INFLUENCE OF THE LOADING RATE AND THE CONCENTRATION OF AN ACTIVE DILUENT ON THE STRENGTH OF EPOXY COMPOSITES AND MODEL ADHESIVE COMPOUNDS

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A study has been made of the loading rate and the concentration of an active diluent on the shear strength of unidirectional epoxy glass- and carbon-fiber-reinforced plastics and the adhesion strength of the model compounds fiber–matrix. It has been shown that the values of the strength of the composites and the interface increase with the loading rate. As the concentration increases, the sensitivity to the loading rate follows a curve with a maximum in the adhesive compounds and it remains constant, in practice, in the composites. The results obtained have been employed in discussion of the mechanism of the process of failure of fiber-reinforced plastics.

Introduction. It is well known that the properties of fiber-reinforced plastics depend not only on the properties of the components but also on the strength of cohesion between the fibers and the matrix. One can assume that the response of a composite to the rate of external action is also related to the manner in which the interface responds to this action. However, direct experimental data confirming (or rejecting) the indicated general assumption are absent, in practice. This is primarily caused by the difficulty of experimental study of the kinetics of failure of the fiber–polymer matrix interface.

In this work, in studying the dependence of the strength of unidirectional fiber composites and adhesive compounds on the loading rate, we have simultaneously investigated the behavior of both. We sought to elucidate, first, the manner in which modification of the epoxy matrix by an active diluent affects the strength and, second, whether it is possible to employ such measurements for refinement of the mechanism of the process of failure in fiber-reinforced plastics.

Experimental. Triethanolaminetitanate-cured mixtures of epoxydian oligomer ÉD-20 (analog of DGEBA) with an active diluent (diethylene glycol DEG-1) were used as the matrices in the composites under study. The concentration of DEG-1 in the mixtures varied from 0 to 50 wt.%, while the loading rates changed 2 to 3 orders of magnitude. To evaluate the adhesiveness of these epoxy matrices we investigated the strength of adhesion between these compounds and a steel wire 150 μm in diameter. The form of the employed model compounds is shown in Fig. 1. The selection of a steel wire as the substrate was motivated by its great methodological advantages: high breaking loads and constancy of the diameter (along the length) ensure the absence of breaks on the wire and good reproducibility of the results, which in turn considerably decreases the number of test specimens and the duration of the experiment. The specimens were cured at a temperature of 160°C for 8 h. The measure of adhesion strength τ_{adh} was the stress necessary for pulling the wire out of the matrix layer (pull-out method):

$$\tau_{adh} = \frac{F_f}{S}, ^*$$

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* For the sake of simplicity, in what follows we omit the subscript "adh" and employ τ instead of τ_{adh} throughout the paper to denote adhesion strength.

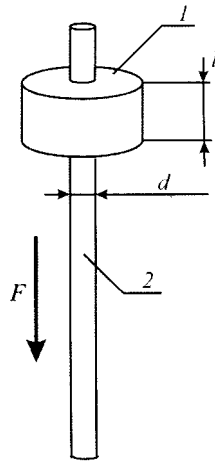
Fig. 1. Diagram of the specimen employed for measuring the adhesion strength in the joints of polymers with fibers of diameter $d \geq 100\,\mu m$: 1) matrix; 2) fiber.
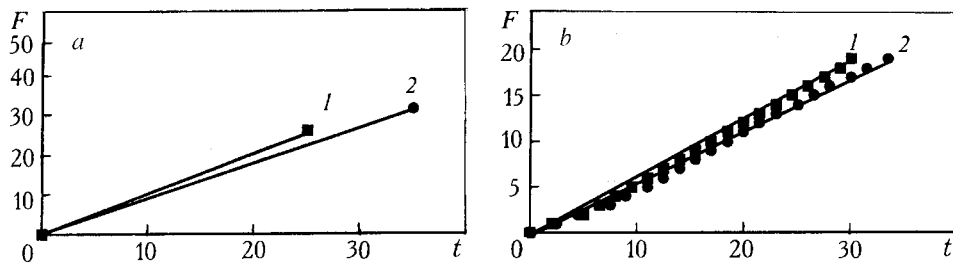

