

## Atomic Mechanism of Fracture of Solid Polymers

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The kinetic theory of breakdown of solids, developed in recent years, considers the mechanical fracture as a cumulative process of interatomic bond dissociation by thermal fluctuations<sup>1-4</sup>.

This concept is based on an experimentally established relation between the lifetime ( $\tau$ ), the tensile stress ( $\sigma$ ), and the absolute temperature  $T$ . Under uniaxial tension the relationship between these values is well approximated by a statistical equation:

$$\tau = \tau_0 \exp. \frac{U_0 - \gamma \sigma}{RT} \quad (1)$$

where  $U_0$  is the bond dissociation energy,  $\tau_0 \approx \frac{1}{\nu}$  is the frequency of atomic vibrations,  $\gamma$  is the coefficient depending on the actual stress on atomic bonds, and  $k$  is Boltzmann's constant.

It follows from this equation that the ultimate stress ( $\sigma_b$ ) is equal to

$$\sigma_b = \frac{U_0}{\gamma} \left( 1 - \frac{kT}{U_0} \ln \frac{\tau}{\tau_0} \right) \quad (2)$$

If  $\left( \frac{kT}{U_0} \ln \frac{\tau}{\tau_0} \right) \rightarrow 0$ , then  $\sigma_b = \frac{U_0}{\gamma}$ . In the extreme case, when the magnitude of  $\gamma$  is close to the atomic volume, the strength of the solid reaches the theoretical value.

\*) In this report the experimental data of V. Korsukov are used.

The relation (1-2) has been repeatedly checked up on various amorphous and crystalline solids having different interatomic bonds.

In terms of the thermal activation theory the mechanism of polymer fracture may be divided into three stages:

1. Excitation of bonds under the action of mechanical stress.
2. Scission of the excited overstressed bonds by thermal fluctuation, and
3. Formation of submicrocracks and their coalescence into larger cracks.

A number of hypotheses on polymer fracture have been suggested, which took into account their complex structure. The presence of two types of bonds: of a strong chemical bond between atoms in polymer chains and a weak Van der Waals bond between macromolecules contributed to the division of these hypotheses into several groups.

According to one of them it is the chemical, or primary, bonds which are broken in polymers under stress. It means, that the time to failure, or lifetime, must be determined by the kinetic of accumulation of the ruptured chemical bonds. In this case the energy parameter  $U_0$  in eq. (1) has the significance of the activation energy of thermal destruction of macromolecules<sup>5)</sup>.

The opposite assumption is based on breakage of intermolecular bonds. Chain molecules slip past each other under load and due to this fact the polymer fracture occurs. In this case the molecular rearrangements will play a decisive role and will determine the time to failure, or the mechanical lifetime. The activation energy,  $U_0$ , of such a process will be determined by the rate of slippage of macromolecular segments<sup>6)</sup>.

At last, a combined hypothesis was suggested. According to it one or the other of the discussed mechanisms of fracture

takes place, depending on the conditions of testing, structure, and temperature<sup>4)</sup>. For instance, at low temperature the fracture of a glassy polymer occurs through scission of chemical bonds. The temperature being relatively high, the polymer fracture occurs through slippage and rearrangements. Unfortunately, the discussed models of polymer fracture are by their nature a priori models, based on general considerations, and not on direct experiments. I shall try, therefore, to discuss the possible mechanisms of fracture on the basis of experimental data, obtained recently by direct methods; i.e., by electron paramagnetics resonance (EPR) and infrared (IR) spectroscopy.

#### 1. Chain Scissions in Stressed Polymers

Scission of interatomic bonds under deformation and in breakdown of polymers was first studied by the EPR method by E.E. Tomashevskii, V.A. Zakrevskii, S.N. Zhurkov<sup>7-8)</sup>. Using this method of registration of the ruptured chemical bonds it was shown that under the action of mechanical stress a homolytic scission of macromolecular chains occurs and free radicals are formed. The rate of free-radical generation proved to grow exponentially with increasing tensile stress and temperature. Besides, it was shown that "mechanical" radicals initiate the local fracture and are responsible for the appearance of submicrocracks in stressed polymers<sup>9)</sup>.

The convincing evidence of the mechanical degradation of molecules has been obtained by mass-spectrometric study of volatile products evolving from polymers in the course of breakdown. The low-molecular products of the mechanical destruction of polymers, studied by V.R. Rogel, O.F. Posdnyakov and Muinov<sup>10-11)</sup> indicated that they are formed as a result of macromolecular chain scissions. At last, it has long been known from the measurements of the molecular weight of polymers that the mechanical loading leads to the rupture of polymer molecules.

