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Potentiality of the triboelastic approach for clarifying the filler reinforcement mechanism in elastomers

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Abstract

The triboelastic approach developed earlier is applied to a set of well-known structure–property relations of elastomers whose structural mechanisms remain debated topics until now. Predictive calculations gained through the triboelastic approach demonstrate good agreement with the accumulated experience and with it they present a new insight into certain as yet unclear mechanisms. The area of application of the proposed approach is examined.

Keywords: Particulate elastomeric composites; Reinforcement mechanism

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1. Introduction

It is common knowledge that solid tiny particles of a micron size or less incorporated into a rubbery matrix increase considerably the modulus and tensile strength of such particulate composites.

The mechanism of this effect discovered in the early 20th century and thereafter widely used in industry is not entirely known (Kraus, 1977; Mullins, 1969; Payne and Whittaker, 1972; Voet, 1980; Edwards, 1990). In spite of huge experience gained by chemists, physicists and mechanicians in a search for its foundation, it remains at a level of qualitative explanations not substantiated by appropriate mathematical modeling. It is of interest to note that chemists usually explain this phenomenon as reinforcement of the rubber with layers contacting with solid particles (Voet, 1980). Mechanicians believe that reinforcement is a manifestation of the growing resistance to crack propagation caused by the presence of filler particles (Smith, 1977).

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Physicists suppose that the effect arises from the aptitude of the rubber molecules, adsorbed by the filler surface, to keep integrity under strain through moving along the interface zone and thus increasing the total number of the resistant structural elements of the composite system (Alexandrov and Lazurkin, 1944, Dannenberg, 1966, Rigbi, 1980, Kraus, 1977; Soos, 1984; Medalia, 1987; Edwards, 1990). The substructure of the elastomer and filler arrangement and its influence on the mechanical properties of composites have been examined by Sharaf and Mark (2002), Vacatello (2002, 2003) and Nakatani et al. (2001).

In a recent paper Moshev and Evlampieva (2003) tried to develop a mathematical model of reinforcement, based on the latter foundation offered by physicists. Accepting their ideas, as a background for simulating the reinforcement phenomenon, a rather rough triboelastic mathematical model of a structural unit has been developed and reported (Moshev and Evlampieva, 2003) with a couple of illustrative examples demonstrating good qualitative agreement between theory and practice. This has awakened an interest in enhancing the model potentiality and in establishing the range of its applicability.

The refined variant of the model, examined in this paper, is based on three-dimensional representation. It allows comparison with a great body of experimental data taking into account the volume loading and the size of filler particles. Additionally, it examines some experimental observations that still require clarification.

2. Theoretical background and model characterization

The model reported by Moshev and Evlampieva, 2003 is based on two major premises. The first takes into account the geometrical peculiarities of the well-reinforced rubbery composites. It assumes that the size of filler particles is so small and their number is so great that the mean spaces between the neighboring particles become appreciably shorter than the contour length of rubber macromolecules. Under such condition one macromolecule can be adsorbed by several adjacent particles forming links between them. The second premise is of physical nature. It considers the behavior of rubber chain as a non-Gaussian one with the upturns due to finite chain extensibility.

Hence the geometry of a unit cell of the model in the initial state (Fig. 1a) might be represented as some length, L_0, of a spring simulating a rubber molecule lying along two substrates, U_m in lengths, simulating the surfaces of the adjacent filler particles and the space, L_g, between them.

It is assumed that the spring is retained on the surface of substrates by the adhesive forces throughout its length with the ends fixed to the outer positions of the substrates. Applying some tensile effort to substrates, as shown in Fig. 1b, results in stretching the elastic bridge L_g with some additional portion of the spring slid off the substrates into a gap between them. Further increase in the tensile force induces enlarged slipping off the spring from the substrates into the bridge between them (Fig. 1c and d) until the sliding area reaches the outer ends of the model. Then both dragged and proper elastic resistances of the spring come into play till the most loaded gap part of the spring breaks down.

