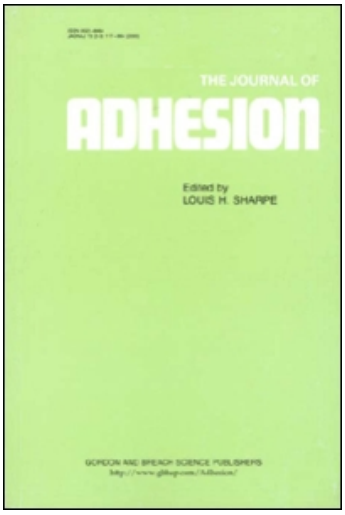

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Determination of Strength of Adhesion Contacts in Filled Elastomers from Elastic Modulus Change

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Determination of Strength of Adhesion Contacts in Filled Elastomers from Elastic Modulus Change

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The concentration of particles of the filler that have separated from the binder is determined by comparing the values of the modulus of elasticity of a filled polymer for the initial sample and after loading with a measured load. Analyzing the curve of the dependence of the concentration of the debonded filler on the stress that has caused the debonding makes it possible to estimate the adhesion strength of the binder-to-filler bond.

KEY WORDS filled polymers; mechanical properties; debonding filler particle; adhesion strength in particulate composites

1. INTRODUCTION

Development and improvement of composites based on elastic binders and particulate fillers calls for information on the strength of the adhesion bond between the filler particles and the binder. Commonly regarded as the measure of strength of the adhesive interaction in an adhesive-substrate system is the mechanical resistance to separation or resistance to breakaway of the adhesive from the substrate.[1]

It is well known that the failure of adhesion joints almost never has a pure adhesion character. As a rule, it proceeds in weak boundary layers;[2] that is to say in the interphase region near the polymer-solid interface. This should be taken into account when we discuss the adhesion joint strength, because the appearance of a weak boundary layer is also a result of adhesion interaction at (or near) the interface.[3]

The breakaway method presupposes a simultaneous break of the bonds over the whole area of the adhesion contact, which is not the case with disperse fillers. In this case, the strength of the adhesion contacts on the filler particle surface with the adhesive can be characterized by the mechanical stress in the interphase region at

the binder-filler interface, at which the filler particle starts separating from the binder and a break in the continuity of the sample occurs.[4]

We suggested earlier several methods for determining the moment of the break of continuity of filled polymers.[5] Each method has its own advantages and drawbacks, but their common drawback is the absence of anything near a substantiated interrelation between characteristics determined experimentally and the concentration of separated filler particles. Another common disadvantage is that the characteristics are measured under conditions of a stressed-strained state, *i.e.*, under conditions where nonlinearity in the viscoelastic behavior of the binder appears, which impedes an unambiguous interpretation of obtained results. Due to this, developing adequate methods for determining the strength of adhesion contacts of disperse filler particles with the binder remains an urgent problem. In this paper we suggest a new approach to the problem.

2. THE THEORY

In contrast to earlier proposed methods, the strength of adhesion contacts is determined from the analysis of the change in the modulus of elasticity of the material that has occurred as a result of a pre-action on the sample by a measured load. The modulus is determined twice: for the first time, in the initial sample, and for the second time, after some portion of the adhesion bonds in the material has been broken. Such an approach ensures a linear viscoelastic behavior of the binder. It also provides the possibility for revealing the interrelation between the modulus of elasticity and the volume concentration of separated filler particles, based on two known facts: increasing the filler concentration appropriately increases the Young's modulus of a composite if there exists a strong enough adhesion bond between the binder and the filler[6,7] and, conversely, reduces it if the adhesion bond is absent or is not strong enough. In the latter case the binder separates from the filler surface in the course of a modulus of elasticity determination even at low stresses and strains.[6,7] It follows that after a break, in some manner, of adhesion contacts in a filled polymer, the Young's modulus of the composite should decrease, the decrease being the more considerable, the greater the portion of the filler that has lost its adhesion bond with the binder. It is the well-known Mullins effect which we try to use here for estimating adhesion strength. Really, a decrease in the Young's modulus of a filled polymer after a preset mechanical action can be evidence that separation of the binder from some fraction of filler particles has occurred. If, moreover, the law of variation of the Young's modulus with varying concentration of separated filler particles, φ_x, is known, then the possibility arises for determining the fraction of separated particles from the Young's modulus change. For this purpose, the relationship between the concentration of separated-off filler particles and the resulting decrease of the Young's modulus of the filled composition should be determined. Results of experimental and theoretical studies[6,7] of the effect of the concentration of non-bonded filler on the value of the relative modulus of a composite are presented in Figure 1. From the presented data it is seen that

