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ON THE DESCRIPTION OF THE PHENOMENON OF FILLED ELASTOMER STRENGTHENING

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Relations invariantly relating the matrix deformation to the composite deformation have been derived. A model that permits obtaining a Mullins effect and explains the multiple increase in the strength characteristics of the composite compared to the matrix is proposed. At the basis of the model is the presence at the matrix–filler boundary of a hard rubber layer. This layer is formed due to the interaction between the active surface of the filler and the rubber macromolecules. The quantitative form of the tension distribution function density of active chains of the mesh explaining the strengthening phenomenon has been substantiated.

One of the main differences between the quasi-elastic properties of rubbers filled with an active filler and those of unfilled ones is that after the first extension–contraction cycle the curve of the second and subsequent cycles lies much lower than that of the first cycle (Fig. 1). If in the first loading cycle the rubber specimen is extended to the value of the relative deformation ε_1, then in the second loading cycle at $\varepsilon > \varepsilon_1$ both curves will coincide [1–3]. This effect, referred to as the Mullins effect, is not of relaxation character if the relaxation spectrum of unfilled rubber is meant. The tested specimen can "rest" for a fairly long time at room temperature but will not go back to the initial state.

The second essential difference of filled vulcanizing agents from unfilled ones is manifest under the conditions of cyclic sinusoidal loads, where there is a sharp dependence of the complex modulus components on the deformation amplitude [4, 5].

The above effects for rubbers filled with active fillers (technical carbon (black), silica (white black), etc.) are usually attributed to the structural changes in both black aggregates (at small deformations) and the rubber matrix (at finite deformations). In so doing, an important role is played by the notions of the presence at the rubber–active filler boundary of a rubber layer of improved hardness and reduced mobility formed as a result of the interaction between the rubber molecules and the active surface of the filler [6–9]. The above notions have received a certain experimental confirmation and cannot be ignored. At the same time, attempts to describe the properties of rubbers on this basis are, as a rule, verbal and are of qualitative character.

The theoretical investigations on the basis of statistical physics give a certain insight into the strengthening phenomenon [10], but it is still impossible to go beyond the one-molecule approximation.

However, the most important feature of filled rubbers is the strengthening phenomenon and not the effects described above. Its point is a considerable increase in the strength properties of filled rubbers compared to unfilled ones [11–13]. Among such properties are: strength at a constant-rate extension, shredding value, fatigue strength, wear resistance, etc. The attempts to explain this phenomenon qualitatively were generalized rather long ago in [4]. A review of the recent works on the rubber–filler interaction is given in [5]. However, these publications do not describe the molecular mechanism of the strengthening phenomenon from which quantitative characteristics could be obtained. Important results have been achieved by using the current methods of statistical physics, structural micromechanics, and computer simulation [13], and the main achievements would be expected along these lines.

We proceed from the fact that the basis for the strengthening phenomenon is the condition of equality of tensions of the active chains of the mesh carrying the applied load. In other words, the tension distribution function density of chains should be close to a δ-shaped one. The idea of equalizing the chain tensions was put forward rather a long time ago [14]. For example, at a critical tension the macromolecule adsorbed on the surface of the filler does not break but is desorbed by one portion and adsorbed by another.

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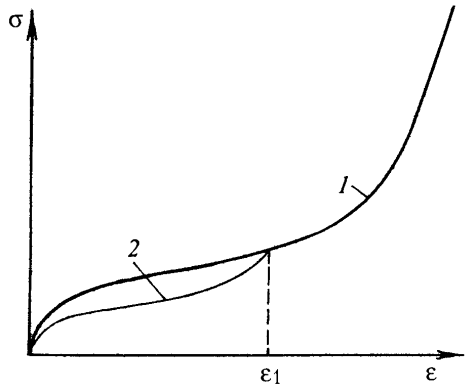

Fig. 1. Stress under uniaxial loading σ versus the relative extension ε: 1), curve of tension under the first loading; 2), second loading for the case where under the first loading the deformation value was ε_1 (for graphic presentation, the σ(ε) curves under the first and second loadings were brought into coincidence at the origin of coordinates).

The situation where the mesh chains are extended uniformly can be represented physically in two cases: 1) in the presence of a strictly regular mesh with an equal number of chains between nodes, without any tipping over, engagement, or other steric interactions leading to a break of regularity; and 2) under the condition of "coming-off" of segments from the hard layer (or "pulling" of segment from the hard layer) at a load on the chain close to but not less than the chain strength. The chains thereby will not break but will carry the load.

It is clear that practical realization of the first case is impossible. The second case is substantiated below.

