

A STUDY OF THE PHYSICAL NATURE OF FRACTURE IN  
COMPOSITE MATERIALS

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INTRODUCTION

This paper represents an attempt to pose problems arising in research into the physical nature of fracture of composite materials in terms of modern ideas encompassed in the kinetic concept of the strength of solids.

According to this concept, fracture should be considered as resulting from a progress of accumulation of defects developing in time from the moment of load application. This process should be characterized not by some critical stress alone, but rather by the rate of defect accumulation at a given temperature regime of loading, or by the reciprocal lifetime of the specimen under load from the moment of loading until failure ( $\tau$ ). An investigation of the temperature - stress dependence of the lifetime leads to the conclusion that for homogeneous solids of various structure the dependence of  $\tau$  on  $\sigma$  and  $T$  over a sufficiently broad range of stress  $\sigma$  and temperature  $T$  can be described by a formula which is the same for all solids (single and polycrystals, glasses, polymers) [1].

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

This expression is frequently called Zhurkov's formula.

The properties of the coefficients  $\tau_0$ ,  $U_0$ , and  $\gamma$ , entering this formula were studied experimentally on various materials. Experiments showed the prefactor  $\tau_0$  to be practically constant for all the solids studied and equal to  $10^{-13}$  s within one or two orders of magnitude, i.e. close to the period of atomic vibrations in solids.

The quantity  $U_0$  which may be treated as an activation energy of fracture varies from one material to another while turning out to be structurally insensitive. The value of  $U_0$  for metals and crystals is found to be closer to the energy of sublimation than self diffusion, and to coincide with the activation energy of the initial stage of the thermal destruction process in the case of polymers. The alloying of metals, their mechanical and thermal treatment, the plastification and orientation of polymers, which change their structure substantially, do not noticeably affect the magnitude of  $U_0$ .

The coefficient  $\gamma$  turns out to be the only structurally sensitive coefficient in Eq. (1) and varies markedly with variation of material structure. The value of  $\gamma$ , which has the dimensions of volume, ordinarily exceeds the volume occupied by atoms in a solid by a factor of several hundred.

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The form of Zhurkov's formula (1) and the properties of the coefficients  $\tau_0$ ,  $U_0$  and  $\gamma$  give grounds for assuming fracture to be a thermally activated process. This process is based on elementary events in thermofluctuation and rupture of atomic bonds in a solid. When subjected to mechanical stress, the energy  $U_0$  required for atomic bond rupture decreases by  $\gamma\sigma$ , the probability of their recombination being reduced.

Such a concept of the nature of fracture of solids was put forward earlier only on the basis of phenomenological studies of the temperature - stress dependence of lifetime found for a large number of materials. The validity of these ideas has been confirmed thereafter by an investigation of the fracture process using direct methods of physical experiment capable of following the development of fracture at the atomic and molecular level. The application of IR spectroscopy, EPR and mass spectrometry make it possible to follow the extension under load of individual macromolecules in oriented polymers, and the rupture of drawn atomic bonds in molecules. It was shown that it is essentially the kinetics of atomic bond rupture accumulation that determines the kinetics of fracture of oriented polymers. This work was described in detail in the monograph [2].

We start from the assumption that application of the kinetic approach to the study of composite fracture will turn out to be fruitful in understanding the physics of fracture of this new and important class of materials. In our opinion it would be wrong to wait for the final solution of nuclear problems in the physics of strength of solids by investigating homogeneous materials with a subsequent transition to the physics of composites.

It is reasonable to start studying the kinetics of fracture of composite materials and to apply to them the kinetic concept of strength from the simplest kind of this material, i.e. unidirectional fibrous composites with continuous filaments. Just as in the case of homogeneous solids, studying the fracture of composites within the framework of the kinetic concept of strength should be started with systematic experiments on the kinetics of fracture and, primarily, with an investigation of the temperature and stress dependence of the lifetime of these materials. Such an investigation may yield valuable information on the nature of fracture in composites. By analogy with studies performed on homogeneous solids [2], one should thereafter employ direct experimental techniques which permit one to follow the process of fracture at the atomic and molecular level. Considering the specific nature of the composite materials, particular attention should be paid to the process of fracture at the interface between the constituents in order to reveal the role of adhesion-bonding between the constituents in determining the strength of composites.

We are able at present to analyse some results obtained in studies of the fracture of composites reinforced with continuous unidirectional filaments, and to formulate problems which should be solved in the future.

