CORRELATION BETWEEN THE STRENGTH
OF FIBER-REINFORCED PLASTICS AND THE ADHESIVE
STRENGTH OF FIBER—MATRIX JOINTS[1]

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The relationship between the strength (σ_c) of unidirectional fiber-reinforced plastics in different stressed states and the interfacial strength of their components is investigated. The shear adhesive strength (τ_0) of fiber—matrix joints determined by the pull-out technique is used as a measure of the interfacial strength. To obtain the correlation curves between σ_c and τ_0, the experimental results are used, where both the plastic and adhesive strength change under the influence of a single factor. In this case, such factors are the fiber surface treatment, nature and composition of polymer matrices, and test temperature. It is shown that the strength of the glass, carbon, and boron plastics increases practically linearly with increased interfacial strength. Such a behavior is observed in any loading conditions (tension, shear, bending, and compression). Sometimes, a small (10-20%) increase in the adhesive strength induces a significant (50-70%) growth in the material strength. Therefore, the interface is the "weak link" in these composites. The shape of the σ_c—τ_0 curves for composites based on the high-strength and high-modulus aramid fibers and different thermoreactive matrices depends on the nature of the fiber and the type of stress state. In many cases, the composite strength does not depend on the interfacial strength. Then, the fiber itself is the "weak link" in these composites.

It is well known that the strength properties of fiber-reinforced plastics depend not only on the properties of the reinforcing filler and polymer matrix, but also on the adhesive strength between them. Therefore, to create composite materials with predetermined properties and to be able to predict any change in their properties under operating conditions, it is necessary to know just how the strength of a composite depends on the adhesive strength of the fiber—matrix joints. This study is dedicated to the analysis of such dependences obtained experimentally. It generalizes both the data published earlier and the results obtained recently by the authors.

The correlation curves of the strength of a reinforced plastic, σ_c, and the adhesive strength τ_0 can be obtained by investigating of the change in the strength of composites and the adhesive strength under the action of one and the same factor. Such factors can be, for example, the nature and composition of the binder, the nature and surface treatment conditions of the fibers, the test temperature, the rate of application of the external load, the curing conditions, the conditions and time of storage, and so on.

Attention must be paid to the following point. The strength of composites in tests of any kind, as well as the strength of adhesive joints, depends on the technology of their production and test conditions. Therefore, when constructing each σ_c—τ_0 dependence, both the composite specimens and the adhesive joints must be manufactured and tested under the same conditions. Usually, this can be achieved only in specially performed tests. Therefore, great care should be exercised when using data from the literature for constructing the σ_c—τ_0 curves.

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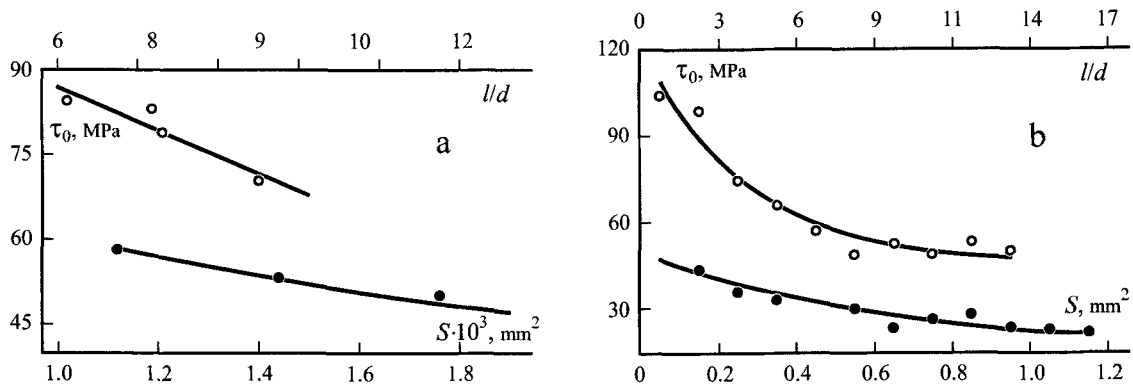

