Hyperelastic structural-mechanical model of filled rubber. Influence of filler dispersion and interfacial properties

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Abstract

The microstructure of filled rubber (heterogeneous filler network in rubber matrix) is modelled by a volume filled with thousands of rigid spherical inclusions. Inclusions could be grouped into secondary structures fractal clusters. Inclusions are connected by damageable links representing the mechanical behaviour of the elastomer in the gaps between filler particles. The formation of the interfacial polymer layer is taken into account. The volume is subjected to stepwise deformation. Hysteresis losses under cyclic loading conditions are modelled by way of breaking links. The influence of the microstructure (filler fraction, cluster/random filler distribution) and properties of interfacial layers, on the macroscopic characteristics of filled elastomers are discussed.

1 Introduction

Reinforcement of elastomers by active fillers, in particular carbon black (CB) improves the mechanical and strength characteristics of rubbers. Elastic properties inherent in unfilled vulcanizates remain unchanged. CB is represented by the primary indivisible aggregates of the order of 0.1...0.2 μm. However, the filler is added to the polymer in a pelletized form (grains of size 1 - 3 mm). During the process of mixing of composite ingredients these grains are somehow separated and distributed throughout the matrix. Depending on the mixing parameters and elastomer viscosity, part of the filler is left in the composite in the form of bulk inclusions micropellets. At the same time CB aggregates in the polymer matrix form secondary structures fractal clusters. At some volume fraction, the filler in the matrix forms a continuous network of clusters. Experimental studies have revealed that the surface of active filler in a rubber is surrounded by a reduced-mobility polymer layer [1]. The thickness of this layer is 2 nm, and it exhibits properties similar to the polymer in a glassy-like state. According to some hypotheses [2], the mobility of molecules increases gradually outward from the surface and at a distance of 10 nm passes into the matrix. One of the effective ways of explaining the mechanical properties of the composites is structural-mechanical modeling. The finite element method is used in the works [5, 6] to determine the macroscopic properties of filled rubber. On the basis of the periodicity cell, the authors examine the stress-strain state, depending on the location [5, 6] and shape [6] of inclusions. Both works describe the effect of stress softening. In the first case [5] stress softening effect is modeled by reducing (result of local ruptures) the number of elastic macromolecular segments in the second [6] - due to the viscoelastic properties of the binder. FEM models are limited by large computational costs and the complexity of calculations arising from the large deformations and on the borders of the hard and soft phases. In the work of Xi and Hentschke [7] filled elastomer is presented by the volume of elements, each of which is either part of the filler or fragment of matrix. The force interactions between the elements exist. Introducing the force response under low shear stress, the authors simulate the Payne effect. We should also mention the work of Garishin and Moshev [8], which is describe the discrete model of behavior of random filler structure in an elastomer matrix under uniaxial loading. In the present work, a structural-mechanical model for filled elastomers is proposed which takes into account the peculiar microstructural features of the material. Inclusions are connected by hyperelastic links. The mechanical properties of these links are dependent on the size of the gap between inclusions and the characteristics of hypothetical interfacial layers.

2 Concept of the model

The structure of the composite is represented as a system of rigid spherical inclusions. For modelling of interfacial interactions the links are used (Fig.1), which are, in fact, the rods pivotally connected to the centres of inclusions and working in tension and compression only. Two types of links are considered: 1. Links between inclusions

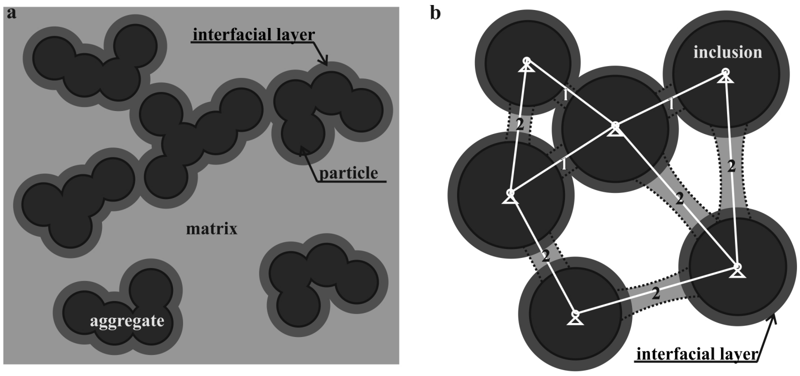

Figure 1: Continuum structure (a) and discrete model (b) of the filled elastomer. Different types of links are indicated by the numerals (description is given in the text).