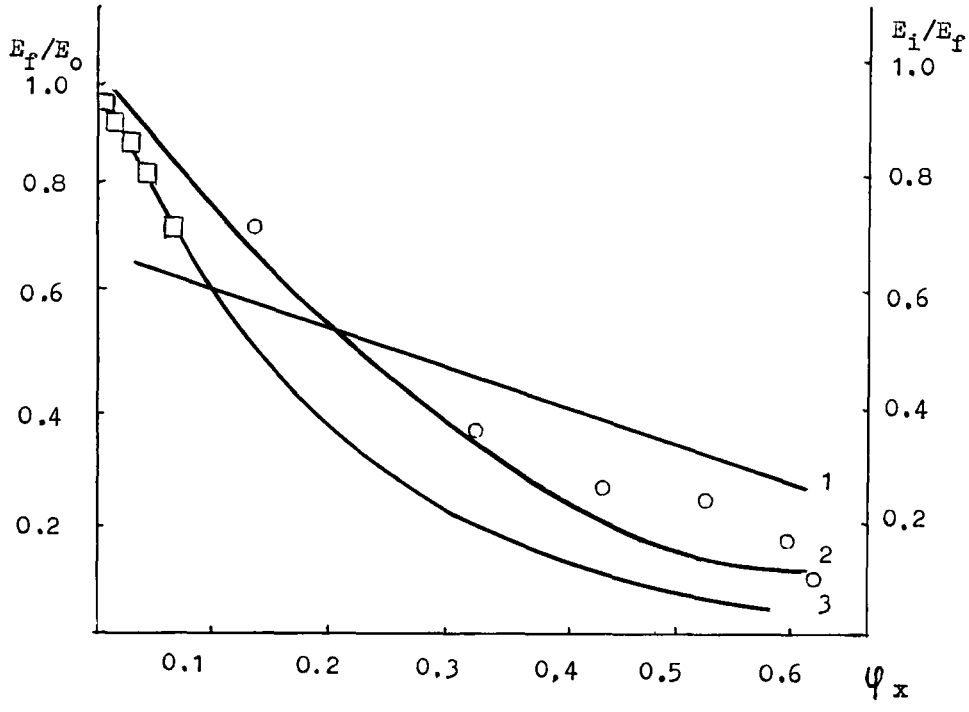


FIGURE 1 Experimental and theoretical dependences of relative Young's modulus of filled polymer on filler concentration in the absence of adhesion bonding. Calculated curves: 1—using eq. (1); 2—using eq. (2); 3—using eq. (4). Experimental data: circles, for PVC—glass bead model samples;[4] squares, for PU—glass bead model samples.

increasing the concentration of an adhesively unbonded filler indeed reduces the relative Young's modulus. Zgaevsky[6] proposed the relation, derived theoretically:

$$\frac{E_f}{E_o} = \frac{2}{3}(1 - \varphi_f), \tag{1}$$

where E_o is the Young's modulus of the binder, E_f the modulus of the filled polymer, and φ_f the concentration of the filler adhesively not bonded to the binder. However, this relationship poorly describes experimental results in the region of low filler concentrations, which is of a particular interest to us.

Experimental results can be much better approximated by the empirical equation, proposed by us:

$$E_f/E_o = e^{-3\varphi_f}. \tag{2}$$

Here, as in (1), E_f, E_o, and φ_f are the composite modulus, the binder modulus, and the filler concentration, respectively.

It can be expected that when a part of the filler in the course of a mechanical action separates from the binder, the filled polymer with unbroken adhesion bonds

will serve as a "binder" for this part of the filler adhesively unbonded. An equation similar to (2) can be applied to such a system. Indeed, when a polymer filled with adhesively bonded particles is treated as a binder characterized by the modulus E_f, then, in the presence of such a binder of an adhesively unbonded filler, whose concentration is φ_x, the same relationship as (2) should exist between the composite modulus E_x, "binder" modulus E_f, and filler concentration φ_x:

$$E_x/E_f = e^{-3\varphi_x} . \quad (3)$$

The E_f value can be determined experimentally in an initial sample with unbroken adhesion bonds and the E_x value can, as well, be determined experimentally after breaking some portion of the adhesion bonds in the sample; hence, equation (3) makes it in principle possible to calculate the concentration of the separated-off filler.

3. EXPERIMENTAL

The experimental determinations of the adhesion bond strength consist of three stages:

1. Determining the Young's modulus of the initial filled polymer specimen from the slope of the initial portion of the stress-strain curve which was obtained under tension with a constant deformation rate.
2. Applying a known force (loading by the required weight or deformation up to the required limit) to the specimen to fracture a portion of the adhesion bonds of the adhesive with the filler.
3. Determining the Young's modulus of same specimen after the force application.

For this purpose we developed and manufactured a test set which can be used to load the specimen in tension at a constant deformation rate and to obtain tensile stress-strain diagram within the limits of stresses and displacements which ensure reliable determination of the Young's modulus both of the initial specimen and of that after the fracture of the adhesion bonds. The set also provides for a known mechanical action upon the specimen by a constant tensile force within the required period of time.

The test set (see Fig. 2) consists of a screw (4) both ends of which are fixed in the ball-bearings (16). One half of the screw has a left-hand thread while the other one has a right-hand thread. When the motor (1) rotates the screw, the nuts (3 and 2) move in opposite directions and deform the specimen (6) fixed in the clamps (5). The dynamometer (7) measuring the specimen resistance to the deformation is fixed to the bottom nut (2). The strain is measured by the displacement inductive sensor (17). In addition, the top end of the screw is fitted with the disk (18) the scale of which provides for visually monitoring the angle of the screw turn as well as the mutual displacement of the nuts (2 and 3). The input of the two-coordinate recorder PDS-21 (8) or the input of the potentiometers KSP-4 (20) are fed by the voltage from the force cell and the strain gauge.

The strain calibration is performed by the disk readings (18). The force calibration

