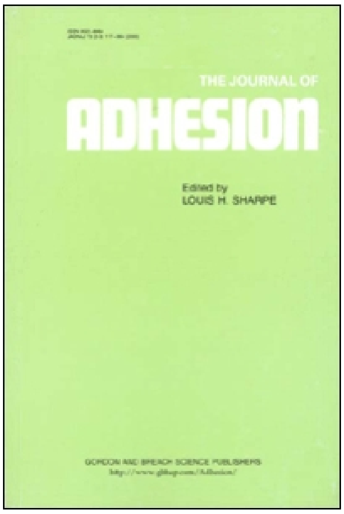

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Babich, V. F. , Lipatov, Yu. S. and Todosijchuk, T. T.(1996) 'Filler Debonding in Particulate-Filled Composites', The Journal of Adhesion, 55: 3, 317 — 327
To link to this Article: DOI: 10.1080/00218469608009955
URL: http://dx.doi.org/10.1080/00218469608009955

J. Adhesion, 1996, Vol. 55, pp. 317–327
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Filler Debonding in Particulate-Filled Composites

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(Received September 27, 1993; in final form July 29, 1995)

The decrease in Young's modulus after mechanically loading particulate-filled composites serves as a measure of the fraction of debonded filler particles.

For composites based on plasticized rubber and fine ammonium perchlorate these effects have been studied for various stresses and for both varying amounts and particle sizes of the filler.

It was found that debonding filler particles during loading is strongly dependent both on the filler concentration and the particle size. Composites with small particles are characterized by higher stresses at which debonding takes place. The effects observed are supposed to be connected with different conditions of the stress distribution depending on the filler particle size and amount. Another reason is the varying fraction of the interphase zone formed at the filler-matrix boundary.

KEY WORDS: Filler debonding; particulate filled rubber; interphase zone; mechanical model; adhesion; mechanical properties; filler size and concentration effects; stress distribution.

NOMENCLATURE

A	The tensile strength of the adhesion joint of the filler particle with the matrix
α	The length of the cube rib modelling the filler in the model of filled polymer
C	The thickness of the binder layer in the model
C_{ij}	The thickness of the binder layers between filler particles
d	Diameter of the filler particle
E_0	The modulus of elasticity of the binder
E_f	The modulus of elasticity of the filler polymer
E_x	The modulus of elasticity of the filled polymer in the presence of some debonded particles
E_{ij}	The modulus of elasticity of the cell in the model of filled polymer
E_j	The modulus of elasticity of the j-th layer in the model
E_M	Modulus of elasticity of the multiparticle model of filled polymer
E_{Mx}	The modulus of elasticity of the multiparticle model in the presence of some debonded particles
i	The number of the vertical row of cells in the multiparticle model
j	The number of the horizontal row

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σ_0	The mechanical stress in the cross-section of the specimen calculated for the initial cross-section
σ_T	The true mechanical stress in the cross-section of the specimen
φ_f	The total volume fraction of the filler particles in the filled polymer
φ_x	The volume fraction of the filler particles not bonded with the binder
φ_{ij}	The local concentration of the filler in the multiparticle model
ε	The relative deformation

INTRODUCTION

The problems of debonding of filler particles has attracted attention ever since the famous work of Mullins.[1] Among new theories describing these effects one has to cite the work done by Vratsanos and Farris.[2,3] Their approach takes into account that the diminishing modulus of filled polymers after loading is connected with both debonding of filler particles and formation of voids resulting from this debonding. The problem is not new and was analyzed many years ago.[4] In some studies[5-10] attempts have been made to predict the viscoelastic properties of composite materials from the properties of their components and the characteristics of their adhesion interaction. However, the reverse aim may be as important, namely, the determination of the adhesion interaction from the properties of the composite. Gent and Park[11] found that for single spherical filler particles, imbedded in inifinite elastic media, the debonding force is proportional to the media modulus and inversely proportional to the square root of the diameter of the particles. Such data allow one to determine the strength of adhesion bonding. It was, however, not clear if the regularities found are valid for highly-loaded polymers.