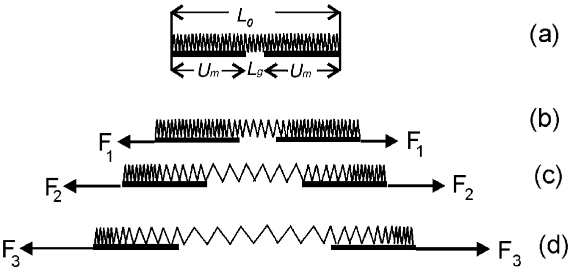

Fig. 1. Geometry of the linearized structural cell.

Two operators govern the mechanical behavior of the model. The first one simulates the highly non-linear elastic resistance of rubber macromolecules as follows

$$\lambda = \sqrt{L_0}(Cthf - 1/f) + 1.0, \tag{1}$$

where λ is the elongation of the spring, L_0 is the length of the spring measured in a number of the virtual segmental units, f is some undefined (arbitrary) measure of the tensile force. Thus the deformation of the spring, ε, can be defined as

$$\varepsilon = \sqrt{L_0}(Cthf - 1/f). \tag{2}$$

The spring is assumed to break down, when tensile force reaches a limiting value equal to 20.0 that corresponds to 0.95 of the spring maximum stretch.

The second operator simulates the adhesive bond strength at the spring–substrate interface. It is represented as

$$f = Tu, \tag{3}$$

where u is the length of the substrate - spring contact, T is the specific adhesive bond strength taken as some constant magnitude per unit of substrate length. If $f < Tu$, no sliding occurs.

These premises and computing procedures concerning the stress-strain relations have been described in detail earlier (Moshev and Evlampieva (2003)). Such linear model has demonstrated rather convincingly its predictive power.

Further research has shown that a slight refinement of the linear model allows expanding its predictive capacities to a three-dimensional structural representation. With this in mind, an isometric regular hexahedral prism, with a filler particle put at the center (Fig. 2a), has been adopted as a representative structural unit for the volumetric representation. The isometric configuration, allowing close packing of structural units, seems most suitable for latter case.

Carbon black as a typical industrial filler has been chosen for the following analysis. Experience evidences that carbon black particles have the irregular dendrite-like shape, which is commonly modeled by the so-called equivalent diameter, D_a, determined experimentally by transmission electron micrography or through specific area measurements. In such cases, D_a can be regarded as some spherical substitute averaging the complicated real shape of the branched carbon black aggregates. The magnitude D_a ranges ordinarily between 20 and 40 nm (Boonstra, 1979).

If the filler particle with diameter D_a touches the cell boundaries (Fig. 2a), then this structural unit can be regarded as that having the maximum packing density with the minimum volume, $V_{\min}$, equal to

$$V_{\min} = (\sqrt{3}/2)D_a^3. \tag{4}$$

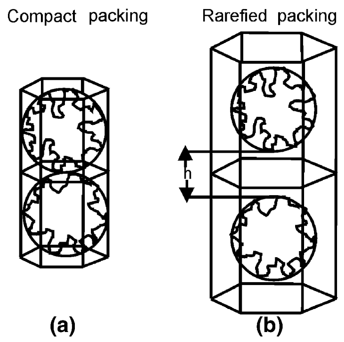

Fig. 2. Geometry of the three-dimensional structural cell.

The volume of the filler particle, V_{f}, inside $V_{\min}$ is obtained by multiplying $V_{\min}$ by the maximum volume fraction, $\varphi_{\max}$, specified for a given carbon black type

$$V_{\mathrm{f}} = (\sqrt{3}/2)D_a^3\varphi_{\max}. \tag{5}$$

The magnitude of $\varphi_{\max}$ is obtained experimentally, more often by means of the so-called dibutylphtalate absorption test (DBPA).

$$\varphi_{\max} = 0.543/(0.543 + \mathrm{DBPA}),$$

where DBPA is a volume of dibutylphtalate needed for filling the voids in 1 g of the pelleted carbon black. Because of the irregular shape of carbon black aggregates, $\varphi_{\max}$ generally does not exceed 0.4 (Medalia, 1987) in contrast to 0.64 for randomly arranged uniform spherical particles.

In the close packing composed of the cells having minimum volume, the filler particles are in touch with each other with a zero gap between them. Since the solid volume fraction φin commonly used rubbers is always lower than $\varphi_{\max}$ (about 0.15–0.3), in actual composites, the filler particles are separated from each other by some spaces, h (Fig. 2b).

