers during the various forms of testing. With strong intermolecular interaction of the chains or for high degrees of crosslinking intense destruction of the covalent bonds is possible with great stresses. All this, including rate and time of deformation, can be reflected both in coefficients  $b_d$  and  $b_i$  and in the pre-exponential factors in equations (6), (7), (16), and (19). This is necessary to be taken into consideration for the quantities appraisal of deformation curves and in the methods of prediction of mechanical properties of polymeric materials. Taking into account the above arguments the deformation mechanism proposed in this work appears to be common for all polymers in the presence of large reversible deformations. It is based on the entropy elasticity of a macromolecular network which causes an increase of the material's flow resistance in the course of deformation. The latter increases the activation energy of jumping of molecular-kinetic units of macromolecules in vacancies.

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