Earlier, we proposed a method for comparative evaluation of the adhesion joint strength in particulate-filled composites.[12] This method is based on the determination of the fraction of debonded filler, φ_x, depending on the value of mechanical stresses, σ_0, in the cross-section of a specimen at which debonding of the filler particles proceeds. It was found that for elastic matrices the smooth dependence $\varphi_x = f(\sigma_0)$ is typical. With increasing applied stress the number of debonded particles gradually increases. The comparison of such dependencies for various systems gives a possibility to estimate the concentration of debonded particles at the same value of σ_0 or to determine the value, σ_0, at which the same concentration of debonded particles exists. The method was based on the theory developed by Zgaewsky,[13] according to which

$$\frac{E_f}{E_0} = (2/3)(1 - \varphi_f) \tag{1}$$

where E_f and E_0 are the Young's modulus of the binder and of the filled polymer, respectively, and φ_f is the concentration of the filler not adhesively bonded to the binder. Experimental results can be much better approximated by the empirical equation:[12]

$$\frac{E_f'}{E_0} = e^{-4.3}\varphi_f. \tag{2}$$

When a part of the filler in the course of mechanical action is separated from the binder, the filled polymer with unbroken adhesion bonds will serve as a "binder" for that part of the filler which is unbonded.[12] For this case

$$E_x/E_f = e^{-4.3}\varphi_x. \quad (3)$$

As was shown in References 2 and 3, the secant modulus, E_x, of the material is a measure of the amount of debonding or the amount of damage sustained by the material at any stress. It is evident that a changing modulus after deformation is connected both with debonding of particles and with formation of voids.[2-4] Therefore, the value E_x includes contributions from both debonding and void formation. Because the amount of debonded particles, φ_x, determines the volume of voids, E_x should depend on φ_x. It is reasonable to suppose that because the volume changes are proportional to the number of debonded particles, the ratio E_x/E_f characterizes that number.

The experimental data[12] show that, for various materials, the dependence of φ_x on the applied stress, σ_0, allows one to compare the concentration of debonded particles at any given stress with the value of the stress corresponding to the same concentration of debonded particles.

Such an approach seems to be sufficient to make a comparative investigation but cannot be applied if we need to estimate the adhesion joint strength, *i.e.* the stress at the polymer-solid interface corresponding to debonding. It is evident that the smooth character of the curves $\varphi_x = f(\sigma_0)$ is connected with the nonuniformity of the stress-strained state of the binder interphase at the phase boundary. Debonding of particles proceeds in those places where the stress level reaches the adhesion joint strength, A. With increasing σ_0 there proceeds a growth in the number of particles which are located in a zone where the local stresses are equal to, or exceed, the adhesion joint strength.

The value of the local stresses at the filler-binder interface depends on the filler concentration, φ_f, and on the granulometric composition of the filler. It is important to establish the influence of the filler concentration and particle size on the process of debonding. If we know the stress corresponding to debonding of a definite amount of filler particles, we can proceed to evaluate the adhesion joint strength as proposed in Reference 12.

The aim of this paper consists in establishing the interrelation between φ_f and particle diameter, d, and the debonding stress, which may give the possibility to determine the adhesion strength from the data on debonding. As we know, such an aim has not been realized up to now.

EXPERIMENTAL

Materials

Composites based on the isoprene rubber SKI (mol.mass 2×10^3), plasticized by transformer oil, were studied. As a filler, ammonium perchlorate was used. The filler was introduced into the reaction mixture which was cured for 5 days at 343 K. The filler concentration was varied in the range 40–70 vol.%. Particles with diameter from 2 to

$160–315 \times 10^{-6}$ m were used. The blocks of cured, filled materials were cut into strips of thickness 7×10^{-3} m. The standard specimens were cut from these strips as described earlier.[12]

Apparatus and Methods

The methods used were described in a previous paper.[12] Their essence consists in the determination of the Young's modulus, E_f, of the filled polymer.

The most distinctive feature of the methods applied are the following. The instant of loading of composite material to destroy adhesion joints and the instant of the determination of their amount are separated in time, *i.e.* one test set is used for the measured loading and another for estimation of the Young's modulus by stretching at a constant rate. Such methods allow one to determine the Young's modulus at conditions where the stresses are very low and where nonlinear effects may be neglected. Simultaneously, the loading used for destroying adhesion contacts may be rather high. However, they act for a very short period of time and, after unloading, the specimen relaxes for a long time. At such conditions, the nonlinear viscoelastic prehistory of the specimen has no influence on the modulus.

