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SHEAR STRENGTH OF EPOXYPOLYSULFONE GLASS-REINFORCED PLASTICS IN A WIDE RANGE OF LOADING RATES

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The shear strength of unidirectional epoxypolysulfone glass-reinforced plastics in the range of six decimal orders of loading rates has been measured. ED-22 epoxydiane resin (analog of DGEBA) modified by PSK-1 aromatic polysulfone served as a matrix. It has been shown that the strength values linearly increase with increasing logarithm of the loading rate; the sensitivity of composites to the rate of application of a force increases with increasing quantity of PSK-1 introduced into the matrix, and the fracture mechanism of composites is the thermofluctuation one. The laws revealed do not differ from those established by us earlier for glass-reinforced plastics based on epoxy binders modified by active diluents.

In [1], the influence of the loading rate on the shear strength of unidirectional epoxy glass-reinforced plastics has been investigated. ED-20 epoxydiane resin modified by an active diluent epoxidized diglycidyl ether of diethylene glycol (DEG-1) served as a matrix in them. Measurements were made at five rates differing by six decimal orders. The present paper is a continuation of these studies. Its aim is to determine the extent of generality of the laws elucidated in [1] for composites based on modified epoxy matrices. Here glass-reinforced plastics in which epoxypolysulfone mixtures are used as matrices are investigated. In recent years, these matrices have been increasingly widely used as binders for composites. With their help, researchers have tried to obtain materials possessing not only high strength and rigidity but also stability to crack extension.

Epoxypolysulfone binders, representing, before hardening, monophase systems, delaminate in the process of hardening [2–4]. Thus, the main difference between the glass-reinforced plastics investigated in [1] and in the present paper is that in the first case composites were obtained on the basis of monophase binders and in the second case — on the basis of heterophase binders.

Experimental. Unidirectional glass-reinforced plastics (GRPs) obtained by wrapping a glass fiber on cylindrical mandrels were investigated. The matrices represented mixtures of ED-22 epoxydiane oligomer and PSK-1 aromatic polysulfone with a molecular mass of 35,000. The content of PSK-1 in the mixtures was 5, 10, 15, and 20 mass·h per 100 mass·h of ED-22. The mixtures were hardened by triethanolaminotitanate (TEAT) or diaminodiphenylsulfone (DADPS). The content of TEAT in all events constituted 10 mass % of the ED-22 mass and the content of DADPS — 30% of the ED-22 mass.

Hardening was carried out in an oven in a stepwise regime: 1 h — 100°C, 2 h — 120°C; 6 h — 160°C for TEAT-hardened matrices; 1 h — 100°C, 2 h — 120°C; 5 h — 180°C for DADPS-hardened matrices. The quality of the glass-reinforced plastics obtained was assessed by their structural characteristics: volume content of components, density, and porosity (see Table 1). From the rings obtained, segments were cut out and subjected to a shearing test by the short-beam method with a three-point loading scheme [5]. The ratio of the length of specimens to their thickness was ~6. And the specimens thereby failed under the action of the shear stresses, i.e., in the experiments we measured the interlayer shear strength τ. Tests were carried out under quasi-static and shock loadings. In the quasi-static experiments, we used a WPM (Instron-type) tension testing machine. Loading of specimens under a low-rate impact was carried out on a plant based on a KSP-2 spring impact testing machine [6, 7]. Both measuring complexes

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TABLE 1. Density and Composition of Glass-Reinforced Plastics Based on Polysulfone-Modified Epoxy Matrices

Hardener	Indices	C				
		0	5	10	15	20
TEAT	V_{fib}	63	57	53	59	59
	V_{pore}	2	2	3	5	3
	ρ	2	1.95	1.88	1.94	1.96
DADPS	V_{fib}	52	48	46	—	59
	V_{pore}	2	3	5	—	5
	ρ	1.83	1.75	1.83	—	1.92