It can be shown that for the adopted geometry of the structural cell

$$h = D_a((\varphi_{\max}/\varphi)^{1/3} - 1). \tag{6}$$

This expression connects the *linear* parameter h with its *three-dimensional* counterpart φ. Identifying h of Fig. 2b with the gapL_g in the one-dimensional model of Fig. 1 provides a basis for using the capabilities of the simple linear model for predicting some important properties of composites as functions of the filler volume fraction φ. Herewith the h-length expressed in nm should be replaced by the L_g-length expressed in segmental units

$$L_g = h/L_{\mathrm{seg}}, \tag{7}$$

where L_{seg} is the length of the macromolecular segment.

An increment in the length of the model during extension is formed as a sum of the current elastic bridge length, L_g, and the portion of the spring pulled out of the substrates. Calculation techniques of the extension curve are described elsewhere (Moshev and Evlampieva, 2003).

From Fig. 2 it follows that the stress, σ, in the hexahedral cell under a tensile force, f, is determined as

$$\sigma = f/S, \tag{8}$$

where S is the cross-section area of the cell.

$$S = (\sqrt{3/2})(D_a + h)^2. \tag{9}$$

Now the current modulus of the cell, E, defined as some secant magnitude, can be calculated.

$$E = \sigma/\varepsilon. \tag{10}$$

Since σ is strongly non-linear, the modulus magnitude becomes a variable as well.

3. Some experimental observations viewed as manifestations of triboelastic structural rearrangements

3.1. Initial modulus reinforcement as a function of the filler volume fraction

For a long time, an unexpectedly high experimental initial modulus, E_0, of carbon black filled rubbers cannot find satisfactory theoretical explanation. Calculations taking into account only the hydrodynamic effect of reinforcement give the values of E_0 that are much below the experimental results. The theoretical amendments offered have also appeared insufficient for filler volume fractions above 0.1 (Fedors, 1979). At present the problem seems to be still unsolved, experimentalists restrict themselves to qualitative assumptions (Harwood et al., 1969; Meinecke and Maksin, 1981). Most likely, these difficulties come from the attempts to seek for the solution of the problem on generally recognized hydrodynamic grounds.

The fact that drastically increased rigidity appears in systems having very fine particles at rather high volume loading safely suggests that this phenomenon has a direct relationship to the geometrical peculiarity of the system. Obviously, the point is that the rubbery layers connecting the adjacent filler particles become smaller than the mean size of rubber molecules and their mechanical behavior *cannot longer be represented by the rubber bulk properties*. Hence modeling such systems should take into account this rubber peculiarity.

The structural model outlined above allows testing the latter approach. By way of illustration let us examine a typical compound containing High Abrasion Furnace (HAF) carbon black ($\varphi_{\max} = 0.33$, $D_a = 40$ nm) and a common hydrocarbon rubber ($L_{\text{seg}} = 2.0$ nm).

Substituting these data into Eq. (6), one gets the dependence of a space h in nm between the adjacent particles on the filler volume fraction $\varphi$and the same value in segmental units.

The initial modulus, E_0, represents the response of the system relative to its virgin state. Hence it can be defined through the given D_a, h and L_g values by the expression

$$E_0 = \frac{6}{\sqrt{3L_g}(D_a + h)^2}, \tag{11}$$

where h is found as a function of φ by Eq. (6) with the resistance f of bridges L_g connecting adjacent particles (Eq. (7)).

Theoretical expression (11) cannot be evaluated directly through experimental checking because it represents E_0 via arbitrary unit of force. Hence a fitting multiplier is needed for comparison of experimental and calculated data. Shifting E_0 values along the logarithmic E_0 scale can readily do such procedure.

Fig. 3 presents the designed curves for HAF carbon (solid line) and for experimental data demonstrated by Fedors (1979) (crosses). It is evident that the theoretical estimations agree well with the experimental results in the range of high reinforcements being the subject of discussion.