Fig. 2. Loading diagrams of the adhesive joints: $\dot{F} = 1$ N/sec (a) [1) $W = 10$ and $S = 0.53$ and 2) 50% and 0.71 mm^2]; $\dot{F} = 0.01$ N/sec (b) [1) $W = 0$ and $S = 0.43$ and 2) 10% and 0.71 mm^2].

where $S = \pi dl$. The produced joints were tested on the adhesiometer created at the Laboratory of Reinforced Plastics of the Institute of Chemical Physics of the Russian Academy of Sciences and enabling one to carry out measurements in a range of rates which covers three decimal orders [1, 2].

The adhesiometer employed, just as most of the breaking machines, ensures measurements at a constant velocity of movement of a movable clamp, i.e., when the deformation rate is nearly constant. However, a small length of the adhesive joints of polymers with fibers and correspondingly small elongations make it impossible to directly measure the deformation. Therefore, in loading of the specimen, one usually records the dependence of the load F on the loading time t, which precisely characterizes the rate of growth of the stresses at the interface:

$$\dot{\tau} = \frac{1}{S}\dot{F}.$$

Typical diagrams of loading of the joints under study, which were obtained at rather high rates, are given in Fig. 2a. It is obvious that the load increases linearly up to failure. On these diagrams, the loading time was no longer than several tens of seconds. For rather low rates the loading time significantly increased. In these experiments, we left the recorder strip immobile and constructed the F–t diagrams from points by fixing the values of F at certain time intervals. It turned out (Fig. 2b) that in this case, too, the dependence F–t is linear up to failure, in practice. Thus, we can state that each of these experiments has been conducted at a constant loading rate $\dot{F} = $ const and the values of the adhesion strength of the polymer–fiber joint have been measured at a constant rate of growth of the tangential stresses at the interface. The procedures of manufacture of the joints, measurement, and processing of results have been described earlier [1, 2] in detail.

To determine the shear strength of unidirectional glass- and carbon-fiber-reinforced plastics in shear ($\tau_{c.m}$) we employed wound rings with an inside diameter of 150 mm, width of 10 mm, and a thickness of ~5 mm. From the
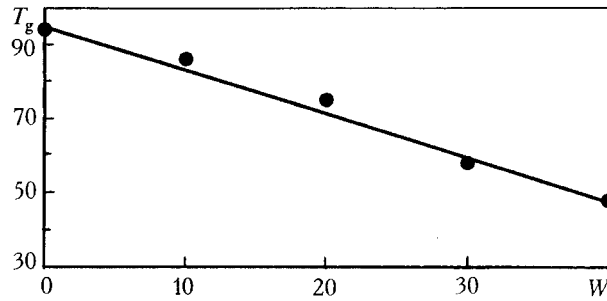
Fig. 3. Adhesion strength τ vs. area of the joints S for the systems modified epoxy resin ED-20–steel wire ($d = 150$ μm) for different concentrations of DEG-1 in the matrix [1, 3) $W = 50$ and 2, 4) 30%] and different loading rates [1, 2) $\dot{F} = 10$ and 3, 4) 0.01 N/sec].

rings we cut segments that were tested for shear according to the short-beam method (three-point-measurement scheme) on an Instron-type machine.

The quality of the produced carbon-fiber-reinforced plastics was evaluated by their structural characteristics: the volume content of the components and the porosity. The content of the fibers amounted to 50–55 vol.%. The porosity turned out to be insignificant (no higher than 1.6 vol.%) and nearly equal for all the components.

The strength of the adhesive compounds and the composites was measured at room temperature and quasistatic loading. The loading rates changed 2 to 3 orders of magnitude.