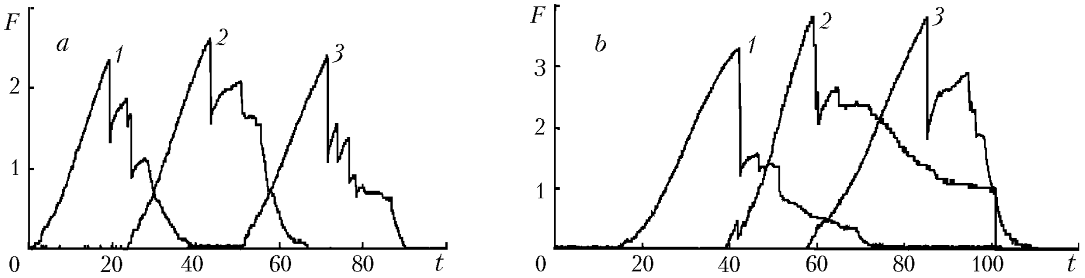

Fig. 1. Typical loading diagrams of unidirectional epoxypolysulfone glass-reinforced plastics [hardeners: TEAT (a), DADPS (b), loading rate 11 mm/min] at a PSK-1 content in the matrix of: 1) 0, 2) 10, 3) 20%. F, kN; t, min.

provided computerized reading and processing of the results. In so doing, one and the same measuring equipment was used. In the process of testing the loading diagrams, i.e., the load–time dependences were registered, which permitted obtaining data on the kinetics of change in the strength at various loading rates.

The loading rates for quasi-static tests were 0.8, 11, and 80 mm/min, for dynamic tests — $2.4 \cdot 10^5$ and $3.24 \cdot 10^5$ mm/min. All measurements were made at room temperature. In all events, the shear-strength value of the glass-reinforced plastics was calculated by the formula [8]

$$\tau_{\text{fr}} = \frac{3F_{\text{fr}}}{4bh}, \tag{1}$$

where the maximum value of the force corresponding to the onset of failure of the specimen failure is given as the height of the first peak in Figs 1 and 2.

Results and Discussion. Figures 1 and 2 show the typical $F-t$ loading diagrams obtained on specimens of glass-reinforced plastics based on modified epoxy matrices with a different quantity of polysulfone introduced into them hardened by TEAT or DADPS at various loading rates (from quasi-static to dynamic ones). It is seen that for all investigated glass-reinforced plastics the shape of the diagrams for both quasi-static and dynamic loadings up to the moment of the first crack formation is practically the same. It depends on neither the quantity of polysulfone nor the hardener type. At small rates of application of a load (see Fig. 1), some nonlinearity of the initial section on the $F-t$ diagrams is noteworthy. This is most probably due to the taking up of the plays in the testing-machine clamps and the specimen injury at the sites of contacts with supports. Nonlinearity is also observed near the top of the first peak. Such a character of change in the load with time under quasi-static loading is observed for matrices of any composition. Under a low-rate impact the load changes in most cases practically linearly up to its maximum value, and a change in the quantity of the modifier and the hardener type leaves the shape of the $F-t$ curves unaltered. If we take the loading time before the appearance of the first crack to be 100%, then the loading time in the nonlinear section constitutes (at the lowest rate) no more than 5–15% for both the glass-reinforced plastics based on the nonmodified epoxy binder and the composites into whose matrix 20% polysulfone was introduced. Under dynamic loading, the part of the nonlinear section decreases to a few percent. Since the extent of the nonlinear sections is small, it may be as-

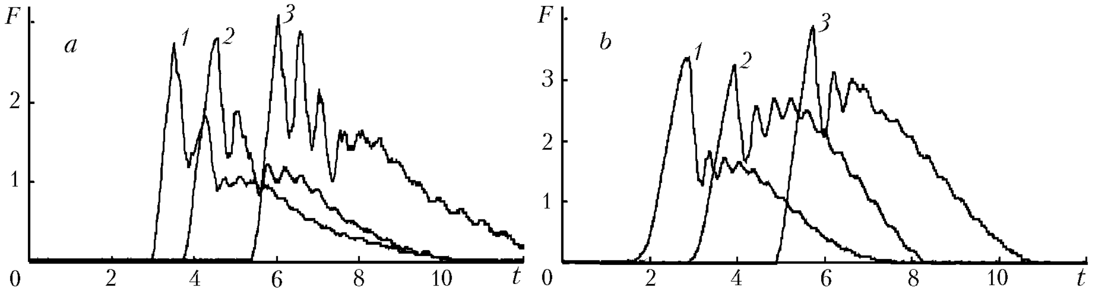

Fig. 2. Typical oscillograms of the impact momentum for unidirectional epoxy-polysulfone glass-reinforced plastics [hardeners: TEAT (a), DADPS (b), loading rate 4 m/sec] at a PSK-1 content in the matrix of: 1) 0, 2) 10, 3) 20%. F, kN; t, msec.