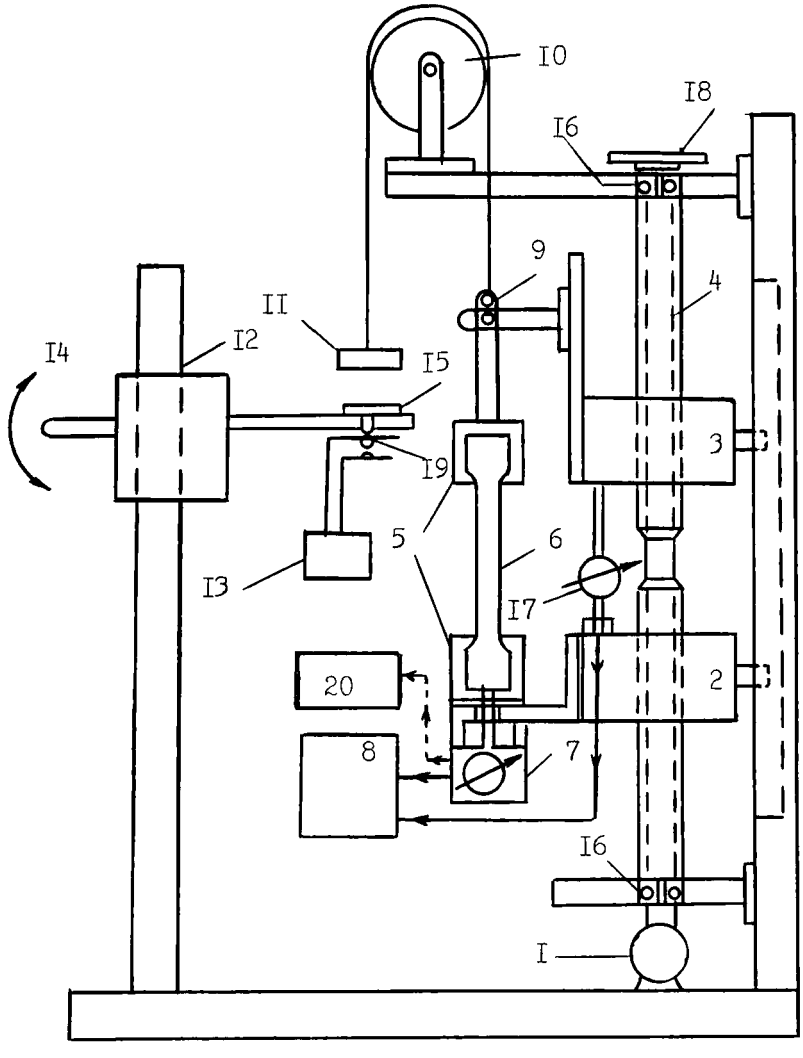


FIGURE 2 Drawing of the experimental device (see the text).

is performed by means of a set of weights on the platform (11). In the course of the force meter calibration the top clamp is relieved of the rigid brace with the nut (3) and the load weight appears to be applied to the dynamometer (7) *via* the thread which runs over the pulley (10) and *via* the specimen (6). When measuring small loads (5–10 g) the calibration of force is performed by means of a high sensitivity spring dynamometer which is fixed between the clamps (5) instead of the specimen to be tested.

The set for the force effect is the combination of the upright (12), load platform (11), pulley (10), and the support (15) which moves up and down.

The specimen (5) made of the composite is fixed to the dynamometer (7) by its bottom end. The top end of the specimen is fixed to the platform (11) with loads *via* the thread which runs over the pulley (10). To load the specimen, a required set of weights is placed on the platform and by the lever (14) the support (15) on which the platform initially rests descends. Thus the specimen appears to be under the tensile stress. A stop-watch or a timer can be used for the standardization of the loading duration. The contacts (19) switch on the timer (13) at the moment when the load separates from the support (15) and appears to be applied to the specimen. As soon as the prescribed time terminates, an audible signal sounds to inform the operator that the loading should be relieved. The loading relief is performed by a turn of the lever (14).

For an experimental test of equation (3), model samples were prepared in the form of 1 mm thick, 10 mm wide, and 80 mm long strips of a polyurethane elastomer, filled with glass beads of about 800 μm in diameter. The surface of some fraction of the beads was treated with a release agent to reduce the strength of their bonding to the binder; these beads were the first to separate off when a filled sample was subjected to tension. The samples were flat and transparent, which made it possible to monitor the number and volume fraction of debonded beads and to determine the correlation between the decline in the Young's modulus of a filled sample and the volume fraction (concentration) of debonded particles.

To find the threshold of stresses and strains at which the filler particles separate in the specimen the determination of the elastic modulus of the initial specimens begins with the minimum values of σ and ϵ which ensure reliable measurement of the desired Young's modulus. Repeatedly loading and unloading the specimen, with a load increase each time, we empirically determine the conditions under which the filler separation in the course of the Young's modulus determination can be ignored. Further on, the specimen is subjected to the action of the known force. This can be performed either on a special test set or by means of the same test set used to determine the Young's modulus if its design provides for that. The duration of the force application and its value are selected by the researcher, taking into consideration the material peculiarities and the operating conditions. In so doing, one should take into account that the accumulation of filler particle separation occurs over time, although most of the particles separate within the first few seconds of the load application. In addition, one should take into consideration that in the case of long-time loading the "residual" and high-elastic strain accumulates in the specimen. After the specimen is relieved of the loading it restores its shape and size. The longer was the period of strain accumulation, the longer is the time during which the shape and size relaxation process occurs. After relaxation the Young's modulus of the specimen should be determined again. In this case, one can use the same procedure of loading (with incrementally increasing loads) and unloading as was used when the initial modulus value was determined. In so far as the separating binder may have the ability to "stick" and "sticks" again to the filler surface, there is a necessity to have some initial stress to overcome that "stickiness" which is aggravated by the atmospheric pressure. Using the cut-and-try method one can determine the load limit which exceeds the "stickiness" limit. Above this limit the Young's modulus becomes less dependent on σ and ϵ within a considerable range.

These are the values of the Young's modulus E_i which characterize the new macrostructure of the specimen related to the separation of some portion of the filler particles. The relationship of the E_i value to the modulus value E_f of the initial specimen contains the information about the amount of the separated filler.

4. RESULTS AND DISCUSSION

Fig. 1 shows the theoretical dependences of $E_f/E_o = f(\varphi_f)$ according to eq. 1, 2 and $E_i/E_x = F(\varphi_i)$ to eq. 4 and to the experimental data.

The experimental data obtained are presented in Fig. 1 (curve 3). The experimental points of the dependence $E_x/E_f = F(\varphi_x)$ can be, in this case, approximated by the formula

$$E_x/E_f = e^{-4.3\varphi_x} \tag{4}$$

Thus, the volume concentration φ_x of debonded particles or the fraction of the debonded filler, $\varphi_o = \varphi_x/\varphi_f$, can be determined by measuring the Young's modulus of a filled elastomer before and after a loading that breaks adhesion contacts. One should take into account that decreasing E_i/E_f may result due to decreasing elasticity modulus E_o in a binder, if that binder is subject to a stress-induced modulus change. To be sure such changes are absent, it is necessary to estimate the influence of a loading on the modulus for a pure binder. To be sure that the decrease in E_f after stress action is related to a break in continuity of a composite, the Poisson's ratio of the composite may be measured, its value decreasing by debonding of filler particles due to increase of the sample volume as a result of the appearance of voids.