#### An Investigation of the Temperature - Stress Dependence of the Lifetime of Fibrous Composites

The first problem that arises when studying the temperature - stress dependence of the lifetime of composites consists in checking whether the functional dependence (1) of lifetime  $\tau$  on acting mean stress  $\sigma$  and test temperature  $T$  for composites is the same as for homogeneous solids.

There is experimental evidence showing Zhurkov's formula (1) to be valid for various fibrous composites subjected to tensile stress with specimens cut along the filament direction. As an illustration, Figure 1 presents data on the temperature - stress dependence of lifetime of a tungsten fiber-copper matrix composite [3]. Similar data are available for polymeric matrix composite [4]. Experimental data similar to those presented in Figure 1 show equation (1) to hold for composites within a certain stress and temperature range. This means that the fracture of composites, just as that of the other solids, should be considered as a thermally activated process of gradual accumulation of defects.

The next problem which can be posed in a systematic investigation of the temperature - stress dependence of lifetime of composites is to study the properties of parameters  $\tau_0$ ,  $U_0$ ,  $\gamma$  in equation (1) and revealing their physical meaning. The final purpose of such studies may be a development of "kinetic rules of mixture", i.e. rules permitting determination of parameters  $\tau_0$ ,  $U_0$ ,  $\gamma$  in equation (1) for composites having data on the corresponding parameters of the composite constituents and taking into account the effect of the mechanical properties of the interface between them. One should develop three rules for the determination of each of three parameters  $\tau_0$ ,  $U_0$  and  $\gamma$  in equation (1), accordingly, for composites with different volume ratio of the fibres.

On the basis of the available experimental data on the properties of  $\tau_0$ ,  $U_0$  and  $\gamma$  in equation (1) for composites, and on the kinetic rules of mixture, the following can be said at present.

#### (a) *First rule of mixture*

The magnitude of  $\tau_0$  for all the composites studied up to now (their number is small) turned out to be constant within experimental errors and equal to  $\tau_{0\text{comp}} = 10^{-13 \pm 2} \text{ sec}$ , i.e., about equal to the prefactors in equation (1) for the composite constituents. Therefore the first rule of mixture may be formulated in the following way: the prefactors in equation (1) for the composite  $\tau_{0c}$ , for fibres  $\tau_{0f}$  and for matrix  $\tau_{0m}$  are approximately constant and equal to  $10^{-13} \text{ sec}$ :

$$\tau_{0c} = \tau_{0m} = \tau_{0f} = 10^{-13} \text{ sec} \quad (2)$$

In accordance with this rule, the physical meaning of  $\tau_{0\text{comp}}$  does not differ from that attributed to the prefactor  $\tau_0$  in Zhurkov's formula for homogeneous solids.

(b) *The second rule of mixture* relates to the determination of the activation energy for the fracture of composites,  $U_{0\text{comp}}$ . Since any composite contains at least two constituents, each of them being characterized by its own activation energy for fracture,  $U_{0f}$  and  $U_{0m}$ , a question arises as to the magnitude of  $U_{0\text{comp}}$  at different volume contents of the constituents.

We will limit ourselves here to a simple case where  $U_{0f}$  and  $U_{0m}$  for the original specimens of the constituents outside the composite are numerically equal to  $U_{0f}$  and  $U_{0m}$  of these constituents in the composite. However, even in this case, a question arises as to how the activation energy of fracture of this composite changes with the changing fiber volume ratio.

The answer to this question can be obtained in experiments on specimens of tungsten fiber-copper matrix composite with different tungsten fiber volume ratio [3,4]. One first studied the temperature - stress dependences

of the lifetime of the constituents of this composite, and obtained the activation energies of fracture of copper and tungsten. Experiments show the activation energy of copper fracture to be  $U_{0m} = U_{0Cu} = 80$  kcal and that of the fracture of tungsten to be  $U_{0f} = U_{0W} = 230$  kcal.

Figure 2 represents a graph of the activation energy of fracture of the copper-tungsten composite vs. volume content of the tungsten fibers,  $U_{0comp}(V_f)$ . At low tungsten fiber content the activation energy of composite fracture is seen to coincide numerically with that of the copper matrix fracture,  $U_{0comp} = U_{0m} = 80$  kcal/mole, whereas at a sufficiently high tungsten fiber content  $U_{0comp}$  coincides numerically with the activation energy of fracture of the tungsten reinforcement  $U_{0comp} = U_{0f} = 230$  kcal/mole.