Figure 1 shows a drawing of the experimental device for loading specimens with a constant load. A specimen of material (1) has a standard shape with cross-section 0.7×0.7 cm and working length 3.4 cm. Its lower end is connected with a load (2) of known mass. The upper end (3) is connected with a control rod (4). With the control rod the specimen is rapidly elongated until the load (2) separates from the support. After the specimen was stretched by the load for 2 sec, the upper end of the specimen was rapidly lowered to full unloading. The rates of lifting, lowering and duration of the load could be changed depending on the properties of material. In our case, the rates of lifting and lowering was 12 cm/sec.

To measure the magnitude of deformation the leading rods (5) were used. The rods were firmly fastened to the lower clamp of the specimen, whereas the upper clamp could glide along the rods due to bearings (6). The bearings push cylindrical sleeves (7) along the rod. After unloading the specimen and relaxing it for 15–30 min, the sleeves stay on the rod where their movement up was stopped. From the position of the sleeves before and after stretching, the magnitude of its displacement and, therefore, the deformation of the specimen could easily be found. The Young's modulus was determined twice: first before loading and then after unloading and relaxation. The modulus was measured at the elongation rate of 2×10^3 cm/sec. The magnitude of deformation does not exceed 10% and the stress 0.015 MPa. As for loading to destroy the adhesion joints, the range of stresses and deformations was within the limits 0.2–0.5 MPa and 5–500%, depending on the size of the filler particles (for fine particles the stress and deformation for rupture of adhesion bonds were rather high).

The true stress, σ_T, especially at high deformation, seems to be impossible to calculate because of the void formation accompanying the adhesion joint breakage. We have no accompanying possibility to control the dilatation induced by deformation. The correction was introduced based on the assumption that the particle is fully debonded and is surrounded by a medium with zero elastic modulus. The concentration of the voids may be taken equal to φ_x. Due to formation of these voids, the

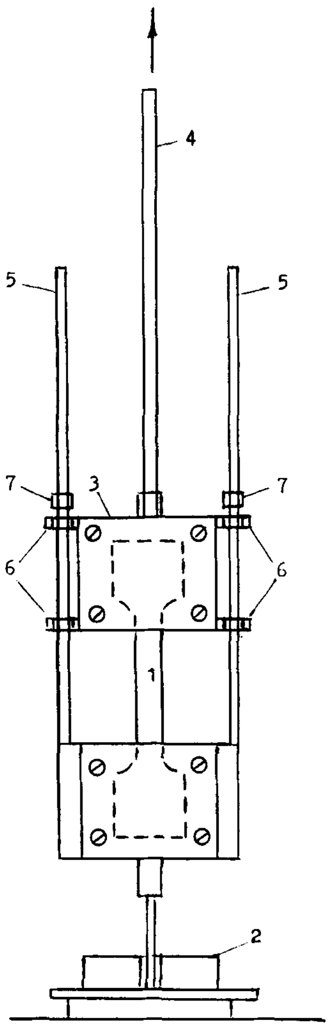

FIGURE 1 Drawing of the experimental device for measured loading.

cross-section of the specimen diminishes $(1 - \varphi_x^{2/3})$ times. Then the value σ_T may be calculated, as:

$$\sigma_T = \frac{\sigma_0(1+\varepsilon)}{(1-\varphi_x^{2/3})} \tag{4}$$

because we could estimate the volume concentration of debonded filler, using Eq. (3). We have used the value σ_T found in this way because the engineering stress cannot be used at high deformations.

For various specimens and different loads the ratios E_x/E_f and values of σ_T have been calculated to plot the dependence of $E_x/E_f = f(\sigma_T)$.

RESULTS AND DISCUSSION

Experimental Data

Four series of specimens have been studied differing in the amount of the filler and in the average size of the particles. Figure 2 shows typical dependencies of the relative decrease in the Young's modulus on the disturbing stress for the specimens with the largest particles. It is seen that with increasing σ_0 a smooth decrease in modulus is observed. This fact testifies to the increasing fraction of debonded filler particles leading to the diminishing modulus.