When studying the filler separation in the model samples, it was noted that not all the particles debond simultaneously and that the number of debonded particles depends not only on the magnitude of the average stress in the sample, but also on the time of duration of the disturbing load.

Two methods of accumulation of adhesion fractures were tried to determine the concentration of the debonded filler as a function of the magnitude of the disturbing stress: deformation of a filled polymer sample of both standard shape and dimensions at a constant strain rate up to a predetermined stress value, and deformation by a constant load during a predetermined time.

The former method is illustrated by the family of curves for one and the same model sample of a filled polymer, which are shown in Fig. 3 and which demonstrate the Mullins effect. Curve 1 was obtained by deformation of an initial sample at a constant rate. The Young's modulus E_f, determined from the slope of the diagram, characterizes the mechanical properties of the filled polymer with practically undisturbed filler-binder adhesion contacts. Curve 2 was obtained for the same sample after its unloading and relaxation. The sample was strained for the second time to higher stresses than for the first time. The Young's modulus E_1, determined from the slope of the initial portion of curve 2, characterizes the mechanical properties of the same sample; however, as the sample has already been subjected to loading and some of adhesion contacts may have been broken, E_1 may differ from the initial E_f. Curve 3 was obtained after the second loading-unloading cycle. Accordingly,

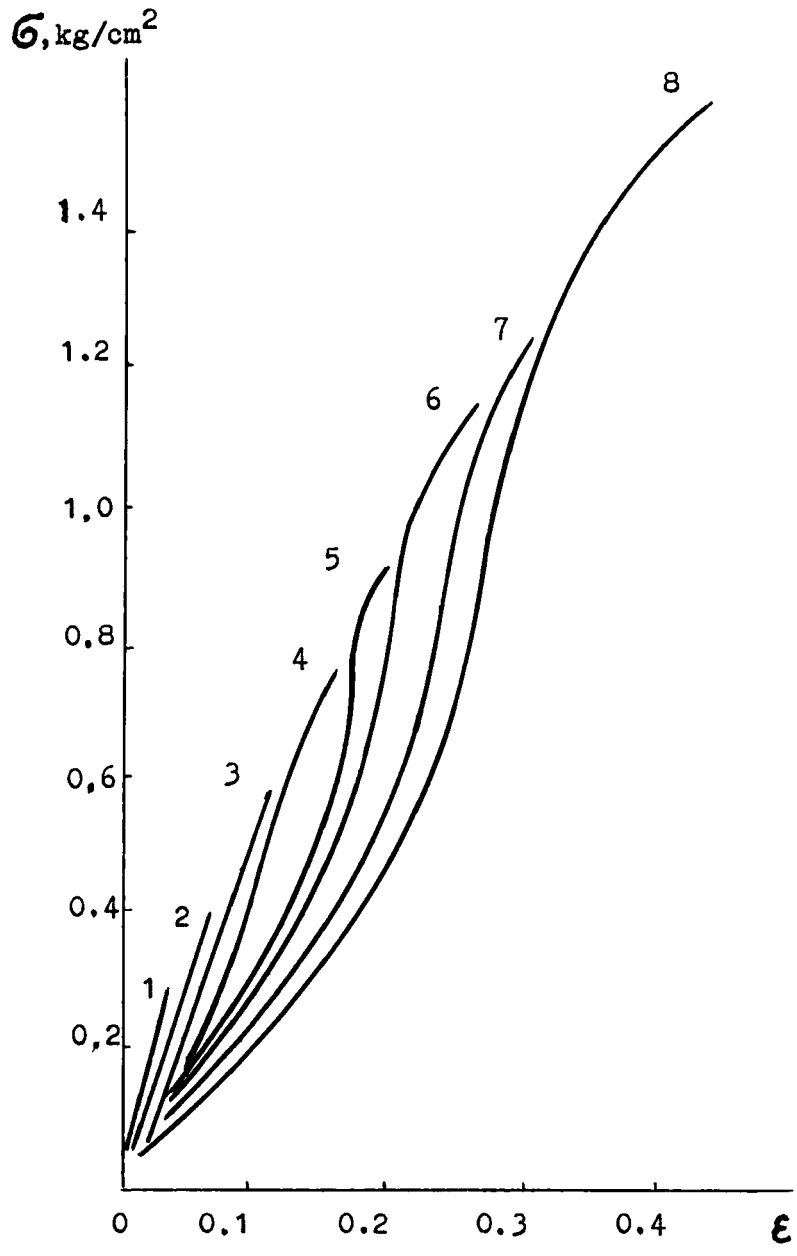


FIGURE 3 Experimental curves of tension at constant rate for model sample of filled polymer. Designations are given in text.

the Young's modulus, determined from it, characterizes the fracture that has arisen in the sample after the second loading. Repeating such a procedure of loading to higher and higher stresses and determining every time the Young's modulus makes it possible to obtain experimentally the E_x dependence on the maximum magnitude of the stress that occurred at the $(x-1)$-th loading. Figure 4 shows such a dependence, derived from the data of Fig. 3. As can be seen from Fig. 4, the E_x value regularly decreases as the maximum stress preceding the E_x determination increases. Unfilled binder did not change its properties over a strain range up to 200%; the E_x decrease with increasing σ_{dist} should be, therefore, regarded as resulting from the separation of an ever-increasing number of filler particles.

