

## MECHANICAL FAILURE OF SOLID POLYMERS

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THE depth and breadth of the physical studies of failure in various materials is determined in many respects by their extent of application in technology. The furthest advances have been made in studying the failure of crystalline materials, especially metals.<sup>[1,2]</sup>

Here we can distinguish three major approaches, which have successively developed from one another: 1) the study of the macroscopic laws of failure, 2) the study of the bulk and local changes in a stressed material preceding and accompanying failure, and 3) the development of a theory of failure. Naturally, these approaches must be undertaken in the study of failure in any type of solids. This article will try to clarify the current status of the problem of the nature of the mechanical failure of solid polymers, principally amorphous ones. It will not pretend to give a complete review of all the material in the literature. It will be confined to discussing only the fundamental physical results obtained in this field in recent years. Only the simplest forms of failure will be discussed, since the failure of polymers in complex stress states, under crushing or cutting, under the action of surface-active media, etc., has been poorly studied. The systematic analysis of data on the effect on the strength of polymers of such factors as the molecular weight, chain structure, degree of crystallinity, scale effect, and orientation, has also not been considered. Some information on these problems can be found in the reviews.<sup>[16,142]</sup>

## I. SOME IDEAS ON FAILURE IN SOLIDS

The first ideas on the mechanism of failure in solids were formulated in some theoretical estimates of the strength of crystal structures.<sup>[3-5]</sup> Here they meant by the strength the stress at which the equilibrium between the external load and the internal forces due to interatomic interaction was destroyed. In the simplest

case, that of tension, the destruction of the equilibrium was ascribed to the separation of adjacent atomic planes normal to the direction of tension to a distance at which the interatomic attraction forces begin to decline. Since all the atomic planes were considered equivalent, failure of a crystal under tension was indeed represented as a simultaneous separation of the crystal into individual atomic planes (into individual atoms under homogeneous tension). The theoretical strength of crystals calculated under these assumptions proved to be hundreds or thousands of times greater than the ultimate strength observed experimentally.

The search for the reasons for this discrepancy has developed along two lines. Some of the researchers<sup>[6]</sup> consider that the lattice theory itself is imperfect. They point out that one must make a correct account of not only the nearest neighbors, but also of the long-range interatomic interactions. The important role of the long-range interactions is illustrated by the example of melting. Here a change practically solely in the long-range order results in a radical change in the properties of the crystal. According to<sup>[6]</sup>, we must first of all refine the theory of the strength of an ideal crystal, and then try to compare it with experiment.

Most of the researchers<sup>[1]</sup> are inclined to consider the conclusions of the theory regarding ideal lattices to be correct. They explain the discrepancy with experiment by the fact that ideal crystals do not exist, and that in real objects failure does not at all occur in the way assumed in the lattice theory.

An impetus toward the emergence of this viewpoint was given by the studies of Griffith based on the energy theory of failure.<sup>[7,8]</sup> Griffith showed that the low strength of solids can be explained by the appearance, even under moderate loads, of great local excess stresses at defects, which inevitably exist in every real material. By defects one usually means empty

microcracks. Under average stresses corresponding to the ultimate strength, the excess stress at the end of one of the cracks becomes equal to the theoretical strength. The crack begins to propagate with a velocity close to that of sound, progressively dividing the specimen into parts. At average stresses below the ultimate strength, the material does not fail. The cracks are stable. Thus, according to Griffith, the discrepancy between the calculations and experiment is explained by the fact that the failure is localized in one or a few of the "weakest" cross-sections of the object, and does not take place simultaneously at all points of the fracture surface.

Subsequently, Griffith's theory has been considerably refined (see [9-13], etc.). Its main assertion on the effect of cracks on the strength of real materials has been most clearly confirmed in the studies of A. F. Ioffe with rock salt. [4]

Surface cracks are the decisive factor for this substance. On the basis of experiments with thin glass fibers, A. P. Aleksandrov and S. N. Zhurkov [14] have called attention to the necessity of taking into account the internal defects. According to [14], the strength-reducing defects are distributed at random throughout the volume of the object, and differ in "degree of danger." On the basis of these concepts, the increase in strength with decreasing dimensions of the specimen (scale effect) could be explained and a mathematically-formulated statistical theory of strength was derived (references [15,16], etc.).

Within the framework of the usual variant of Griffith's theory, failure arises "at a critical point," i.e., only at a strictly defined stress. Consequently, the ultimate strength must characterize the degree of imperfection of the material and define the mean stress level at which it can remain for an indefinitely long time without failure.

However, experiment shows that solids can fail under the action of loads several times smaller than the ultimate strength. In engineering practice this phenomenon is called "static fatigue."\* For a long time it was considered to be something incidental to the seemingly general type of failure according to Griffith's scheme, and as something characteristic of only certain materials or under specific conditions, e.g., when corrosive media act on the specimen.

The studies of S. N. Zhurkov and his associates in recent years have shown that the phenomenon of static fatigue can be observed in any solid, when tested either in air or in a high vacuum. It turned out that static fatigue is described by approximately the same empirical laws for materials of the most varied structure. These studies permitted them to state that failure is a result of irreversible changes in the material, whose rate of accumulation is determined by the value

\*The terms "delayed failure," "long-term strength," "static failure," etc. are also used.

of the stress, the temperature, and the structure of the material. This implied that there is no point in speaking of the ultimate strength as being the stress at which the object is on the verge of failing unless one specifies the time over which this stress acts. According to Zhurkov, the course in time is one of the most essential features of the mechanical failure of all solids.

## II. EXPERIMENTAL STUDIES OF FAILURE OF SOLID POLYMERS

### 1. Test of the applicability of Griffith's method

According to Griffith, the free energy  $F$  of a stressed elastic object containing a crack is composed of the elastic energy  $U$  stored in the object and the surface energy  $S$ . We assume that  $S$  varies only because of changes in the dimensions of the crack, and that the boundaries of the object are not displaced (the external forces do no work). The condition for equilibrium in the object, i.e., stability of the dimensions of the crack, is defined as

$$\frac{\partial F}{\partial l} = \frac{\partial U}{\partial l} + \frac{\partial S}{\partial l} = 0, \quad (1)$$

where  $l$  is the characteristic dimension of the crack.

The possibility of describing the experimental data on polymers using quantitative relations derived from condition (1) for various cases of fracture has been tested only recently.

In [17,18], tension tests were carried out on polymethylmethacrylate and polystyrene specimens containing previously introduced open cracks of "natural" configuration (superficial cracks). The depth  $l$  of the cracks could be varied by grinding off the cracked surface of the specimen. The dimensions of the specimens were also varied. It turned out that the ultimate strength  $\sigma_f$  increases in proportion to the quantity  $1/\sqrt{l}$  (Fig. 1). Here hundredfold changes in the rate of extension did not result in appreciable deviations from this law. This result agrees with the formula derived from condition (1):

$$\sigma_f = \sqrt{\frac{2ET}{\pi l}}, \quad (2)$$

which relates the ultimate strength  $\sigma_f$  with the elastic

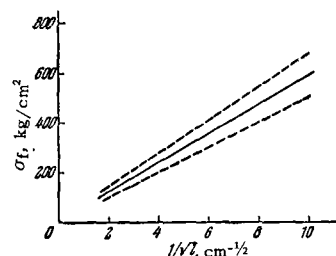


FIG. 1. Graph of the relation of the ultimate strength  $\sigma_f$  to the reciprocal of the square root of the length  $l$  of the open crack for polymethylmethacrylate. Calculated from data of [17]; solid line—mean relation; dotted line—limits of deviation of the data,  $\theta = 20^\circ\text{C}$ .

modulus  $E$ , the specific surface energy  $T$ , and the dimensions of the crack. This formula has been derived for an infinite elastic body under homogeneous tension, containing a transverse crack of length  $2l$  situated perpendicular to the direction of tension. The specific surface energy  $T$  of the polymers was calculated by use of Eq. (2). It proved to be  $(3 \pm 0.8) \times 10^5$  erg/cm<sup>2</sup> for polymethylmethacrylate and  $(1.7 \pm 0.6) \times 10^6$  erg/cm<sup>2</sup> for polystyrene.<sup>[17,18]</sup>

In <sup>[19,20]</sup>, the failure of polymers upon splitting by a wedge was studied according to Griffith's scheme. A diagram of the experiments is shown in Fig. 2. In order to ensure linear propagation of the crack, the specimen was compressed along the direction of splitting. This method made it possible for the first time to carry out a "controllable" failure while maintaining a simple geometrical configuration of the failing object. An analysis of this case using Eq. (1) leads to the following relation between the length  $l$  of the equilibrium crack, its aperture  $\delta$ , the width  $b$  of the specimen, and the constants of the material:

$$\frac{\delta^2}{l} = \frac{64}{3} \left( \frac{l}{b} \right)^3 \frac{T}{E}. \quad (3)$$

The experiments were performed on polymethylmethacrylate and polystyrene at room temperature. The specimen dimensions and length of the equilibrium cracks were varied over wide ranges. The experimental data plotted in coordinates of  $(\delta^2/l)^{1/3}$  versus  $l/b$  were represented by curves that asymptotically approached the theoretical straight lines in the region of large  $l/b$  (Fig. 3). It was shown in <sup>[21]</sup> that if one calculates the elastic energy of the specimen more rigorously, the experimental relations fit more closely to the theoretical. The calculated specific surface energy  $T$  at room temperature proved to be  $4.8 \times 10^5$  erg/cm<sup>2</sup> for polymethylmethacrylate, and  $2.5 \times 10^6$  erg/cm<sup>2</sup> for polystyrene, i.e., near the values obtained in <sup>[17]</sup>.