sumed that the glass-reinforced plastics deform quasi-elastically up to the moment the first crack grows and the stress growth rate on the specimen $\dot{\tau}$ remains constant during the experiment. In all cases it can be determined by the slope of the linear section of the diagrams: $\dot{\tau} = 3\dot{F}/4bh$. Earlier, in [1], we also noted that upon introduction into the epoxy matrix of the DEG-1 active diluent the nonlinearity region near the breaking load somewhat expands. In so doing, the investigated glass-reinforced plastics at a low-rate impact undergo elastic deformation. Under quasi-static loading, the diagrams also show a small nonlinear section preceding the first crack, and the loading time in the nonlinear section constitutes (at the lowest rate) no more than 2% for the composites based on the nonmodified epoxy binder and does not exceed 8–12% in the composites into whose matrix 30–50% of DEG-1 active diluent was introduced.

Further (upon extension of the first crack) failure of the materials depends on both the quantity of polysulfone and the hardener type. Failure of all specimens is followed by multiple cracking. This shows up as the appearance on the $F-t$ diagrams of several peaks whose height decreases as the fracture process develops. Under the conditions of quasi-static loading, as the polysulfone content is increased in the TEAT-hardened epoxy matrix, the level to which the load decreases as a result of the appearance of the first crack pointing to the degree of injury of the material at this instant of time remains practically unchanged with increasing PSK-1 content in the matrix and constitutes 70% of the maximum value of F. For the glass-reinforced plastics based on DADPS-hardened matrices, an increase in the modifier concentration leads to an increase in the level of loads needed for secondary cracking. For instance, in the glass-reinforced matrices based on the nonmodified matrix the load upon secondary cracking reduces by about one-half, and for the glass-reinforced plastics containing 10–20% polysulfone in the matrix it reduces by about one-third of the maximum. Moreover, the absence of clearly defined secondary peaks at a concentration of PSK-1 of over 10% points to a weak cracking of these composites (compared to the glass-reinforced plastics based on TEAT-hardened epoxy matrices).

An increase in the received load upon the formation of the first crack is also characteristic of the glass-reinforced plastics tested under the conditions of dynamic loading. For instance, for the epoxy plastic the appearance of the first crack leads to a decrease in the received load by nearly one-half, which points to a considerable injury of the specimen. At the same time, for the composites based on polysulfone-modified epoxy resin, upon reaching the ultimate stress, the load decreases to a much lesser extent, which is indicative of a smaller injury of the composites. For example, the glass-reinforced plastic based on a TEAT-hardened matrix containing 20% polysulfone upon secondary cracking is able to receive up to 90% of the maximum load, and the glass-reinforced plastic based on the same matrix but hardened to DADPS — up to 80%.

The diagrams obtained have made it possible to calculate the strength of the glass-reinforced plastics in a wide range of loading rates.

Figure 3a shows the shear strength of the glass-reinforced plastics under quasi-static loading. It is seen that the introduction of polysulfone practically does not influence the strength of the composites. The shear strength is also independent of the hardener type. The slight increase in the values upon introduction of 5 mass % of polysulfone is comparable to the scatter of data. Under the conditions of dynamic loading (4 and 5.4 m/sec, Fig. 3b), the strength of the composites based on TEAT-hardened matrices increases with increasing modifier concentration. The maximum strength increase was registered for the 20% content of polysulfone in the matrix and constitutes 10% at a

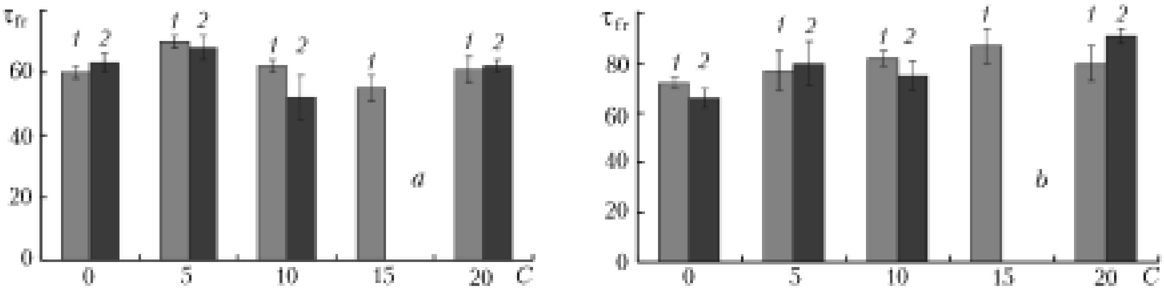

Fig. 3. Shear strength of unidirectional glass-reinforced plastics based on epoxypolysulfone matrices versus the quantity of polysulfone introduced into the matrix (hardeners: TEAT — 1, DADPS — 2) at a loading rate of: a) 11 mm/min; b) 4 m/sec. τ_{fr}, MPa; C, mass %.