Fig. 1. Adhesive strength τ_0 vs. the joint area S upon adhesion of the EDT-10 epoxy binder (based on DGEBA) (○) and PSK-1 poly(arylene sulphone) (●) to the carbon fibers of diameter $d = 7$ μm (a) and steel wire of diameter $d = 150$ μm (b).
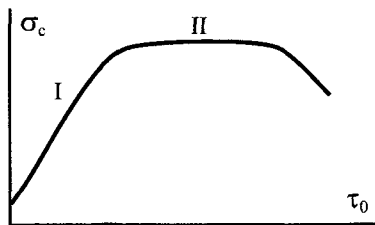

Fig. 2. Strength of a composite as a function of the adhesive strength of fiber—matrix systems.

Since the fiber together with the adjacent binder layer forms the unit cell of any fibrous composite, examination of the adhesive strength in just such a cell makes it possible to maximally approach the conditions existing in the reinforced plastic. Several ways for determining the adhesive strength in a fiber—matrix system are known, namely different variants of the pull-out technique [1-7], the method of fragmentation [8-11], and the push-out method [12-14]. In the present study, we will employ the data obtained for the fiber-polymer matrix joints using the pull-out technique.

The experimental values of the adhesive strength τ_0 depend on the shape and sizes of the test specimen [1, 2, 4-6, 15-17]. When determining the degree of adhesion to fibers of constant diameter d, the values of τ_0 decrease monotonically with increase in the area S (length l) of the adhesive joint. Some of these curves obtained for fibers of "small" and "large" diameters are given in Fig. 1. The dependence of τ_0 on S reflects the nonuniformity of distribution of the tangential stresses (residual and applied) at the interface between the fiber and the polymer matrix.

The existence of a markedly expressed dependence of the adhesive strength on the sizes of joints requires that, in each series of tests on the strength of composites and the adhesive strength of components, the σ_c—τ_0 curves be constructed using the values of τ_0 for joints of similar sizes (at the same values of S, l, and l/d). Wherever possible, the values of τ_0 obtained for joints with a sufficiently large area S, for which $l/d \geq 10$-20 and the values of τ_0 vary only slightly with change in S, must be used. As shown in [1, 2], these are the values that most precisely reflect the fracture conditions at the interface in actual composites.

The character of the relation σ_c—τ_0 depends on which element is the "weak link" in the composite. If such a "weak link" is the interface, an increase in the adhesive strength τ_0 will result in growth in the composite strength σ_c. On the contrary, at high values of σ_c, either the fibers or the matrix will be the "weak link," and τ_0 will not depend on σ_c. This fact is illustrated in Fig. 2 (the scheme shows also a possible region where the strength σ_c decreases with increased τ_0).

Thus, elucidation of the character of the dependence σ_c—τ_0 allows us to detect the localization of the "weak link" in a composite material.

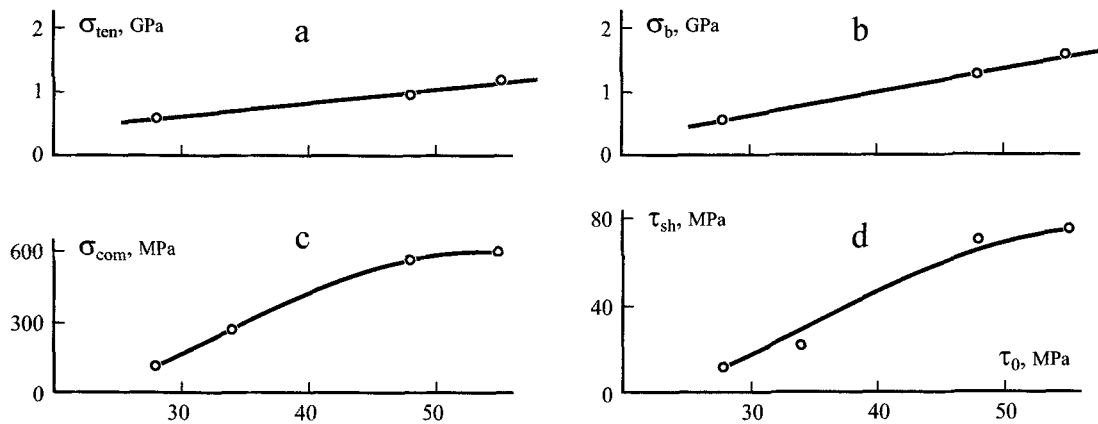Let us clear up to what extent the experimental data confirm the scheme offered.