In <sup>[22]</sup>, analogous experiments on the same polymers were performed at various temperatures. It

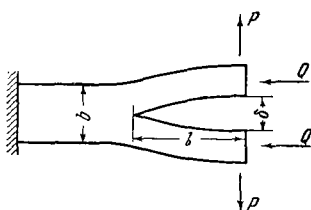


FIG. 2

FIG. 2. Diagram of the experiments on controlled failure in splitting by a wedge.<sup>[19]</sup>

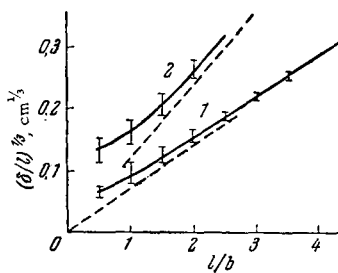


FIG. 3

FIG. 3. Experimental graphs of the relations of  $(\delta^2/l)^{1/3}$  to  $l/b$  for polymethylmethacrylate (1) and polystyrene (2).<sup>[19]</sup> The limits of deviation of the data are indicated;  $\theta = 20^\circ\text{C}$ . Dotted line = the theoretical relation.

turned out that when the temperature was raised from  $20^\circ$  to  $80^\circ\text{C}$ , the surface energy increases by a factor of  $1\frac{1}{2}$ . In <sup>[23]</sup>, Griffith's hypothesis was applied to the analysis of the tearing of rubber. Here the surface energy was as much as  $3 \times 10^7$  erg/cm<sup>2</sup>.

All these experiments show that in an entire series of cases, the failure of solid polymers, as for other materials, can be described by quantitative relations derived from Griffith's hypothesis. However, we cannot consider them to be proof of the generality of this hypothesis, treating failure as being a "critical" breakdown of equilibrium in the body + crack system. Conversely, we can see its limitations even within the limits, e.g., of the experiments on splitting. Indeed, when one decreases the load, the splitting cracks in polymers do not close, in contradiction to what is implied by Griffith's scheme. The value of  $T$  proves to be greater upon splitting in wetting liquids than in air.<sup>[20]</sup> This means that the ultimate strength must rise according to Eq. (2). However, in fact the strength of polymers under tension in liquids declines. Also, the phenomenon of gradual, rather than instantaneous, establishment of equilibrium crack dimensions in splitting and other facts do not fit Griffith's scheme.

In the above-mentioned studies it was shown that  $T$  is a constant. Griffith ascribed to it the meaning of the surface energy. For a polymeric substance, the latter should be no greater than the energy of the chemical bonds per cm<sup>2</sup>. With closest packing, the energy of the C—C bonds amounts to  $\sim 5 \times 10^2$  erg/cm<sup>2</sup>. This is a thousand times smaller than experiment indicates for the value of  $T$ .

The reason for this discrepancy consists in the fact that the failure of polymers is accompanied by a considerable deformation of the material in the region of the end of the crack. Practically all the elastic energy released in the growth of the crack is used up in bringing about this deformation.\* This is confirmed also by more direct observations. Thus, it has been noted in <sup>[24,25]</sup> that fracture surfaces of polymers seem brilliantly colored in reflected light. This is evidence of the existence of a thin surface layer of oriented polymer material (subjected to "cold" drawing). An analysis of the interference patterns observed at the ends of the cracks in polymethylmethacrylate<sup>[28]</sup> led to the conclusion that failure is preceded by the formation of a narrow wedge-shaped zone of altered polymer material. We see from the photograph of the emergence of a cleavage crack at the specimen surface (Fig. 4) that the width of this zone (twice the thickness of the surface layer) for polymethylmethacrylate at room temperature amounts to  $\sim 4 \mu$ . If we assume that the stresses and strains at the end of the crack are no less than the corresponding macroscopic quantities referred to the instant of rupture ( $\sigma_f \approx 8 \text{ kg/mm}^2$ ,  $\epsilon_f$

\*An analogous pattern had been previously established for metals.<sup>[26,27]</sup>

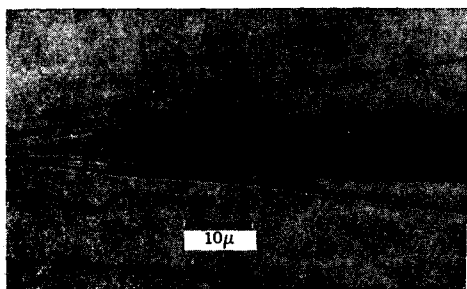


FIG. 4. Micrograph in reflected light of the end of a crack made by splitting a wedge in polymethylmethacrylate,  $\theta = 20^\circ\text{C}$ .

$\approx 0.1$ ), we can easily calculate that the energy of the local deformation per unit area of the crack surface must be no less than  $10^4$  erg/cm<sup>2</sup> for this polymer. This calculation directly shows that what the quantity  $T$  characterizes is namely the local-deformation process preceding failure. Since for polymers the deformations around the crack are irreversible in the usual sense of this word,\* the quantity  $T$  is a measure of the dissipation of energy, and loses the meaning of being a thermodynamic parameter, as Griffith thought.

This same effect has had the result that, in an attempt<sup>[129]</sup> to compare the theoretically-calculated values of the rate of propagation of a Griffith crack † in an ideally-elastic object with the experimental data obtained upon fracture of polymethylmethacrylate sheets, a sharp discrepancy between calculation and experiment was observed in the initial stages of failure.

The possibilities of the phenomenological approach to failure in real materials, the groundwork of which was laid by Griffith, are far from exhausted yet.<sup>[13]</sup> However, as we see from what has been said, at present this approach permits us to analyze the failure of polymers only under the conditions that we can represent them by the model of a material obeying Hooke's Law. Usually this is true in the last "rapid" stages of failure. In the initial stages of failure, which are the most interesting from the physical standpoint, the relaxation laws of the mechanical behavior of the polymer in the failure zone and the inevitably concomitant time effects are manifested; the energetic theories of failure do not describe these stages. Considerably more information along this line has been obtained by studying static fatigue in polymers.

\*That is, they do not disappear upon removal of the load, although they can be removed by heating above the softening temperature. Such deformations in polymers are commonly called "retarded elastic" ones.<sup>[128]</sup> The laws for their appearance have a clearly marked relaxation character. In essence, they are a "delayed" rubbery deformation, the rate of establishment of which depends markedly on the stress and the temperature.

†To do this, one must also take into account in Eq. (1) the kinetic energy of the motion of the material as the crack grows.

## 2. Time-dependence of the strength of polymers

The fundamental experimental characteristic of the resistance of a material to static failure is its mechanical life (breaking time), or the time  $\tau$  elapsed from the instant of loading with a constant load to the instant of failure. The fundamental law to be determined experimentally is the relation of the breaking time  $\tau$  to the stress  $\sigma$  and the temperature  $T$ , usually termed the temperature-time-dependence of the strength. Most often, one determines the breaking time under uniaxial tension, while ensuring constancy of the tensile stress independently of the amount of deformation of the specimen with the aid of special apparatus.<sup>[29-34]</sup> Considerably more rarely, mainly in applied studies, the time-dependence of the strength is studied in other stress states.

The literature contains information on the temperature-time-dependence of the strength under tension for polystyrene,<sup>[35-37]</sup> polymethylmethacrylate and its copolymers,<sup>[38-42]</sup> polyvinylchloride,<sup>[85]</sup> ebonite,<sup>[42]</sup> polyamides,<sup>[35,43,44]</sup> cellulose derivatives,<sup>[35,41,45,42,32]</sup> and fibers made of capron, polypropylene, teflon, and other polymers.<sup>[46-50]</sup> The static failure of polyvinylchloride has also been studied under homogeneous tension,<sup>[31,52]</sup> polymethylmethacrylate under torsion and bending,<sup>[53]</sup> and laminated plastics under compression.<sup>[54]</sup> Static failure of polymers in the rubbery state has been studied in<sup>[55-57]</sup> and elsewhere.

The basic problem to be solved in the cited studies consisted in determining the analytic form of the empirical relation between  $\tau$ ,  $\sigma$ , and  $T$ . The best-known studies in this regard are those of S. N. Zhurkov and his associates. In their very first paper<sup>[35]</sup> they showed that the relations

$$\tau = Ae^{-a\sigma} \text{ for } T = \text{const}, \quad (4)$$

$$\tau = Be^{\frac{U}{kT}} \text{ for } \sigma = \text{const}, \quad (5)$$

which had been previously been established<sup>[46]</sup> for fibers of nylon, rayon and cotton, give a good description of the breaking time under tension for a large number of polymer (and non-polymer) materials.

An example confirming the validity of Eq. (4) is given by the data on polymethylmethacrylate<sup>[39]</sup> (Fig. 5,a). It is valid for this material at  $20^\circ\text{C}$  over a range of variation of the breaking time of 8-9 orders of magnitude. However, in some cases the linear dependence between  $\log \tau$  and  $\sigma$  implied by Eq. (4) does not hold even at room temperature (Fig. 5,b, ebonite, from the data of<sup>[42,58]</sup>). Usually this phenomenon is explained by a change in the properties of the original material during the time that it is under load. The reason for the change in properties could be crystallization<sup>[35]</sup> or orientation hardening<sup>[58]</sup> under tension.\* From this standpoint, it is hard to explain the behavior

\*There is no consensus with regard to crystallization (cf.<sup>[35]</sup> and<sup>[55,56]</sup>).