We will describe the method for calculating the principal deformations of the rubber matrix (assuming that its stressed-strained state (SSS) is homogeneous depending on the principal deformations of the composite). Then we will describe the model of deformation of a cross-linked composite "rubber–active filler" without assuming that the active filler particles are destroyed.

Relationship between the Composite Deformation and the Matrix Deformation. The volume degree of filling of the composite φ is defined by the relation

$$\varphi = \frac{V_\mathrm{f}}{V_\mathrm{c}} = \frac{V_\mathrm{c} - V_\mathrm{m}}{V_\mathrm{c}} = 1 - \frac{V_\mathrm{m}}{V_\mathrm{c}} \,. \tag{1}$$

In the deformation process the composite has the principal values of the degrees of extension Λ_i (i = 1, 2, 3). The matrix deforms by the principal values λ_i (i = 1, 2, 3). It is correct to introduce the values of λ_i only on the assumption that the matrix deformation is homogeneous when the composite deformation is homogeneous. As a matter of fact, it is not so, but we do not know any other reasonable assumption permitting analytical calculations.

Consider the restructions on the functionals $\lambda_i(\Lambda_i, \varphi)$:

$$\lambda_i\,(\Lambda_i, \varphi) = \begin{cases} \Lambda_i & \text{at} \quad \varphi = 0 \,, \\ \infty & \text{at} \quad \varphi = 1 \,. \end{cases} \tag{2}$$

Assume the incompressibility conditions of the composite and matrix

$$\Lambda_1\Lambda_2\Lambda_3 = 1 \,, \quad \lambda_1\lambda_2\lambda_3 = 1 \,. \tag{3}$$

From the absolute hardness of the filler particles relation (2) follows. Relation (3) reflects the invariability of the composite volume and matrix in the deformation process, which is satisfied for rubber. Proceeding from (2) and (3), we can write the following particular form for $\lambda_i(\Lambda_i, \varphi)$:

$$\lambda_i = \Lambda_i^{f(\varphi)} \,. \tag{4}$$

The function $f(\varphi)$ from (4) can be given as

$$f(\varphi)=\frac{1}{1-\varphi^{n}} \tag{5}$$

or

$$f(\varphi)=\exp\left(\frac{n_1\varphi^{n_2}}{1-\varphi^{n_3}}\right). \tag{6}$$

Relations (4)–(6) are particular cases of the expressions satisfying the conditions of (2) and (3).

Comparison with experiment can be performed in the following way. An elastic potential U_m that describes well the properties of unifilled rubber (matrix) is selected. For expressions (5) or (6), n–n_3 constants at which the best agreement between the deformation curves of filled rubber in an arbitrary complex SSS and the calculated dependences is observed are calculated. This procedure can be carried out with the use of multiple parameter optimization methods [15]. As a result, if, for example, for unfilled rubber, a Khazanovich–Bartenev potential of the form [16]

$$U=\beta\,(\lambda_1+\lambda_2+\lambda_3-3) \tag{7}$$

has been used, then the expression for the elastic potential of filled rubber in the form of the first term of the Ogden potential [17] (this potential was also proposed by K. F. Chernykh [18])

$$U=\sum_n \frac{\mu_n}{\alpha_n}\,(\Lambda_1^{\alpha_n}+\Lambda_2^{\alpha_n}+\Lambda_3^{\alpha_n}-3) \tag{8}$$

will be obtained.

Analogous reasoning can be used for any other known potentials. In each of them, the principal degrees of extension will be raised to some power in accordance with expressions (4)–(6).

Is this enough to obtain a good expression for the elastic potential of the filled rubber? As the results of [15] show, this is not enough. The Chernykh, Ogden, and all other potentials where the deformation parameter is raised to some power describe the experiment with a large error. Expressions with a different structure are more exact for the essentially nonlinear behavior of the filled rubber [15].

One can get out of this difficulty purely phenomenologically. Let us return to expression (4) and see that we have not simplified the situation. We have ignored the fact that the following form of the function $\lambda_i(\Lambda_i,\ \varphi)$ is more general:

$$\lambda_i=\Lambda_i^{f(\varphi,J)}, \tag{9}$$

where J is any function of invariants of the composite deformation tensor. In other words, the exponent, depending on (4), varies at different deformations of the composite. In this case, expressions (5) and (6) should be changed by adding, for example, to the numerator a polynomial in J in the form of a multiplier.

This technique has the right to exist and deserves more careful consideration. However, here one will have to introduce additional parameters connected with J, which will complicate the problem. Therefore, we will try to investigate in more detail the general features of the composite deformation and use this in analyzing the problem stated in the present paper — to explain the strengthening phenomenon at the molecular level.