Fig. 3. Strength of a unidirectional epoxy GFRP as a function of the adhesive strength of the corresponding fiber—matrix joints in tension (a), bending (b, segments of thin rings, $L/h = 40$, $L = 76$ mm, where L and h are the length and thickness of specimens), compression (c), and shear (d, measured by the short-beam method at $L/h = 5$ and $L = 24$ mm). The values of τ_0 were varied by modifying the fiber surface. Alkali-free glass fiber + EDT-10: $S = 7 \cdot 10^{-3}$ mm^2, $d = 13$-15 μm, and $l/d = 10$-13.
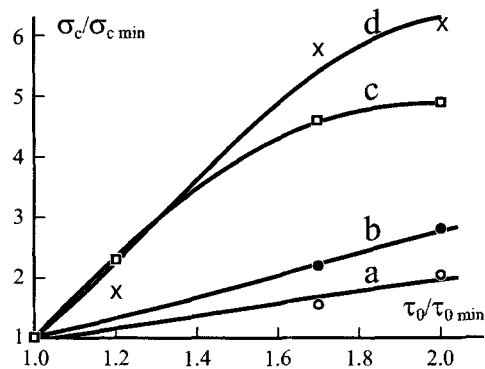

Fig. 4. Strength of an epoxy GFRP under different loading conditions vs. the adhesive strength of the components (according to the data in Fig. 3).

Modification of the interface. A most direct answer to the question on the relation between the degree of adhesion and the properties of a composite can be given by tests where its characteristics vary only due to changes in the adhesive strength. These tests can be carried out if, in producing the composites, the fiber and matrix remain the same, whereas the degree of adhesion is changed by modifying the surface of the fibrous filler.

The data in Fig. 3 illustrate the mechanical behavior of epoxy glass-reinforced plastics (EDT-10 binder) based on fibers coated with finishing agents and antiadhesives. These composites are obtained on the basis of alkali-free glass (an analog of E-glass) fibers formed from filaments directly upon drawing them out of the glassmelting vessel. The coatings were applied to the fiber surface during the pull-out. AGM-9 γ-aminopropyltriethoxysilane (0.1% water solution) was used as the finishing agent and dimethyldichlorosilane (DMDCS) (3% solution in CCl_4) and K-21 organic silicon liquid (10% solution in benzene) as the antiadhesives. To fix the coatings, the fibers were thermally treated ($130°C/0.5$ h) and then used to make flat and ring specimens by pressing and winding, respectively. It follows from the data in Fig. 3 that the treatment of fibers by antiadhesives not only reduces the adhesive strength but also decreases considerably the strength indices of the plastic in tests of all kinds. The relatively low values of the characteristics of glass-reinforced plastics in tension and compression can be explained by the rather low content of fibers and their damage upon rewinding the filaments which have not been cemented together. The drop in strength of the composite is especially pronounced in shear. According to the increasing sensitivity to the action of antiadhesives, the tests may be arranged as follows: tension, bending, compression, and shear. This is most evident in Fig. 4, where the relative change in the strength of a composite is shown as a function of the adhesive strength.

The strength of glass-reinforced plastics based on fibers finished with aminosilane increases just as the adhesive strength. This holds true for stress states of any kind.