with the initial gap δ_0 <20 nm, which has a common special layer with a thickness 10 nm. 2. Links between inclusions that do not have common intersecting layers ($\delta_0 \geq$ 20 nm) and interact in the material via the elastomer matrix. The external load changes the location of inclusions and the configuration of links. Shortly speaking, the links are irreversibly broken under a particular load. In addition, the case where the special layers are absent, i.e. the properties of links coincide with the properties of the matrix, is analyzed.

3 Mechanical interaction of the pair of inclusions in the elastomer

The force due to the stretching or compression of the link between two inclusions was determined by the finite element method by analyzing the stress-strain state in the gap between two rigid inclusions embedded in a hyperelastic low compressible polymer (Poisson ratio – 0.495). In the calculation, an elastomeric matrix was assigned the properties of unfilled styrene butadiene vulcanizate, and the corresponding experimental uniaxial tension curve was approximated by the third-order Ogden potential.

For simplicity, we suggest that the forces occur in the gaps between the nearest carbon black particles of the neighboring aggregates (Fig.2a). The particle radius is assumed to be equal to 15 nm. The special layer is divided into 5 equal parts with the corresponding elastic modulus: E_i = 60, 30, 7, 5, 3 MPa (Fig. 2b). The modulus of the matrix is 1 MPa. In the case of inclusion interaction in the absence of a special layer, $E_i = 1$ MPa. It is assumed that the inclusion is an absolutely rigid one, and the interface between the inclusion and the matrix is in perfect adhesion. As a cohesive failure criterion for the structural element, we have taken the Gent

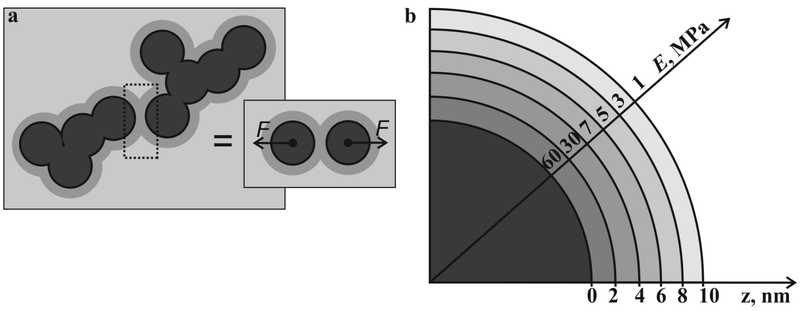

Figure 2: Carbon black aggregates in the matrix surrounded by a special layer and the structural element for calculating force interactions (a); elastic modulus of the layer versus the distance from the surface (b).

approach [3]: $< \sigma > = 5/6E$, where $< \sigma >$ is the hydrostatic stress in the center of the gap between inclusions; E is the elastic modulus in the center of the gap. The plots of force F versus elongation in the gap λ_g up to the point at which the fracture begins are presented in Fig.3. The results indicate that the structural elements with specific layers begin to fracture at lower deformation, and the resulting force is twice as much as the force for elements without specific layers.

4 Structural – mechanical modelling

The microstructure is modelled as a cube non-uniformly filled with spheres of equal size. The minimum acceptable space between the spheres is 2 nm. The spheres are assembled into fractal clusters. Comprehensive analysis of fractal structure and the synthesis algorithms are given in work [4]. Apart from the clustered structure, the