The relaxation behavior of the composites and the adhesive joints was characterized by their sensitivity to the rates of application of the external load (absolute and (or) relative changes in the strength with a change of one order of magnitude in the loading rate), i.e., to the quantities m and M for the composites

$$m = \frac{d\tau_{c.m}}{d \log \tau_{c.m}} \; ; \quad M = \frac{d\tau_{c.m}}{\tau_{c.m}^{m} d \log \tau_{c.m}} \tag{1}$$

and the coefficients k and K for the adhesive joints

$$k = \frac{d\tau}{d \log \dot{\tau}} \; ; \quad K = \frac{d\tau}{\tau^{m} d \log \dot{\tau}} \; . \tag{2}$$

The quantities M and K are convenient for comparing of the sensitivity of the corresponding strengths to the rate of external action in different systems.

Results and Their Discussion. The results obtained are given in Figs. 3–9. Figure 3 shows the manner in which the adhesion strength of the model compounds changes with the loading rate, the composition of the adhesive, and the dimensions of joints. It is obvious from the figure that the strength of the interface depends on the loading rate: the values of the adhesion strength increase with rate. We emphasize that the unmodified resin ED-20 forms one of the strongest (as compared to other epoxy resins [1, 2]) interfaces in interaction with the steel wire.

From Fig. 3 it is also obvious that the values of τ depend on the dimensions of the adhesive joint, decreasing with increase in S. Such a decrease in τ is a common phenomenon. One observes it for joints of thermoreactive and thermoplastic polymers with fibers of any nature and any diameter if the measurements have been performed at $T < T_g$ of the polymer [1–5]. As is well known [1, 2, 6–8], the character of such a dependence is due to the statistical scale factor (increase in the probability of appearance of a hazardous defect with increase in the dimensions of the specimen), to the nonuniform distribution of tangential stresses occurring at the fiber–polymer interface in the case of application of the external load, and to the action of residual stresses occurring at the interface in manufacture of the specimens and their heat treatment (mainly in their cooling to the testing temperature T).

As the amount of the active diluent added to the matrix increases, the dependence $\tau(S)$ becomes less pronounced, which seems natural. Indeed, diethyleneglycol DEG-1 employed for modification of the epoxy matrix serves as its plasticizer: its addition decreases T (Fig. 4). The value of the residual stresses acting at the interphase boundary
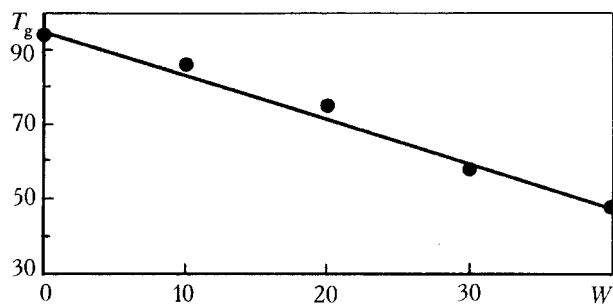
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Fig. 4. Vitrification temperature T_g of the epoxy resin ED-20 modified by an active diluent vs. concentration W of the added DEG-1.
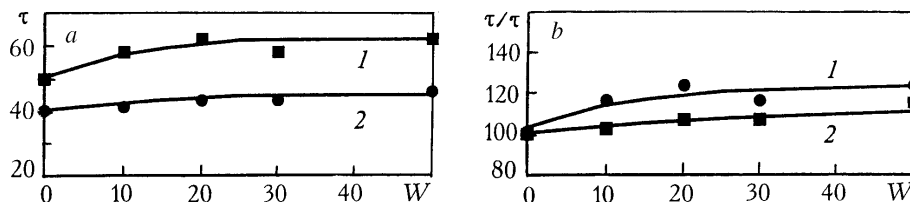

Fig. 5. Adhesion strength τ of the joints modified epoxy resin ED-20–steel wire ($d = 150$ µm) vs. concentration W of the DEG-1 added to the resin: 1) $\dot{F} = 10$ and 2) 0.01 N/sec; a) in absolute (MPa) and b) relative (%) units ($\tau_0 = \tau$ at log $\tau = 2$ and $S = 0.65$ mm^2).

is in proportion, in the first approximation, to $\Delta T = T_g - T$ ($T \approx 20^{\circ}$C in our case). The quantity ΔT decreases with T_g, the residual stresses decrease and their distribution becomes more uniform. This precisely leads to a steeper dependence τ–S.