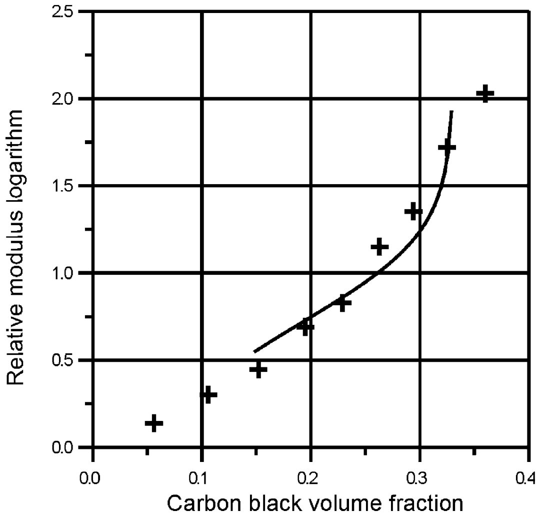

Fig. 3. Initial modulus versus filler volume fraction.

Thus, it may be safely suggested that the drastically increased initial stiffness of rubber composites at higher volume filling results from very high stiffness of the short molecular chains connecting the adjacent filler particles in the virgin state of the system. Their rigidity is vastly greater than the rigidity characteristic of the bulk gum rubber.

3.2. Initial modulus reinforcement as a function of the filler particle size

As follows from Eq. (6), the mean spaces between particles are dependent not only on their volume fraction but also on the diameters of filler particles. With φ held constant, the smaller is the size of particles, the lesser becomes the space between them, and, consequently, the shorter the molecular chains connecting particles. Therefore, the filler size diminution alone should increase the initial modulus of rubber composites.

This effect was demonstrated by Alter (1956), who generalized the available experimental data concerning this point for various filler sizes at various volume fractions. According to Alter's results, the effect is typical of small particles having diameters less than 200 nm. The increase in the modulus becomes greater at higher filler concentrations. A marked influence of the size of filler on the modulus was experimentally established likewise by Schwarzl et al. (1970).

The computed dependence of the initial modulus (in arbitrary units) on the diameter of filler particles (for input parameters of Section 3.1) is shown in Fig. 4. It demonstrates the slackening of dependency with size of particles and with decrease in filler concentration, which agrees well with experimental observations.

3.3. Reinforcement as a function of the bond strength

In Sections 3.1 and 3.2, two structural sources of high initial modulus in particulate composites are examined. They are: (1) small size and rather high volume fraction of structural elements and (2) short macromolecular chains connecting the adjacent filler particles. However, as soon as the interface sliding begins, one more factor, i.e., the adhesive strength, T, enters into action. It predetermines the evolution of the already framed initial modulus of composites. Fig. 5 illustrates importance of this factor with reference to a rubbery ($L_{\text{seg}} = 1.5$) composite loaded with 25% by volume HAF black ($D_a = 30$ nm, $\varphi_{\max} = 0.352$). The tensile curves of individual cells for adhesive strengths varying from 0.1 to 10 have been calculated.

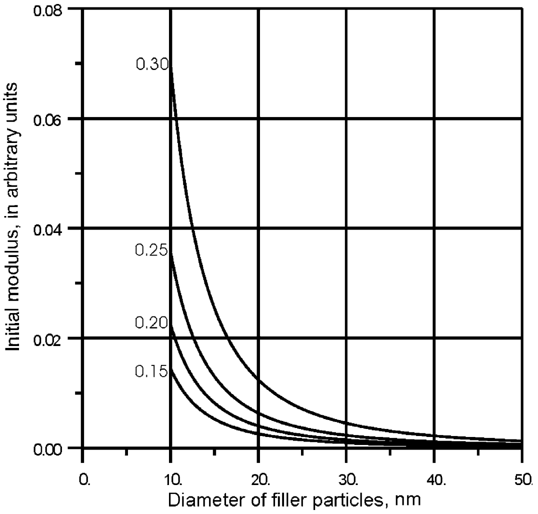

Fig. 4. Initial modulus versus size of filler particles at various filler volume fractions (indicated near the curves).