An increase in the strength of composites with increased τ_0 was observed not only for glass-reinforced plastics based on alumoborosilicate fibers but also for plastics reinforced with fibers of VMP composition (an analog of S-glass). It is clearly seen from Figs. 3 and 4 that the strength of unidirectional epoxy glass-reinforced plastics also increases with increased interfacial strength. In this case, the more marked the change in the strength of the composite with varying interfacial strength (the more sensitive is the test type to the state of the interface), the earlier (at smaller values of τ_0) the σ_c—τ_0 dependence tends to weaken. However, the σ_c—τ_0 curve never reaches region II of the scheme in Fig. 2.

Let us now consider the dependence of the adhesive strength of components and the strength of composites on the method of surface treatment of boron fibers. A typical method of surface modification is treatment in solutions of nitric acid. For example, upon etching of the fibers in a 58% solution of HNO_3 at 117°C, with increased time of etching, the adhesive strength of the system of boron fiber—epoxypolyisocyanate binder varies according to a curve with a maximum [1, 2]. Boron plastics based on such fibers and the epoxypolyisocyanate binder have better mechanical characteristics. In this case, their strength varies symbatically with the strength of the interface. A small (17%) variation in the interfacial strength leads to a much greater (55%) change in the bending strength of boron plastics (for more details see [1, 2]). Thus, for boron plastics, as well as for glass-reinforced plastics, the relation between the strength of the composites and the interfacial strength that is increased by modification of the fiber surface is described by section I of the σ_c—τ_0 curve (see Fig. 2).

To increase the strength of CFRPs, different methods of oxidizing treatment of the filler are frequently used [18, 19]: oxidation by hot air, treatment by ozone, and electrochemical activation by anodic oxidation. In addition, the surface of carbon fibers is treated by special finishing agents [18, 19].

By activating the fiber surface, it is possible to raise the strength of their adhesion to the polymer matrices. Thus, upon electrochemical treatment of the UKN-5000P fibers, the interfacial strength τ_0 in joints with the EDT-10 binder increases by 28%. In this case, the physicomechanical characteristics of CFRPs based on the EDT-10 binder and treated fibers also improve. The strength of CFRPs increases especially significantly in shear (by 130-160%) and compression (160%), and to a lesser degree in tension (by 43%) and bending (40%).

The growth in the shear strength of epoxy CFRPs with increased adhesive strength at the interface is reported in [3]. Similar to the case of glass-reinforced plastics, a tendency to go beyond the limits appears on the τ_{sh}—τ_0 curve at large values of τ_0. However, in the case of CFRPs, it was also impossible to reach the range of values where the properties of the composite did not depend on the adhesive strength: the dependence σ_c—τ_0 again fell in region I of the scheme given in Fig. 2.

Modification of the nature and composition of the polymer matrix. The shape of the curves describing the correlation between the composite strength and the interfacial strength upon modification of the filler surface, i.e., in the "purest" form when the strength of the components is invariable, was considered above. However, in practice, when producing composite materials, it is of great importance to know how their properties vary upon use of different polymer matrices. Therefore, the problem on the effect of the nature and composition of the matrix on the properties of the interface and the character of the dependence σ_c—τ_0 is also of interest.

In [2, 3], it was shown that the strength of unidirectional glass-reinforced plastics based on thermoreactive binders of different nature (epoxy, phenolformaldehyde, and polyester) increases with increased degree of adhesion. This is also true both for unidirectional glass-reinforced plastics based on relatively low-modulus alkali-free glass fibers and for glass-reinforced plastics on the basis of high-modulus fibers of VMP composition. In this case, the correlation curves σ_c—τ_0 for materials reinforced with glass fibers of different nature are different. At a high degree of adhesion, an increase in the adhesive strength does not lead to a proportional increase in the strength of the plastic: the slope of the σ_c—τ_0 curve decreases gradually. This regularity is never broken whatever the stress state.