It also follows from Fig. 3 that the τ–S curves referring to different loading rates are approximately parallel to each other. The problem of how the change in the rate of external loading influences the form of the τ–S curves has been considered in [1, 2]. It was shown that the measured value of the adhesion strength for joints with a contact area S can be written in the form

$$\tau(S) = \tau_{loc} - \tau_T(S) . \tag{3}$$

The value of τ_{loc} is determined only by the physicochemical interaction at the interface and does not depend on the geometry of the specimens, the conditions of their fastening, and some other details of the experiment. It is precisely this value that represents the characteristic of a given interacting pair. The value of τ_{loc} can be determined from experimental data in extrapolation of the $\tau(S)$ curve to zero

$$\tau_{loc} = \lim_{S \to 0} \tau_{exp} = \lim_{S \to 0} (F/S) .$$

The value of the residual stresses in (3) depends on the physicochemical characteristics of the adhesive and the substrate and on the dimensions of the joints, increasing with S. These stresses are formed in the process of manufacture of joints in temperature treatment and subsequent cooling to room temperature. They exist in the specimens until the external load is applied to them and accordingly do not depend on the loading rate. Therefore, for two different rates of loading we can write (3) in the form $\tau_1 = \tau_{loc1} - \tau_T$ and $\tau_2 = \tau_{loc2} - \tau_T$. Whence $\tau_1 - \tau_2 = \tau_{loc1} - \tau_{loc2}$ or, introducing the notation $\tau_1 - \tau_2 = \Delta\tau$, we have

$$\Delta\tau = \tau_{loc1} - \tau_{loc2} = \text{const} . \tag{4}$$

Relation (4) holds for joints of any dimensions. Thus, if the ideas developed are correct, for any S the adhesion strength must differ by the same value of $\Delta\tau$ for two different rates of loading; accordingly the τ–S curves referring
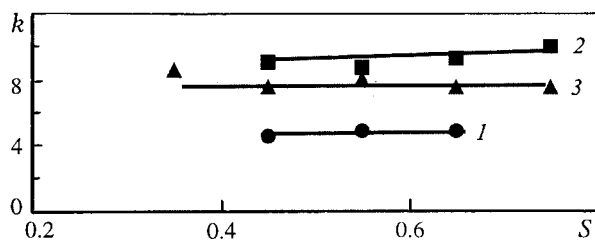
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Fig. 6. Coefficient k (MPa) vs. area of the adhesive joint S (mm^2). The values of k have been calculated from formula (2): 1) $W = 0$, 2) 20, and 3) 30%.
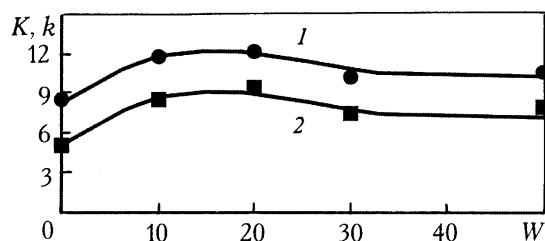
Fig. 7. Sensitivity of the interface of the rate of application of the external load for compounds with different contents of the active diluent DEG-1 in the matrix in relative (%) (curve 1) and absolute (MPa) (curve 2) units, $S = 0.65$ mm^2.

to these rates must be parallel to each other. However, from Fig. 3 it is obvious that the τ–S curves are parallel to each other only approximately. The absence of strict parallelism is explained by the fact that the nonuniformity of the field of shear stresses at the interface is caused not only by the nonuniform distribution of "internal stresses" which have already been spoken of but also by the nonuniformity of the field of external (applied) stresses. Since the external load is applied with different rates, relation (4) holds only approximately.

It is noteworthy that nearly parallel τ–S curves have been observed earlier [1, 2] for the joints of epoxydian, phenolformaldehyde, and polyether matrices with a steel wire of diameter 150 μm.

