CURRENT STATE AND PROSPECTS FOR DEVELOPMENT OF THE PHYSICAL
THEORY OF BRITTLE STRENGTH OF POLYMERS

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Various mechanisms of brittle fracture and theories of the time
dependence of the strength of rigid polymers are examined. The
effect of various types of mechanical losses (deformation, dynamical,
surface) on polymer strength and life is analyzed. The principal
shortcomings of Griffith's theory of strength are pointed out. From
an examination of the two basic mechanisms of brittle fracture of
polymers—nonthermal and thermal (thermal fluctuation)—it is con-
cluded that the latter is the more important. A comparison is made
of the fluctuation theory of polymer strength with new experimental
data on polymethyl methacrylate, and the causes of the transition
from brittle to nonbrittle fracture are discussed. The effect of
molecular orientation on the strength of polymers is examined on
the basis of the fluctuation theory of strength.

All polymers pass into the brittle state at sufficiently
low temperatures. The brittleness temperature for
most polymers is below 20°C. In the temperature
region of the brittle state, polymers experience a
characteristic fracture similar to that observed in
brittle solids and especially glass. Brittle fracture is
the most dangerous type of fracture; therefore its in-
vestigation in polymers is a matter of some urgency.

From the point of view of strength theory, brittle
fracture is a simpler phenomenon than other types of
polymer fracture. This is because when polymers
fracture in the nonbrittle rigid and high-elastic states
the molecular orientation and other structural changes
of the polymer under load become an important factor.
It is natural, therefore, that most success should
have been achieved in the development of the theory
of the brittle strength and its time dependence. How-
ever, even here there are many problems of the phys-
tical theory of these phenomena that have not yet been
solved or whose solution is debatable.

We will analyze below the possible mechanisms of
brittle fracture of polymers in close connection with
the problem of the fracture of solids in general, ex-
amine theories of the time dependence of strength,
and point out further directions in the development of
the theory of polymer strength.

The difficulties in the development of the theory of
brittle strength of polymers are explained in part by
the impossibility of direct visual observation of the
transition from brittle to nonbrittle fracture. In non-rittle fracture, which often outwardly has all the
features of brittle fracture, local structural changes
(molecular orientation near the tips of microcracks,
cross strands strengthening the walls of microcracks,
etc.) go unnoticed. The empirical equations of fatigue
in regions of brittle and nonbrittle failure generally
have the same mathematical form.

In many studies these circumstances lead to a
formal approach to interpreting the physical meaning
of experimental data. In this connection we will dis-
cuss in the concluding part of the article the differ-
ence between the time dependence of polymer strength
in the brittle and nonbrittle temperature regions
without a detailed examination of the mechanism of
nonbrittle fracture of solid polymers.

The state of the problem of the strength of poly-
mers in nonbrittle rigid and high-elastic states is to
be examined in subsequent publications.

Low-strength and high-strength (defect-free) ma-
terials. All commercial materials contain internal
and surface defects, which lower their strength in
comparison with the natural strengths inherent in
the structure of the material itself. Henceforth in
this article we will mean by defects micro- and sub-
microcracks, microdiscontinuities, and other stress
raisers present in a specimen before loading that are
not characteristic molecular or supermolecular
structural motifs of the material itself.

Brittle solids, representatives of which are in-
organic glasses and rigid polymers at sufficiently
low temperatures, can be divided into high-strength
and low-strength materials with respect to the mech-
anism and the character of fracture. The main dif-
fERENCE BETWEEN THEM IS THAT THE FORMER HAVE NO
initial micro- and submicrocracks and other defects,
whereas such are present in the latter. Low-strength
materials contain initial microcracks or submicro-
cracks mainly in the surface layers. Their breaking
stress depends strongly upon the scale factor and
surface-active medium, but relatively little on chem-
ical composition. A broad scatter of the strength
etc. values is observed for these materials.

Griffith's first physical theory of strength [1], and
most subsequent theories, pertain to low-strength,
brittle materials. The presence of initial micro-
breaks leads to a mechanism of failure differing from
the mechanism of failure of high-strength materials.
Thus, in materials containing initial microcracks the
rupture cracks begin to grow after the application of
loads exceeding the safe load. In brittle bodies the
initial microcracks are characterized by their more
or less sharp distribution with respect to degree of
dangerousness. Therefore, the strength and life of
brittle materials are determined for all practical
purposes by the growth of one, or more rarely
several, of the most dangerous microcracks. As a
result low-strength glass breaks into macroparts.