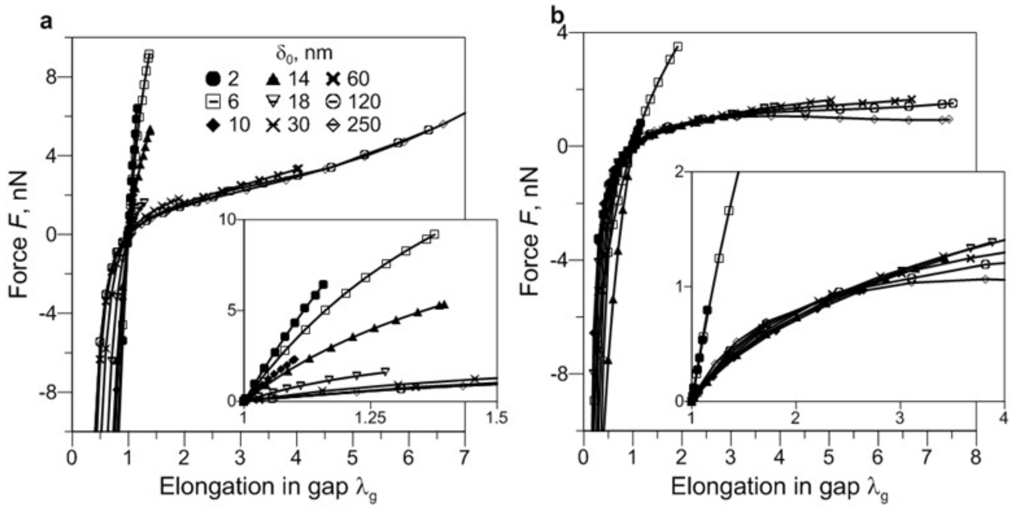

Figure 3: Plots of force F versus elongation in the gap for different initial gaps δ_0: (a) inclusions are surrounded by a specific layer; (b) characteristics of the layer coincide with the matrix.

case of random filler distribution is also considered. The filler volume fraction in the investigated structures is 0.13 (30 weight parts of filler).

By virtue of the constancy of the volume, the structure is deformed by the step-wise displacement of inclusions. After each deformation step, the coordinates of inclusions are refined in the context of forces that occur in links. This is done by minimizing the local elastic energy of links. The minimization is performed by the Nelder - Mead method. On achieving the optimal state of all the inclusions, the configuration of links is specified: at maximum elongation, the link is broken. The part of the material in the gap with the broken link begins to respond to compressive forces only and makes no resistance in other cases. If the breakage of links takes place, then the equilibrium seeking for the system is repeated. When a new optimal state of the structure is found, the structural-mechanical characteristics of the system are determined, and the next step of loading is performed.

5 Results and discussion

Two uniaxial stretching compression cycles with an increasing amplitude (elongation ratio λ was equal to 2 and 4) were applied to each structure. Example of the initial and stretched 4-times structure is shown in Fig. 4. At a certain local elongation of the gap between inclusions the corresponding link was broken. The typical behaviour of the rupture of the links is shown in Fig. 5a. At λ less than the maximum value (unloading or repeating loading), the number of broken links remains unchanged. Thus, the rupture of links leads to the hysteresis of the stress-strain curve (Fig. 5b), which is typical of filled rubbers. The stress of links of the clustered model without layers, starting at $\lambda = 2.5$ in Fig. 6a, reaches its maximum and then begins to diminish; no material reinforcement takes place. The reason is that the forces caused by the deformation of the material in the gap between two

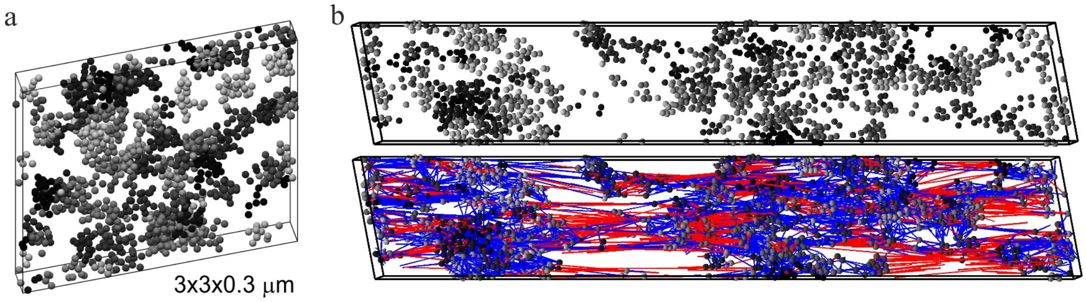

Figure 4: Fragment of the model clustered structure before loading (a), after stretching 4 times (b). Unbroken links are shown in green and blue, and broken links in red. Clusters are shown in different shades of gray.