Addition of the active diluent DEG-1 to epoxydian resin ED-20 changes the strength of the interface. In the range of concentrations of the active diluent of 0 to 50%, the adhesion strength monotonically increases (Fig. 5). The increase in the values of τ depends on the loading rate: it attains 24% for $\dot{F} = 1$ N/sec and 16% for $\dot{F} = 0.1$ N/sec (Fig. 5). The character of the adhesion strength–concentration of the modifier curves is independent of the dimensions of the tested specimens. The improvement in the cohesive strength with increase in the concentration of diethylene glycol is most probably due to the decrease in the level of residual stresses.

We emphasize that the increase in τ with the amount of the modifier is also characteristic of bipolymeric matrices with phase layering, such, for example, as epoxy resin–polysulfone [9]. However, the interface strength for these systems follows a curve with a maximum, while the increase in the values of τ is observed for low (to 10%) concentrations of polysulfone.

In accordance with what has been said above, the change in the adhesion strength of the systems under study must weakly depend on the dimensions of the joints in variation of the loading rate (see Fig. 6).

Remaining constant, in practice, in the investigated range of areas for such an amount of the active diluent in the matrix, the coefficient k nonmonotonically changes with increase in the concentration of DEG-1 as part of the binder (Fig. 7). The sensitivity is maximum for the matrices containing 10 to 20% diethyleneglycol. For these concentrations the sensitivity is 1.7 to 1.9 times higher than that in the unmodified matrix.

Figure 7 also gives the coefficients K characterizing the relative change in the adhesion strength with a change of one decimal order in the loading rate (see (2)). This sensitivity is also maximum in binders containing 10 to 20% DEG-1: we have $K = 12$–12.5% for them. Thus, study of the adhesion strength in the fiber–matrix systems shows that the addition of the active diluent to the epoxydian binder can change the sensitivity of the interface to the rate of application of the external load 1.5 times.

For one investigated matrix containing 10% DEG-1, we investigated earlier [10] the adhesion strength in compounds with glass and carbon fibers directly employed for manufacture of glass- and carbon-fiber-reinforced plastics. The experiments were conducted at different loading rates covering three decimal orders. It turned out that, although the absolute values of the strength of the interface in the compounds markedly differ (see Table 1), the sensitivity to a rate change in the systems in question is equal, in practice: $K = 10$–12%. For the sake of comparison, the table gives the value of the coefficient K obtained in the present work in investigating the adhesion of this matrix to a steel wire. The equality of the coefficients K in adhesion to the fibers of different chemical nature and different diameters enables us to say that the sensitivity in the unit cell of a fiber-reinforced plastic to the rate of application of the ex-

TABLE 1. Adhesion Strength and Sensitivity to the Rate of Loading of the Fiber–Modified Epoxy Matrix Joints

Fibers	d	l	$S \cdot 10^3$	k	K	τ^{**}
Carbon[*]	7.1	56.5	1.2	10.5	12	68
Glass[*]	13.5	165	7.0	4.5	10	38
Steel	150	1300	650	8.5	12.5	56

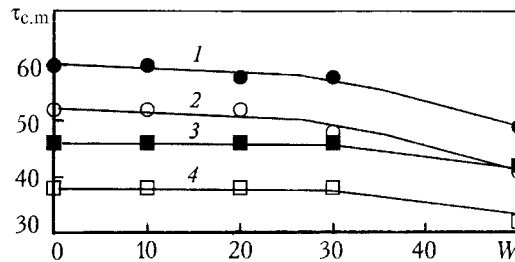Note: [*]According to the data of [10]. [**]At $\log \dot{\tau} = 0$.

