The model of elastomeric composite based on the filler cluster network and special interfacial polymer layers

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Abstract

Rubber reinforcement by filler is due to the continuous filler network and strong interfacial interactions. It is assumed that the polymer, at a distance of 2 nm from the surface of inclusions, is in a glassy state, then its elastic modulus decreases, and at a distance of 10 nm it converts into a matrix. The model is represented by a volume filled with fractal clusters. These clusters of spheres-inclusions are connected by elastic bonds, whose properties are dependent on the gap between inclusions. Structural parameters are obtained from the analysis of micro-images of filled rubbers. The force response of bonds to loading is determined by solving the pair interaction problems by the finite element method. The behavior of the model "samples" under uniaxial loading conditions is studied taking into consideration bond failure criteria.

1 Introduction

Filler reinforcement of rubber is caused by the formation of a continuous filler network and strong interfacial interactions. Investigations indicate that at a distance of 2 nm from the surface of inclusions a polymer is in a glassy-like state, then its stiffness decreases in a non-linear fashion, and at a distance of 10 nm a polymer converts into a binder state. In paper [1], the authors suggested that this behavior could be used to change the glass transition temperature of a polymer near the proximity of particle surface. The present paper describes the results of numerical simulation of the behavior of filler network at the structural level using finite element techniques. Based on these results, a model is developed for evaluating the degree of reinforcement of a composite. The model is a volume filled by fractal clusters. Structural parameters (particle sizes, cluster fractal parameters) are obtained from the analysis of the AFM images of materials [2]. Spherical inclusions occurring in clusters are stuck together with elastic bonds, and their properties are dependent on the space between inclusions.

2 The model

A filler network is a branched combination of structural elements. By a "structural element", we mean two closely located inclusions surrounded by a special layer and placed in an infinite elastomeric matrix. Application of the finite-element method to the description of the behavior of the loaded structural element indicates that part of an elastomeric material in the space between inclusions experiences basic load. This fact allows us to use the structural element filler network instead of a composite medium during the development of the model.

The structure of the material is represented as a volume filled with fractal clusters consisting of spherical inclusions. The fractal parameters of clusters and their number per volume unit can be determined from the analysis of AFM micro-images of rubber surfaces [2]. Figure 1 presents a fragment of the simulated structure of rubber (the content of carbon black - 30 phr). Filler aggregates are spheres. The minimum acceptable distance between the surfaces is 3 nm. Deformation (stretching/compression) is applied along the

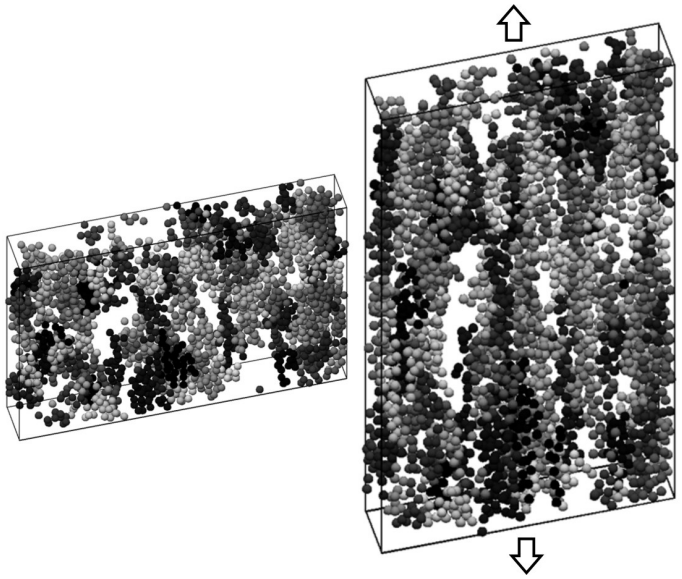

Figure 1: Fragment of the simulated filler network in the elastomeric matrix before and after double stretching. Different clusters are indicated in shades of grey.

vertical axis in a stepwise manner as follows. The upper boundary of the fragment is shifted, and the spheres are displaced proportionally to their place in the material subject to the constancy of volume. After that, the coordinates of inclusions are defined more exactly with account for interactions.

Initially, the material is in an equilibrium state. Under loading, the inclusions held together by bonds sustain forces responsible for changes in the structural mechanical configuration of the system. The forces will be discussed in detail later.