The experiments listed have clearly demonstrated that the mechanical stress results in scission of chemical bonds in polymer molecules. None of the experiments, however, has

provided the answer to the question of a connection between macromolecular chain scission and polymer fracture. It was not clear whether the chain scission is the chief cause of the loss of strength process or it is only an attendant event which is due to molecular slippage.

To answer this question it is necessary to establish if the time to failure,  $\tau$ , is a single-valued function of the kinetics of chemical bond scission. For this purpose the fracture of stressed polymers was studied by IR spectroscopy. The end groups formed as a result of chain scissions were registered. The concentration of the ruptured bonds in stressed polymers was measured by the intensity of the characteristic absorption band in the infrared region of the spectrum. The possibilities of this method for studying the problem of mechanical fracture of polymers are treated in the paper by V.K. Vettegrov, S. Veliev, I.I. Novak and S.N. Zhurkov<sup>12</sup>).

To study ruptured bonds which appear under load it is convenient to use the differential spectrum measured on a double-beam spectrometer. The deformed specimen was placed into one channel of this spectrometer and a reference undeformed specimen was placed into the other channel. Under these conditions the device registered directly the number of end groups formed under mechanical load.

As an illustration Fig. 1 shows a differential spectrum of oriented polyethylene which was subjected to tensile test. The spectrum is seen to consist of a number of selective absorption bands. The difference in optical density of each band  $D = D_s - D_o$  is proportional to the concentration of end groups of the ruptured bonds. The absorption bands with maxima  $910 \text{ cm}^{-1}$ ,  $965 \text{ cm}^{-1}$ ,  $1380 \text{ cm}^{-1}$ , and  $1740 \text{ cm}^{-1}$  are known to belong vinyl ( $\text{R}-\text{CH}=\text{CH}_2$ ), vinylene ( $\text{R}-\underset{\text{R}}{\text{C}}=\text{CH}_2$ ), methyl ( $\text{R}-\text{CH}_3$ ) and oxygenated ( $\text{R}-\underset{\text{O}}{\text{C}}-\text{H}$ ) end groups, respectively.

When a polyethylene molecule is broken in the absence of oxygen the first three end groups are formed; in atmospheric conditions the fourth group containing oxygen is added. The spectroscopic study of stressed polymers has indicated that formation of end groups occur under a very small load and starts long before the specimen breaks down into parts. The rate of the end group generation turned out to increase sharply with increasing tensile stress and temperature.

These data enabled us to employ the spectroscopic technique to study in detail the process of the chemical bond dissociation and end group accumulation in stressed polymers under different conditions.

The IR spectroscopic method of studying chemical changes, which occur in a polymer specimen, shows considerable advantages over the EPR measurement of free radicals. During the experiment the radicals are partly lost due to recombinations. The spectroscopic measurements are, therefore, more reliable and independent of the experimental conditions owing to stability of end groups.

The spectroscopic technique was used to study the kinetics of chemical bond scission under uniaxial tension in creep conditions. The accumulation of end groups with time was measured at constant tensile stress ( ) and temperature (T).

The experiments were carried out in steps on a long thin polymeric strip. When time  $t_1$  was over the specimen was unloaded and the concentration of end groups,  $C_1$ , was measured. Then the specimen was reloaded for time  $t_2$ , then it was unloaded and a new concentration,  $C_2$ , was measured, etc. In this way a successive number of values:  $C_1, C_2, C_3, \dots, C_b$  corresponding to times  $t_1, t_2, t_3, \dots$  were found. By these data the curve of the end group accumulation at  $\sigma = \text{const.}$  and  $T = \text{const.}$  was plotted.

2. Kinetics of Interatomic Bond Scission in Stressed Polymers

The mechanical destruction of chemical bonds was studied on high-strength oriented polymers: high- and low-pressure polyethylene and polypropylene in atmospheric conditions.

The band  $1740\text{ cm}^{-1}$  belonging to the aldehyde group proved to be convenient as an analytical end group.

Fig. 2 shows a typical experimental curve of the aldehyde group accumulation in polyethylene at given  $\sigma$  and  $T$ .

The kinetics of end group accumulation is seen to be described in all the cases by similar curves.

