Cyclic strength of polyester acrylate composites

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Abstract. The results of a study of the cyclic strength of polyester-acrylate composites are presented. The mechanical properties of the samples were determined on a Shimadzu Autograph AG-X Series universal testing machine. Test process management and pre-processing of data obtained on this machine are performed using the TRAPEZIUM X * 1 software. The measurements were carried out with a constant velocity of movement of the active capture of 3 mm / min. The compression force was directed along the long axis of the sample. The cyclic mechanical impact on the sample was carried out according to the following scheme: “loading to a certain maximum stress σmax in a given cycle → complete unloading at the same speed → five times repeating the cycle with a given load σmax → repeating the five times cycling procedure with a stepwise change in maximum load σmax until the sample is destroyed. It is shown that a characteristic feature of the load – strain curves during cycling is the presence of hysteresis, which is especially significant in the first cycle. The first compressive loading of the sample leads to significant changes in the structure of PEA. In the second and subsequent cycles, the difference between the loading and unloading curves of the sample is noticeably smaller and depends little on the cycle number. Then the state of the sample is stabilized, and subsequent cycling affects it much weaker. It is characteristic that the maximum difference between the losses in the first and subsequent cycles is observed at the minimum initial voltage. At maximum loads, the unloading curve is steeper than the loading curve, and at low loads, vice versa. Hysteresis losses increase with increasing maximum load in the cycle, which corresponds to an increase in the contribution of the plastic component to the total deformation of the sample. The E (σ) dependences obtained during loading in the first cycle practically coincide with the loss curves. In subsequent cycles, a slight quantitative change in these curves is observed without changing their general nature. The dependences obtained by unloading the samples are fundamentally different from the dependences obtained by loading. In this case, the discrepancy between the E (σ) curves during loading and unloading in the composite is slightly weaker than in pure PEA.

1. Introduction
Interest in studying the physicomechanical properties of polymer composites has not waned for more than 50 years. This is due to a significant variety of their mechanical properties [5-20]. Polymeric materials can be flexible and brittle.

Earlier [2,4], the results of compressive and bending strength tests of composites based on polyester acrylate (PEA) MGF-9 were obtained. Tests were conducted in order to optimize the composition and technology of obtaining these materials. In this article, these data are analyzed to
obtain additional information about the mechanisms that form the mechanical properties of this class of materials. Additional experiments were also carried out to study the mechanical relaxation in them.

The need to study the cyclic strength of materials is due to their possible operation under vibration loads. The specificity of concrete fatigue is associated with the manifestation of relaxation, the interaction of microdestructions. The development of these processes is determined by the state of the structure of the composite and the influence of many structure-forming factors on the strength, elastic-plastic and other properties of composites. When a load is repeatedly applied to concrete, the properties of the creep diagrams, called vibration creep, are intensified. It is believed that the main cause of the destruction of composites subjected to intense cyclic loads is the formation of main cracks in the composites. Since the process of destruction of any solid material includes the processes of formation and development of microcracks. The introduction of a finely divided filler determines the presence of a branched interface (interphase boundaries) in the composite, which serve as sources of microcracks and, consequently, an increase in the probability of their formation under certain conditions. Under conditions of poor adhesion of the filler and the matrix, a microcrack, having reached the interphase boundary, easily propagates along it, which leads to a rather rapid destruction of the material.

2. Materials and Methods

To obtain the composite material the following were used: as binder - oligoester acrylate of the MGF-9 brand, hardener - cyclohexanone peroxide PCON-2 and a curing accelerator - cobalt octoate OK-1. The filler was ground quartz sand of different fractions of the Smolensky deposit of the Republic of Mordovia. Mixtures were prepared manually. Samples were made in metal forms pre-lubricated with paraffin. To study the mechanical properties, rectangular samples with dimensions of 10x10x30 mm were used.

The mechanical properties of the samples were determined on a Shimadzu Autograph AG-X Series universal testing machine. Test process management and pre-processing of data obtained on this machine are performed using the TRAPEZIUM X * 1 software. The measurements were carried out with a constant velocity of movement of the active capture of 3 mm / min. The compression force was directed along the long axis of the sample.

The elastic modulus was determined with an increase and decrease in compressive force until the specimen fractures, as well as the work of deformation and hysteresis losses during mechanical cycling in different stress ranges. The formal (effective) modulus of elasticity, defined as the tangent of the angle of inclination of the deformation curve, was also calculated. In the future, this value will be called simply a module.

The cyclic mechanical impact on the sample was carried out according to the following scheme: “loading to a certain maximum stress σmax in a given cycle → complete unloading at the same speed → five times repeating the cycle with a given load σmax → repeating the five times cycling procedure with a stepwise change in maximum load σmax until the sample is destroyed ”. For an example in fig. Figure 4 shows a screenshot of the control computer of one of the experiments with cycling.

All measurements were performed under normal conditions.