Simplicity and a good reproducibility are advantages of this method of accumulation of adhesion fractures. Its drawback consists in that the duration of action of disturbing stresses does not remain constant from cycle to cycle: since the strain rate is maintained constant, the achievement of higher stresses requires a longer time, *i.e.*, the higher the σ_{dist}, the longer the sample is in a loaded state and the

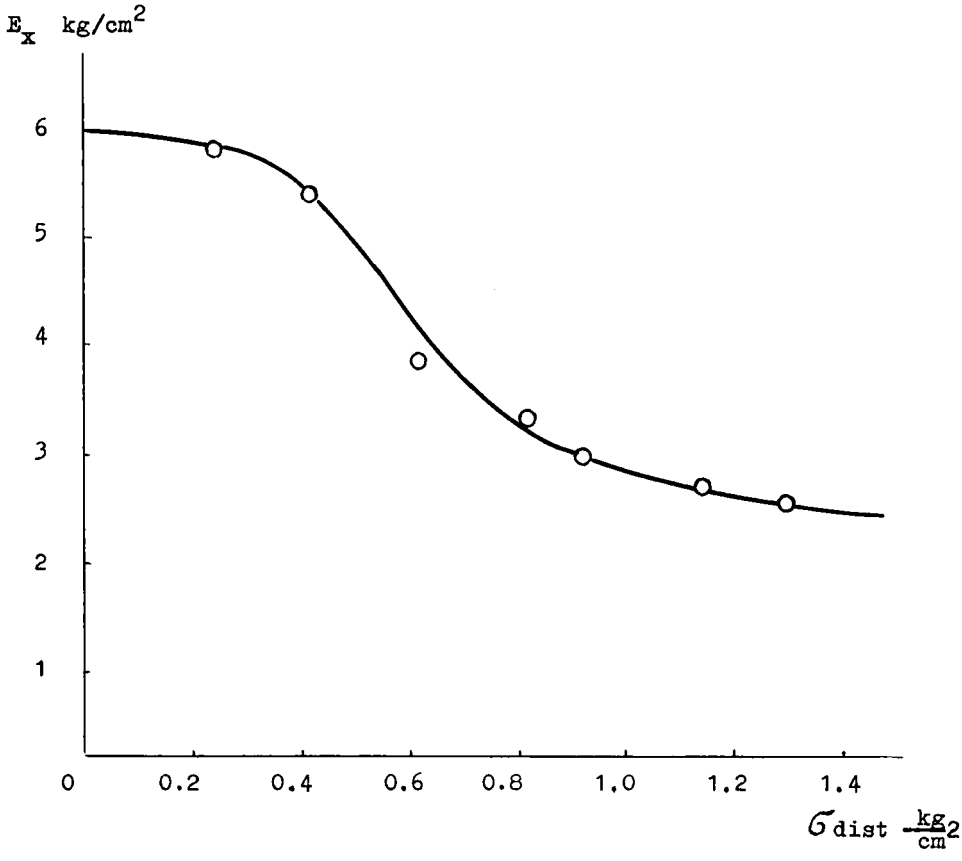


FIGURE 4 Experimental dependence of E_x on σ_{dist} from data of Fig. 2.

greater the time needed for the relaxation processes to occur after the loading. All this complicates the interpretation of the experimental dependence of E_x on σ_{dist}. For the second method of accumulation of adhesion fractures a sample of a filled polymer is tensioned by a constant weight. The duration of the load can, in this case, be identical for all the predetermined loads. To substantiate the selection of the time during which the sample is held under load, an experiment for revealing the effect of this holding time τ on the E_x value at constant loads of different values was conducted. The dependence of $E_x/E_f = f(\tau)$ on σ_{dist} is shown in Fig. 5. From the presented data it follows that, within the stress range studied, the duration of the load exerts a relatively weak effect on the E_x/E_f value and that the main fractures of adhesion contacts occur during the first few seconds after the loading; when the load is removed, the strain relaxation process proceeds rapidly enough. Based on the above, it can be recommended that a constant load applied to the sample under investigation for a few seconds will effect the fracture of adhesion contacts.

Thus, the experimental determination of the fraction of the debonded filler includes the following stages: (1) determination of the Young's modulus of the initial sample; (2) mechanical action on the sample in order to fracture a part of the adhesion contacts; (3) strain relaxation after the action; and (4) determination of the Young's modulus E_i of the sample with partly debonded filler.

The concentration of the debonded filler can be calculated from the E_x/E_f ratio value (see equations (3) and (4)).

As can be seen from Figs. 4 and 5, an increase of σ_{dist} results in a decrease of the

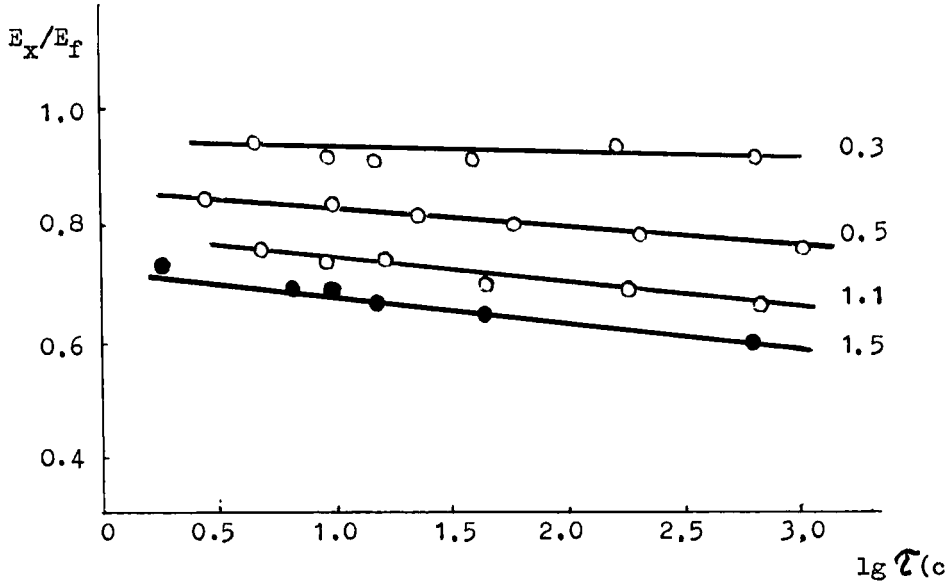


FIGURE 5 Experimental dependences of the ratio E_x/E_f on duration of sample loading. Corresponding stress magnitudes (kgf/cm^2) are indicated at curves.