The quantitative analysis of these curves has shown that they are well described by the first-order reaction equation

$$\frac{dC}{dt} = K (C_* - C_t) \quad (3)$$

where  $C_t$  is the concentration at time  $t$ ,  $C_*$  is the final concentration at  $t = \infty$ , and  $K$  is the rate constant of the end group generation reaction under load. Integrating eq. (3) we obtain the following expression for the end groups, formed during time  $t$ .

$$C_t = C_* [1 - \exp. (- Kt)] \quad (4)$$

This equality was numerically checked on a computer. The experimental data on concentrations  $C_1, C_2, C_3 \dots C_b$  were used to determine the optimal values of parameters  $K$  and  $C_*$ , satisfying eq. (3). The calculated curve  $C(t)$  for optimal parameters  $K$  and  $C_r$  is shown in Fig. 2. The experimental data are denoted by marks. It is clearly seen that the kinetics of end groups accumulation obeys the first-order monomolecular reaction law. This enables us to correlate the kinetics of molecular chain scissions with the mechanical fracture of solid polymers.

For this purpose we have to know the stress dependence of  $K$  and  $C_*$ . Table I lists the estimated values of  $K$  and  $C_*$  for polyethylene.  $K$  is seen to vary strongly with the increase in mechanical stress while  $C_*$  is practically constant. The  $K = f(\sigma)$  curve turned out to be rather steep. The stress being increased from  $20\text{ kg/mm}^2$  up to  $40\text{ kg/mm}^2$  the 10,000 fold increase in  $K$  was observed.

The mechanical rupture was found to be closely connected with macromolecular chain scission. The results of spectroscopic measurements (Fig. 3a) are plotted in Arrhenius coordinates:  $\lg K = f(\frac{1}{T})$ . It turned out that at constant  $(\sigma)$  the dependence of the rate constant  $K$  on temperature is governed by Arrhenius equation:  $K = K_0 \exp. (E_s/RT)$ .

The stress is seen to change the slope of curves, i.e., it changes the motivation energy,  $E_A$ . The more is the mechanical stress on the polymer, the less is the activation energy, and hence, the dissociation of chemical bonds is more probable and new end groups are formed easier.

The dependence of the activation energy  $E_A$  on tensile stress is well approximated by the linear function

$$E_s = E_A - \alpha \sigma \quad (5)$$

Substituting this equality into Arrhenius equation we obtain

$$K = K_0 \exp. (- \frac{E_A - \alpha \sigma}{RT}) \quad (6)$$

This expression takes into account the dependence of the rate constant  $K$  both on the temperature,  $T$ , and on the mechanical stress,  $\sigma$ .

The study of mechanical destruction of three polymers verified the validity of this formula. The kinetic parameters:  $K_0, E_A, \text{ and } \alpha$ , which determine the end group generation rate are listed in Table 2.

### 3. Relationship between the Lifetime of Polymers under Load and Kinetics of the End Group Generation

The similarity between the formulae (6) and (1) attracts one's attention. Both the mechanical lifetime,  $\tau$ , and the rate constant of the bond rupture,  $K$ , depend exponentially on the temperature  $T$ , and stress,  $\sigma$ . Both formulas are similar to Arrhenius equation with the term depending on mechanical stress ( $\gamma\sigma$  and  $\alpha\sigma$ ) introduced into it.

This similarity makes us find a more close relationship between the seemingly different mechanical and chemical processes. The possibility appears to establish if the chemical chain scission serves as the basis of the mechanical fracture of polymers. If the mechanism of fracture of polymers is identical to the interatomic bond scission, the kinetic constants of these processes ( $\tau_0$ ,  $U_0$  and  $\gamma$ ) and ( $\frac{1}{K_0}$ ,  $E_A$  and  $\alpha$ ) must be equal, respectively. If the interatomic bond rupture only accompanies mechanical fracture, this identity will not exist. With this in mind we rewrite Eq. (1) and (6) in the form

$$(U_0 - \gamma\sigma) = RT \ln \frac{\tau}{\tau_0}; \quad (E_A - \alpha\sigma) = RT \ln \frac{K_0}{K}$$

Left sides of these equations are the effective activation energies:  $U_* = U_0 - \gamma\sigma$  and  $E_* = E_A - \alpha\sigma$  under applied stress.

The values of  $U_0$  and  $K_0$  necessary for calculation of the effective activation energies were found by extrapolating the linear dependence shown in Fig. 3.