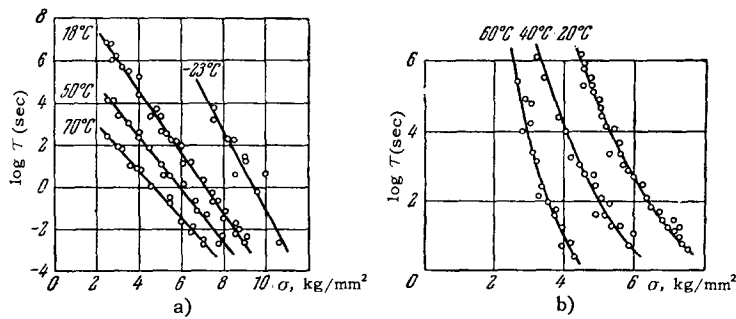


FIG. 5. Time-dependence of the strength for polymethylmethacrylate (a), and for ebonite (b)<sup>[58]</sup> at various temperatures.<sup>[39]</sup>

of ebonite, since crystallization and orientation hardening are observed only at high strains. For ebonite at 20°C, where the non-linearity of the experimental log τ-σ relation is already evident, the strain does not exceed 7-8%. Possibly this case is an example of a premature "natural" deviation from Eq. (4), such as is observed only in the low-stress region for other polymers. In this region, Eq. (4) loses its physical meaning, since it implies that the material fails at σ = 0. The breaking time of a real specimen cannot be less than the time for propagation of elastic vibrations over distances equal to the transverse dimension of the specimen. Hence, Eq. (4) is also limited in applicability on the high-stress side.<sup>[60]</sup>

As for Eq. (5), it is confirmed by all the existing experimental data for polymers. The graph of the log τ - 1/T relation for polymethylmethacrylate and ebonite is given (Fig. 6) as an example. The analysis of these relations shows that the quantity U in Eq. (5) is a linear function of the stress having the form U = U<sub>0</sub> - γσ (Fig. 7), where γ is a constant. In contrast to solid polymers, it has been shown that U is independent of the stress for rubbers.<sup>[55,56,61]</sup> An expression of the type

$$\tau = A\sigma^{-m}e^{\frac{U_0}{kT}} \quad (6)$$

has been proposed<sup>[61]</sup> to describe the temperature-time dependence of the strength of rubbers.

Bearing in mind what we have said concerning Eq. (4) and the fact that direct measurements of the temperature-dependence of the breaking time are restricted to a rather narrow temperature range by vir-

tue of the strong dependence of τ on σ, we must take an equation of the following form in order to describe rigorously the temperature-time-dependence of the strength of polymers:

$$\tau = f(\sigma, T)e^{\frac{U_0 - \gamma\sigma}{kT}} \quad (7)$$

In order to determine f(σ, T) exactly, we need a further extension of the range of stresses and temperatures in determination of the breaking time and a thorough statistical treatment of the data. An attempt to determine f(σ, T) more precisely for polymethylmethacrylate is found in <sup>[62]</sup>.

As S. N. Zhurkov has shown,<sup>[39]</sup> we can neglect the dependence of the coefficient of the exponential term on σ and T over a considerable range of stresses and temperatures, and describe the experimental breaking-time data by the relation

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{kT}}, \quad (8)$$

where τ<sub>0</sub>, U<sub>0</sub>, and γ are constant coefficients. The same relation had been previously established for metals. Here it turned out<sup>[39,63,64]</sup> that in most cases the coefficient τ<sub>0</sub> is 10<sup>-11</sup>-10<sup>-13</sup> sec, coinciding with the characteristic vibration period of the atoms in the crystal, U<sub>0</sub> is numerically equal to the energy of sublimation of the given metal, while γ depends on conditions of specimen preparation, such as cold work, annealing, etc.

Recently S. N. Zhurkov and S. A. Abasov have studied the long-term strength of fibers of rayon, polypro-

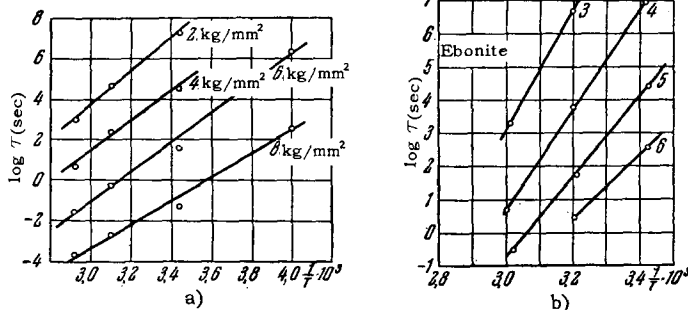


FIG. 6. Temperature-dependence of the strength for: (a) polymethylmethacrylate, and (b) ebonite, drawn from the data of Fig. 5. The numbers give the stress in kg/mm<sup>2</sup>.

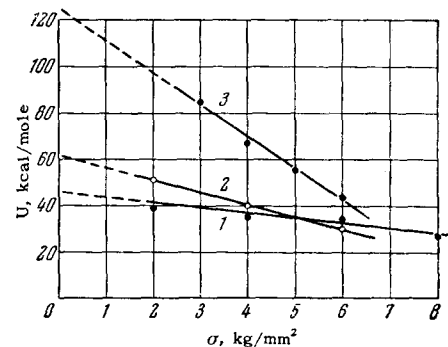


FIG. 7. Graphs of the relation of the coefficient U to the stress for 1-polymethylmethacrylate,<sup>[39]</sup> 2-celluloid,<sup>[17]</sup> and 3-ebonite.<sup>[58]</sup>

pylene, capron, and other polymers.<sup>[47-50]</sup> They established that Eq. (8) holds for all cases. An analysis of the change in the coefficients in this equation as one goes from one type of polymer to another, or varies such characteristics as the degree of orientation, the plasticizer content, and the degree of polymerization for a given polymer, showed the following. The coefficient  $\tau_0$  remained constant in all cases, being  $10^{-12}$  sec. The value of  $U_0$  proved not to depend on orientation, plasticizer content, or molecular weight, but varied only when one went from one polymer to another. An essential feature was that  $U_0$  coincides to a high degree of precision with the values given in the literature for the activation energy of the process of thermal decomposition of the corresponding polymers. Just as with metals, only the coefficient  $\gamma$  proved to be structure-sensitive. Every influence that increase the breaking time, such as an increase in the degree of stretching of fibers made of a given polymer, leads to a regular decrease in  $\gamma$ . Conversely, changes in the structural characteristics that decrease the breaking time bring about an increase in this coefficient. We should especially note a study of the effect of the degree of polymerization performed on capron fibers.<sup>[50]</sup> The degree of polymerization was varied by decomposition of the fibers by ultraviolet illumination. This method permitted strict fixation of the other parameters (e.g., the orientation of the macromolecules). They were able to establish a quantitative relation between  $\gamma$  and the degree of polymerization  $P$  in the form of the equation

$$\frac{1}{\gamma} = \frac{1}{\gamma_\infty} - \frac{p}{\gamma_\infty P}$$

(where  $P$  and  $\gamma_\infty$  are constants). This result had been predicted theoretically in<sup>[65]</sup>. The experimental relation of  $\gamma$  to  $P$  for capron is shown in Fig. 8.

These laws made it possible for Zhurkov to formulate the following ideas on the physical peculiarities of the process of failure of polymers.<sup>[46]</sup> The fact that the strength is time-dependent and that the empirical time laws are general for all solid polymers permits one to state that failure is a kinetic process, and that time is a fundamental characteristic of fail-

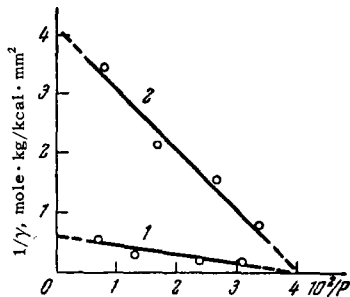


FIG. 8. Graphs of the relation of the coefficient  $\gamma$  to the degree of polymerization  $P$  for capron. 1—Oriented fiber; 2—unoriented fiber.<sup>[50]</sup>

A comparison of the activation energy  $U_0$  of the failure process with the activation energy  $Q_0$  for thermal decomposition and the theoretical energies  $W_0$  of the corresponding C—C bonds

| Material               | $U_0$ ,<br>kcal/<br>mole <sup>49</sup> | $Q_0$ ,<br>kcal/<br>mole* | $W_0$ ,<br>kcal/<br>mole <sup>56</sup> |
|------------------------|--|---------------------------|--|
| Teflon                 | 75.0                                   | 76—80                     | 69.6                                   |
| Polypropylene          | 56.0                                   | 55—58                     | 55                                     |
| Polymethylmethacrylate | 54.0                                   | 52—53                     | —                                      |
| Polystyrene            | 54.0                                   | 55                        | 52.5                                   |
| Polyvinylchloride      | 35.0                                   | 32                        | 36                                     |

\*From various source references.

ure. The form of the temperature-dependence of the breaking time is evidence that failure is an activation process whose rate essentially depends on the energy  $kT$  of the thermal fluctuations. Now, the pre-exponential coefficient  $\tau_0$  is equal to the period of vibration of the atoms linked by chemical bonds. Also, the value of  $U_0$  equals the energy of the chemical bonds, depending on the structure of the side substituents<sup>[66]</sup> (see the table). Further,  $U_0$  coincides with the activation energy of thermal decomposition and does not vary with the factors determining the intermolecular interaction. These facts indicate that failure in polymers is based on a process of breaking of chemical bonds. This process requires the surmounting of the energy barrier  $U_0 - \gamma\sigma$ , whose value depends on the stress. From this standpoint, failure of polymers is a mechanochemical process in which the role played by the mechanical stress amounts to accelerating the reaction of C—C bond breakage through thermal fluctuations. However, an important role is played here by the intermolecular interactions, since the lowering of the energy barrier is determined by the quantity  $\gamma$ , which depends on the factors determining the inter-chain interactions. In Zhurkov's opinion, the quantity  $\gamma$  is a characteristic of the uniformity of distribution of the load over the polymer chains.

We can consider these ideas to be directly confirmed by some experiments showing that macroradicals are formed in the mechanical crushing of polymers (reference<sup>[144]</sup>, etc.), and that the chemical products generated in thermal decomposition and failure are similar.<sup>[145]</sup> However, we must note that there are experiments<sup>[146]</sup> comparing the amount of macroradicals formed in crushing with the free surface formed and with the molecular weight of the crushed material. These experiments indicate that the breaking of chemical bonds and the formation of macroradicals may not be the primary act in the failure of

polymers.\* The process of thermal decomposition is also a complex combination of many reactions, and the problem of the meaning of the activation energy for thermal decomposition has not yet been elucidated.