Analogous data have been obtained for the entire series of specimens, namely, E_x/E_f decreases with growth in σ_0. As a rule, larger decrease in E_x/E_f is observed for the specimens with higher filler content. These data my be explained in the following way. Even if the ratio φ_x/φ_f would be constant, φ_x should be higher for greater φ_f. Earlier it was established[12] that $E_x/E_f = e^{-4.3}\varphi_x$. Then, at higher φ_f the relative modulus decrease will be larger. However, another reason may exist, namely the influence of the filler on the magnitude and distribution of stresses in the matrix between filler particles.

It is more convenient to present the experimental data in coordinates φ_x/φ_f and σ_T, because the deformation of the samples by the load is different depending on the filler concentration. To have more correct results, one also has to consider that, after debonding of some fraction of filler particles, some voids should appear in the specimen around the particle. As a result, the redistribution of applied stresses should proceed leading to increased loading of those parts of the specimen where debonding of filler particle has not yet taken place.

Figure 3 presents the same data as in Figure 2 in coordinates φ_x/φ_f and σ_T. It is seen that the fraction of debonded filler really increases with increase in φ_f.

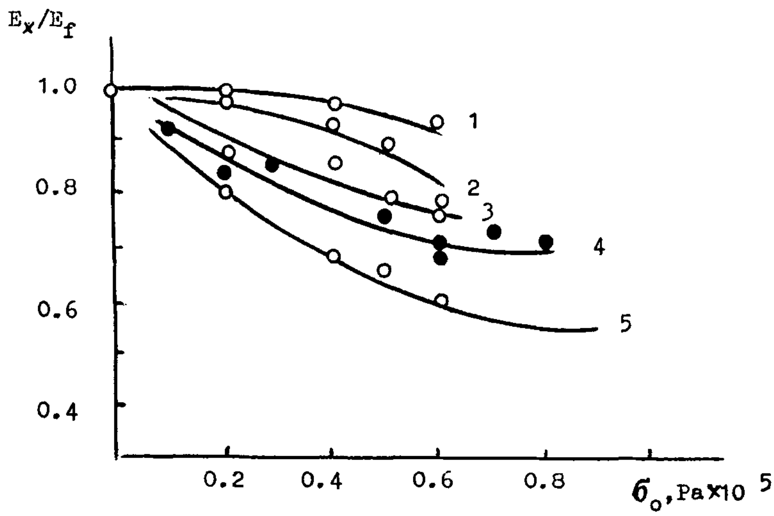

FIGURE 2 Dependencies of the relative diminishing Young's modulus on the value of deforming load for specimens with various filler concentration (vol.%), φ_f: (1) 0.45, (2) 0.50, (3) 0.55, (4) 0.60, (5) 0.65. Particle size $1.6–3.15 \times 10^{-4}$ m.

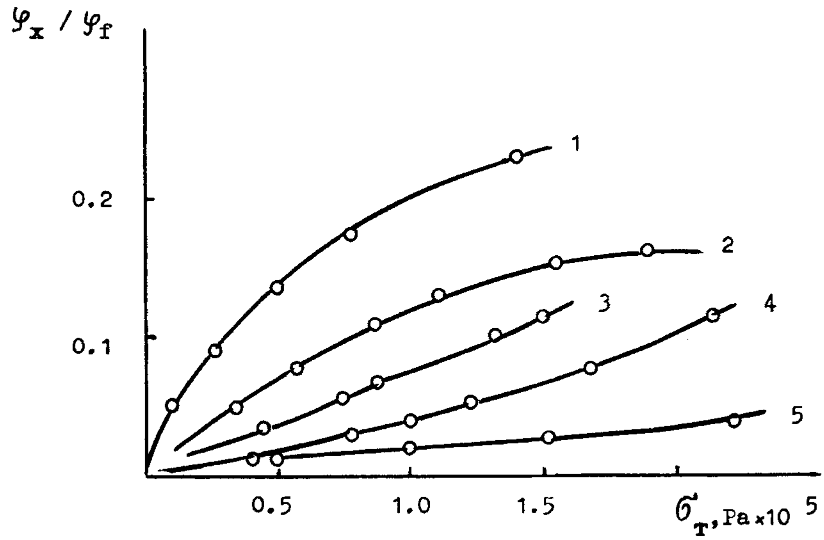

FIGURE 3 Dependence of the fraction of debonded filler on the true stress for various filler concentrations (vol.%): (1) 0.65, (2) 0.60, (3) 0.55, (4) 0.50, (5) 0.45. Particle size 1.6–3.15 × 10^{-4} m.