$U_*$  and  $E_*$  found in this way and calculated for different  $\sigma$  are shown in Fig. 4. This figure shows that the activation energies of the processes of mechanical and chemical destruction are equal at any value of mechanical stress. The dependence of both activation energies on tensile stress is the same. The coincidence of the slopes of the curves means that the coefficients  $\gamma$  and  $\alpha$ , as well as  $\tau_0$  and  $\frac{1}{K_0}$ , are equal. Hence, eq. (1) and (6) coincide. The initial energy barriers,  $U_0$  and

$E_A$ , found by independent measurements of lifetime and the kinetics of the end group accumulation, are listed in Table 3. The last column of the Table presents for comparison the activation energy,  $E_T$ , for thermal degradation of the same polymers, taken from the papers by V.R. Regel and O.F. Pozdnyakov<sup>11</sup>). The equality of the activation energies indicates that a connection exists between mechanical, mechanochemical, and thermal destruction of polymers.

In the original unloaded state at  $\sigma = 0$  the energy barriers of the processes compared turned out to be equal. This fact enables us to substitute the parameters of the kinetics of chemical bond rupture -  $\tau_0$ ,  $U_0$  and  $\gamma$  - for  $\frac{1}{K_0}$ ,  $E_A$ , and  $\alpha$  in the kinetic equation of fracture (1) and (2<sup>o</sup>). Having substituted these parameters we obtain: for the mechanical lifetime:

$$\tau = \frac{1}{K_0} \exp. \frac{E_A - \alpha\sigma}{RT} \quad (1a)$$

and for the tensile stress ( $\sigma_b$ ):

$$\sigma_b = \frac{E_A}{\alpha} \left[ 1 - \frac{RT}{E_A} \ln (K_0 \tau) \right] \quad (2a)$$

In this form the expression have a clear physical meaning. The constants  $K_0$  and  $E_A$  are the universally adopted Arrhenius constants, accepted in the physicochemical kinetics. The obtained kinetic equation for strength and lifetime of a polymer under load shows clearly that mechanical fracture should be considered as a thermal activation process of degradation of mechanically stressed interatomic bonds. In this case the role of mechanical stress in this process becomes clear. In the stress field the interatomic bonds are deformed. Due to this fact the activation energy for the bond rupture  $U_0$  decreases down to the value  $U_* = U_0 - \gamma\sigma$ . The more is the stress on the interatomic bond, the more is the probability of breakdown of a polymer under load, and the less are its strength and lifetime.

#### 4. Connection between the Number of Ruptured Bonds and the Breakdown of Polymers

The dependence of lifetime on the kinetics of the end group formation enables one to find a criterion for the mechanical stability of a polymer and its breakdown into parts.

The curves of the end group accumulation presented in Fig. 2 were measured up to the polymer breakdown at  $\sigma = \text{const}$ . The last point on the accumulation curves, indicated by special marks, correspond to the prebreaking end group concentration,  $C_b$ , at which the breakdown occurs.

To find a relationship between the ultimate stress  $\sigma_b$  and the number of scissions in chain macromolecules the summation was carried out over all end groups of various types, formed in the polymer to the moment of breakdown.

/ The number of scissions of macromolecules in one half of the number of end groups/ The value of the ultimate stress under uniaxial loading was varied by the change of temperature and duration of the test. In addition to the measurement in creep conditions the limiting concentration  $C_b$  was estimated in the conditions of a smoothly increasing load and deformation. The results obtained on the samples of oriented polyethylene and polypropylene are shown in Fig. 5. As one can see the total concentration of the ruptured bonds,  $C_b$ , is constant and for a given polymer does not depend on the value of the ultimate stress, temperature, and conditions of fracture. As the experiments show, the concentration  $C_b$  is a characteristic parameter, which determines the prebreaking state of a polymer and the occurrence of the breakdown under load.

The breaking concentration of the ruptured bonds in polyethylene and polypropylene turned out to be equal to  $10^{18}-10^{19} \text{ cm}^{-3}$ , i.e., it constitutes approximately 1/1000-1/10000 of all the interatomic bonds in polymer chains. If we assume that the ruptured bonds are distributed over the volume uniformly, then it is difficult to understand, why the polymer fails at such a low

concentration. It turned out that this difficulty can be easily overcome. As V.S. Euksenko, A.J. Slutsker, S.N. Zhurkov et al.<sup>13)</sup> showed in their paper, the ruptured bonds are distributed over the volume nonuniformly. The ruptured bonds are localized in microregions, forming the disc-shaped submicrocracks. Such incipient microcracks are the microconcentrators of stress. They initiate the polymer breakdown.