Model of Deformation of the Cross-Linked Composite "Rubber–Active Filler." Consider the processes that occur at a deformation in the system "active filler–rubber near-boundary layer–rubber matrix." All previous calculations were based on the absence of the hard layer. If it is present, then it is necessary to use in relations (2), (4)–(6), and (9) φ_{ef} instead of φ:

$$\varphi_{ef}=\varphi_f+\varphi_b\,. \tag{10}$$

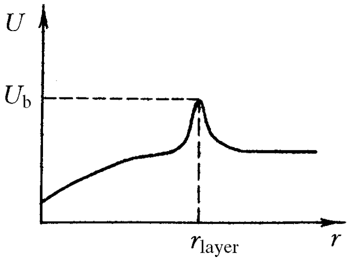

Fig. 2. Potential of the macromolecule segment U as a function of the distance r from the active surface.

The effective degree of filling φ_{ef} is determined by the volume portions of the filler φ and the hard boundary rubber layer φ_b.

The model describing the deformation of the elementary cell of the cross-linked "rubber–active filler" composite uses the experimental fact that there occurs an interaction between the filler surface and the macromolecules [5]. This interaction leads to the formation in the vicinity of the filler particle of a hard macromolecular layer with a low level of conformation mobility. It is believed that the above layer is in the pseudoglassy state. Under a load the composite experiences a three-axis loading, since along the surface of the filler particle movement of rubber macromolecules is impeded.

As a result of such an interaction, the segments situated near the surface not only are in a potential well, but are also separated by the barrier U_b from the vulcanizate in a highly elastic state (Fig. 2). The nature of this potential barrier is associated with the energy that has to be expended in displacing along the filler particle surface the macromolecular segments interacting strongly enough with the active surface of the filler. Such a displacement is needed to prevent the formation of a free volume at the site which the segments of the macromolecule left when it was extended. And it is possible to escape this barrier only in the case where the external action on this macromolecule (e.g., the extending force) will lower the effective height of this barrier. The return to the pseudoglassy state with a higher hardness when the extending load is removed will require very much time, since there are no external actions lowering the potential barrier. The return to the initial state occurs at a higher temperature, which is observed experimentally [4, pp. 22–24].

This phenomenon is in qualitative agreement with induced elasticity of extension. In either case, their nature is essentially nonequilibrium. If the problem is solved by the equilibrium statistics methods, then the size of the barrier U_b at the boundary between the layer and and cross-linked rubber in the highly elastic state will not influence the value of φ_b.

Note that there is no clearly defined boundary between the near-boundary layer between the hard rubber layer and the matrix, which is in a highly elastic state. This boundary is blurred and the potential barrier is wider than is shown in Fig. 2. However, this fact in no way affects the above qualitative considerations.

Thus, the value of φ_b should depend on the voltage applied to the rubber specimen and on the barrier size U_b. To solve the problem invariantly, we consider the dependence of φ_b on the function of invariants of the deformation tensor J:

$$\varphi_b\,(J_{\max}) = \varphi_{b,\text{in}} - CJ_{\max}\,. \tag{11}$$

Here $J_{\max}$ is the largest value of the quantity J that has ever been obtained in the history of the deformation of a composite.

The form of the right-hand side of dependence (11) can be complicated by adding terms containing the highest degrees of $J_{\max}$.

The central point in understanding the Mullins softening effect when the return to the initial state after the load is removed and the repeated extension occurs along the curves lying much lower than the initial curve (Fig. 1) is the following. The effective degree of filling, which has decreased in the deformation process, does not increase (does not regain the initial value) when the load is removed. Consequently, the secondary extension after the removal of the load will occur at a lower value of the effective degree of filling φ_{ef} than the first extension. And this is the

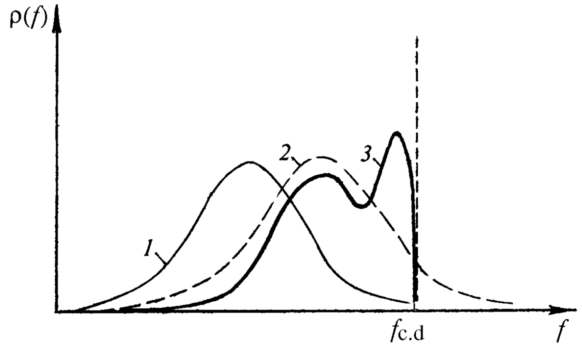

Fig. 3. Tension distribution function density of chains ρ(*f*) in the initial state (1), at affine displacement of ends (2), and with regard for the "coming-off" of segments from the near-boundary hard layer (3).

reason why the secondary extension curve will lie lower than the curve of the first extension but will connect it upon reaching the maximum degree of extension attained in the first extension.