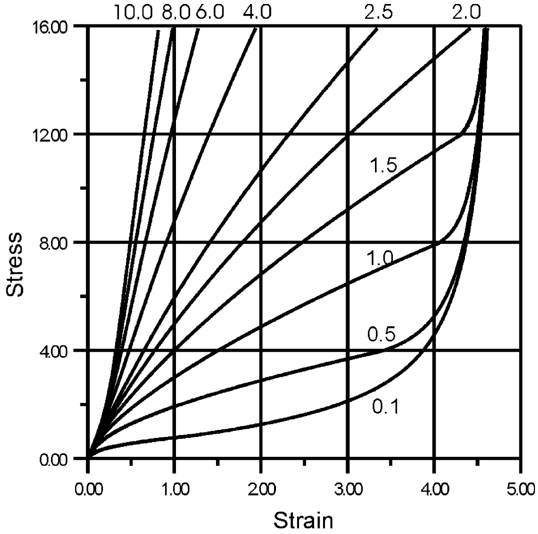

Fig. 5. Tensile curves of the structural cell at various adhesive strengths (indicated near the curves).

Fig. 5 demonstrates that, generally, the growth of T helps in maintaining the magnitude of the initial modulus. The growth of T from 0.1 up to 2 does not influence breaking deformations, which remain close to maximum 4.5, in this instance. However, at higher adhesive strengths, breaking strains start quick going down.

Real composites are randomly composed systems with cells varying in a local filler volume fraction. The ultimate stresses and strains of individual cells are distributed around specified mean values. The tensile curves of the objects including a multitude of random structural cells become random as well including their breaking efforts, f_b, and strains, ε_b.

To clarify this point, a discrete model composed of inhomogeneous structural cells has been developed like that examined earlier by Moshev and Evlampieva (1997). This model is a representative of the so-called bundle systems (Hansen and Hemmer, 1998). It consists of M cross-sections connected in tandem, each cross-section representing a bundle of N parallel random cells clamped at both ends. According to Moshev and Garishin (1993), a non-uniform distribution close to the normal law has been synthesized for samples completed with random structural cells.

As an illustration, random samples have been composed for $M = 3$ and $N = 3$. Tensile curves, based on the input data of Fig. 5, have been calculated for various T values in the interval from 0.3 up to 10.0.

Fig. 6 depicts ε_b–T, f_b–T and ε_b–f_b relationships. It is seen that the maximum breaking effort (about 16.0) together with the maximum breaking deformation (about 3.5) correspond to the intermediate value of T about 2.0. These results agree well with experimental data gained by Edwards and Fischer (1973) and Voet (1980).

The interrelation ε_b–f_b is in the qualitative consent with the experimental failure envelope demonstrated by Smith (1977). Triboelastic treatment makes clearer the physical essence of this relation. The increasing T in numerical experiments simulates decreasing temperature or increasing rate of extension in realistic tests.

3.4. Payne effect

In the early seventies, Payne and Whittaker (1972) demonstrated data on cyclic deformation of HAF black filled butyl rubber. A nearly constant high elastic modulus is observed at very small strain amplitudes

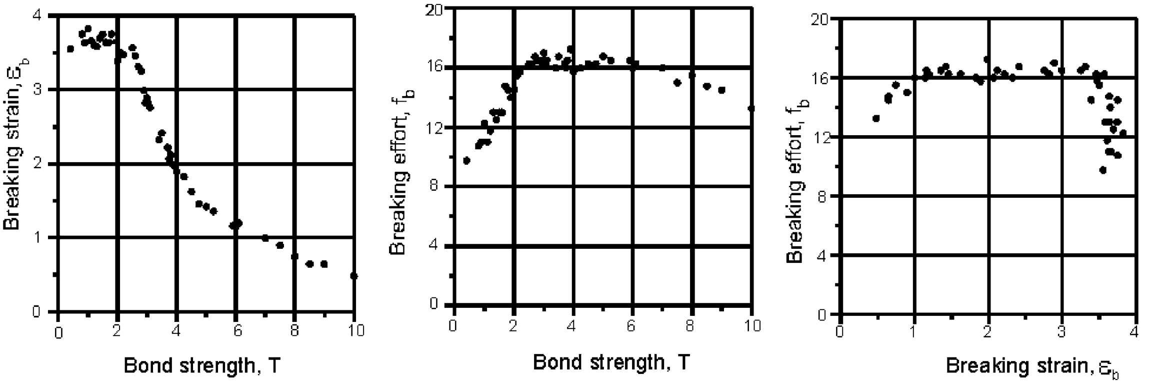

Fig. 6. Failure curves for ε_b and f_b versus T bond strength.

of less than 0.1%. It drops rapidly beyond 1%. However, at strain amplitudes beyond 10% modulus leveling off appears. This behavior is more pronounced at higher black loading, while it disappears below 10% volume loading. The effect is reversible provided enough time is allowed for recovery. The first explanation of this phenomenon was that the low strain modulus was caused by the network formed of carbon black dendritic aggregates and that the decrease of the modulus with strain amplitude was due to the breakdown of the carbon black structure at low strains. However, in the later 80s Medalia (1987) showed that it disagrees with facts.