The estimation shows that when the concentration of the ruptured bonds is  $C_b = 10^{19} \text{ cm}^{-3}$  and the submicrocrack sizes range from 100 Å up to 1000 Å, a system of neighbouring microconcentrators of stress is formed. Interacting with each other by their stress fields, the submicrocracks coalesce into larger cracks, which in their turn unite with small cracks and form eventually a main crack, which breaks the specimen down into parts.

Thus, at a low concentration of ruptured bonds,  $C_b$ , the mechanism of scission of stressed chemical bonds is completed by the polymer breakdown.

#### Discussion

After the appearance of the first theoretical paper by A. Tobolsky and H. Eyring (1943) (6) the slippage of macromolecules was usually considered as the main mechanism of the polymer fracture under load. A low binding energy of secondary bonds and their mobility led to the conclusion that the intermolecular mechanism of fracture of polymers was the most probable.

Later E.E. Tomashevskii, S.H. Zhurkov et al.<sup>7)</sup>, employing the EPR method for the study of the micromechanism of fracture, registered the rupture of chemical bonds by the appearance of radicals. The relation between the formed "mechanical" radicals and the strength of polymers was established. The free radical generation rate proved to grow componentially with the increasing load and to obey the equation

$$\frac{dR}{dt} = A \exp. (a \quad ).$$

On the basis of these facts the question about the nature of bonding forces, responsible for strength of solids, was reconsidered in favour of the chemical bond rupture.

However, K.L. DeVries, D.K. Roylance and M.L. Williams<sup>14)</sup> in one of their recent papers, concerning the study of the mechanism of fracture by the EPR method, called in question the model of the chemical bond rupture as the basis of the polymer strength. It was caused by the fact that the free radical generation rate decreases under constant load.

Indeed, it followed from the thermal-fluctuation equation  $\frac{dR}{dt} = A \text{ cap } (a \bar{\sigma})$  that the radical accumulation rate at  $\bar{\sigma} = \text{const}$  must be constant. In the experiments a continual decrease of the rate with the increase in time was observed, which was similar to that, shown in Fig. 2 for the end groups. From these facts the authors drew the conclusion that the assumption of the thermal-fluctuation scission of chemical bonds was wrong and that the free radical generation rate was not an independent process, but was determined by the rate of intermolecular rearrangements. The results of direct observations of the chemical bond rupture, which have been presented above, make it possible to understand whether the doubts of the authors are valid.

It is quite evident that the processes of formation of radicals and end groups are interconnected. V.A. Zakrevskii, V.E. Korsukov, V.S. Euksenko et al.<sup>9)</sup> showed that the scissions of chemical bonds are initiated by "mechanical" radicals due to radical reactions. Each radical formed under stress reacts with neighbouring macromolecules and leads to the destruction of many chain molecules. The kinetics of accumulation of radicals and end groups must, therefore, obey a common law.

The checking has shown that the first-order equation can be applied to the radicals, too. The rate of formation of "mechanical" radicals at  $\bar{\sigma} = \text{const}$ . proved to be well described

by the equation  $\frac{dR}{dt} = K_R (R_* - R_t)$  where  $K_R$  is the rate constant and  $R_t$  and  $R_*$  are the running and final concentrations of radicals.

Two solutions of the above equation are possible:

The first is when the limiting concentration  $R_* \gg R_t$ . In this case  $R_t$  may be neglected and the equation for the free radical generation rate will be  $\frac{dR}{dt} = K_R \cdot R_* = \text{const}$ . Only this result was taken into account by the authors of the paper<sup>14)</sup> and led them to the denial of the atomic mechanism of fracture.

Another solution is, however, possible, when  $R_* \sim R_t$ . In this case the free-radical generation rate will not remain constant. It will diminish with the decreasing difference  $(R_* - R_t)$ .

The analysis of the experiment data for a number of polymers shows that the second case takes place. The limiting concentration  $R$  proved to be comparable to  $R_t$ . Thus, the decrease of the free-radical generation rate with time under constant tensile stress is due to the decrease of the number of overstressed bonds, the thermal fluctuation scission of which determines the low concentration of radicals  $R_*$ . In other words, one need not reconsider the mechanism of polymer fracture.

I. Becht, K.L. deVries and H.H. Kausch<sup>15)</sup>, when discussing the models of fracture of polymer fibres, set up the hypothesis that two mechanism-interatomic and intermolecular are possible. Depending on experimental conditions one or the other mechanism takes place. They believe that below the glass transition temperature,  $T_g$ , the strength is defined by scission of chemical bonds. At elevated temperatures in an high-elasticity state a polymer breaks down into parts due to molecular rearrangements and slippage of chain molecules.