We repeat that the softening effect in the proposed interpretation is essentially nonequilibrium. It can only be explained from the viewpoint of physical kinetics.

It is easy to give the above considerations in mathematical form and get analytical expressions to describe the real dependences obtained experimentally in an arbitrary complex stressed-deformed state.

Let us illustrate the theory by an example of potential (7) describing the properties of unfilled cross-linked rubber. In this case, the elastic potential of unfilled rubber will be of the form

$$U = \beta\,(\Lambda_1^{\alpha_n} + \Lambda_2^{\alpha_n} + \Lambda_3^{\alpha_n} - 3)\,, \tag{12}$$

where the quantity α_n is defined by relation (5)[*]:

$$\alpha_n = \frac{1}{1 - \varphi_{\mathrm{ef}}^{n}} = \frac{1}{1 - (\varphi_{\mathrm{f}} + \varphi_{\mathrm{in}}\,(J))^{n}} = \frac{1}{1 - (\varphi_{\mathrm{f}} + \varphi_{\mathrm{b,in}} - CJ)^{n}}. \tag{13}$$

Thus, the elastic properties of the filled rubber can be described by potential (12) containing three adjustable parameters: β, *n*, and *C*. The quantity φ_{f} is given and the constant $\varphi_{\mathrm{b,in}}$ is determined experimentally or by computer simulation methods.

We now turn to the explanation of the effect of multiple increase in the strength of filled noncrystallizing rubbers as compared to unfilled ones.

Figure 3 shows the curves of the tension distribution function density for various cases. Curve 1 corresponds to the initial (nondeformed) state, and ρ(*f*) is bell-shaped[**]. The chains practically do not break, since the quantity $f_{\mathrm{c.b}}$ is in the region where ρ(*f*) is equal to zero.

If the chains are dead-linked to the filler particles, then in the case where an extending load is applied the ρ(*f*) plot will shift to the right (curve 2). The right branch of the plot will appear beyond the ultimate strength of one chain and all chains corresponding to this part of the plot will break. The strength of the material thereby will not be too high, since at the breaking sites of stretched chains located in the right-hand part of the plot there will appear overtensions on the neighboring chains, which will lead to the formation of an incipient microcrack and further destruction.

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[*] One can also use relation (6), but this is only in the case where the accuracy attained by means of (5) is insufficient.

[**] At the current stage of devolopment of the theory, a concrete form of the distribution function has not been calculated. The best available way to obtain it is to use numerical modeling methods. Knowledge of the exact form of this function is not necessary for understanding what follows.

A different picture is observed in the case where stretched chains "come off" from the near-boundary layer. If the "coming-off" load is slightly smaller than the chain strength, then all stretched chains will carry the load and the form of the distribution function density will correspond to curve 3 (see Fig. 3). In the limit, $p(f)$ will become δ-shaped. The strength will be much higher than for curve 2. The breaking extension, too, will be higher, since there are no regions of overtensions formed by the presence of broken chains.

The strengthening mechanism described above can be extended to crystallizing unfilled rubbers in which the strength approaches that of filled rubbers. In this case, strengthening is achieved due to the "coming-off" of segments of stressed chains from crystallites. All the other reasonings hold good.

Apparently, an analogous strengthening method is applicable for oligomer rubbers with rigid end groups forming the microphase.

NOTATION

σ, stress, MPa; ε, relative extension; φ, volume fraction of composite filling; V_f, filler volume in the composite, m^3; V_m, matrix volume in the composite, m^3; V_c, composite volume, m^3; Λ_i and λ_i, degrees of extension of the composite and matrix along the principal axis i; n, n_1, n_2, n_3, parameters selected from comparison with experiment; U, elastic potential of filled rubber, J/m^3; U_m, elastic potential of the matrix, J/m^3; β, α, μ, elastic potential constants; φ_{ef}, volume fraction of composite filling with regard for the hard rubber layer in the pseudoglassy state located in the near-surface layer around the filler; φ_f, volume fraction of composite filling with the filler proper; φ_b, volume fraction of composite filling determined by the volume of the hard rubber layer; U_b, potential barrier height between the state of the macromolecule segment in the near-boundary layer and the highly elastic state, J/mole; r, distance from the active surface; r_l, thickness of the hard rubber layer on the surface of the filler particle, m; C, adjustable parameter; $\rho(f)$, chain tension distribution function density of macromolecules f; δ, Dirac function. Subscripts: f, filler; m, matrix; c, composite; b, near-boundary layer; layer, layer; ef, effective; max, maximum; c.d, chain destruction; in, initial.

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