Many studies have shown<sup>[41,45,46,35,40,67]</sup> that the total time elapsed up to failure does not depend on how the load has been applied: continuously until the specimen breaks, or with interruptions ("rests") of any length. The fact that the breaking time in an ordinary test is equal to the sum of the periods that the specimen is under load in the case of interrupted loading remains valid, independently of the conditions of "rest" of the specimens, whether they be at the temperature of the experiment, or at temperatures above the softening point, or under irradiation.<sup>[40,42]</sup> These observations show that the characteristic peculiarity of the development of failure in the course of time is its irreversibility. Every action of a force on the material causes it to lose the ability to resist a subsequent stress. In<sup>[68]</sup>, a series of hypotheses has been proposed, stemming from the fact of irreversibility of failure, and permitting one to describe quantitatively the process of accumulation of "partial" failures. The simplest of these amounts to the idea that the condition for fracture must be that the sum of the partial times of action of the load must equal unity. For stepwise loading, the condition for fracture can be written as

$$\sum_i \frac{\Delta t_i}{\tau(\sigma_i)} = 1, \quad (9a)$$

and for continuous loading, as

$$\int_0^{t_f} \frac{dt}{\tau[\sigma(t)]} = 1, \quad (9b)$$

where  $\Delta t_i$  is the time of action of the  $i$ th loading, and  $\tau(\sigma_i)$  is its corresponding breaking time, and  $t_f$  is the time elapsed until fracture when the load is continuously varied in time according to  $\sigma = \sigma(t)$ .

Equations (9) have served as the basis for experimental comparison of the time-dependences of the strength with the results of tests in tension at constant rate and with cyclic loading.<sup>[67]</sup> The object of study was polymethylmethacrylate films. They were able to show that if one knows the parameters of the time-dependence of the strength [A and  $\alpha$  in Eq. (4)], then with the aid of Eqs. (9) one can predict the results of tests having other loading schedules. This means that the time effects in failure, which are especially plainly manifested in experiments under constant loading, also occur under any other types of loading.

One cannot always make a quantitative transfer from the static laws to the dynamic ones with the aid of Eqs. (9). For massive polymer samples, the basic reason

for this is that one cannot take into account the overheating of the specimens in the dynamic tests. In the cases in which these and other methodological difficulties have been eliminated,<sup>[70]</sup> one still cannot get complete agreement between the dynamic and static breaking times. In<sup>[70]</sup>, this is explained by the fact that under the dynamic conditions the value of  $\gamma$  in Eq. (8) cannot be considered to be constant. Indeed, if we ascribe to the quantity  $\gamma$  the meaning of being a measure of the uniformity of distribution of the load at different points of the specimen, its value for polymers must be determined by the processes of stress relaxation at local defects. Naturally, these processes can take place in different ways under static and dynamic loading.

A considerable deviation of the data from specimen to specimen is unavoidable in experiments to determine the breaking time. The nature of the statistical distribution of breaking times for polymers has been studied experimentally in<sup>[35,40]</sup>. On the basis of an analysis of the laws governing the deviations in the breaking times, the authors of<sup>[71,72]</sup> have proposed methods of statistical treatment of the data on the time-dependence of the strength, and have discussed the problem of taking the deviations into account in extrapolating the time-dependence into the region of long breaking times. The latter fact is of great technical significance, since the direct determination of practical service lives (breaking times of  $\tau \sim 10^7$  sec and longer) is difficult. Methods of extrapolating the experimental breaking-time data based on the form of the analytical relation  $\tau = \tau(\sigma, T)$  are described in<sup>[73-75]</sup> and elsewhere.

It has been shown in<sup>[40,42]</sup> that for polymers of similar chemical structure (e.g., pure and plasticized polymethylmethacrylate and copolymers based on it), the graphs of the time-dependence of the strength ( $\log \sigma$  versus  $\tau$ ) for a single temperature are parallel and displaced from one another along the  $\sigma$  axis. The shift in the graphs is correlated with the values of the strength of the polymers in tests under stretching at a constant rate of deformation. This implies the practically-important conclusion that one can estimate the resistance of polymers of similar structure to static failure from their strengths in fracture, provided that the time-dependence of the strength of one of them is known. This fact is in full accord with the results of<sup>[67,70]</sup>.

### 3. The relation between the laws of failure and deformation

In testing polymers for long-term strength, we can easily note that they deform like other solids. The process of accumulation of strain at a constant load (creep) has been the subject of numerous investigations. One of the main problems is the search for simple empirical laws describing the dependence of

\*See also<sup>[140]</sup>, which indicates that the breaking of chemical bonds occurs not only at the fracture surface, but also in the interior of the continuous material.

the deformation in creep on the time, the temperature, and the stress, that are suitable for technical calculations. The best-known in this regard are the studies of Marin and Findley (see, e.g., the reviews [76-78]). An entire series of studies has been devoted to establishing the general rheological laws for the creep of polymers on the basis of Boltzmann's superposition principle. [79-82] The molecular nature of creep in polymers has been discussed in [81-84].

Usually creep and failure of polymers are studied and discussed separately. As a rule, the experimental studies on creep have been performed at low stresses, where the time until failure is hard to determine experimentally. Under these conditions, one traverses only the initial region of the creep. Conversely, the long-term strength is studied under relatively high stresses, and most often without recording of the creep curves (the strain-time relation). In the theoretical studies, failure is considered as a process involving the breaking of the bonds that give strength to the polymer. The breaking of these bonds is not considered in the study of creep.

The joint study of creep and long-term strength is of great interest as the first stage in solving the general problem of how the processes of deformation and failure of polymers are related. Furthermore, it is necessary in connection with the application of polymers in stress-bearing structures. Such studies have been widely undertaken for metals. Their fundamental result consists in the fact that a regular relation could be established between the macroscopic characteristics of failure and deformation under static loads. It has been shown in [85-89] and elsewhere that there is a simple empirical relation for metals between the breaking time  $\tau$  and the rate of steady-state creep  $v$ :

$$\tau v^a = A, \quad (10)$$

where  $a$  and  $A$  depend on the temperature and the nature of the material. This relation is implied by the fact that the relations of  $\tau$  and  $v$  to the stress and the temperature are of the same type. [88]

Studies have been conducted in [90] on the laws of accumulation of creep deformation up to the instant of fracture in solid polymers. It was shown that under these conditions the deformation laws become considerably more complicated, as compared with those observed in the usual creep tests. Thus, one could not find a well-defined stage of steady-state creep for all polymers. Usually the creep curves show an entire series of regions in which the rate of deformation varies with the time according to different laws. At the same time, it seems impossible to separate the deformation process into physically distinct stages. In most cases, only retarded-elastic deformations accumulated in all the regions.

As was stated above, the resistance to static failure is characterized by the breaking time  $\tau$ . The ratio  $1/\tau$  can be considered to be a measure of the mean

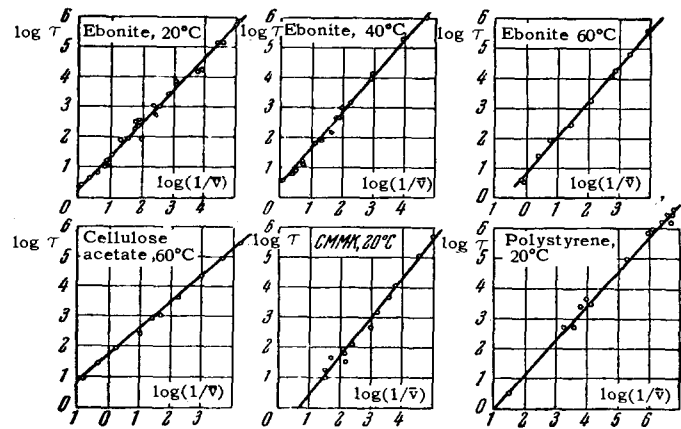


FIG. 9. Experimental relations between the logarithms of corresponding values of the breaking time and the rate of creep for various polymers. [91] For polystyrene the symbols  $\circ$  indicate data that can be determined from other studies.

rate of failure under the given conditions. If we take into account the noted peculiarities of creep in polymers and a number of other considerations (e.g., the equivalence of different characteristics of the creep), we might consider [42,91] that in analyzing the relation between failure and deformation in terms of the experimental creep curves, it suffices to characterize the rate of deformation by its mean value

$$\bar{v} = \frac{\epsilon_f - \epsilon_e}{\tau}$$

Here  $\epsilon_e$  is the elastic deformation under load, and  $\epsilon_f$  is the deformation at the time of fracture. The corresponding values of  $1/\tau$  and  $\bar{v}$  for various polymers have been compared in [91]. As is implied by the experimental relations (Fig. 9), the quantities  $1/\tau$  and  $\bar{v}$  are related by the equation

$$\frac{1}{\tau} = \bar{v}^m A, \quad (11)$$

which is fully analogous to (10). The coefficients  $m$  and  $A$  depend on the temperature and the type of polymer. For example, for polymethylmethacrylate  $m$  varies from 1.3 to 1.1 as the temperature is raised from 20° to 80°C.

For metals in many cases,  $m = 1$ . [88] This means that the relation of the rate of creep to the stress and the temperature is expressed by an exponential formula having exactly the same numerical coefficients as the corresponding expression for the breaking time. Hence the conclusion has been drawn in [88] that for metals the processes of failure and deformation are of the same physical nature. However, this does not exclude other assumptions.

The existence of Eq. (11) indicates that we can propose a mutual relation between failure and deformation for polymers as well. As has been stated,  $m \neq 1$  for polymers, and it varies with the temperature. This means that the rates of accumulation of failure and



deformation, as characterized by the quantities  $1/\tau$  and  $\bar{v}$ , vary to different extents when the experimental conditions are varied. Thus, if  $m > 1$  (polymethylmethacrylate, ebonite, polystyrene, and other polymers), we can say that failure is retarded more than deformation with decreasing stress. Conversely, if  $m < 1$  (cellulose acetate), we can assume that deformation "lags" behind failure, etc. Thus, this relation shows that for polymers failure and deformation are different processes.