To confirm this point of view the authors presented the experimental data on concentration of "mechanical" radicals, formed in cutting of nylon-6 fibres at different temperatures.

Fig. 5 (a dotted line) presents the results of their experiments. If cutting is carried out below  $T_g$ , the radicals are formed in great quantities. At elevated temperatures, however, the concentration of free radicals falls abruptly and above the glass transition temperature it is practically absent. From these data the authors concluded that the mechanism of rupture changed. Below  $T_g$  the chemical bonds are ruptured and above the glass transition temperature radicals are not formed and the rupture occurs through intermolecular rearrangements and slipping. This conclusion seems at first sight to be convincing. The question arises, however, whether the temperature dependence of the number of radicals is not connected with their high reactivity. The drop of the free-radical concentration above  $T_g$  could be due to their rapid recombination in a high-elasticity state of a polymer.

As it has been noted the measurement of the number of scissions by the end groups by spectroscopic method shows advantages over the EPR method. The end groups are stable and are preserved for a long time. So the measurement of their concentration can serve as a control measure in registration of radicals. A comparison between the data obtained by the two methods of study of ruptured bonds was, therefore, conducted. The same figure gives the results of this comparison obtained for nylon-6 and polyethylene.

One can easily see that the free-radical concentration fall above  $T_g$  is not confirmed by spectroscopic measurements. The concentration of end groups in the broken specimens remains constant and equal  $C_b$ , irrespective of whether the sample breaks down below or above the glass transition temperature.

Though the discussed papers failed to prove experimentally the intermolecular mechanism of fracture the question of the role of secondary bonds in mechanical fracture of polymers is as yet open to discussion. The molecular rearrangements in orientational strengthening, for example, are sure to influence

strongly the strength. But it is not necessarily explained by the change of fracture mechanism. In our opinion, the influence of intermolecular forces on strength is accounted for by their participation in the redistribution of the external load among atomic bonds. Owing to macromolecular rearrangements the stress on the chemical bonds being ruptured changes abruptly. In the stressed polymer the overstressed microregions are formed, the real stresses in which can exceed the average by a factor of hundreds. The existence of such highly overloaded interatomic bonds has been recently proved by direct measurements by the deformation of the absorption bands in the IR spectrum under load<sup>1)</sup>. The fraction of such overstressed bonds is not large and it is comparable to the value of the limiting concentration  $C_*$ , which has been discussed above. Such highly overloaded bonds, formed by macromolecular rearrangements, are however, ruptured first of all. They initiate the local fracture and serve as the centres of nucleation of submicrocracks. The measure of such overstressed bonds is the structure-sensitive coefficient  $\chi$ , entering into the critical equation of strength (1). The larger is the structural coefficient  $\chi$ , the higher is the overstress on the bond being ruptured and the less is the time and load which are required to break the polymer.

On the contrary, the external load being distributed more uniformly, the coefficient  $\chi$  decreases and, therefore, the real strength of the material increases. In this aspect, the immediate task in the development of the theory of strength is, in our opinion, the establishment of a functional relationship between the structural coefficient and rheological rearrangements under load and the polymer structure.

This investigation is based mainly on the results obtained in the Laboratory of Physics of Strength in Leningrad. We should like to thank the workers of our laboratory whose studies enabled us to formulate and finish this work.



We express our sincere gratitude to Dr. I.I. Novak and Dr. V.I. Vettegren for the method of spectroscopic study of the ruptured bonds, developed by them, which was used in this work.

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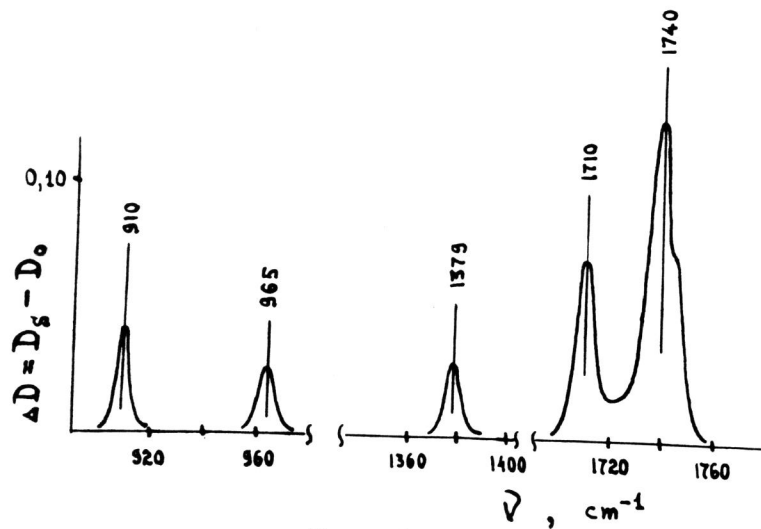


Fig. 1

Fig. 1: Difference infrared spectrum between an untreated oriented polyethylene and one stressed at room temperature.