To find the equilibrium position of inclusions, after each loading step, we search for a minimum of local potential energy of the k-th inclusion provided that other inclusions having common bonds with the k-th are fixed. Minimization is done using the Nelder-Mead method. This allows us to consider all inclusions and to choose new coordinates corresponding to the expected equilibrium of the structure. And again, the coordinates of inclusions are adjusted until a condition for a discrepancy in the elastic energy of the entire system is fulfilled.

We assign the properties of pure styrene-butadiene rubber (SBR) to the elastomeric matrix of the structural element. The curve illustrating the uniaxial loading of the unfilled SBR is approximated by the 3rd order Ogden elastic potential with 6 material constants. To realize the properties of interphase, we separated the 10 nm thick region into 5 layers with a thickness of 2 nm. Changes in the rigidity of interfaces away from the surface of filler particle are set by the power law dependence:

$$E_j = E_m(79.02z^{-1.59+1}), j = 1...5$$

where E_m is the elastic modulus of the matrix (1 MPa), E_j is the elastic modulus of the j-th layer (the layer is enumerated from the surface of the inclusion), z - is the distance

to the surface of inclusion along the radial line. Proposed relation yields the following stiffness relationships: the strength of the 1^{st},...,5^{th} layers is, respectively, 80, 15, 7, 3 times stronger than matrix. Inclusions are assumed to be perfectly rigid spheres. The radius of inclusions in all structural elements is equal to 40 nm (the average size of N220 carbon black aggregates in the examined SBR/30).

The macroscopic model of a composite involves three types of structural elements (Fig. 2a). The first type consists of structural elements with a common glassy layer. These are structural elements formed by the inclusions located at a distance of $\delta_0 < 4$ nm, where δ_0 is the thickness of the gap between inclusions. The second type includes structural elements having common, less rigid, interfacial layers when $4 < \delta_0 < 20$ nm. The third type consists of structural elements with interfacial layers that do not intersect when $\delta_0 > 20$ nm. In this case, the pair interaction of inclusions is performed by means of the matrix layer.

The first and second types of elements are formed before loading the model, and their number does not increase during deformation. The third type of elements can be formed between a pair of inclusions during deformation if the distance between the surfaces of these inclusions $< 3R$ (the estimate was obtained from the solution of the corresponding finite element problem). More details about a failure criterion for all types of elements are given below.

The degree of particle interaction was evaluated by comparing the stress-strain state of the loaded structural element obtained for different values of the initial size of the gap δ_0 (Fig. 2b). Loading was realized by applying a force to the centers of inclusions and directed along the line that connects these centers.

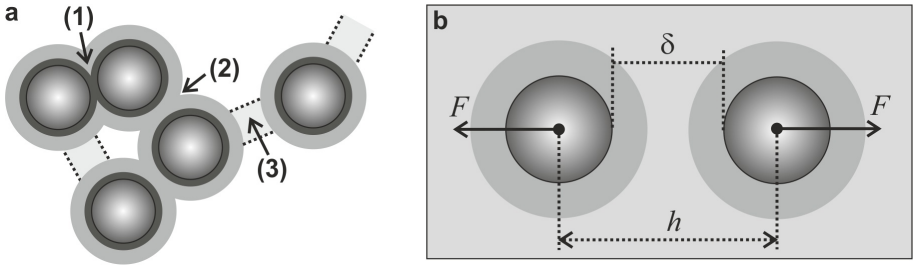

Figure 2: Types of structural elements (a). The loading pattern is plotted for the third type of structural element (b).

The problem of determining the stress-strain state of a structural element is solved by the finite element method in the axisymmetric formulation. Calculations are carried out for δ_0 equal to 2; 3; 3.5; 5; 7; 9; 11; 13; 15; 17; 19; 30; 40; 80; 200 nm.

The analysis of maximum principal stresses in the cross section of the gap gives the time instant at which one can observe the onset of rupture in the middle of the gap of the structural element. In this case, use is made of the Gent criterium [3] predicting cohesive failure of an elastomer in the gap between inclusions at a time when the maximum principal stresses exceed the value of the elastic modulus of the material at each point of the cross section of the loaded bond. This moment defines the final state of the bond, after which the relationship loses its primary strength, acquiring the properties inherent in the matrix.

Figure 3 shows the initial (a) and final (b) states of the second type of structural element with the initial size of the gap - 13 nm. In the gap between inclusions, one can see the area of maximum principal stresses corresponding to the final state of the structural element. A darker shade of gray shows the region with the highest values of maximum principal stresses. Maximum possible elongation of the gap λ_δ^{max} equal to 1.15.