The difference between failure and deformation of polymers is especially clearly marked in experiments with interrupted loading and annealing of the deformed specimens during the period that they are in the unloaded state.<sup>[42,91]</sup> It turns out that in distinction from failure, which always accumulates irreversibly, independently of the "rest" conditions of the specimens, the deformation process is reversible in the sense that annealing reverses the creep deformation, and permits one repeatedly to reproduce anew the entire course of accumulation of deformation. This result indicates that Eq. (11) is limited in significance, being valid only under certain test conditions: when the load acts continuously and the stress and the temperature are kept constant throughout the experiment. Under these conditions, as (11) implies, failure takes place only at a strictly fixed deformation. In the annealing experiments, fracture can occur at considerably lower deformations, although the breaking time remains the same for the same  $\sigma$  and at the previously-set  $T$ . This implies that failure is a local process encompassing small regions of the material and directly related to the deformation of these regions alone. Evidently, as has been shown, in not nearly all cases will the macroscopic characteristics of the deformation be correlated with the local deformation in the failure zone. From this standpoint, further precision in the relation between  $\tau$  and  $\bar{v}$  in order to elucidate the physical nature of the interrelation between failure and deformation is not of great significance.

#### 4. Crazing of polymers under mechanical loads, propagation of failure cracks, and morphology of fracture surfaces

In studying the mechanism of failure, one inevitably must come up against the problem of the origin and growth of cracks. The theoretical treatment of this problem involves great mathematical difficulties and the introduction of arbitrary assumptions, even in simple cases. Hence, experimental studies on cracks are of very great significance. For many materials, e.g., silicate glasses in an atmosphere of dry air, it is very difficult to detect the cracks and follow their growth under the conditions of a long-term strength test. It is considerably easier to observe the cracks in solid polymers. Hence it is often suggested to use

them as model objects to study the failure of solids in general.<sup>[38,92-94]</sup>

We must define crazing of solid polymers as the appearance of thin ("hairline") superficial cracks. In transparent polymers (organic glasses), the cracks are easily detected by their intense luster, or reflection of light from their surfaces. Thus the term "silvering" of organic glasses has come into use, which will be used as an equivalent to the term "crazing."

Here we are discussing the crazing of polymers due to mechanical load alone. Unstressed polymers also can craze under the action of organic and inorganic solvents, ultraviolet, electron, and nuclear irradiation, weather conditions, and other factors.<sup>[38,95-98]</sup> However, in most of these cases, the initial cause of crazing is also mechanical stress due to internal inhomogeneities in the material.<sup>[38,95,99]</sup>

Although the first observations of crazing of polymers go back to the beginning of the thirties,<sup>[100]</sup> up to now it has been mainly the subject of applied investigations. The fundamental problems of these studies consist in the development of methods of estimating resistance to crazing<sup>[101-103]</sup> and of improving this characteristic in polymers. Among the latter methods, we should mention those such as preliminary stretching (orientation),<sup>[104,105]</sup> surface coatings,<sup>[106,107]</sup> and the chemical cross-linking of linear macromolecules.<sup>[106,42]</sup>

The studies concerned with elucidating the general laws of crazing, its nature, the structure of the cracks, etc., are not numerous. In<sup>[108]</sup>, the kinetics was studied of the crazing of polystyrene under a constant tensile load. The "degree" of crazing was estimated from the intensity of the light scattered by the cracks. It turned out that the curves for creep and for relaxation of deformation after unloading are analogous in form to those for the variation in time of the light intensity under analogous conditions. Hence it has been concluded that the appearance and growth of the crazing cracks is one of the causes of creep in polystyrene, since the cracks must relieve the stress in the surface layer of the material. In<sup>[38,92]</sup> the time-variation of the length of the surface traces of the crazing cracks and their concentration on the surface was studied in polymethylmethacrylate specimens with varying plasticizer contents under constant tensile force. It was shown that the traces of the cracks are arranged perpendicularly to the tensile stress. The number of cracks per  $\text{cm}^2$  of surface first increases, and then remains constant until the specimen fails. The higher the stress is, the greater the concentration of cracks and the smaller their dimensions. The rate of growth in length of the surface traces of the cracks declines monotonically with time. The stress-dependence of the time  $\tau_0$  elapsed until the appearance of the first microscopically-visible cracks is analogous to the corresponding relation for the breaking time  $\tau$

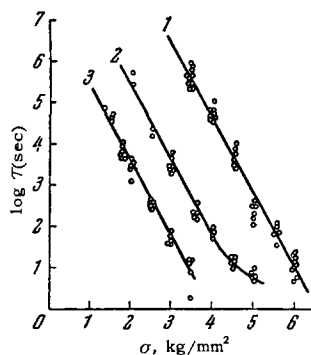


FIG. 10. Polymethylmethacrylate (data from<sup>[92]</sup>). 1—Relation of the breaking time to the stress at 25°C; 2 and 3—relation of the logarithm of the time until appearance of the first crazing cracks to the stress at 25° and 45°C.

(Fig. 10). Evidently,  $\tau_0 \ll \tau$ . Hence, the conclusion has been drawn in <sup>[92]</sup> that the time until failure is determined by the rate of growth of the crazing cracks, rather than by the rate of formation of invisible failure "nuclei," and that the time-dependence of the strength of polymers is directly related to the laws for the former process.

Data for polystyrene on the kinetics of growth of crazing cracks from the surface into the interior of the material are given in <sup>[109]</sup>. It turned out that the cracks grow into the interior at a constant rate depending on the tensile load. It was also noted there that polystyrene cracks during the time that it is under load. There have been attempts to use this effect in metals and crystals to analyze the changes occurring in the stressed material.<sup>[4,110]</sup> In <sup>[111-113]</sup>, optical and electron-microscopic methods were used to study distortions in the surfaces of polymers arising from crazing. They showed that the material expands near the cracks, and signs of strong shear deformations are observed at the ends of the cracks. They showed that there are no cracks whose traces on the surface are shorter than a certain limit. This amounts to  $\sim 2\mu$  for polymethylmethacrylate. The refractive index in a crack is less than that in the continuous material. Hence it was concluded that the crazing cracks are empty. Upon annealing, all traces of the cracks and surface distortions vanish.

The prior assumption has been made in most of the cited studies that the crazing cracks in solid polymers are identical with the failure cracks of the type of the Griffith cracks, i.e., that they are wedge-shaped empty discontinuities. The observed regularities are explained from this standpoint, although no decisive confirmation is provided for it.

The first indications that the crazing of polymers under load cannot be directly reduced to the growth of failure cracks are found in <sup>[36,109,114]</sup>. They observed no appreciable loss of strength in experiments on the crazing of polystyrene under constant tensile loads. Even when many of the crazing cracks had

completely transected the specimen, its strength was diminished by no more than 30–40% with respect to the original value. At the same time, its deformability increased. These and other facts are explained in <sup>[36,109,114]</sup> as follows. A bulk amorphous linear polymer is not a conglomerate of uniformly entangled macromolecules, but a system of rodlike formations, or "domains." The domains consist of macromolecules in parallel arrangement, and are distributed at random in the bulk polymer. Under a tensile load, part of the domains become exfoliated from one another. Other domains, having an orientation near the direction of tension, turn about and take up the load. The features that were taken to be empty cracks are actually regions of accumulation of microscopic exfoliations, linked by intact domains oriented in the direction of tension. The existence of orientation in crazed polystyrene is indicated by x-ray diffraction patterns, while the possibility of combination of macromolecules into elongated supermolecular formations is indicated by electron-microscope observations.\* It is assumed in <sup>[36,109,114]</sup> that crazing is much more similar to the process of deformation than to failure in the sense of formation of empty cracks.

These concepts on the nature of crazing of solid polymers have been confirmed and developed in <sup>[28,59,115-117]</sup>. A method has been developed for microscopic observation of crazing cracks in transparent polymers. It permits one to estimate precisely the dimensions of these structures (Fig. 11) from interference patterns. The method has been applied to study the growth of cracks in polymer specimens stretched by a constant force at various temperatures of experiment. At the same time, the breaking time and creep deformation were determined. The experiments, which were performed with polymethylmethacrylate and linear cross-linked polystyrene, made it possible to discover the following characteristic differences of crazing cracks from classical failure cracks. During the time that the specimen is under load, the crazing cracks can attain dimensions comparable with its cross-section, and even transect it completely at many places. The dimensions of the cracks at the moment of rupture becomes greater as the stress is reduced. Even after the specimen has been completely "transected" by cracks, the time until rupture amounts to a considerable fraction of the total breaking time: 20–25% for polymethylmethacrylate, and 70–90% for polystyrene. The interference pattern of the crazing cracks does not change when the load is removed from the specimen, nor upon long standing at room temperature. This means that the dimensions of these cracks do not vary upon removal of the load, in distinction from failure cracks. Upon annealing, the intensity of

\*In recent years, the formation of supermolecular "bundle" structure in linear amorphous polymers has been studied by V. A. Kargin and his associates.<sup>[130]</sup>