The increase in the strength of glass-reinforced plastics with increased degree of adhesion between the polymer matrix and fiber is characteristic not only of materials based on thermoreactive net binders, but also of those based on heat resistant thermoplastic matrices, as shown in Fig. 5. The figure shows a comparison between the results of measuring the adhesive strength and the shear strength of glass-reinforced plastics in the case where the polymer matrix consists of PSK-1 poly(arylene sulfone) modified by different amounts of liquid-cristalline polyether (LC polyether) — the product of copolycondensation of hydroxybenzoic acid and ethyleneterephthalate (60 : 40).
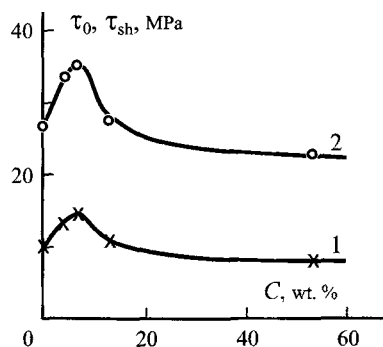
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Fig. 5. Adhesive strength τ_0 of a glass/fiber—thermoplastic/matrix joints (1) and the shear strength τ_{sh} (2) of GFRP vs. the amount $\tilde{N}$ of LC-polyether (wt.%), added to the poly(arylene sulphone) PSK-1.

The thermoplastic polymers that have appeared recently, such as poly(arylene sulfone), polysulfides, polyketones, and thermoplastic polyimides, combine highly elastic strength properties with high deformability. However, since their melts possess high viscosity, which exceeds that of, for example, epoxy oligomers by several orders of magnitude, it is difficult to use thermoplastic binders for producing composites reinforced with continuous fibers.

One of the most promising ways of decreasing the viscosity of polymer melts is their modification by polymers which have a rather low viscosity in a particular temperature interval. The possibility of using the LC polyether as the modifying additive to poly(arylene sulfone) for obtaining a unidirectional ribbon prepreg to produce a glass-reinforced plastic on its basis was also investigated in this study.

The LC polyether content in the blends was 2, 5, 10, and 50 wt.%, respectively. The blends were prepared in a "Brabender" double-rotor mixer at 250°C in 10 min. As follows from the data in Fig. 5, the character of the change in the composite strength and in the adhesive strength of the fiber—matrix joints is the same: with increased percentage (C) of LC polyether in the polymer blend, the dependences τ_0—C and σ_c—C are described by curves with a maximum. It should be noted that the maximum strengths of the composite and interface are achieved practically at the same composition of the blend. The increase in the shear strength of glass-reinforced plastics at a 2-8% content of LC polyether reaches 25%.

A similar pattern was also observed when examining the influence of modification of polyisocyanates by monomeric additives and polyisocyanurate by telechelic rubbers [20, 21]. It was found that the relation between the adhesive strength and the strength of unidirectional wound CFRPs is described by curves with a maximum. The maximum values of σ_c and τ_0 are also observed at small (5-10%) content of rubbers.

Thus, for glass, carbon, and boron plastics, an increase in the strength at the binder—fiber interface leads to an increase in the strength of the materials. This is also true in the case of surface modification of the reinforcing filler, as well as with any changes in the nature and composition of the matrix. All the dependences σ_c—τ_0 belong to region 1 of the scheme shown (see Fig. 2).

However, such relation between the strength of a unidirectional composite and the adhesive strength of the binder—fiber system is not always observed [1, 2, 22]. It turned out that the strength of plastics based on polyheteroarylene (SVM) fibers of SVM type and binders of different nature (epoxy and epoxy phenolic) does not depend on the adhesive strength of their components (Fig. 6). It is seen that, when τ_0 changes from 40 to 60 MPa, the strength of the composites for all types of stress state remains constant: the dependence σ_c—τ_0 falls in region II of the scheme in Fig. 2. This is probably associated with the failure character of the material and with some structural features of the fibers. The monofibers examined consist of separate highly oriented high-strength fibrils poorly bonded together in the transverse direction. Due to such structure of the fibers, the strength of these plastics, even when loaded along the fibers, is determined by the strength of the fiber, since the bond between the fibrils proves to be the "weak link."