Figure 4 shows the plot of the λ_δ^{max} as a function of δ_0 (Fig. 4a) and force F (Fig.4b)

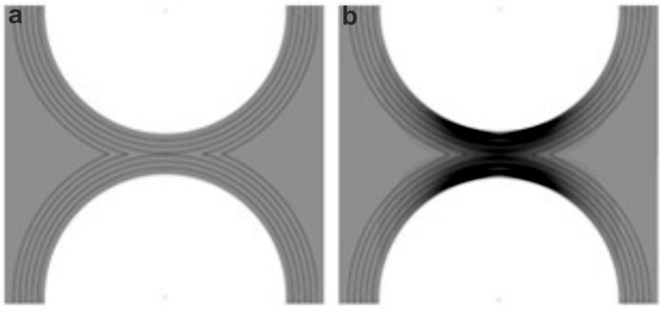

Figure 3: Primary (a) and stress-strain (b) state of 2nd type of structural element with the initial of the gap δ_0=13 nm.

which occurred in the structural elements. Calculations of λ_δ^{max} (Fig.4a) make it possible to conclude that the material fails in the gaps at relatively low elongation.

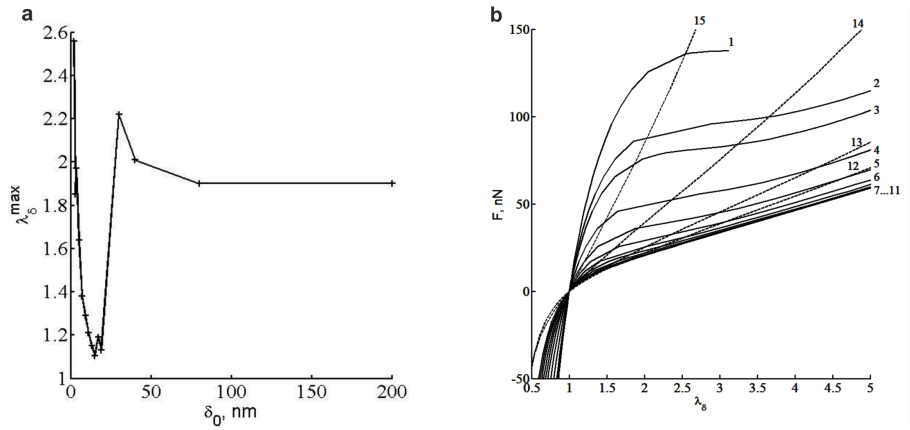

Figure 4: Local rupture elongations (a) and forces (b) for different initial gaps.

It should be noted that, in the region with intersecting layers $\delta_0 < 20$ nm, this elongation decreases with increasing gap. In practice, however, filled rubber compounds fail at much higher values of elongation, which holds valid for SBR/30 demonstrating an elongation of 450%. This is possibly due to the fact that the stretching of polymer chains begins on the surface of inclusions. Moreover, under the action of bonding forces filler network inclusions (Fig. 4b) form ensembles and then move in clusters under loading. Therefore, a condition for a local break of the material in the gap may appear in the case of strong macro stretching of the sample.

3 Results and discussion

The efficiency of the model was verified on the material SBR filled with 30 phr of carbon black. The average particles size is 40 nm, the fractal dimension of clusters is 1.73, the scaling factor is 0.17, and the number of clusters is 9 per one μm^3 [2]. Based on these parameters, the filler network was synthesized in the volume of 3x3x2 μm. The fragment of this network is shown in Fig. 1. The total number of inclusions was 8900. Inclusions formed 560 clusters overlapping in space. The strain step was 0.5 nm. The model "sample" was subjected to a stretching - compression with an increasing amplitude. Macroscopic stresses in the cross-section of the "sample" under uniaxial loading conditions is calculated

as

$$\sigma_z = \sum F_z/L^2 + \sigma_m(1 - \phi_L - \phi),$$

where F_z is the projection of force in the bond (observed in the cross-section) onto the deformation axis; L is the current cross-sectional area; σ_m is the stress of the unfilled matrix calculated using the Ogden potential; ϕ_L is the portion of the material with bonds in this cross-section; ϕ is the filler content. A criterion for the macroscopic sample failure is the lack of all cross-sectional bonds (in this work, it is not achieved). Figure 5 presents the total macroscopic stress (a) and local elongations in the gaps with a common glassy layer (b). A slight deviation of stress from zero at λ=1 can be attributed to errors of