TABLE 2. Zhurkov-Equation Coefficients Obtained for Epoxypolysulfone Glass-Reinforced Plastics

Hardener	Indices	C				
		0	5	10	15	20
TEAT	B_1	59	67	62	57	59
	B_2	2.3	1.5	3.7	5.6	5.6
	B	0.04	0.02	0.06	0.1	0.1
	γ	2445	3839	1521	1001	1001
	U_0	218	330	169	132	134
DADPS	B_1	63	66	47	—	62
	B_2	1	3.3	5.3	—	5.7
	B	0.02	0.05	0.11	—	0.09
	γ	5859	1690	1061	—	981
	U_0	440	185	125	—	136

loading rate of 4 m/sec and 24% at 5.4 m/sec. The τ_{fr} value for the glass-reinforced plastics based on DADPS-hardened matrices at a concentration of polysulfone of 20% increases by about 35% at both dynamic loading rates. The increase in the strength in these cases is likely to be due to the improvement of the dissipative properties of the modified matrices. The slight decrease in the shear strength at a 10% PSK-1 content (loading rate of 11 mm/min) is due to the increased porosity of the specimens (Table 1). These data demonstrate the advantages of epoxypolysulfone matrices over epoxyrubber ones, in using which the shear strength of the composites begins to decrease even at 3–5% of the modifier [9].

The dependence of the shear strength on the loading-rate logarithm for the glass-reinforced plastics based on epoxy matrices with a different content of polysulfone is given in Fig. 4. It is seen that in the range of six decimal orders in each investigated glass-reinforced plastic the τ_{fr} values obtained by "fast" and "slow" application of the load fall well on one straight line. Thus, for each investigated composite

$$\tau_{fr} = B_1 + B_2 \log(\dot{\tau})\,. \tag{2}$$

The coefficient $B_2 = d\tau_{fr}/d \log(\dot{\tau})$ characterizes the change in strength caused by a change in the loading rate by an order of magnitude, i.e., the response of the material to the rate of application of the external force, its "sensitivity" to the rate of external action.

From Table 2 it is seen that this sensitivity in using TEAT-hardened nonmodified resin is equal to 2.3 MPa and that for DADPS-hardened nonmodified resin is $\approx$1 MPa. But for the glass-reinforced plastics based on ultimately modified matrices the value of B_2 increases to 5.6 MPa for both types of hardeners. The observed trend is even more pronounced if the sensitivity to the loading rate is expressed in relative units $B = B_2/B_1$. According to formula (2), $B_1 = \tau$ at $\log \dot{\tau} = 0$, i.e., at $\dot{\tau} = 1$ MPa/sec. The data presented in Table 2 show that at a high content of polysulfone

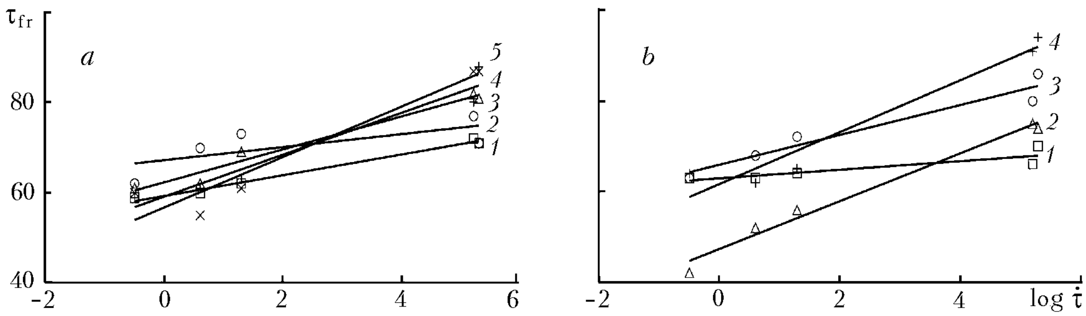

Fig. 4. Shear strength of unidirectional glass-reinforced epoxypolysulfone plastics versus the loading-rate logarithm [hardeners: TEAT (a), DADPS (b)] at a PSK-1 content in the matrix of: a) 1) 0, 2) 5, 3) 10, 4) 15, 5) 20%); b) 1) 0, 2) 5, 3) 10, 4) 20%. τ_{fr}, MPa; log $\dot{\tau}$, MPa/sec.