Let us consider the experimental dependencies of σ_T on φ_f for filler particles of different size (Fig. 4). It is seen that for fillers with large particles σ_T diminishes with increasing φ_f (curves 3 and 4), whereas for small particles (curve 1) the opposite is true. This may be connected with the role of the interphase formed at the filler-matrix interface.[2] For filler with large particles the fraction of the interphase should be

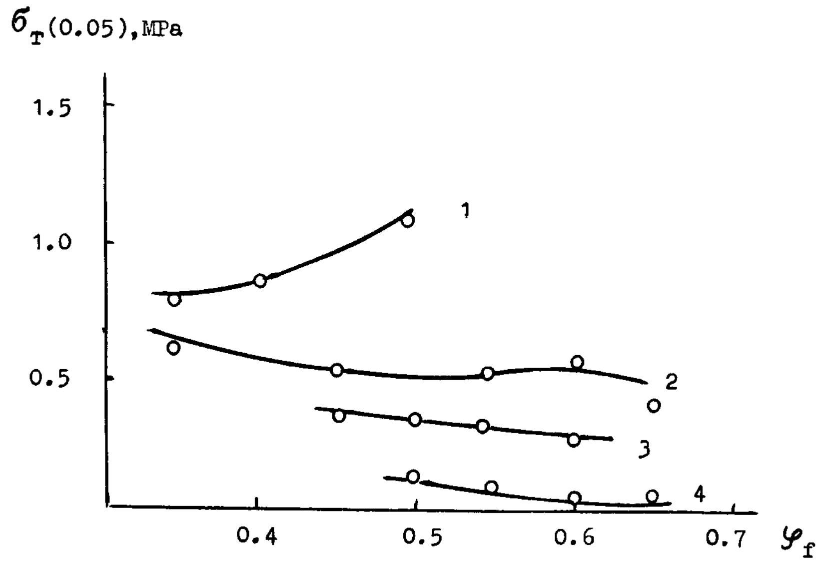

FIGURE 4 Dependence of the stress, corresponding to the debonding of 5% of particles, on the filler concentration at various particle diameters: (1) 1–2, (2) 10–12, (3) 85–100, (4) 160–315 × 10^{-6} m.

comparatively small and the shape of the σ_T *versus* φ_f curves is determined only by the concentration of stresses in the matrix interlayers between filler particles, leading to diminishing σ_T with increase in φ_f.

For small particles, the fraction of the interphase is much larger and cannot be neglected when considering the stress distribution. It is possible that the contribution of the interphase determines the increase in σ_T with increasing φ_f (increasing in φ_f leads, as is shown, to increasing amounts of the interphase layers).

Figure 4 shows also the increase in the adhesion joint strength with diminishing particle size. According to Reference 6, for a single glass particle imbedded in an inifinite polymeric matrix the average stress at debonding of the particle is in inverse proportionality to the square of the diameter of the particle. To prove this statement in the case under consideration, we have presented the data (Fig. 4) at $\varphi_f = 0.5$ in various coordinates (Fig. 5). It is seen that the best correlation between the adhesion joint strength and the particle diameter was observed when σ_T was plotted as a function of $1/d^{1/3}$ or $\log(1/d)$.

Model Representation

Thus, we have established that the adhesion strength in particulate-filled composites does depend on both the filler particle size and concentration. To understand these