Fig. 8. Shear strength of the unidirectional epoxy composites $\tau_{c.m}$ (MPa) vs. content W (%) of the active diluent DEG-1 in the matrix: 1, 2) glass-fiber-reinforced plastics; 3, 4) carbon-fiber-reinforced plastics; 1, 3) $\dot{F} = 800$ and 2, 4) 2 N/sec.
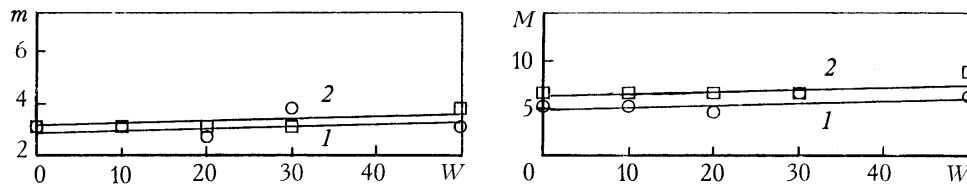

Fig. 9. Coefficients m and M for unidirectional epoxy glass-fiber-reinforced plastics (1) and carbon-fiber-reinforced plastics (2) vs. content of the active diluent DEG-1 in the matrix.

ternal action is mainly determined by the nature of the matrix. No direct measurements of the adhesion strength in compounds with glass and carbon fibers were performed for matrices containing different amounts of DEG-1. However, it is beyond reason to assume that the regularities obtained in such experiments will differ from those observed for the composition with 10% DEG-1. Therefore, it may be thought that in adhesion to commercial glass and carbon fibers, the cohesive strength increases with the amount of the added modifier and the sensitivity to the rate of application of the external load follows a curve with a maximum.

The influence of the loading rate and the composition of the matrix on the strength of unidirectional glass and carbon-fiber-reinforced plastics is shown in Fig. 8. It is obvious that the shear strength changes weakly if the amount of active diluent does not exceed 30% and it decreases by 10–20% (as compared to the strength of the composites based on an unmodified epoxy matrix) when the concentration of DEG-1 attains 50%. With decrease in the loading rate the form of the $\tau_{c.m}$–W curves remains constant and only the absolute values of the shear strength change.

The sensitivity to the loading rate in absolute units (values of the coefficient m) is presented in Fig. 9 for glass- and carbon-fiber-reinforced plastics. It is obvious that the values of m are not only low ($m \cong 3$ MPa) but are also equal for both composites. The values of the coefficients M are also very close for the glass- and carbon-fiber-reinforced plastics: for all the composites they amount to 5 to 7% (Fig. 9).

A comparison of Figs. 7 and 9 shows that the character of the concentration curves $k(W)$ and $m(W)$ and accordingly $K(W)$ and $M(W)$ is different: the extremum dependence of the coefficients on the amount of the modifier (plasticizer) for adhesion and the absence of the dependence on W for the composites. Such an absence of the correlation between the strength of the plastic and the strength of the interphase boundary in its unit cell suggests that (within the investigated loading rates) the interface is not the "weak" link of these fibrous composites and their failure does not depend on the cohesive strength of the components. For plastics reinforced with nonpolymer fibers (glass,

boron, carbon) such an independence is observed for the first time as far as we know. In this respect, we can speak of the uniqueness of the materials under study.

CONCLUSIONS

The data obtained show that a parallel study of the rate dependences of the strength of fibrous composites and the adhesion strength in fiber–matrix compounds and an analysis of the correlation dependences plastic strength–interface strength provide new information on the localization of the process of failure in such materials.

NOTATION

d, diameter of the fiber, μm; l, length of the adhesive joint, μm; S, area of the adhesive joint, mm^2; t, time, sec; F, load applied to the specimen at the instant of time t, H; F_d, load under which the adhesive joint fails, N; $\dot{F}$, rate of growth of the load applied to the specimen, N/sec; $\dot{\tau}$, rate of growth of the stress applied to the specimen, MPa/sec; τ, shear strength, MPa; τ_T, temperature residual stresses, MPa; k and K, absolute and relative changes in the adhesion strength with a change of one order of magnitude in the loading rate, MPa and %; m and M, absolute and relative changes in the strength of the composites with a change of one order of magnitude in the loading rate, MPa and %; W, concentration of the active diluent in the matrix, wt.%; T, temperature, $^{\circ}$C. Subscripts and superscripts: loc, local; f, failure; g, glass transition (vitrification); adh, adhesive joint; c.m, composite material; 0, modifier-free (for W = 0); m, maximum; exp, experimental.

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