(20%) the change in the strength of the glass-reinforced plastic caused by a change in the loading rate by an order of magnitude can reach 10%.

Analogous dependences were obtained by us earlier [1] for glass-reinforced plastics based on an epoxy matrix containing DEG-1 active diluent. It was shown that the "sensitivity" upon introduction into the epoxy oligomer of active diluent increases: in using nonmodified resin B_2 = 2.3 MPa, and for glass-reinforced plastics based on modified matrices B_2 is equal to 4–7 MPa. In relative units, the change in the strength of the glass-reinforced plastic caused by a change in the loading rate by one order of magnitude can reach 10–15% (at 30–50% of active diluent).

The linear change in the strength caused by a change in the logarithm of the rate of external action is highly general. Under quasi-static loading, not only the tensile and compressive strength of glass fibers of various diameters (10–200 μm) and glass-reinforced plastics based on various polymers (epoxy, polyester, butvar-phenol), but also the strength of adhesive joints of polymers with fibers and the strength of flat adhesive joints obey this dependence [10, 11]. The results presented in Fig. 4 indicate that the shear strength of the epoxy glass-reinforced plastics linearly increases with increasing log $\dot{\tau}$ as well and (at least for unidirectional materials) the change in the tensile and shear strengths is described by the same mechanisms.

The straight lines given in Fig. 4 make it possible to conclude that the epoxy glass-reinforced plastics also fail in shear by the thermofluctuation mechanism. Indeed, the dependence of strength on the loading rate is manifestation of the stress dependence of durability. The question of how to calculate the durability (lifetime t^* under a load at a constant stress) if the strength under the other loading conditions is known was considered in [12, 13]. These investigations have shown that if one assumes that the fracture process is irreversible and the fracture arising under the action of a stress at each given instant of time is independent of the fracture that has already taken place in the material and is only connected with the value of the stress σ acting at a given instant of time, then the process of superposition of "partial" fractures can be characterized, using the Baily criterion [14]. For continuous monotonic loading this condition is written as

$$\int_0^{t_{\max}} \frac{dt}{t^*(\sigma)} = 1 . \tag{3}$$

Let the loading rate $\dot{\sigma}$ be constant and the relation between the durability $t^*(\sigma)$ and the stress be described by the Zhurkov formula [12]

$$t^* = A \exp(-\alpha\sigma) = t_0^* \exp[(U_0 - \gamma\sigma)/kT] , \tag{4}$$

where A and α depend on the material properties and temperature:

$$\alpha = \gamma/kT , \quad A = t_0^* \exp(U_0/kT) . \tag{5}$$

Then integration of (3) at a constant temperature yields the known relation [12]

$$\sigma_{\mathrm{fr}} = A_1 + A_2 \log \dot{\sigma}, \tag{6}$$

and it is assumed thereby that the product $\alpha\dot{\tau}A \gg 1$. The coefficients A_1 and A_2 are related to the coefficients of the durability formula α and A by the relations

$$A_2 = \frac{2.3}{\alpha}, \quad A_1 = \frac{2.3}{\alpha} \log A\alpha. \tag{7}$$

Thus, when the exponential law holds for the durability t^*, the dependence of the stress σ_{fr} on the loading rate (at $\dot{\sigma}$ = const) is linear in the semilogarithmic coordinates. Expressions (4) and (6) were first obtained and used for the simplest types of loading — uniaxial static tension at a constant load and quasi-static tension at a constant rate, respectively. The results of the present investigation show that the rate dependence of the strength τ_{fr} of epoxypolysulfone glass-reinforced plastics is also described by an expression analogous to (6).

It has been shown above that the growth rate of the load on the specimens of the investigated glass-reinforced plastics and in both the dynamic and quasi-static experiments can be considered to be constant. Therefore, it is reasonable to consider expression (2) as a confirmation of validity of the Zhurkov formula (4) also in describing the durability of solids (at least of unidirectional glass-reinforced plastics) subjected to the action of shear stresses. This fact agrees with the ideas that the role of activation processes is important in failure.

The Zhurkov formula serves as a mathematical expression of the kinetic conception of strength. The knowledge of its parameters (γ and U_0) permits predicting the properties of a material. It is easy to calculate the parameters γ and U_0 in shear, knowing the coefficients B_1 and B_2 of Eq. (2).