Figure 2 shows also that the change of activation energy from  $U_{0m} = 80$  kcal/mole up to  $U_{0f} = 230$  kcal/mole occurs practically in a jump at a certain value of the fiber volume ratio,  $V_f = V_f^*$ . Assuming that at this fiber volume ratio  $V_f^*$  the strengths of the matrix and the reinforcement in the composite become equal, i.e.,  $\sigma_f V_f^* = \sigma_m(1 - V_f^*)$ , then for an estimate of  $V_f^*$  we may write

$$V_f = \frac{\sigma_m}{\sigma_f + \sigma_m} = \frac{\gamma_f}{\gamma_f + \gamma_m \left( \frac{U_{0f} - C}{U_{0m} - C} \right)} \quad (3)$$

where

$$C = RT \ln \frac{T}{T_0}$$

such an evaluation yields for our case  $V_f^* = 7.5\%$  which is not in disagreement with experiment.

Thus the second rule of mixture for the simplest case of  $U_{0f}$  and  $U_{0m}$  remaining in the composite the same as outside it may be expressed in the following way:

$$\begin{aligned} U_{0comp} &= U_{0m} \quad \text{for } V_f < V_f^* \\ U_{0comp} &= U_{0f} \quad \text{for } V_f > V_f^* \end{aligned} \quad (4)$$

As already pointed out, in more complex cases  $U_{0comp}$  may differ from  $U_{0f}$ , and sometimes from  $U_{0m}$ , at  $V_f > V_f^*$  and  $V_f < V_f^*$  respectively.

(c) *The third rule of mixture* should permit us to estimate the magnitude of  $\gamma_{comp}$  from data on  $\gamma_f$  and  $\gamma_m$  and from information on the mechanical properties of the interface between the constituents. The experimental data available are, however, insufficient to be able to formulate this rule for a general case. One may expect the development of this rule to turn out to be a particularly difficult problem because of the structural sensitivity of the coefficient  $\gamma$  in equation (1).

One may consider here the simplest case to the well-known "static rule of mixture" [5].

$$\sigma_{comp} = \sigma_f \cdot V_f + \sigma_m \cdot V_m \quad (5)$$

where  $\sigma_f$ ,  $\sigma_m$  are the strengths, and  $V_f$ ,  $V_m$  the volume contents of the fibers and matrix, respectively in the composite.

Then for  $\gamma_{comp}$  the following relation should hold:

$$\begin{aligned} \frac{1}{\gamma_{comp}} &= V_f \cdot \frac{1}{\gamma_f} \frac{U_{0f} - C}{U_{0m} - C} + V_m \frac{1}{\gamma_m} \quad \text{for } V_f < V_f^* \\ \frac{1}{\gamma_{comp}} &= V_f \cdot \frac{1}{\gamma_f} + V_m \cdot \frac{1}{\gamma_m} \frac{U_{0m} - C}{U_{0f} - C} \quad \text{for } V_f > V_f^* \end{aligned} \quad (6)$$

where

$$C = RT \cdot \ln \frac{T}{T_0}$$

One may expect, however, that an estimate of  $\gamma_{comp}$  by equation (6) will frequently be wrong. This formula, just as equation (5), does not take into account the effect of defects at the interface between the constituents on the composite strength. Equations (5) and (6) do not also include the fact that the structure and strength properties of the matrix, and sometimes of the fibers as well, may change in the process composite manufacture. This means that the magnitudes of  $\gamma_f$  and  $\gamma_m$  in the composite are different from those for the original constituents. Further work on improvement of the third rule of mixture (as well as in the determination of corrections to the static rule of mixture) should take into account these complicating points.

An analysis of the parameters  $\tau_0$ ,  $U_0$  and  $\gamma$  in equation (1) for composites and of problems in the development of kinetic rules of mixture shows that the systematic investigation of the temperature - stress dependences of the lifetime of model composites may yield valuable information on the process of composite fracture. Therefore further studies of the kinetics of composite fracture both on composites of other type and on specimens cut at an angle to the filament orientation, as well as at other regimes of loading and different kinds of stresses should be considered as promising. The studies of the temperature - stress dependence of lifetime should be accompanied by direct observations on the appearance and growth of cracks at different stages of the process, and with a recording of the distribution of stress in the fibers and matrix in time. This will permit to develop in more detail the kinetic rules of mixture and to reveal the physical meaning of the parameters  $\tau_0$ ,  $U_0$  and  $\gamma$  in the formula for lifetime.

The mechanism of fracture in polymer matrix composites can be explored by the same experimental techniques as the ones used in the study of polymer fracture. Among them are IR spectrometry, radiospectroscopy (EPR and NMR), mass-spectrometry and small-angle x-ray scattering. The possibilities offered by these methods in studies of fracture of composites can be illustrated by results of the research performed in Leningrad Physical-Technical Institute, Academy of Sciences of the USSR [6-8]. These results can be summarised as follows.