3. Results

3.1. Strength.

The results of measurements on samples of composites with different fractions of sand (coarse - K, medium - C, fine - M), carried out in [4], are shown in Table 1.

Table 1 Results of measurements on samples of composites with different fractions of sand

| Fractional composition | Strength composition | bend |
|------------------------|----------------------|------|
First, we note that in this work, not absolute, but relative values of the characteristics were given.

In figure 1, the same data are presented depending on the fraction of the sand fraction. Based on the set of experimental points, trend lines in the form of polynomials of the second degree are drawn. The reliability criterion for the approximation of R² is quite high (> 0.96 for compression tests and > 0.92 for bending tests).

Based on the data presented, the following patterns can be distinguished:

a. The finest fraction of the filler affects the strength most, increasing it.

b. The dependence of strength on the fraction of a certain fraction of the filler is nonlinear, and the strongest at low concentrations of the fine fraction. In other words, the strength of the composite is not an additive function of the fractional composition of the filler.

c. The ratio of the shares of the large and medium fractions, although it affects the strength of the composite, is substantially less than the proportion of the fine fraction.

d. The possibility of approximating the data by polynomials of the second degree allows us to suggest that a maximum is possible on the dependence of the strength characteristics on the degree of grinding of the filler (for compression tests, a weak maximum is even observed in Fig. 1).

Additional tests showed that the strength and ductility of a composite are generally lower than that of pure PEA (see Figs. 2 and 3 below). Upon destruction, part of the sand is easily separated from the sample (poured out). In the works devoted to polymer composite materials [1,3], the main reasons for the hardening of polymers by highly dispersed filler particles are the costs of external energy for the formation of a large number of microcracks near the filler particles. In our case, the opposite is true: the introduction of filler with poor adhesion to the polyester matrix leads to easier formation and growth of microcracks. The distinguishing features of the composites studied in this work are the significantly greater strength (hardness) of the particles compared to the matrix and the insufficient adhesion of the filler particles to the matrix. An analysis of the results of the studies with necessity leads to the conclusion that the deformation of these materials is mainly due to the processes in the material of the polymer matrix, while the destruction occurs mainly along the interphase boundaries.
3.2. Effective module.

Figure 2 shows the stress-strain relationships obtained during the compression test to fracture of PEA samples without filler and composite with a fine fraction of silica sand. Already purely visible you can see the significant difference between these two entries.

![Figure 2](image)

**Figure 2.** Loading diagrams during compression of samples: PEA without filler (left) and with sand (right). Screenshots from the control computer.

More detailed information about the processes that occur in the material during its deformation can be obtained by analyzing the behavior of the effective module \( E = \frac{d\sigma}{d\varepsilon} \) during the deformation of samples. In Figure 3 shows the dependences of this quantity on current voltage values for pure PEA and composite.

a. The effective modulus of composites is significantly higher than that of pure PEA, while the situation is opposite with respect to the ultimate strength. Therefore, the molecular mechanisms responsible for the resistance of the material to deformation (exponent - modulus) and fracture (exponent - tensile strength) are different.

b. The process of deformation of the PEA and the composite can be divided into several stages, which is reflected in the different form of the \( E (\sigma) \) curve in its different sections. Initially, there is a strong increase (several times) in the effective module in a narrow voltage range with a maximum reached and its subsequent relatively slow decrease. It could be assumed that the initial increase in the module is due to purely technical reasons associated with the experimental conditions. However, in experiments with composites, a portion of the curve with similar behavior is also observed, and it occupies a much wider stress interval (compare the upper and lower curves in Fig. 3). Therefore, it was concluded that there is a deeper (physical) reason for such module behavior.

The declining section of the \( E (\sigma) \) curve for PEA ends with a gentle minimum in the stress range between 20 and 30 MPa. Then again, a near-linear increase in the module with increasing voltage follows. Finally, the destruction of the sample is preceded by a slight decrease in modulus. On the curve \( E (\sigma) \) of the composite (the lower curve in Fig. 3), only the first two sections are visible, which are shifted to the region of high stresses (to the right in the figure), so that the sample is destroyed already at the second stage of deformation.

A change in the nature of the dependences \( \sigma (\varepsilon) \) and \( E (\sigma) \) indicates a change in the molecular structure of the material and a corresponding change in the molecular mechanism of its deformation during loading. It is difficult to draw any conclusions about the details of these mechanisms based on the test results described here. Additional research is needed by other methods, including the use of computer simulation.

As mentioned above, the strength of the composite "PEA + quartz sand" is less than the strength of the original resin. At the same time, the resistance to elastic and plastic deformation of the composite
is much stronger, which is expressed in the increased effective modulus (elastic modulus) of the composite. This contradiction indicates the complexity of the physical (molecular) mechanisms of deformation and fracture of composite materials. The opposite effect of two factors (a decrease in the mobility of fragments of macromolecules and an increase in the number of sources of microcracks) leads to the fact that, at sufficiently high stresses preceding the destruction of the samples, the effective modulus of the composite substantially decreases and approaches the values characteristic of pure resin.