E_x/E_f ratio, *i.e.*, in a growth of φ_x. Consequently, φ_x is a function of the disturbing stress σ_{dist}. An analysis of the form of the function can be useful in calculating the strength A of adhesion contacts. Possible versions of the dependence of φ_x on σ_{dist} are shown in Fig. 6. Curve 1 characterizes the case where the separation of the filler on reaching a certain σ occurs avalanche-like. A characteristic point of the curve is that corresponding to the σ_{dist} value at which a sharp increase in the separation rate occurs. In earlier publications,[5] proceeding from the assumption that the entire sample resistance force is concentrated solely at the cross-sectional area of all the filler particles in the sample cross-section plane, it was proposed to calculate A with the formula:

$$A = \frac{\sigma_{o\,dist}}{2\varphi_f^{2/3}}, \tag{5}$$

where $\sigma_{o\,dist}$ is the stress corresponding to the beginning of the avalanche-like separation of the filler.

A version of the dependence of φ_x on σ_{dist}, shown by curve 2 in Fig. 6, where characteristic points are absent, is, however, possible as well.

One of the causes of such a behavior may be a nonuniformity of the stress-strain state of binder interlayers, as a result of which the filler debonding will occur at the places where the stress has reached the level of the adhesion or cohesion strength.

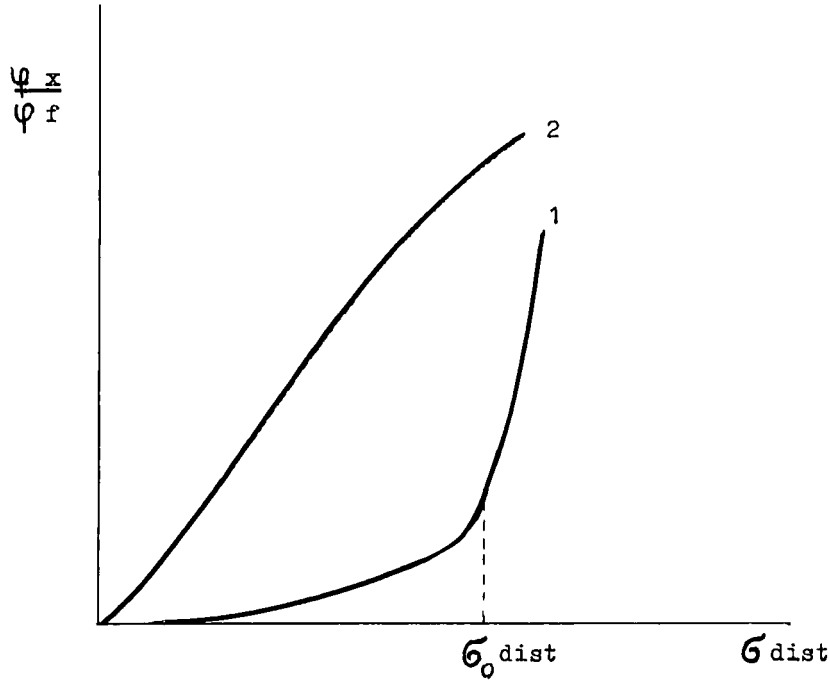


FIGURE 6 Typical form of the dependence of filler concentration on average stress in sample.

As σ_{dist} increases, more and more such places will occur and an ever-increasing number of filler particles will debond. To evaluate the adhesion strength in such a case, consider the simplest model of an elementary cell of a filled polymer, illustrated in Fig. 7. The cell is a polymeric cube with an edge length a. Filler particles of a spherical shape have a diameter D. The shortest distance between particle surfaces is d. If such a cell is deformed so that the absolute deformation is Δa, then the strain of a polymer at point K will be $\epsilon_f = \Delta a/a$. The absolute deformation of the polymeric interlayer at point P will, as well, be Δa, since the filler is a high-modulus one and, therefore, does not deform practically. The strain at point P will be of $\epsilon_p = \Delta a/a$. Hence

$$\epsilon_p/\epsilon_f = \Delta a/d : \Delta a/a = a/d \tag{6}$$

Since a>d, then, as can be seen from eq. (6), the deformation a in places where particles come most close to each other and, consequently, also the stress in the same places in the binder interlayer will be appreciably greater than in other places. A purely geometric analysis shows the volume concentration of the filler to be $\varphi_f = \pi D^3/6a^3$, wherefrom

$$a = D\left(\frac{\pi}{6\varphi_f}\right) \text{ and } d = a - D = D\left[\left(\frac{\pi}{6\varphi_f}\right)^{1/3} - 1\right]$$