Figure 6 also shows the correlation dependences σ_c—τ_0 for different types of loading of plastics based on Armos fibers — aramid fibers of other types. It is seen that all these plastics have practically the same shear strength (the deviations do not exceed 13%), while the difference in strength of the composites in compression reaches 30%. However, for the latter type of loading, the dependence of the composite strength on the interfacial strength is also poorly expressed. The constancy of the strength under these loading types, as in the case of plastics based on SVM fibers, can be explained by the particular structure of monofibers. Thus, at
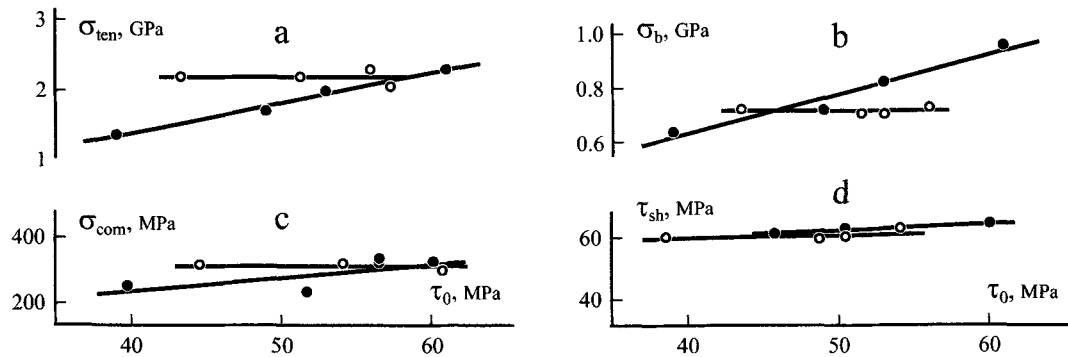
Fig. 6. Strength of a unidirectional aramid-fiber-reinforced plastic (OFRP) vs. the adhesive strength of the components. The OFRP based on the Armos (●) and SVM (○) fibers in tension (a), bending (b), compression (c), and shear (d, $L/h = 5$).
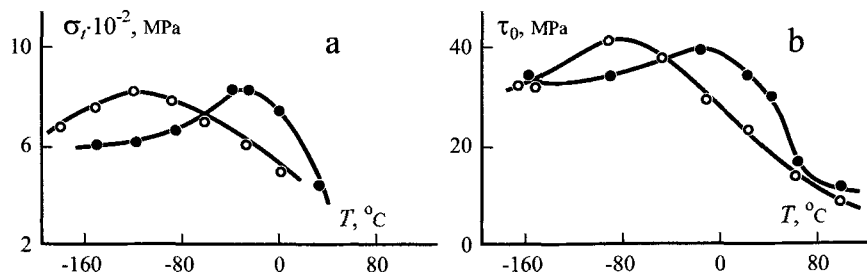

Fig. 7. Effect of the test temperature on the tensile strength of a unidirectional glass-fiber-reinforced plastic (a) and on the adhesive strength of a fiber—matrix system (b) with butvar-phenolic (○) and epoxy-phenolic (●) adhesives. $S = 1 \cdot 10^{-2}$ mm^2, $d = 10$ μm, and $l/d \cong 30$.

room temperature, the systems considered form joints with a sufficiently strong interface and ensure production of unidirectional materials with rather high shear (65 MPa) and compression (260-330 MPa) strengths.