![Graph of effective modulus vs. voltage](image)

**Figure 3.** The dependence of the effective module on the voltage. PEA without filler (top), composite with a fine fraction of sand (bottom).

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3.3. Cycles.

A characteristic feature of the load – strain curves during cycling is the presence of hysteresis, which is especially significant in the first cycle (Fig. 4). The first compressive loading of the sample leads to significant changes in the structure of PEA. In the second and subsequent cycles, the difference between the loading and unloading curves of the sample is noticeably smaller and depends little on the cycle number. Then the state of the sample is stabilized, and subsequent cycling affects it much weaker. It is characteristic that the maximum difference between the losses in the first and subsequent cycles is observed at the minimum initial voltage.
At maximum loads, the unloading curve is steeper than the loading curve, and at low loads, vice versa. This feature is observed in all cycles, as a result of which it can be concluded that stress relaxation processes prevail in the initial stages of unloading (high stress region), and strain relaxation processes prevail in the final stages (low stress region).

The dependence of losses on hysteresis on the maximum load in the cycle is shown in Fig. 5. As can be seen, the hysteresis losses increase with increasing maximum load in the cycle, which corresponds to an increase in the contribution of the plastic component to the total deformation of the sample.

The relatively large energy losses due to hysteresis during cycling indicate that most of the deformation is plastic. Naturally, an increase in voltage leads to an increase in the number of elements that have made irreversible movements, and, accordingly, to an increase in losses. A decrease in losses with an increase in the number of cycles is evidence of stabilization of the structure, a decrease in the number of elements capable of irreversible movement. Plastic deformation of polymeric materials is carried out mainly due to the irreversible movement of fragments of macromolecules. A decrease in the effective cross section of the resin material when replacing part of its volume with filler particles limits in some way freedom of movement, which may be one of the reasons for increasing the effective modulus of the composite, however, it is not the only and, presumably, not the main one. The
second possible reason is a decrease in the tangential (along the interphase boundary) mobility of fragments of macromolecules that provide plastic deformation of the matrix.

An experiment was conducted with cycling while fixing the maximum stress (Fig. 6 on the left) and maximum deformation (Fig. 6 on the right). When stress is fixed, creep occurs. As can be seen from Fig. 7, this leads to a significant increase in hysteresis losses. When the deformation is fixed, the process of stress relaxation is accompanied by a decrease in losses, which is consistent with the data shown in Fig. 5.

Figure 6. PEA without filler. Left - fixing the maximum strength for 60 s; on the right - fixing the maximum deformation for 60 s.

Figure 7. PEA without filler. Losses in the first cycle: 1 - without fixation; 2 - fixing the maximum voltage; 3 - fixing the maximum deformation.

The experimental data obtained during cycling were further processed to calculate and analyze the behavior of the effective module. In Fig. 8 shows the $E(\sigma)$ dependences obtained from the loading and unloading diagrams of PEA and composite samples at a maximum cycle stress of 20 MPa.
Figure 8. The dependence of the effective module on strength during cycling up to 20 MPa: at the top - PEA without filler, below - a composite with a fine fraction of sand.

The $E(\sigma)$ dependences obtained during loading in the first cycle naturally coincide with the data shown in Fig. 5. In subsequent cycles, a slight quantitative change in these curves is observed without changing their general nature. The dependences obtained by unloading the samples are fundamentally different from the dependences obtained by loading. First of all, the module values obtained at the beginning of unloading are several times (sometimes almost an order of magnitude) greater than at the end of loading. Then, the loading and unloading curves $E(\sigma)$ intersect, so that in the low-stress region, the values of the module during unloading are even less than under load. This fact confirms the position expressed at the beginning of this section that stress relaxation predominates at the beginning of unloading, and creep processes prevail at the end of it.

In conclusion, we note that the discrepancy between the $E(\sigma)$ curves during loading and unloading in the composite is slightly weaker than in pure PEA, as can be seen from a comparison of the upper and lower graphs in Fig. 8.

Conclusion
1. The mechanical tests of cured polyester acrylate resin and composites based on it with silica sand as a filler were carried out.
2. The finest fraction of the filler affects the strength the most, increasing it can increase the strength of the composite.
3. The dependence of strength on the fraction of a certain fraction of the filler is nonlinear, and the strongest at low concentrations of the fine fraction. In other words, the strength of the composite is not an additive function of the fractional composition of the filler.

4. The ratio of the shares of the coarse and medium fractions, although it affects the strength of the composite, is substantially less than the proportion of the fine fraction.

5. The possibility of approximating the data by polynomials of the second degree allows us to suggest that a maximum is possible on the dependence of the strength characteristics on the degree of grinding of the filler (for compression tests, a weak maximum is even observed in Fig. 1).

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