A model polymer - polymer composite made up of strong polyvinyl alcohol filaments embedded in an epoxy matrix has been studied by IR spectroscopy [6]. Bifunctional diisocyanate was introduced between the epoxy and the filaments as a coupling agent. Diisocyanate was shown to form chemical bonds with both the matrix and the filaments. In the course of heat

treatment of this composite, new absorption bands naturally appear in IR spectrum.

These chemical bonds at the interface between the constituents turned out to be carrying considerable stress thus strengthening substantially the composite.

This is evidenced by the frequency shift of the corresponding absorption band maxima under load.

IR spectroscopic measurements carried out on composites made up of polypropylene filaments in a polyethylene matrix showed also that the matrix which was originally nonoriented becomes partially oriented in a layer adjoining the oriented reinforcement. Such effects should be taken into account when calculating the strength of a composite.

Mass spectrometry was employed to investigate thermal desorption of very thin polymer layers from metal surfaces [7]. The interaction of polymers with the substrate, as was shown, can reduce substantially the activation energy of thermal degradation of polymers. The same authors studied the kinetics of water liberation from the surface of glass filament heated in vacuum. The presence of a mono-molecular water layer on the surface of glass filaments was shown to reduce considerably the activation energy of their fracture and, accordingly, their strength. This phenomenon is explained by dissociation of stressed chemical bonds between the silicon and oxygen atoms in the surface layer of glass facilitated by the reaction of hydrolysis in a presence of water. This effect accounts for the experimentally observed changes in the activation energy of fracture of glass-fiber reinforced composites depending on the presence or absence of even traces of water at the interface between the glass filaments and the polymer matrix.

Small-angle x-ray scattering permitted to detect the formation of submicrocracks of two types in model polymer-polymer composites under load [8]. One of them is ascribed to the reinforcement, and the other, to matrix or the interface between the constituents. When combined with the acoustic technique, this method will yield valuable information on the formation and kinetics of growth of micro- and submicrocracks in composites.

The examples presented indicate that the methods employed earlier in the studies of the nature of fracture of homogeneous solids provide important data also on the fracture of composites at the microlevel. Combination of these methods with phenomenological studies of the kinetics of fracture of composites should be used as a basis for research into the nature of the fracture of composites.

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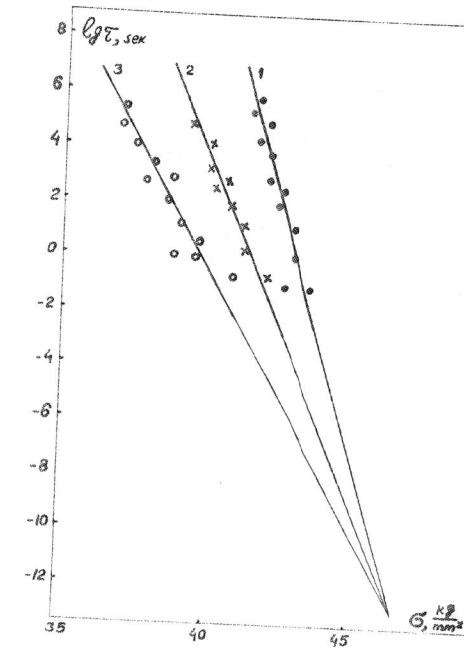


Figure 1 The temperature - stress dependence of the lifetime of tungsten-fiber copper-matrix composite. The volume ratio of tungsten fibers  $V_f = 10\%$ . Temperatures, °C : 1 +18; 2 +150; 3 +300.

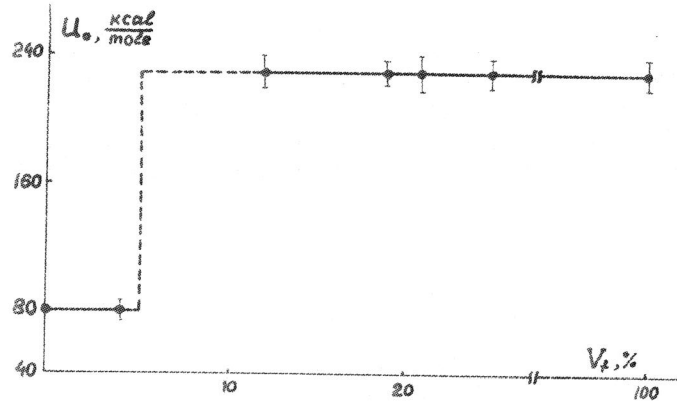


Figure 2 The activation energy of fracture ( $U_c$ ) of Cu - W composite versus the volume ratio of tungsten fibers.