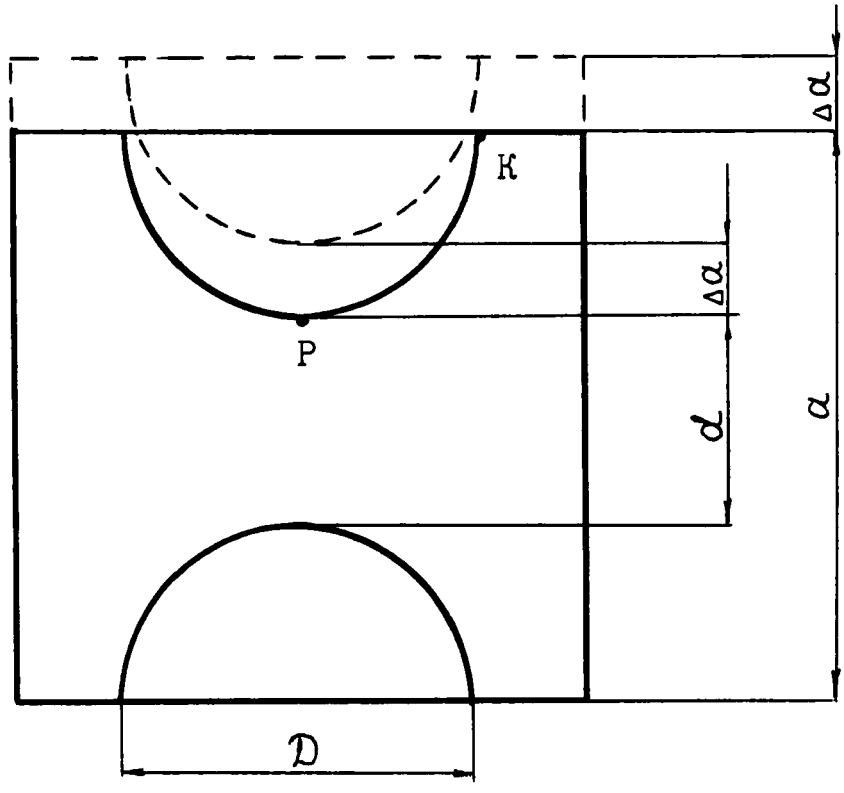


FIGURE 7 Elementary cell of filled polymer

This allows the a/d ratio to be expressed in terms of the filler concentration φ_f.

$$\epsilon_p/\epsilon_x = \frac{a}{d} = \left(\frac{\pi}{6\varphi_f}\right)^{1/3} / \left[\left(\frac{\pi}{6\varphi_f}\right)^{1/3} - 1\right], \tag{7}$$

i.e., the higher φ_f, the greater the nonuniformity of the deformation. From eq. (6) it is seen that the ϵ_p/ϵ_f ratio can reach an appreciable value at high enough φ_f. This means that in some places the strain of the polymeric interlayers and, consequently, also the stress in these places, are much greater than the average ones even at low average stresses.

It should be pointed out that eq. (7) is valid to some extent only at small enough strains and the a/d ratio will decrease as the interlayer strain increases, since d increases in the course of deformation. This means that corrections allowing for the two effects should be applied to eq. (7). To allow for the effect of the decrease of the a/d ratio we will assume that the $(a+\Delta a)/(d+\Delta a)$ ratio should be considered after the straining. Substituting the corresponding a and d values and

$$\Delta a = \epsilon_p \cdot d = \epsilon_f \frac{a}{d} \cdot d = \epsilon_f \cdot a$$

into the equation, we obtain:

$$\frac{\epsilon_p}{\epsilon_f} = \frac{a+\Delta a}{d+\Delta a} = \frac{\beta(1+\epsilon_f)}{\beta(1+\epsilon_f)-1} \tag{8}$$

where

$$\beta = \left(\frac{\pi}{6\phi_f}\right)^{1/3}$$

The pattern of variation of the maximum to the minimum strain ratio is visualized in Fig. 8, where it is seen that the ϵ_p/ϵ_f value decreases as the sample strain, *i.e.*, σ_{dist}, increases. This phenomenon is especially marked at a high enough filler concentration. If the magnitude of stress in the most strained places of the interlayer is assumed proportional to the magnitude of the strain, then the following equation can be proposed to calculate the adhesion bonding strength A for the case of a smooth increase of the concentration of the debonded filler (curve 2 in Fig. 5):

$$A = \sigma_{dist.\,i} \frac{\epsilon_{pi}}{\epsilon_{fi}} = \sigma_{dist.\,i} \frac{\beta(1+\epsilon_{fi})}{\beta(1+\epsilon_{fi})-1}, \tag{9}$$

where ϵ_{f_i} are strains of the composite, corresponding to $\sigma_{dist.\,i}$.

Apart from an increase in the distance between particles, straining of samples involves also a decrease in the sample cross-sectional area. Due to this, the true stress can greatly exceed the average stress calculated for the initial cross-section of the sample. Moreover, a redistribution of stresses in the binder occurs as some fraction of filler particles debond. All this complicates the calculation of the strength of the adhesion bonding of particles to the binder. Therefore, the magnitude of the disturbing stress at which the concentrations of the debonded filler are identical, rather than the adhesion bonding strength itself, can be compared in analyzing adhesion characteristics of different binder-filler systems. Concentrations of the