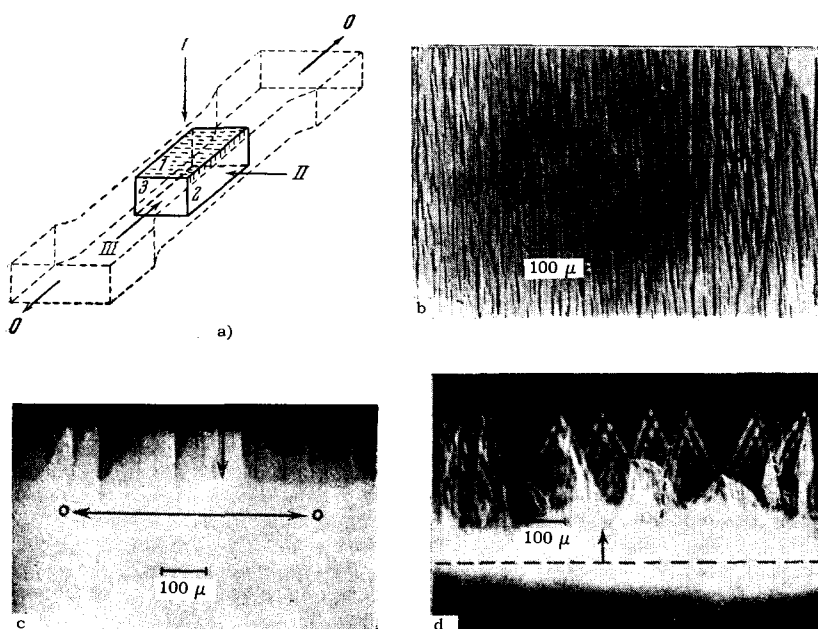


FIG. 11. a) Diagram of possible ways of observing the cracks; I, II, III—directions of observation; O—O = direction of tension. b) Surface traces of crazing cracks in polymethylmethacrylate as observed in transmitted light in direction I; O—O = direction of tension. c) Crazing cracks as observed in transmitted light in direction II; O—O = direction of tension; the direction from the surface to the center of the specimen is indicated by the arrow. d) The same, as observed in reflected light in the direction III; the direction from the surface to the center of the specimen is indicated (from<sup>[115]</sup>).

the interference decreases, and the bands disappear on going through the softening temperature without being displaced. The appearance of a mass of true cracks growing from the surface into the interior of the material would have to result in a monotonic decline in the measured value of the elastic modulus, owing to the decrease in the effective cross-section of the specimen. The elastic modulus of crazed polymer specimens practically does not differ from that of the original material, no matter how large and numerous these crazing cracks are.

In <sup>[118]</sup>, the kinetics of growth of open cracks has been studied in films of cellulose acetate under tension by a constant force. They showed that the open cracks grow in an accelerated fashion, since the stress  $\sigma'$  at the end of a crack, which is proportional to the stress  $\sigma_l$  in the intact portion of the specimen, increases with increase in the crack length  $l$ :

$$\sigma' \sim \sigma_l = \frac{\sigma_0}{1 - \frac{l}{L}},$$

where  $\sigma_0$  is the initial stress, and  $L$  is the width of the specimen. The instantaneous velocity  $V$  of growth of the crack depends on the stress according to

$$V = V_0 e^{\frac{\beta \sigma_0}{1 - \frac{l}{L}}}.$$

Under these same conditions, crazing cracks grow at a constant velocity depending on the initial stress according to  $W = W_0 e^{\beta \sigma_0}$ . This means that their growth does not result in an essential stress redistribution, as in the case of open cracks. This implies that the rate of growth of crazing cracks does not depend on the relation between the dimensions of the cracks and those of the cross-section of the specimen. This fact is illustrated by the example of the laws observed in

specimens of various dimensions prepared from polymethylmethacrylate tested at identical stresses and temperatures (Fig. 12). The opposite picture would be observed for failure cracks under the condition that the breaking time should be independent of the specimen dimensions: the curves for the variation of the absolute dimensions of the cracks should diverge, while those for the variation of the relative dimensions should coincide.

These data are sufficient to permit us to state that crazing cracks in polymers are not cracks in the usual sense of the word, although they resemble them in external appearance. Actually, they are wedge-shaped regions of microexfoliations that are for the most part isolated from one another. The intervals between the microexfoliations are regions of strongly deformed polymer material that has been subjected to orientation hardening.\* The strains in these regions, as shown by estimates based on comparing the dimensions of the cracks, their number, and the macroscopic deformation of the specimen, are hundreds of times greater than the strains in the material surrounding the crack. The crazing of polymers under load, like the similar phenomenon of "milky" whitening, which consists in the formation of a mass of microexfoliations distributed uniformly throughout the volume,<sup>[38,119]</sup> is a consequence of the existence in amorphous linear polymers of supermolecular structures such as elongated "bundles" or "domains." The lateral interaction between the latter is relatively small, and apparently does not contribute appreciably to the strength.

The definition of failure is generally accepted to be a process of separation of a stressed object into parts

\*In<sup>[147]</sup>, the existence of "braces" in the crazing has been shown by direct observation.

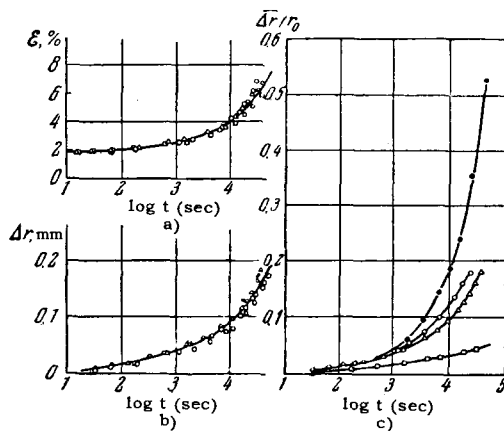


FIG. 12. Polymethylmethacrylate containing 6% dibutyl phthalate,  $\sigma_0 = 4.6 \text{ kg/mm}^2$ ,  $\theta = 20^\circ\text{C}$ ; specimens of various dimensions. [59] a) Creep curves; b) curves for the increase in the mean depth  $\Delta r$  of the crazing cracks, c) curves for the increase in the mean relative depth  $\Delta r/r_0$  of the crazing cracks;  $r_0 =$  cross-sectional radius of the specimen;  $\bullet - r_0 = 0.5 \text{ mm}$ ;  $\circ - r_0 = 0.7 \text{ mm}$ ;  $\Delta - r_0 = 1 \text{ mm}$ ;  $\square - r_0 = 1.5 \text{ mm}$ .

through formation of new free surfaces, i.e., through transection by an empty crack. It is quite clear that we cannot identify the crazing of polymers as discussed above with such a process. From this standpoint, conclusions on the laws governing failure based on experiments on crazing cracks alone (e.g., in [92,93]) are unconvincing. Still, there are a number of data showing that crazing is closely connected with failure. This is indicated by the existence of simple empirical laws relating the breaking time  $\tau$  with the rate  $W$  of growth of crazing cracks. [42] They are analogous in form to Eq. (11), which relates the breaking time to the rate of creep. Experiment also shows that certain of the crazing cracks determine the site of localization of rupture. We can see this easily by comparing the dimensions of the so-called "smooth zones" on the fracture surfaces of polymer specimens with the dimensions of the crazing cracks existing in them [115,42] (Fig. 13). Finally, a thorough microscopic study has been made of the structure of the end of a stable and slowly-growing failure crack in polymethylmethacrylate under "controlled" failure conditions. [28] These experiments showed that phenomena analogous to crazing take place near the end of the failure crack, and precede complete failure of the polymer.

The data presented, along with measurements of the surface energy, permit us to state with assurance that the failure of solid polymers, as with all other materials, involves a roster of other processes, which are a sort of "preparation" of the material for failure. For amorphous linear polymers, e.g., polymethylmethacrylate, these processes can be reduced to the formation of a local system of microexfoliations and to the deformation and hardening of the continuous regions of the material between them, within the zone immediately adjacent to the end of the failure crack. Failure consists in the continuous incision of this zone

and its re-formation upon growth of the failure crack. It is quite clear that the rate of failure will depend on the rate of relaxation of stresses in the pre-failure zone, the concentration of microexfoliations, the nature of the changes in properties in the continuous regions in this zone when they are deformed, and other factors. The quantitative laws governing these processes are not yet known.\*

One of the long-known ways of getting information on the laws governing failure is to study the morphology of the fracture surfaces. It was noted long ago that one can distinguish on the failure surfaces of solid polymers a series of zones having a characteristic relief: a "mirror" or smooth zone, a zone of small steps having hyperbolic or parabolic profiles, and a zone of rough fracture. [38,120,121] The relation between the dimensions of the zones depends on the stress, the rate of deformation, the temperature, and the molecular weight of the polymer [114,122,123,141]. If we decrease the stress or increase the temperature, the size of the smooth zone increases; the hyperbolic and rough-fracture zones are, so to speak, crowded out of the limits of the specimen. The microscopic study of the relief of failure surfaces has made it possible for the first time to construct a concept of the laws of propagation of failure cracks in solid polymers. [38,120,121] The smooth zone usually has a nearly circular profile, and is the trace of a single "initial" failure crack. Sometimes we can discern on it the "origin" of the failure, or the defect which proved to be the source of the crack. Since the dimensions of the smooth zone are practically independent of the dimensions of the specimen being tested under the given conditions (Fig. 13; see also [141]), we can state that it is formed by the transformation of one of the crazing cracks into a failure crack. The appearance of the hyperbolic fractures, with their vertices pointed toward the smooth zone, is due to the appearance of secondary failure sources that grow in the form of circular cracks in planes parallel to the plane of propagation of the initial crack. One can determine from the geometric form of the fracture boundaries what the relation is between the velocities of propagation of the initial and the secondary cracks. [38] Interferometric studies show considerable irreversible shear microdeformations at the fracture boundaries. [121,124] The fine-grained rough relief and the interference color observed in reflected light in the smooth zone and the hyperbolic zone are due in origin to the "domain" structure of the polymer, and to the exfoliation and orientation of "bundles" of molecules. Electron-microscope study of the failure "sources" shows that they are lens-shaped cavities of diameter  $\sim 0.3 \mu$ . [121] The existence of these same cavities has been found in the x-ray study of crazed

\*The first attempt to take these effects into account has been made very recently by G. M. Bartenev and I. V. Razumovskaya [FTT 6, 657 (1964), Soviet Phys. Solid State 6, 513 (1964)].