The triboelastic approach makes the Payne effect fully transparent and comprehensible. As was assumed above, the elastic modulus at very small deformation is high since the spaces between the filler particles are bridged by very short molecular chains, which are much stiffer than those in the full-length molecular networks. At the very beginning of extension, while the virgin structure of the composite is not yet considerably changed, the system keeps its initial high modulus. However at higher stresses, macromolecules begin sliding into the spaces between particles. The length of chains connecting particles rises and their elastic resistance drops.

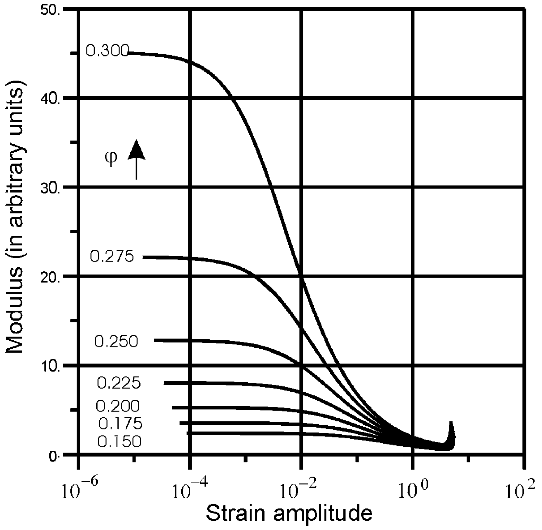

Fig. 7. Calculated Payne effect at various filler volume fractions (indicated near curves).

This effect is reversible. After unloading the system tends to the initial state under the action of the thermal molecular motion. Since the phenomenon is of an interfacial nature, obviously, it is more pronounced at higher filler loading and smaller particle sizes.

Fig. 7 demonstrates the Payne effect calculated through triboelastic modeling. The input data taken for calculation specify commonly used HAF carbon black (DBPH = 1.0, $\varphi_{\max} = 0.352$, $D_a = 30$ nm) and hydrocarbon rubber ($L_{\text{seg}} = 2.0$ nm). Computed curves for various filler volume fractions agree well with experimental data published by Boonstra (1979).

4. Discussion

As follows from the above investigation, the reinforcement phenomenon is manifested in two ways. In the first one it is observed as an unexpectedly high initial modulus, arising from matrix stiffening within closely spaced nano-sized particles. Under extension, the matrix layers between the particles start to lose initial stiffness, due to molecular slippage from the filler surface into the gaps between the particles. This process results in the fall of the modulus with the correspondent flattening tensile curve.

If the adhesive resistance is moderate (say, T is less than 2.0 as in Fig. 5), sliding spreads over the whole length of the substrates (Fig. 1), whereupon the proper highly non-linear resistance of the spring joins to the drag resistance already accumulated. This provokes a steep modulus upturn manifesting the reinforcement due to finite chain extensibility. This case accounts for the S-shaped form of many tensile curves.

When the adhesive strength is sufficiently high (say, T is more than 2.0 as in Fig. 5), the breaking effort comes about without bringing the whole spring into sliding. This case provides tensile curves with gradual ascent due to gradual build-up of dragged resistance. In this case, the high breaking effort stems from the finite chain extensibility as well.

So, the high breaking stresses should be referred to the capacity of the reinforced rubber to bring the macromolecules in the state close to their limiting extensibility.

A conversion of the usual bulk rubber properties into a new much more stiff mechanical state, caused by a nano-scale nature of rubber particulate composites, implies that widely used phenomenological relations, which put mechanical properties of composites in direct dependence on those of the bulk matrix phase, seem to be hardly justified from the physical point of view.

Verification of the predictive capacities of modeling has been carried out via comparison of theoretical calculations with well-known experimental relationships, demonstrated by Alter (1956), Payne and Whittaker (1972), Smith (1977) and Fedors (1979), and revealed good agreement.