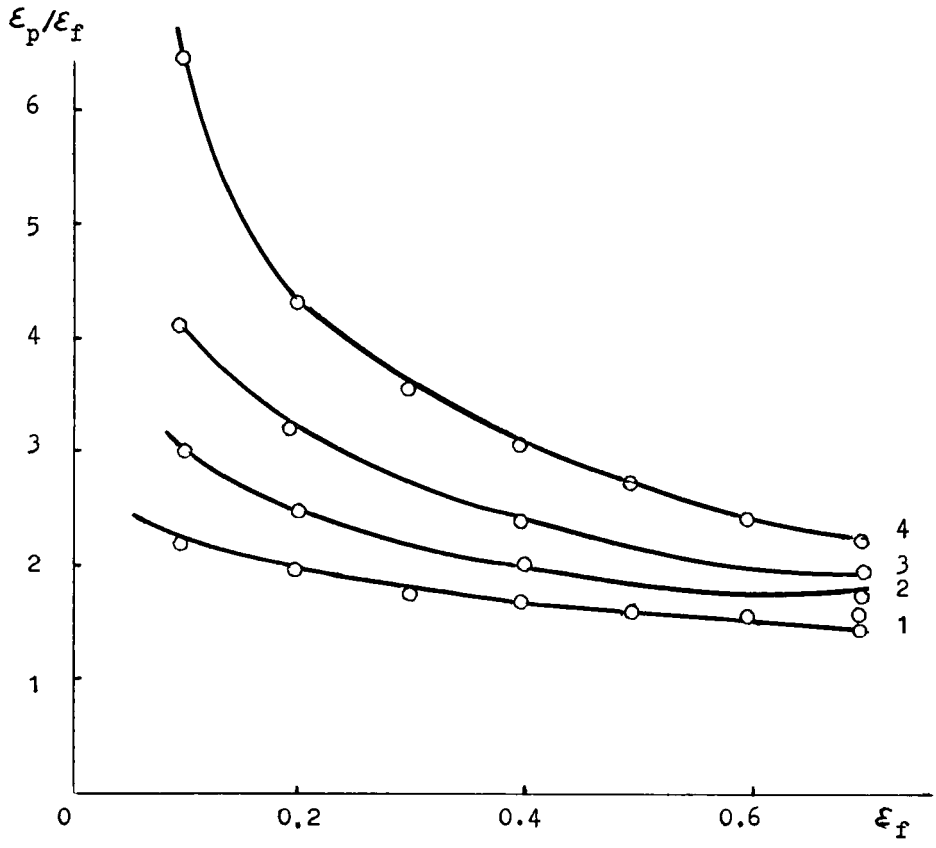


FIGURE 8 Calculated dependences of ϵ_p/ϵ_f on ϵ_f at various filler concentrations: $1-\varphi_f=0.1$; $2-\varphi_f=0.2$; $3-\varphi_f=0.3$; $4-\varphi_f=0.4$.

debonded filler at one and the same magnitude of the disturbing stress can also be compared. As an example, comparison of the efficiency of some chemical additives, introduced into the binder to improve its adhesion to the filler, is presented in Fig. 9.

The comparison is based on determining the concentration of the debonded filler in samples of a number of compositions, differing in the concentration and nature of epoxy resins added to the binder. The concentration of the debonded filler was determined using eq. (4) after the samples had been tensioned by a load of 3 kgf/cm^2 during 2 s. As can be seen from Fig. 9, within the concentration range studied, increasing the concentration of every one of the additives reduces the concentration of the debonded filler, *i.e.* increases the adhesion strength, but the efficiency of the additives is different. In particular, the adhesion strength of binder-to-filler contacts is most efficiently increased by epoydiane resin ED-20.

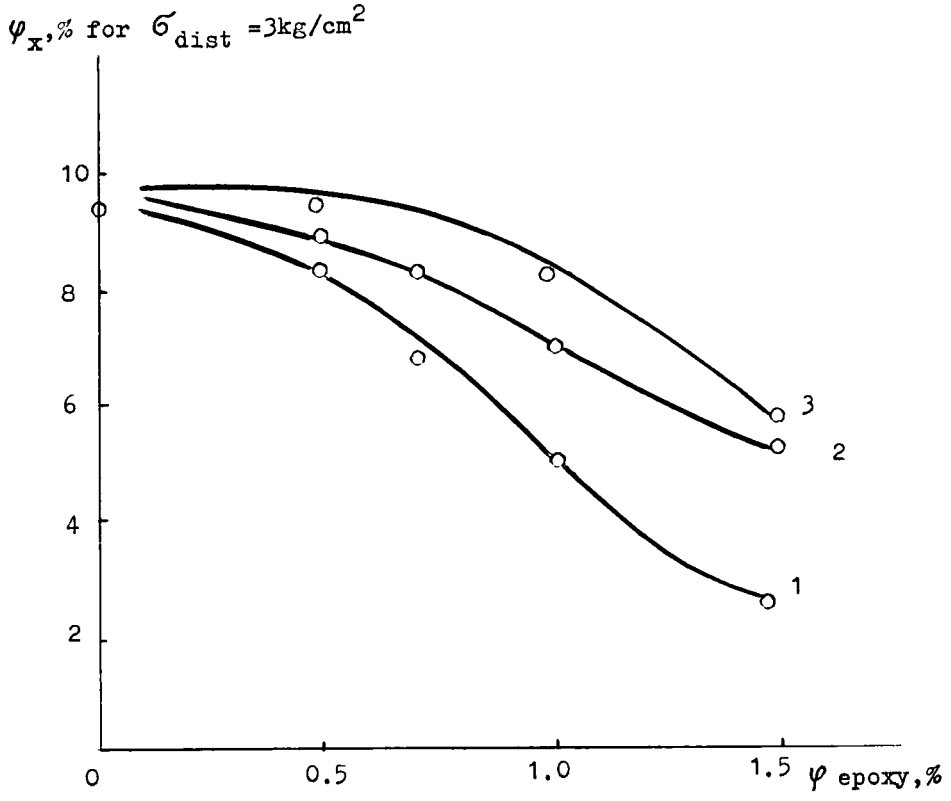
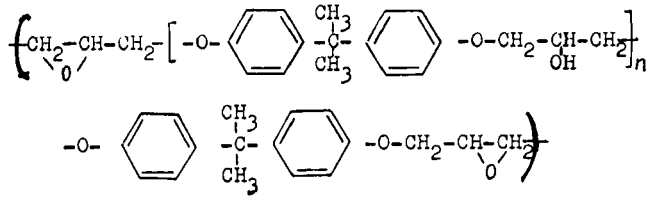
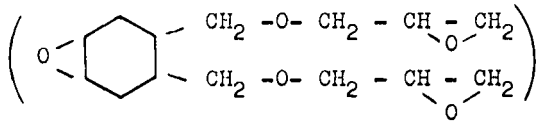


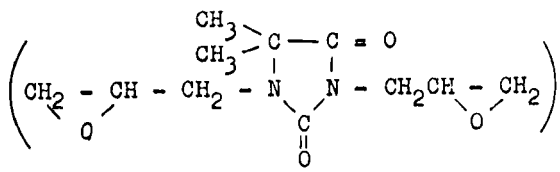
FIGURE 9 Dependence of debonded filler concentration on content of additive in binder for various additives: 1-epoxydiane resin ED-20



2–alicyclic diepoxide UP-650



3–heterocyclic diepoxide containing imidazole cycle, EG-10



CONCLUSIONS

The studies presented here have experimentally ascertained a decrease in the modulus of elasticity of an elastic composite at separation of filler particles from its binder. The relative decrease of the modulus can serve as a basis for estimating the concentration of the debonded filler, and correlation of the amount of the debonded filler with the magnitude of the disturbing force that caused the debonding can be used to estimate the strength of bonding of disperse filler particles to the binder.

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