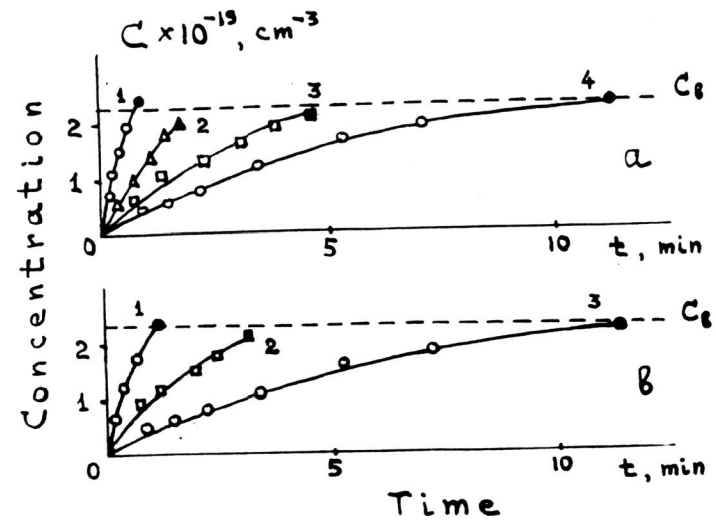


Fig. 2

Fig. 2: Dependence of concentration of end (aldehyde) groups in stressed oriented polyethylene on time.

- a) at room temperature
  - 1.  $\sigma = 36 \text{ kg/mm}^2$ ; 2.  $35 \text{ kg/mm}^2$ ; 3.  $33 \text{ kg/mm}^2$ ;
  - 4.  $28 \text{ kg/mm}^2$
- b) under uniaxial tension  $\sigma = 28 \text{ kg/mm}^2$ 
  - 1.  $T = 340^\circ\text{K}$ ; 2.  $319^\circ\text{K}$ ; 3.  $293^\circ\text{K}$

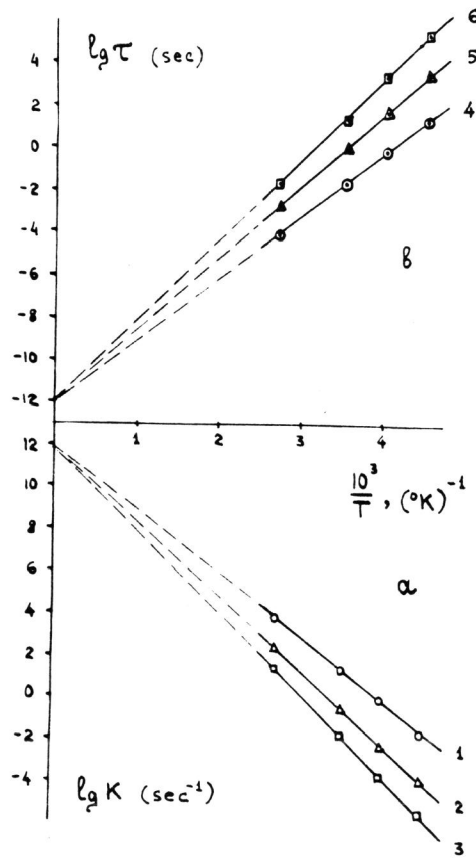


Fig. 3

Fig. 3: Dependence of the rate constant  $K$  (Fig. 3a) and lifetime (Fig. 3b) on temperature. The tensile stress is (1-4)  $40 \text{ kg/mm}^2$ ; (2-5)  $30 \text{ kg/mm}^2$ ; (3-6)  $20 \text{ kg/mm}^2$