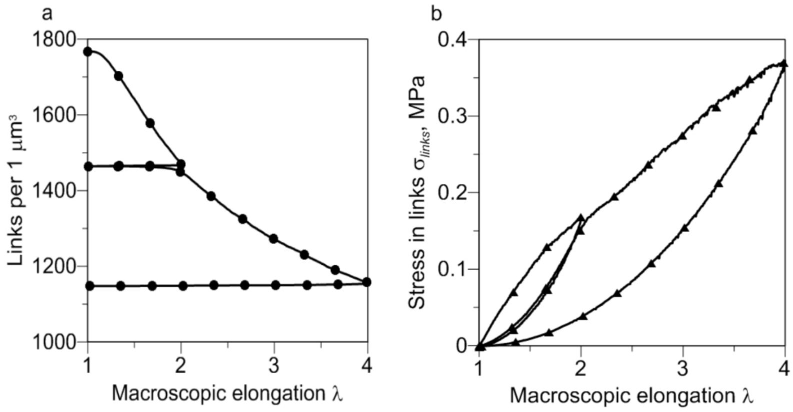

Figure 5: Typical response of the structure to elongation number of links (a) and their stress (b).

inclusions without layers (Fig.3b) do not increase for $\delta_0 > 20$ nm. At the same time, despite the fact that the links in the material with layers are broken at lower elongation, their elastic properties of layers have the reinforcement effect on the composite. Based on the obtained results, it can be concluded that the model with the layers with variable stiffness is more appropriate to describe the mechanical behavior of filled elastomers than others. The stresses in randomly filled structure are higher than in the clustered (Fig. 6b). This is due to the fact that the random distribution of inclusions is more homogeneous compared to that of clusters. Hence, in the structural-mechanical model of random structure many through-matrix links occur, that is, the matrix fraction working under deformation increases. So, this is accompanied by an increase in stresses.

6 Conclusions

A structural-mechanical model for describing the eleastic behavior of filled elastomers has been proposed. The model explicitly takes into account the peculiar properties of the microstructure of the material and interphase interactions in it. The behavior of part of the polymer placed in the gaps between inclusions has

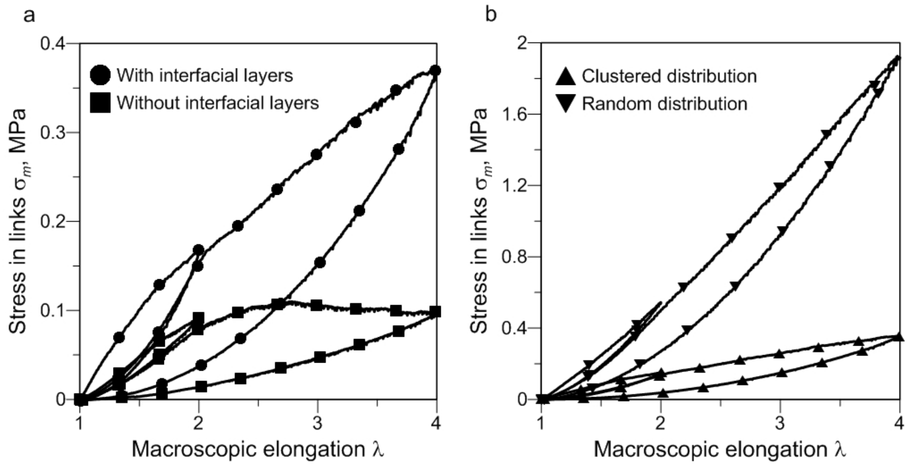

Figure 6: Stress in links vs. elongation of the structure: (a) comparison of the structures with and without layers; (b) comparison of clustered and random distribution.

been modeled by links with nonlinear elastic force response. At some stretch factor the elastomeric link is broken, which allows us to model the Mullins effect at the macrosopic level.

The results of simulation of cyclic stretching-compression of materials with clustered and random distribution of inclusions are presented. The cases where polymer layers with variable stiffness are present or absent around inclusions (the layer of macromolecules adsorbed on the active surface of inclusions) have been examined. Based on the structural-mechanical model, it can be concluded that the absence of interfacial layers of variable stiffness does not lead to the reinforcement effect characteristic of filled vulcanizates.

Acknowledgements

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