The model under consideration allows estimating of the field of its application as regards the filler concentration and the size of particles. In the former case, it may be assumed that the continuous media mechanics approach becomes preferable, when the mean space between the filler particles is sufficiently large, for instance, it exceeds the size of a macromolecular tangle that can be taken equal to 50 nm (Leblanc, 1995). Then, for HAF carbon black ($\varphi_{\max} = 0.325$, $D_a = 50$ nm) and $h = 50$ nm, Eq. (6) gives φ close to 0.1. The upper limit of concentration is defined by the maximum packing capacity of the filler, i.e., by $\varphi_{\max}$, which for common carbon blacks ranges between 0.2 and 0.4.

In the latter case, the minimum size of filler particles is that which becomes too small for producing softening segmental sliding. Obviously, this size should be somewhat greater the segmental length (1.5-2.5 nm), i.e., about 5–10 nm. The upper limiting size can be found from Eq. (6) after substitution therein the critical input data ($h = 50$ nm, $\varphi_{\max} = 0.35$, $\varphi = 0.25$). The maximum D_a is found to be equal to 420 nm.

The experiments with reinforcing of carbon black filled *non-cross-linked* rubber, performed by Leblanc (1995), demonstrated the leading role of the carbon black-rubber complex originating within the compound during its preparation and showed that the modulus of this complex is at least three times higher than that of gum rubber. Hence, in analyzing the reinforcement problems, it would be more properly to assume that carbon black reinforces not the rubber *network* but strictly the rubber molecules without regard if they are cross-linked or not.

Microstructure investigations performed in the past few decades draw attention to the fact that the structure of carbon black-rubber blends on nano-level is far from theoretical random distribution. Pouchelon and Vondracek (1989); Reichert et al. (1993), Cai and Salovey (2001); Yatsuyanagi et al. (2001) paid attention to a strongly stressed inhomogeneity of filler distribution in the virgin carbon-black-filled samples. Their structure looks consisting of rather densely packed particles and areas completely free from them. This peculiarity is unlikely a shortcoming of the mixing process. The appearance of such integrated meso-structures, called supernetworks, is thought to be a spontaneous process.

Seemingly, the model examined in this paper can assist in the comprehension of the super-network formation. The accidental coalescence of two carbon black aggregates during the mixing process joins them by short polymer chains and transforms into a rather stiff object, which cannot be broken thereafter by weaker mixing stresses. Next aggregate can adhere to this pair in the same manner and so on. Mixing stresses cease the process of unbounded agglomeration bringing it to some equilibrium state.

The model considered is not adjusted to describe temporal phenomena, such as stress relaxation and creep. This drawback seems to be remediable under the assumption that the bond strength depends on the rate of the interface sliding. The search in this direction will be explored further.

5. Conclusions

A refined version of the triboelastic model developed earlier has been offered. It demonstrates the reinforcing and softening structural mechanisms governing the complicated mechanical behavior of particulate rubbery composites.

The reinforcement phenomenon, investigated in terms of the triboelastic approach, takes account of the finite extensibility of highly non-linear elastic rubber molecules, the degree of adhesive bonding between rubber and filler particles, the capacity of rubber molecules to overcome adhesion under stress and move along the rubber-filler interface.

The approach proposed enables one to follow the microscopic structural changes beginning with a virgin state of a system and ending in its failure.

It is shown that there are two different sources of reinforcement, one acting in the initial stage of model loading and the other-prior to failure. The initial high modulus of the composite arises due to the fact that the densely packed nano-particles are bridged by the short molecular chains that are much stiffer than the full-length molecular networks. The high non-linear resistance of the strongly stretched rubber molecules just before their breakdown causes the next reinforcement manifestation observed as an upturn on the stress-strain curves prior to sample failure.

Verification of the predictive capacities of modeling has been carried out via comparison of theoretical calculations with well-known experimental relationships and revealed a good agreement. The bounds of the triboelastic approach concerning both the size of filler particles and the filler volume concentration agree well with those observed experimentally.

Formation of filler-matrix supernetworks is regarded as a phenomenon of spontaneous agglomeration of nano-particles having higher stiffness.

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