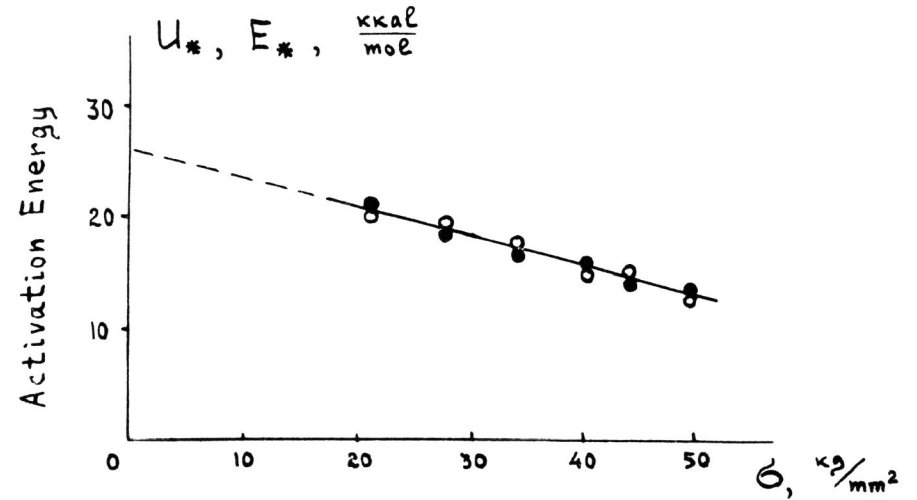


Fig. 4

Fig. 4: Dependence of the effective activation energy  $U_*$  and  $E_*$  on stress,  $\sigma$ , for oriented polyethylene  
 O - in life test  
 ● - by measurement of end groups

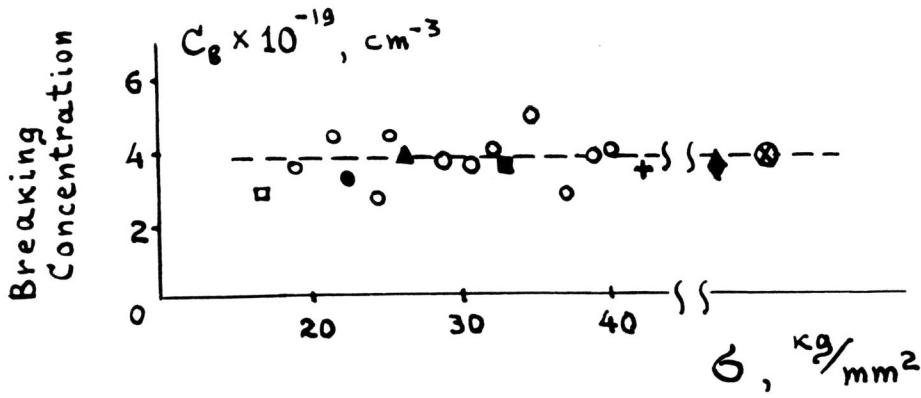


Fig. 5

Fig. 5: Dependence of the prebreaking concentration,  $C_b$ , on conditions of breaking test.  
 For polyethylene which is broken in creep conditions:  
 (+) 200°K; (■) 273°; (○) 293°, (□) 373°; (●) 333°;  
 (▲) 323°  
 (◆) - testing under uniformly increasing deformation  
 (⊕) - testing under uniformly increasing stress

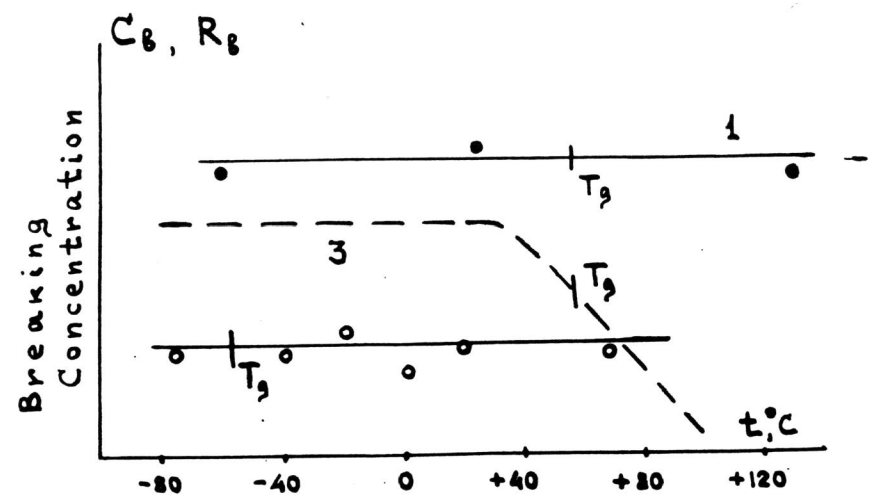


Fig. 6

Fig. 6: Dependence of the prebreaking concentration  $C_r$  on temperature  
 2. polyethylene  
 4. nylon-6  
 The curve 3 - by the data of the paper (15)