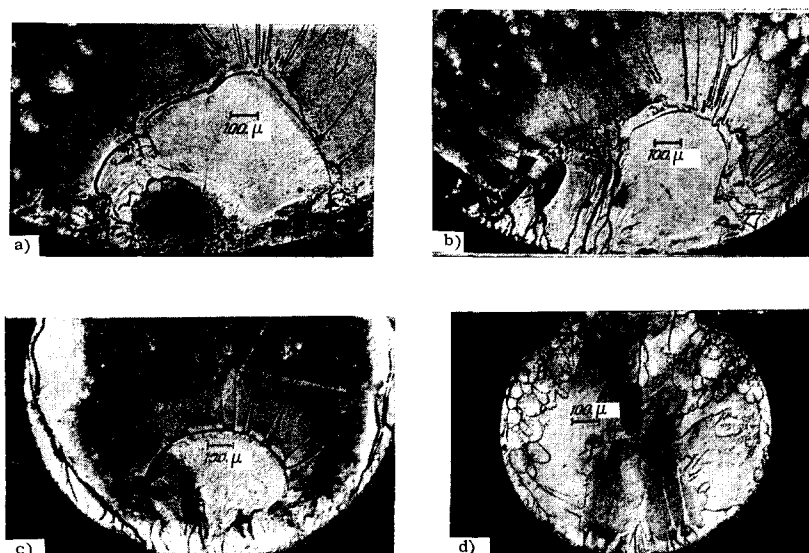


FIG. 13. Failure surfaces of specimens of various dimensions made of polymethylmethacrylate containing 6% dibutyl phthalate, at  $\sigma_0 = 4.6 \text{ kg/mm}^2$ ,  $\theta = 20^\circ\text{C}$ , in reflected light at the same magnification.<sup>[42]</sup> a)  $r_0 = 1.5 \text{ mm}$ ; b)  $r_0 = 1.0 \text{ mm}$ ; c)  $r_0 = 0.7 \text{ mm}$ ; d)  $r_0 = 0.5 \text{ mm}$ ;  $r_0$  = cross-sectional radius of the specimen (cf. Fig. 12).

and “milky” polymer specimens.<sup>[119]</sup>

The coarse-relief zone arises from the branching of the rupture cracks and the deviation of their growth directions from the normal to the tensile stress.<sup>[125]</sup> It corresponds to the greatest rate of failure. A comparison of direct measurements of the rate of propagation of failure cracks in polymethylmethacrylate with the relief of the failure surface<sup>[126,127]</sup> has confirmed these ideas.

As we see from the above, the topography of fracture surfaces indicates the very complex nature of the propagation of failure cracks, especially in the last stages, when secondary failure nuclei appear and branching takes place in the fracture crack.

### III. THE THEORY OF STATIC FAILURE OF POLYMERS AND OTHER SOLIDS

In most current studies, failure is considered to be a process of crack growth consisting of two stages: 1) the stage of “slow” crack growth until stresses near the critical stress appear at one of the cracks, and 2) the stage of “fast” crack growth by the Griffith mechanism. The problem of the growth of Griffith cracks is usually considered within the framework of the “equilibrium” theories of elasticity and thermodynamics. The solution of the problem of the growth of cracks under loads below the ultimate strength, i.e., the explanation of the nature of static fatigue, has required the introduction of kinetic concepts.

Murgatroyd<sup>[131]</sup> has explained static fatigue of silicate glass by ascribing a two-phase structure to it. The time course of failure was treated as involving the gradual increase of stresses in the elastic phase up to the critical value, owing to relaxation of stresses in the viscous phase. This scheme can be normally applied to any viscoelastic bodies. Orowan<sup>[132]</sup> thinks that static failure takes place by variation in the de-

gree of “danger” of Griffith cracks, owing to gradual decrease in the surface energy through adsorption of moisture and surface-active substances on the walls of the cracks. From this standpoint, the strength should not be time-dependent in vacuo, as is confirmed in<sup>[133]</sup>. However, there are data contradicting Orowan’s ideas.<sup>[134]</sup>

In<sup>[135-137]</sup>, a relation was assigned a priori between the rate of crack growth and the stress at the end of the crack. Thus they derived a theoretical relation between the breaking time and the load in the form  $\tau = C\sigma^{-\gamma}$ , agreeing with the experimental data for glass and rubbers.<sup>[55,56]</sup> In essence, here they chose a law of crack movement satisfying the cited experimental relation of  $\tau$  to  $\sigma$ .

In many studies, the time-dependence of the strength has been considered on the basis of molecular-kinetic concepts. Taylor<sup>[138]</sup> considers that under any load an object contains bonds whose strains are near the ultimate values. The kinetics of failure consists in the process of concentration of such bonds into a single cross-section through thermal fluctuations. He assumes that the activation energy  $U$  of this process depends on the stress as  $U = U_0/\sigma$ . In this case, the time for concentration of the critically strained bonds into a single cross-section, i.e., the breaking time is

$$\tau = Ae^{\frac{U_0}{\sigma kT}}$$

This corresponds to the experimental relation for glass established in<sup>[139]</sup>.

The first study on the interpretation of the molecular nature of static fatigue of polymers is that of Tobolsky and Eyring.<sup>[82]</sup> They suggested that the breaking time is determined by the rate of the activation process of bond breakage, whose nature was not specified in advance. Under a mechanical stress, the recombination of broken bonds can be neglected.

Then the rate of decline of the number  $N$  of unbroken bonds per  $\text{cm}^2$  of cross-section is defined as

$$-\frac{dN}{dt} = ANTe^{-\frac{\Delta F}{kT}} e^{-\frac{\sigma\lambda}{kT}}$$

Here  $\lambda$  is the deformation of a bond at the point of rupture, and  $\Delta F$  is the free-energy barrier to be overcome in the rupture of bonds when  $\sigma = 0$ . Integration of this expression under the condition that  $N = N_0$  initially and  $N = 0$  at the moment of rupture, respectively, gives the following expression for the breaking time:

$$\tau = A \frac{N_0}{\sigma} e^{-\frac{\Delta F - \sigma\lambda}{N_0 kT}}$$

As is stated in [82], the data on the breaking time of polymer fibers in [46] correspond to values  $\Delta F = 27$  kcal/mole and  $N_0 = 7 \times 10^{12} \text{ cm}^{-2}$ . However, it is difficult to relate these values to the characteristic molecular bonds existing in polymers.

In fact, Coleman [43] has developed the same theory, and arrived at an expression for the breaking time under constant tensile force in the form:

$$\tau = A \frac{\epsilon_B}{T} e^{-\frac{U_0 - (1 + \epsilon_B)\lambda S \sigma}{kT}}$$

where  $\epsilon_B$  is the strain in the specimen at the breaking point. He assumed that the relative stretch in the bonds and in the entire specimen were the same. A treatment of the data for nylon-66 fibers using this relation has shown that as one increases the degree of extension of the fibers,  $U_0$  decreases from 41 to 36 kcal/mole, while the product  $\lambda S$  decreases from 567 to 200  $\text{\AA}^3$ . If we identify  $S$  with the cross-sectional area per chain, then at the greatest extension  $\lambda$  proves to be approximately the distance along the chain between adjacent hydrogen bonds. Hence he concluded that, in the polyamides, failure involves breaking of hydrogen bonds. However, it is still not clear why the quantity  $U_0$ , which in meaning is a characteristic of the same bonds, is tens of times greater than the energy of hydrogen bonds.

G. M. Bartenev [60] has proposed a theory of failure of polymers in which crack growth is considered to be due to the breaking of bonds at the end of the crack by thermal-motion fluctuations. The existence of over-stresses in a crack shifts the equilibrium in the reaction of breakage versus reformation of bonds in favor of breakage. He assumes that a group of bonds can participate simultaneously in the elementary event of rupture. He also assumes that when the critical stresses have been attained, a "fluctuation" crack is transformed into a Griffith crack. He derived the following formula for the breaking time under constant load:

$$\tau = A \frac{T}{\sigma} e^{-\frac{Q - q\sigma}{kT}}$$

where  $Q$  has the meaning of the energy of the group

of bonds participating in the elementary fracture event, and  $q$  is the volume of these bonds. He assumes that in polymers no changes occur in the properties of the material near the end of the crack. The nature of the bonds is not specified.

V. E. Gul' [142] considers that the failure of polymers is due to the gradual activated rupture of intermolecular bonds and the increase in the stresses on chemical bonds up to the critical values. As we see, Murgatroyd's ideas are concretized here on the molecular level. He assumes that the load on the chemical bonds increases in proportion to the probability  $e^{-U/kT}$  of breaking of the intermolecular bonds, and in inverse proportion to the rate  $v$  of crack growth. By assuming that

$$U = U_0 - \gamma\sigma, \quad v \sim \frac{1}{\tau^m},$$

he derived a formula for the breaking time:

$$\tau = \frac{k}{(\sigma - \sigma_x)^m} e^{-\frac{U_0 - \gamma\sigma}{kT}} n,$$

where  $k$ ,  $m$ ,  $n$ , and  $\sigma_x$  are empirical constants. For small values of  $\sigma$ , this expression agrees with the experimental data for rubbers, and for large values of  $\sigma$ , with those for the breaking times of solid polymers.