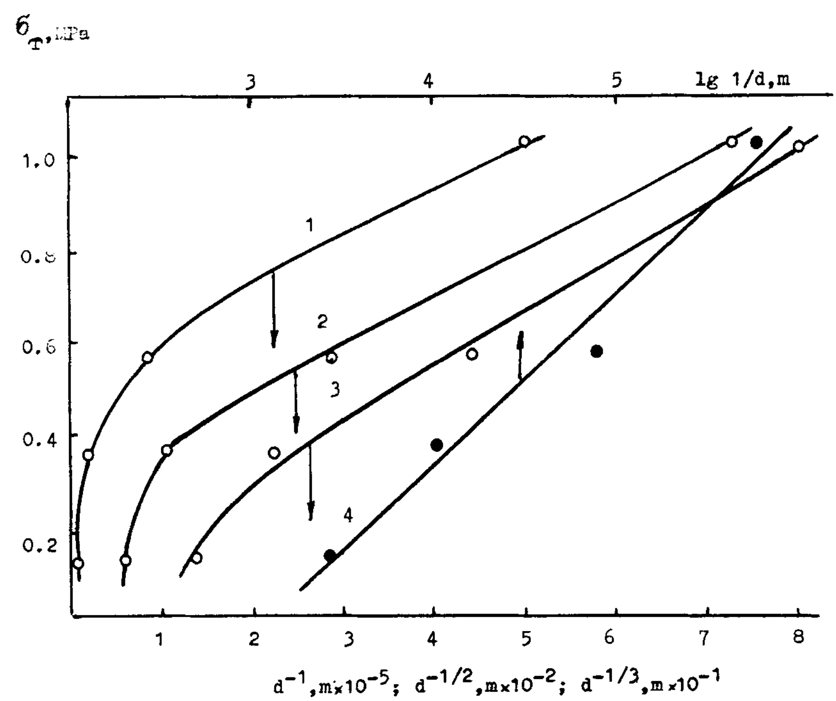

FIGURE 5 Dependence of the stress of debonding of 5% of particles on the filler size in various coordinates: (1) σ_T *vs* d^{-1}, (2) σ_T *vs* $d^{-1/2}$, (3) σ_T *vs* $d^{-1/3}$, (4) σ_T *vs* $\log d^{-1}$.

results, we have made some preliminary calculations using the following mechanical model (Fig. 6). The cross-section of a specimen consists of 49 cubic particles arbitrarily disposed with different thickness of the matrix layers between them. The same figure presents the elementary cell of this model. For the cell $(b - a) = c$. Filler concentration is $\varphi_f = a^3/b^3$, at $b = 1$, $\varphi_f = a^3$. It is supposed that the average thickness of the matrix layers between particles is $c = 1 - \varphi_f^{3/2}$. The deviations of the layer thickness from the average value is taken to be no more than 0.5–2 c. For the calculations it was also assumed that cells in the rows are deformed in parallel, whereas the rows are deformed in series.

As the modulus of elasticity of a filler is some times larger than E_0, the local modulus, E_{ij}, of each ij-th cell in the multiparticle model may be represented approximately by E_0 and the local volume concentration of a filler, φ_{ij}, in this cell in the following way:

$$E_{ij} = E_0(1/C_{ij}) = \frac{E_0}{1 - \varphi_{ij}^{1/3}}. \tag{5}$$

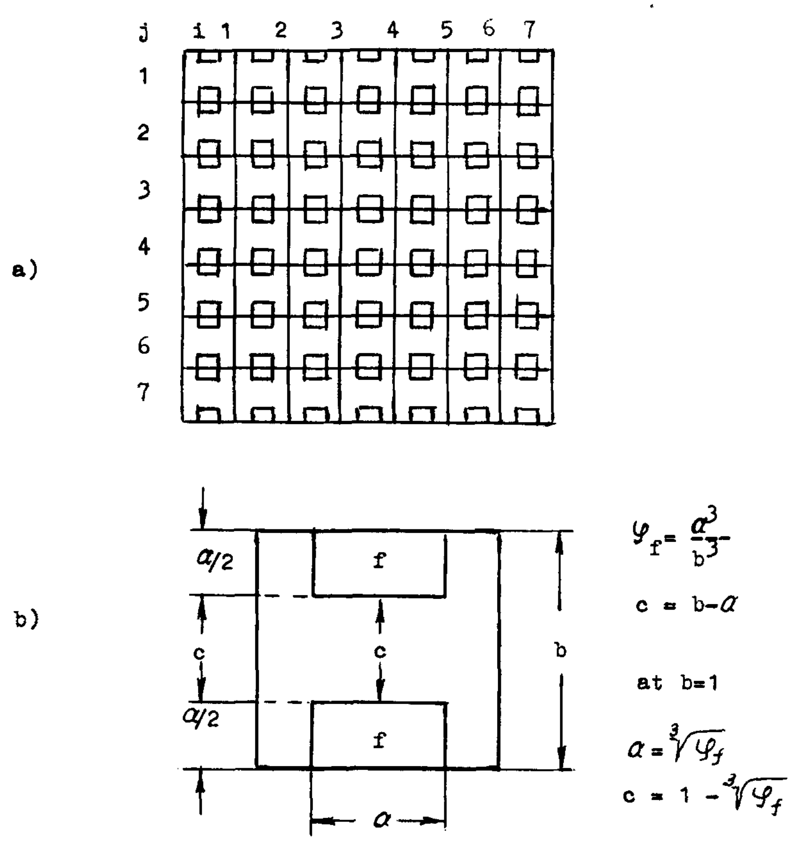

FIGURE 6 The mechanical model of the particulate filled-composite (a) and elementary cell (b).