However, unlike SVM fiber-based materials, the behavior of Armos fiber-reinforced plastics in tension and bending differs from that in shear and compression (Fig. 7): with increased adhesive strength, the strength of the materials increases (up to 40-46% with respect to the lowest values observed). This is the first case known to us where the character of the dependence σ_c—τ_0 turns out to be different at different stress states: in tension and bending, this dependence corresponds to section I of the curve in Fig. 2, whereas, in compression and shear, it falls in the region II. One can speculate that, with further increase in τ_0, the tension and bending strengths will no longer depend on the interfacial strength and that this is caused by the different sensitivity of the composite strength to the adhesive strength of the components under loading of different types (by the different slope of section I of the σ_c—τ_0 curve). Something like that was observed for the σ_c—τ_0 curves in the case of glass-reinforced plastics. The verification of this conjecture requires further investigations.

Variation of the test temperature. The interfacial strength and the properties of composites can be changed by varying not only the nature and composition of binders but also the properties of the matrix. This can be realized, for example, by varying the test temperature.

Figure 7 shows the results of examining the strength of the adhesive matrix—fiber joints and the tensile strength of SVAM-type glass-reinforced plastics based on butvar-phenolic and epoxy-phenolic binders in the temperature interval from 20°C up to the temperature of liquid nitrogen [1, 2]. It is seen from this figure that the course of the temperature-dependent strength curves of the composites is similar to that of the temperature curves of the adhesive strength: the temperatures at the maximum of the τ_0— σ_c curves for both glass-reinforced plastics coincides with that for the τ_0—T curve.

The strength of the glass fibers in the interval from +20 to -200°C varies only slightly. The strength of the binders at temperatures from 25 to -195°C was not examined. However, by analogy with the change in the strength of other polymers, it can be as-
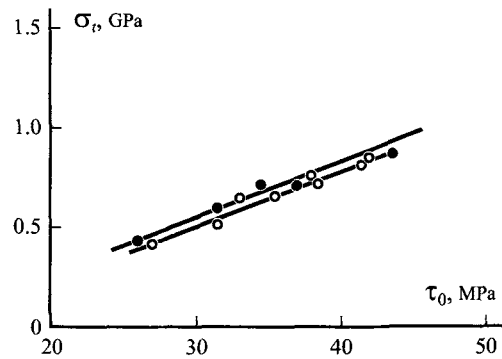
Fig. 8. Correlation curves σ_t—τ_0 (according to the data in Fig. 7).

sumed that their strength in any case will not decrease with decreasing temperature. Therefore, it is most probable that the decrease in the strength of glass-reinforced plastics is caused by the weakening of the interface owing to increased thermal residual stresses. Such an assumption is confirmed by comparing the strength of the glass-reinforced plastic with the adhesive strength of the polymer—fiber system (Fig. 8). It is seen that, within the whole temperature interval examined, the strength of the composites increases linearly with increased degree of fiber-binder adhesion (i.e., corresponds to section I of the curve in Fig. 2). We should note that the change in the strength of composites is similar to the change in the interfacial strength only for joints of sufficiently large sizes ($l/d \geq$ 10). For $l/d <10$, the σ_c—T and τ_0—T curves are no longer similar. At small l/d, the maximum on the τ_0—T curve disappears, and the adhesive strength monotonically increases with decreased temperature. From here it follows that the stress distributions in the specimens used for determination of the adhesive strength of polymer—fiber joints by the pull-out technique (at $l/d >10$) and in the real composite are close to each other and that the microjoints utilized for determination of the adhesive strength truly model the unit cell of a fiber-reinforced plastic.

Conclusions

An analysis of the dependence σ_c—τ_0 allows us to judge the location of the "weak link" in a composite. Under the action of different factors (surface modification of the filler and matrix, change in the nature of the binder, variation in the test temperature and curing conditions [1, 2]), changes in the strength of the composites based on inorganic fibers, as well as in the adhesive strength of fiber—matrix joints, are described by similar curves. This points to the fact that the failure of the composite is determined by its "weak link" and that such a "weak link" is the interface. The strength of the aramid-fiber-reinforced plastics based on different thermoreactive binders does not depend on the adhesive strength of the composites, because the bond between the fibrils forming the fiber is the "weak link."

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