According to Bueche, [37] the only bonds participating in failure of polymers are chemical bonds. He ascribes to each of these a potential curve having a barrier  $U$  whose height depends on the load  $F$  per bond as  $U = U_0 - F\delta$  (where  $\delta$  is the deformation of the bond at the breaking point). He takes into account the fact that upon breaking of each bond, the stress on the unbroken bonds is increased. He takes as the breaking time  $\tau$  the time necessary for breaking of all the stressed bonds occurring in the cross-section of the specimen. Bonds are considered to be stressed when they are parallel to the axis of tension (one-third of all bonds for an isotropic polymer). The breaking time is calculated from the condition  $p\omega\tau \approx 1$ , where

$$p = e^{-\frac{U_0 - F\delta}{kT}}$$

is the probability of breaking of a bond, and  $\omega$  is the vibration frequency. The condition  $p\omega\tau = 1$  determines the time  $t$  at which the load on the unbroken bonds begins to increase sharply. On transforming from  $F$  to the average stress  $\sigma$ , Bueche obtained

$$\tau = \frac{1}{\omega} e^{-\frac{U_0 - 2.7\delta S \sigma}{kT}},$$

where  $S$  is the cross-sectional of a C—C bond ( $\sim 10^{-15} \text{ cm}^2$ ), and  $\omega$  is the characteristic vibration frequency of the bond. Using his data on breaking times for polystyrene and polyethylmethacrylate, Bueche calculated that  $\delta \geq 4 \text{ \AA}$ . That is, the C—C chemical bond must stretch threefold in breaking. If we assume that  $U_0 = 60$  kcal/mole, then Bueche's data and his formula imply that the vibration frequency  $\omega \approx 10^{40} \text{ sec}^{-1}$ ,

which is also unreasonable. Later, [143] Bueche tried to perfect his theory by taking into account the fact that the directional distribution of the bonds and the distribution of the stress over the bonds are chaotic. He assumed that failure begins with the breaking of the most heavily stressed bonds, and continues by successive breaking of bonds around the perimeter of a circular planar crack. With these factors taken into account,  $\omega$  and  $\delta$  proved as before to be considerably larger than expected. Then he made the assumption that the increase in the stress on the chemical bonds arises not only from their decrease in number, but also from relaxation of the stresses in some of the stressed bonds through viscous slip of the polymer chains with respect to one another (Murgatroyd's system). This effect proved to be very large. The new final formula for the breaking time

$$\tau = \frac{A}{\omega_0} e^{-\frac{\sigma a}{N_0 k T}}$$

contains, instead of the characteristics  $\omega$ ,  $\delta$ , and  $U_0$  of individual bonds, those of the segmental motion of the macromolecules: the amplitude  $a$  and the frequency  $\omega_0$  of segment vibrations. The segment length is assumed equal to the length of the monomer unit, although obviously the representation of a solid polymer by the model of a system of absolutely flexible chain molecules is not justified. Besides, the last equation implies that  $\tau$  increases with the temperature. This contradicts Bueche's own experimental data.

A. I. Gubanov and A. D. Chevychelov [65] have refined the first variant of Bueche's theory. They use the Morse potential to describe the potential energy of adjacent atoms in the chain. The probability  $p$  of irreversible breaking of a single bond is assumed equal to the difference in probabilities of dissociation of the stressed bond and of its recombination after "unstressing" upon dissociation:

$$p = e^{-\frac{\Delta E}{kT}} - e^{-\frac{D}{kT}},$$

where  $\Delta E$  is the potential barrier for dissociation of the stressed bond, and  $D$  is the dissociation energy of a free bond. By calculating the relation of  $\Delta E$  to the load and taking as the condition for rupture the equation  $p\omega\tau = 1$ , the authors [65] derived the following formula for the breaking time:

$$\ln \frac{\tau}{\tau_0} = \frac{D}{kT} - \ln \left\{ \exp \left[ \frac{a\sigma e}{kTN} \left( 1 + \ln \frac{2D}{a\sigma} N \right) \right] - 1 \right\}. \quad (12)$$

Here  $\tau_0 = 1/\omega$ ,  $a$  characterizes the curvature of the potential well near the minimum,  $N$  is the number of stressed bonds per  $\text{cm}^2$ , and  $e$  is the base of the natural logarithms. For polymers having carbon chains, for which the orders of magnitudes of  $D$  and  $a$  are known, in an experimentally-attainable range of  $\sigma$  and  $T$ , Eq. (12) can be written approximately as

$$\ln \frac{\tau}{\tau_0} = \frac{D}{kT} - \frac{\gamma\sigma}{kT}, \quad (13)$$

where  $\gamma \sim 1/N$ . Equation (12) has been compared with the experimental data [47] for oriented polymer fibers. The quantity  $D$  was assumed equal to the activation energy  $U_0$  of the failure process determined in [47] by treatment of the experimental data by Eq. (13). The theoretical curves were calculated for disordered and ordered polymers. We see from Fig. 14 that only in one case (Capron) do the theoretical curves fit the experimental ones on both sides. As a rule, the slope of the theoretical curves [the coefficient  $\gamma$  in Eq. (13)] is smaller than the slope of the experimental relations. This means that the experimental strength is lower than the minimum theoretical strength. The reasons for the discrepancy could be such effects as the finite length of the polymer chains, inhomogeneity in the type of cracks, etc. The account taken of the finite length of the chains in [65] gives the result that the effective number  $N_1$  of chains bearing the load proves to be smaller than the total number  $N$  of chains per  $\text{cm}^2$ :

$$N_1 = N \left( 1 - \frac{p}{P} \right),$$

where  $P$  is the degree of polymerization and  $p$  is a constant characterizing the mutual friction between the chains. This leads to a corresponding dependence of the coefficient  $\gamma$  on the degree of polymerization. As was stated, this is confirmed by experiment.

If we examine the molecular theories of failure of polymers as a whole, we cannot but convince ourselves that they are to be considered only as the initial attempts at treatment of this process. The authors of many studies have been satisfied with qualitative agreement of the theoretical formulas for the breaking time with the empirical relations, without taking into account the fact that other authors have arrived at the same result by starting from completely different assumptions. The fact [16] has not been taken into account that many experimental data can be described by different empirical laws. These contradictions have been nowhere discussed. Many of the theoretical formulas for the breaking time imply that  $\tau$  is finite when  $\sigma = 0$ .

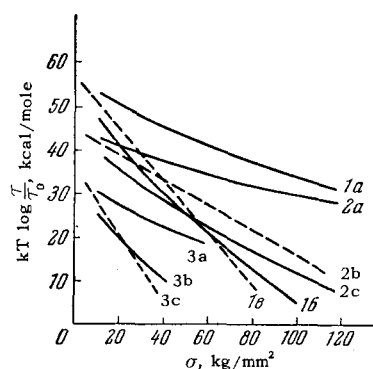


FIG. 14. A comparison of the theoretical relations for the breaking time with the experimental. [65] 1—Polypropylene; 2—capron; 3—polyvinylchloride. a) and b) Calculated for the ordered and disordered polymers, respectively; c) Experimental, for the ordered fibers.

One can put up with this well-known defect of expressions such as Eq. (8) when they are proposed only for description of the experimental data within a limited range of stresses. All the theoretical formulas hold only for the case of tension ( $\sigma > 0$ ); in compression ( $\sigma < 0$ ) they imply that  $\tau$  increases with the load. Experiment<sup>[54]</sup> leads to the opposite result. One could consider the criterion of the validity of a theory to be that the coefficients such as  $U_0$  and  $\gamma$  in the theoretical formula for the breaking time as derived from comparison with experiment should agree numerically with the characteristic values based on calculation from the molecular mechanism of failure. However, most often the value of only one of these coefficients agrees with the adopted molecular model. In a number of cases,<sup>[37,143]</sup> attempts to get complete quantitative agreement of calculation with experiment lead to contradiction of the original model. We can cast doubt on certain of the fundamental assumptions of the theories, such as the unreserved application of the absolute-reaction-rate theory to individual bonds in a solid polymer without taking into account cooperative effects, the formal transition from the average macroscopic stresses to the forces acting on the individual bonds, and the treatment in most cases of failure as being a bulk, rather than a localized process, etc.

The theoretical studies have also made no essential contribution to elucidating the fundamental question of the nature of the elementary event of failure, even as to indicating the most probable nature of this event or aiding in setting up the appropriate experiments. It suffices to say that the most highly developed conception of failure due to S. N. Zhurkov, according to which the failure of polymers is a process of breaking of chemical bonds by thermal fluctuations in a stress field, could be formulated only on the basis of experiments that had been set up independently of the theoretical studies, the detailed theoretical analysis of which is a task for the future.

Quite understandably, this lag of theory behind experiment is occasioned in many ways by the lack of a general theory of amorphous substances.

#### IV. CONCLUSION

The problem of the laws and nature of failure in polymers is at present one of the central problems in polymer physics. In many ways, success in the practical application of these materials depends on the solution of this problem. As we see from what has been said above, the study of failure in polymers has become the object of numerous studies increasing in number from year to year. Especial attention has been drawn to the time effects in failure, which apparently are of prime significance for polymers. The fundamental empirical laws governing these effects and their relation to other time-dependent processes proceeding simultaneously with failure have been established. At-

tempts have been made to study the processes of alteration of the polymer material that precede failure and evidently determine many of the laws governing the latter. An entire series of hypotheses has been advanced on the molecular mechanism of failure. The first experimental data have been obtained on the breaking of chemical bonds in failure and on the similarity of this latter process with that of thermal decomposition.

Nevertheless, it is difficult to draw a complete physically lucid and finished picture of failure in polymers, just as with other solids. Apparently, the reason for this consists in the fact that thus far the major efforts of researchers have consisted in establishing the macroscopic laws of failure such as the temperature-time dependence of the strength, and in trying to explain these laws directly on the molecular level. Bearing in mind the defects of the molecular theories of failure and their limited possibilities with regard to bulk solid polymers, conceivably we should consider the most reliable way to elucidate the nature of this phenomenon to be the accumulation of experimental material permitting us to bridge the gap between the macroscopic laws of failure and the molecular laws that it is based on. In this regard, we should mention the necessity of solving the problems of the origin of failure cracks in a continuous polymer, the laws of growth of cracks in the "slow" stage of failure, the quantitative characterization of the processes of microdeformation and microfracture that take place at the ends of the cracks and in the adjacent "prefailure" zone, the further study of the physicochemical processes in failure, etc. Luminescence and electrification observed during failure of polymers have not been studied at all. The connection must be made between failure and the existence of supermolecular structures, such as bundles, domains, spherulites, etc. The idea has not been ruled out that their role here will prove to be the same as that of grains, etc., in the structures in polycrystals. Apparently, only when these and many other complex problems have been solved can we consider the problem of the nature of failure in polymers to have been elucidated.

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