From equations analogous to (5) and (7) it follows that

$$\gamma = \frac{2.3}{B_2} kT, \quad U_0 = 2.3kT\left(\frac{B_1}{B_2} - \log\frac{2.3}{B_2} - \log t_0^*\right). \tag{8}$$

The values of the structure-sensitive parameter γ calculated by formula (8) are given in Table 2. It is seen that as the binder composition changes, there is also a change in the coefficient γ with increasing content of polysulfone, γ decreases. For the TEAT-hardened nonmodified matrix $\gamma = 2.3 \cdot 10^3$ cm^3/mole, and for the DADPS-hardened one $\gamma = 5.9 \cdot 10^3$ cm^3/mole; for the matrix containing 20% of PSF $\gamma \approx 1 \cdot 10^3$ cm^3/mole for the two types of hardeners. Such a decrease in γ seems to be fairly likely: γ shows the degree of overstress of bonds, which can decrease due to the plasticization of the binder. In so doing, there is also a decrease in the values of the zero-point activation energy U_0 (Table 2). Earlier this approach was used for glass-reinforced plastics based on DEG-1-modified epoxy matrices [1], for which, on the basis of a binder with 10% of DEG-1, U_0 = 156 kJ/mole. This value practically coincides with the value of U_0 = 159 kJ/mole obtained in studying the rate dependence of the tensile strength of glass veneers (thin — of thickness 0.1–0.2 mm — unidirectional glass-reinforced plastics) on the same binder [10, 11]. The values of U_0 for the glass-reinforced plastics based on epoxy matrices containing about 10% polysulfone also agree with this level of activation energies: they are equal to about 125–185 kJ/mole (see Table 2). Such an agreement enables us to state with more certainty that the process of tensile and shear fracture is determined by the rupture of the same bonds. We can speak with the greatest probability of the rupture of bonds at the fiber–matrix interface.

Thus, the results obtained in the present work show that the laws of change in the shear strength for the glass-reinforced plastics in which epoxypolysulfone matrices serve as binders do not differ from those for the glass-reinforced plastics based on the same epoxy matrices plasticized by the DEG-1 active diluent [1]. In both kinds of glass-reinforced plastics, the shear strength linearly increases with increasing logarithm of the loading rate. The sensitivity to the rate of application of the external action increases with increasing quantity of the modifier introduced into the epoxy resin. The fracture mechanism, as for tension, is a thermofluctuation one. In other words, independent of whether the structure of modified epoxy matrices is homogeneous or heterogeneous, the shear strength of the glass-reinforced plastics obtained on their basis with a wide variation of the rates of external action is described by the same mechanisms.

NOTATION

A, constant in the Zhurkov durability equation, sec; A_1, A_2, coefficients of Eq. (6) relating the tensile strength of a solid to the stress growth rate in the specimen, MPa; B, coefficient showing the relative change in the shear strength of glass-reinforced plastics caused by a change in the loading rate by one decimal order; B_1, B_2, coefficients of Eq. (2) relating the shear strength of glass-reinforced plastics to the stress growth rate in the specimen, MPa; b, specimen width, mm; C, content of polysulfone in the epoxy oligomer, mass %; F, current value of applied force, kN; F_{fr}, maximum force value, kN; h, specimen thickness, mm; k, Boltzmann constant, J/deg; T, absolute temperature, ^oC; t, current time, msec or min; dt, action time of stress $\sigma(t)$, sec; t_{max}, time before rupture, sec; $t_0^* = 10^{-12}$–10^{-13} sec for all solids; $t^*(\sigma)$, durability of a body under continuous stress σ, sec; U_0, apparent activation energy of the fracture process, kJ/mole; V_{fib}, volume content of fiber in the composite, vol. %; V_{pore}, volume content of pores in the composite, vol. %; α, constant of the Zhurkov durability equation, 1/MPa; γ, structure-sensitive coefficient connected with the concentration of stresses, cm^3/mole; ρ, composite density, g/cm^3; σ, continuous stress, MPa; τ_{fr}, shear strength of glass-reinforced plastics, MPa; τ, shear strength, MPa; dot over symbol, time derivative: $\dot{F} = dF/dt$, $\dot{\sigma} = d\sigma/dt$, $\dot{\tau} = d\tau/dt$. Subscripts: fib, fiber; pore, pores; fr, fracture.

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