A FRACTAL MODEL OF REINFORCEMENT
OF ELASTOPLASTIC NANOCOMPOSITES

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Within the framework of fractal analysis and percolation theory, an alternative model of reinforcement of filled polymers is offered. Practically, this model can be used only to describe the reinforcement of nanocomposites, because, according to the treatment considered, a pronounced reinforcement can be reached only at ratios of filler particle diameter to the statistical segment length of about 10 and less. A theoretical calculation showed a good qualitative and quantitative agreement with experiments. The type of reinforcement mechanism of composites is determined by the type of the space (fractal or Euclidean) in which the structure of the polymeric matrix is formed.

The effect of reinforcement of elastomers with finely dispersed fillers is crucial for some branches of industry, especially for the manufacture of rubbers. In this connection, the term “reinforcement” is primarily associated with the improvement of mechanical properties of filled elastomers. The numerous studies on this problem made it possible to conclude that the size of filler particles affects the properties of filled rubbers considerably [1]. Thus, there exist several classifications of filler types as functions of filler particle diameter, which can roughly be summarized as follows: “diluting” fillers (i.e., not giving a noticeable reinforcement), with particle sizes of 1000 to 8000 nm; “semi-reinforcing” fillers, with particle diameters from 100 to 1000 nm; “reinforcing” ones, with particle sizes of 10-100 nm (sometimes, “super-reinforcing” fillers, with particle diameters of ~10-35 nm, are distinguished) [1].

In [2], a reinforcement mechanism is suggested for dispersedly filled polymers with a glassy polymer matrix. This mechanism is based on the assumption that the skeleton of filler particles forms a fractal space that “disturbs” the polymer matrix structure (increases its fractal dimension $d_f$), which determines the increase in such mechanical properties of composites as the elastic modulus $E_c$, yield point $\sigma_y$, etc. Thus, the basic condition for this reinforcement mechanism is the formation of the structure of a polymer matrix in a fractal space [2, 3]. However, it is quite obvious that there exist at least two cases where this mechanism does not work. First, this happens when the skeleton of filler particles does not form a fractal structure. Second, this mechanism is not applicable to describing rubbers, since the value of $d_f$ for them is close to the dimension of the enveloping Euclidean space $d$ ($d = 3$), and thus an increase in $d_f$ upon introduction of a filler is impossible in view of the general rule $d_f < d$ [4].

The purpose of the present study is to suggest an alternative fractal mechanism for describing the reinforcement of rubbers upon introduction of finely dispersed fillers, i.e., elastomeric nanocomposites, into them.

For theoretical calculations, eight sizes of filler particle diameter \( D_a \) in the interval of 5-80 nm were chosen arbitrarily; according to the data in the literature [5], the average values of the specific surface \( S_u \) (m\(^2\)/g) were evaluated for them. These data allowed us to calculate the fractal dimension of the surface of filler particles \( d_s \) according to the equation [6]

\[
S_u = 410 \left( \frac{D_a}{2} \right)^{d_s - d}
\]

The characteristic ratio \( C_\infty \) for rubbers was estimated by the equation [7]

\[
C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}
\]

where \( d_f = 2.95 \) [8].

The length \( l_{st} \) of the statistical segment was determined as follows [9]:

\[
l_{st} = l_0 C_\infty
\]

where \( l_0 \) is the length of skeletal link of the basic chain, equal to 0.154 nm [10].

As follows from the condition \( d_f = 2.95 \), for rubbers (the value of \( d_f \) mentioned above is maximum for real solid bodies [8]), these materials can be regarded as fractal objects. Estimates by Eq. (1) show that the value of \( d_s \) for the fillers chosen varies within the limits of 2.2-2.85. This makes it possible to interpret the intercomponent layer in filled rubbers as a result of interaction of two fractal objects (the polymer matrix and the surface of filler particles) for which there exists a unique linear scale \( l \) determining the distance of interpenetration of these objects [11]. Since the elastic modulus of the filler is much higher than that of the rubber, the above-mentioned interaction is reduced to the penetration of the filler in the polymer matrix; then \( l = l_{int} \), where \( l_{int} \) is the thickness of the interfacial layer [12]. In this case, we can write [11]

\[
l_{int} \sim a \left( \frac{D_a}{2a} \right)^{2(d-d_s)/d},
\]

where \( a \) is the lower linear scale of the fractal behavior, which for polymers is assumed equal to \( l_{st} \) [12].

From comparing experimental data, it follows that the coefficient of proportionality in relation (4) is equal to 0.5 [12]. Assuming that the intercomponent layer is spherical with external and internal radii \( R = D_a/2 + l_{int} \) and \( r = D_a/2 \), respectively, from geometrical considerations, we obtain the formula for calculating its relative content \( \phi_{int} \).