Then the modulus of each i-th horizontal row of cells, E_j, is expressed through the moduli of each of seven cells present in this row as

$$E_j = \varphi_{1j}E_{1j} + \varphi_{2j}E_{2j} + \cdots + \varphi_{7j}E_{7j} \tag{6}$$

where j varies from 1 to 7.

Correspondingly, the modulus of the whole model, E_M, consisting of seven horizontal rows, will be written through their moduli and volume fractions, φ_j, of each row as

$$\frac{1}{E_M} = \frac{\varphi_1}{E_1} + \frac{\varphi_2}{E_2} + \cdots + \frac{\varphi_7}{E_7} \tag{7}$$

From the values of the moduli of the rows, the relative deformation, ε_r, of each row is calculated for a given applied stress. The relative deformation of the interlayers of a matrix will be here $1/c$ times higher as compared with the deformation of the cell. The particle is supposed to be debonded if the deformation of the interlayer exceeds some arbitrary value (we have chosen 100% at $E_0 = 0.1$ MPa). Knowing the volume fraction of debonded particles, φ_x, and having calculated the modulus of the model after debonding, E_{Mx}, one can plot the dependence of $E_{Mx}/E_M = f(\sigma_T)$.

Figure 7 shows the dependence of the Young's modulus of the model on the applied load for various concentrations of filler particles. It is seen that increasing the applied stress leads to a diminishing of the ratio E_{Mx}/E_M. For higher values of φ_f the intensity of diminishing of that ratio increases. In such a way even a simplified model predicts the dependence of the adhesion joint strength in particulate-filled systems on the filler concentration.

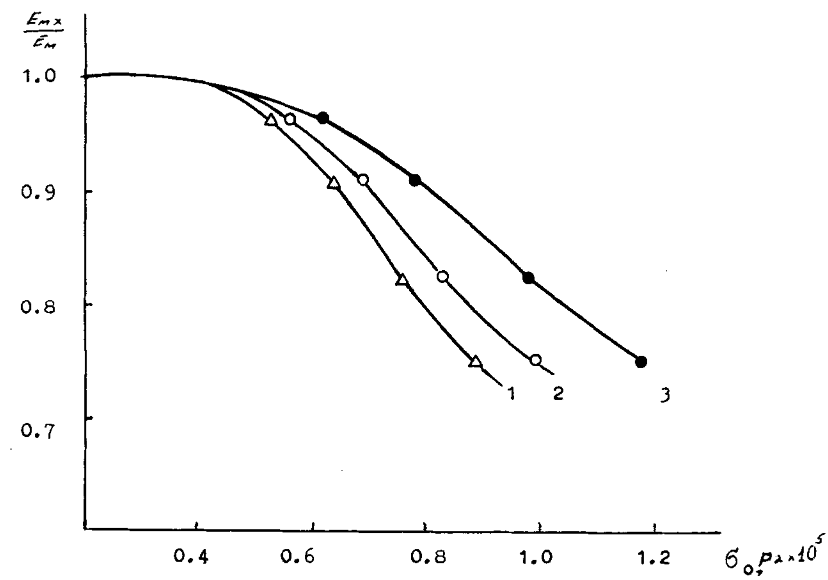

FIGURE 7 Calculated dependencies of $E_{Mx}/E_M = f(\sigma_0)$ at various filler concentrations (vol.%): (1) 0.3, (2) 0.5, (3) 0.7.

CONCLUSION

The experimental study of the influence of the filler concentration and particle size on the debonding of particles from the matrix has shown that the effects are strongly dependent both on the particle size and filler conncentration. Composites with small particles are characterized by the higher stresses at which debonding takes place. Diminishing particle size leads also to increases in the adhesion joint strength which are inversely proportional to the cubic root of the particle diameter. The effects observed are supposed to be connected with different conditions of the stress distribution depending on the fraction of the matrix in the interphase zone at the filler-matrix phase boundary.

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