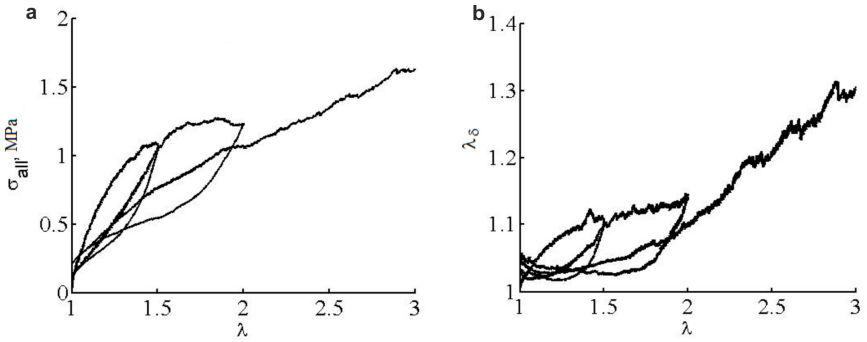

Figure 5: Total macroscopic stress (a) and local elongations in the gaps with a common glassy layer (b).

numerical solutions. As one can see, the use of broken bonds permitted the description of the material softening effect already at the stage of elastic behaviour. A significant contribution to stresses was made by the material in the gaps between the inclusions with the primary common glassy layer. Interestingly, the local elongations in these gaps turned out to be 2...2.5 times less than the macroscopic elongation of the "sample" (Fig. 5b). This can be explained by the fact that strong forces prevent the separation of inclusions until the local rupture elongation occurs.

In the case of cross-linking of the non-glassy material in the gaps, a contribution of bonds of type 2 was lower by an order of magnitude (0.04 MPa at λ=3). For comparable local elongations, the forces were much smaller.

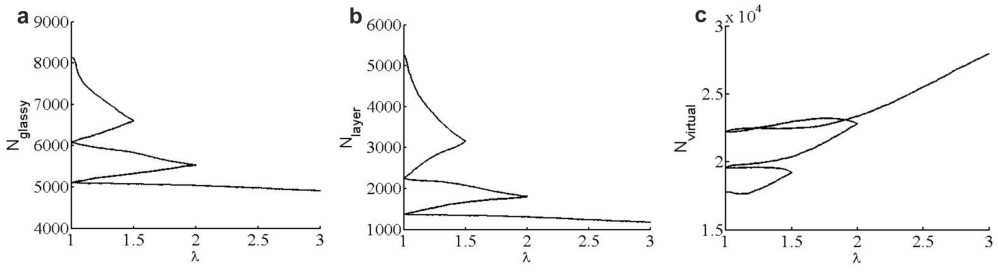

Figure 6: Changes in the number of links of 1st (a), 2nd (b) and 3rd (c) types.

It is seen that the rate of changes in bonds of 1st and 2nd types is high enough at the initial stage of loading up to λ=1.5. The reason is that the continuous filler network is broken into separate areas, where inclusions combined in ensembles move. Within these ensembles, inclusions interact via the material with varied properties. Between these ensembles, inclusions interact via the matrix (links of third type).

4 Conclusion

We have developed a model for describing the elastic mechanical behavior of the filled elastomer. The model takes into account the cluster structure of a filler network and the behavior of interfacial layers, which show the same force response to deformation as nonlinear elastic rods. Application of failure criteria for composite materials in gaps (failure of glassy and less rigid interfacial layers) allowed us to describe the Mullins effect. However, it should be noted that the use of pure elastic properties of the material in gaps cannot provide an adequate description; some bonds connecting inclusions reach their critical state too early. This is supported by the fact that at a 3-fold elongation the real filled SBR/30 gives stress of 4 MPa, which is 2.5 times higher than the value obtained for the model developed here (Fig. 5a). Hence, the necessity for the transition to the elastic-plastic properties of the material in the gaps between inclusions arises. Our current investigations focus on testing the proposed model for different filler networks and on developing a model with more complex properties in gaps.

Acknowledgements

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References

[1] Long, D. Lequeux, F. 2001. Heterogeneous dynamics at the glass transition in van der Waals liquids, in the bulk and in thin films. European Physical Journal E: Soft Matter 4(3): 371-387.

[2] Morozov, I.A. 2013. Identification of primary and secondary filler structures in a polymer matrix by atomic force microscopy images analysis methods. Polymer composites: In Print.

[3] Gent, A.N. 1984. Failure process in elastomer at or near a rigid spherical inclusion. J. Material Sci. 19: 1947-1956.

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