High-strength materials are obtained only in in-
dividual laboratories. For example, glasses obtained
by special chemical treatment of their surfaces [2, 3]
are virtually free of surface microcracks and have a
high strength (300–400 kgf/mm²); defect-free glass
fibers [4,5] without surface defects have a high strength (300–350 kgf/mm²), which depends not at all upon the length and only slightly on the diameter of the fiber; they break into a large number of microfragments and even into "dust"; there is practically no scatter of the strength values when a series of such specimens is tested.

Since microcracks are absent in high-strength glasses in the initial state, the main stage of the process of fracture of these glasses is due to the occurrence of many submicrocracks at weak places of the microstructure under the effect of stress and temperature. Consequently, we can assume that fracture of high-strength materials occurs in two stages: in the first stage many microdefects develop, and in the second stage there is a rapid growth of microcracks, leading to disintegration of the specimen into microfragments. The failure of defect-free glass fibers probably occurs in this manner.

The development of a physical theory of fracture of high-strength materials, on which the Problem Laboratory of Polymer Physics of the Lenin Moscow State Pedagogical Institute is working, is a matter of the future. In this article we will examine problems of the physics of the fracture of low-strength brittle polymers, in particular, their different fracture mechanisms. Thus we will devote prime attention to a discussion of various mechanisms of crack growth and the dissipation of elastic energy during fracture.

*Molecular model of a crack and its growth mechanism in brittle material. The molecular model of a crack (Fig. 1) is a generalization [6–8] of the well-known Griffith and Rebinder models. Breakage of the bonds between atoms (for polymers the C–C bonds or other chemical bonds of the principal valence chains) occurs at the boundary of transition from "continuity" to a free surface (broken line). In Fig. 1 atoms 1–6 are still within the body, and 7–11 and beyond are on the free surface; consequently, the breakage event reduces mainly to the transition 6–7.

Because of thermal motion and fluctuations, the atoms at the tip of the crack acquire, from time to time, sufficient kinetic energy to break or restore the bonds between them. In this case the process of breakage and restoration of the bonds is accompanied by an expenditure of kinetic energy for overcoming potential barriers U and U' (Fig. 2). The kinetic energies of the particles equal to these barriers are, respectively, the energies of activation of the processes of breakage and of restoration of the chemical bond. The difference of the potential barriers U – U' is the potential surface energy, which is practically equal to the free surface energy associated with a single fluctuation.

The potential energy of atoms within the body can be regarded, with some approximation, as a function of the distance between particles in the direction of extension, i.e., as a function of the distance between atoms x, and the potential energy of the particles on the free surface (after breakage of the bonds), as a function of the distance x' (see Fig. 1). In an unloaded solid x = λ₀, which corresponds to the bulk equilibrium interatomic distance, and x' = λ₁, which corresponds to the equilibrium interatomic distance in the surface layer. Consequently, the left minimum (see Fig. 2) corresponds to the bulk equilibrium position of particles far from the crack; the right minimum corresponds to the equilibrium position of particles on the free surfaces of the crack. The maximum on the potential curve arises as a consequence of the fact that the nearest neighbors in the following atomic layers affect the process of bond breakage. Their interaction with atoms reaching the surface of the microcrack after breakage of the bonds is characterized by the interatomic distance x', this distance being maximum near the tip of the crack (see Fig. 1). In an unloaded material the probability of finding particles in the left minimum of the potential energy curve is greater than in the right minimum. If there are no corrosion processes or surface-active medium (factors which are disregarded here), then the crack after unloading closes up to the defect at which it was formed. In loaded material the tensile stress promotes breakage of the bonds and impedes their restoration; consequently, less kinetic energy is required for breaking the bonds, and a correspondingly greater kinetic energy is needed for their restoration than in the unloaded state. Upon increase of tensile stress the probability of the bonds breaking increases, and that of their restoration decreases. At relatively large stresses breakage of the bonds becomes more probable and the microcrack grows. The stress σ = σ₀, at which the probabilities of breakage and restoration of the bonds are equal and the microcrack does not grow, is the safe stress.

At very low temperatures, near absolute zero, there is practically no thermal motion. Therefore, there is also no kinetic energy, which is needed for the transition from one minimum of potential energy to the other. Under these conditions the cracks, for all practical purposes, do not grow at any stresses smaller than some critical stress σ₉, to which corresponds the critical overstress at the tip of the microcrack σ₉*. Their ratio β = σ₉*/σ₀ is the stress concentration factor.

Nonthermal and thermal (fluctuation) fracture mechanisms. We have examined above the fluctuation mechanism of fracture of low-strength solids, the general concepts of which were expressed long ago. An idea of this mechanism of fracture was first expressed in clear form by Smekal [9]. According to Smekal, increase in the intensity of thermal fluctuations with rise of temperature leads to an increase in the probability that the thermal energy together