Structural modeling of nanostrands formation in dispersedly filled elastomers

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Abstract

It is well known that filling carbon black to rubbers significantly improves their strength and deformation properties. One possible explanation for this phenomenon is that the nanofiller creates a huge amount of uniformly distributed micro-breaks to facilitate transfer of the rubber matrix from complex stress state into the system of many uniaxially loaded fibers (strands). Therefore, rupture efforts for them to be much higher than the corresponding values for the same elastomer in an undirected condition.

Appropriate structural model of an elastomeric composite was developed to verify this hypothesis. It is based on a new criterion of deformation strength, taking into account the possibility of an anisotropic hardening of the elastomer under the stretching.

The results of computer simulation showed that in case of a new strength criterion using matrix breaks occurred not in the gap between the inclusions, but on some removal from it. Thus, the formation of a weakened zone in the form of a "hollow ring" occurred around the gap between the particles, that is quite be interpreted as a possible appearance of the elastic strand between the particles.

1 The object of study

Rubbers are one of the most important and common industrial polymers. These materials belong to the class of dispersed-filled elastomeric composites, the specific feature of which lies in the fact that their basis is a continuous low-modulus, highly elastic rubber phase (matrix) with solid granular filler particles (dispersed phase) embedded.

A lot of practical experience has been accumulated in the creation of rubbers for various purposes by now. However, the progress in this area of material science is still hampered by insufficient knowledge of structural mechanisms for formation of mechanical behavior of filled elastomers. Some mechanical properties of rubbers still remain the subject of discussions among materials scientists.

One such issue is the effect of rubber hardening when carbon black dispersed particles are embedded into it [1, 2, 3, 4]. It is known since the beginning of the XX

century, that filling rubber by carbon black (20-30 % by volume) greatly improves its operational properties: enhances the stiffness, rupture force increases 5–15 times, the limiting deformation in 2–4 times, and the smaller size of the filler particles, the stronger is reinforced material [5].

To explain these changes in terms of classical mechanics to date have not succeeded. This problem is one of the most important in modern mechanics of elastomers, because true understanding of hardening mechanisms will reduce the time and costs for experimental development of composite materials with predetermined properties and move to the calculation methods of design[6].

Most researchers agree that when the filled elastomer is deformed, structural changes occur in it, for the description of which additional hypotheses and assumptions are required. This work is devoted to the verification of one of these hypotheses. Its essence lies in the fact that nanoparticles have a huge surface of interphase contacts, which turns a significant portion of matrix into a bounded, that is, more durable state. At the same time the granular nanofiller composite creates a huge amount of uniformly distributed micro-breaks to facilitate transfer of the rubber matrix from complex stress state into the system of many uniaxially loaded fibers —nanostrands. Therefore, rupture efforts for them to be much higher than the corresponding values for the same elastomer in an undirected condition.

The presence of such formations is confirmed experimentally [7]. Studies of the nano-structure of the filled natural rubbers in the extended (up to the prebreaking) state using atomic-force microscopy methods, which were being carried out in ICMM UB RAS [8, 9], experimentally also confirmed this fact. Fig. 1 shows nanoscans of pre-stretched rubber containing carbon black particles. It is easy to see both the strands and the aggregates of soot particles they connect.

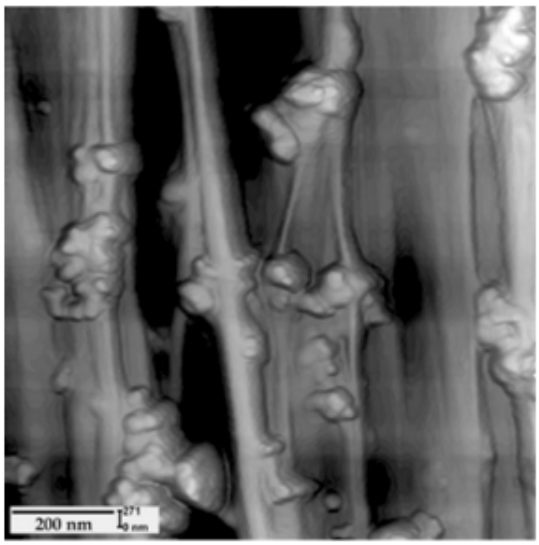


Figure 1: Stretched high-strength bonds between aggregates of carbon black particles obtained by atomic force microscopy

2 Methods

The structural model of the dispersed filled elastomeric composite was developed for description and analysis of the effect of nanostrands appearance under deformation. It is based on new deformation criterion of strength (1), considering the possibility of anisotropic strengthening of elastomer (due to the reorientation of the molecular chains in the direction of the load application).

$$f(\lambda_1, \lambda_2, \lambda_3) = \frac{\lambda_e}{\beta \sum_{i=1}^{3} \exp(-\alpha \lambda_i^2) - 1} < A, \tag{1}$$

$$\lambda_e = \sqrt{(\lambda_1 - \lambda_2)^2 + (\lambda_2 - \lambda_3)^2 + (\lambda_1 - \lambda_3)^2},$$

$$\boldsymbol{V} = \sum_{i=1}^{3} \lambda_i \boldsymbol{n_i} \otimes \boldsymbol{n_i},$$

where λ_e the invariant of left tensor of tension $\boldsymbol{V}$ (analog of the intensity of deformations), $\boldsymbol{n_i}$ - the orthonormalized three of its eigenvectors (in the current configuration),λ_i corresponding main extension ratios, α and β are constants chosen from experiments (biaxial loading of the elastomer);A - tensile strength of the destruction. The main feature of the criterion that a tensile or compression biaxial its value will be higher than when a uniaxial deformation (this is at the same strain intensity). That is, when the uniaxial loading material collapses later than in the case of two or triaxial deformation.$\lambda_1 = \lambda, \lambda_2 = 1/\lambda^x, \lambda_3 = 1/\lambda_1\lambda_2$
Fig. 2 represents the dependences of deformation criterion f for various for various relations between $\lambda_1, \lambda_2, \lambda_3$, illustrating this property (assuming that the medium is incompressible). It was accepted that x is varied from -1 to $1/2$. Constants α, β are taken by the equal 0.5. It is evident on the graph that the curve l ($x = 0.5$), corresponding to uniaxial stretching, lies below all.

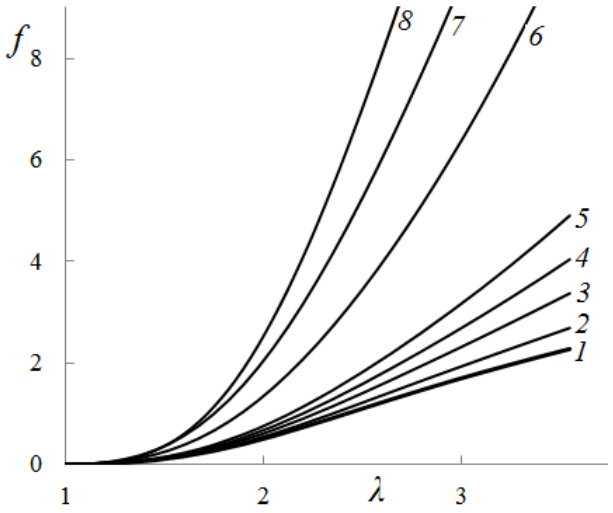


Figure 2: Dependence of the strength criterion f on the main extension ratios on different axes: (1) x= 0.5; (2) 0.25; (3) 0.1; (4) 0; (5) -0.1; (6) -0.5; (7) -0.75; (8) -1.

3 Results discussion

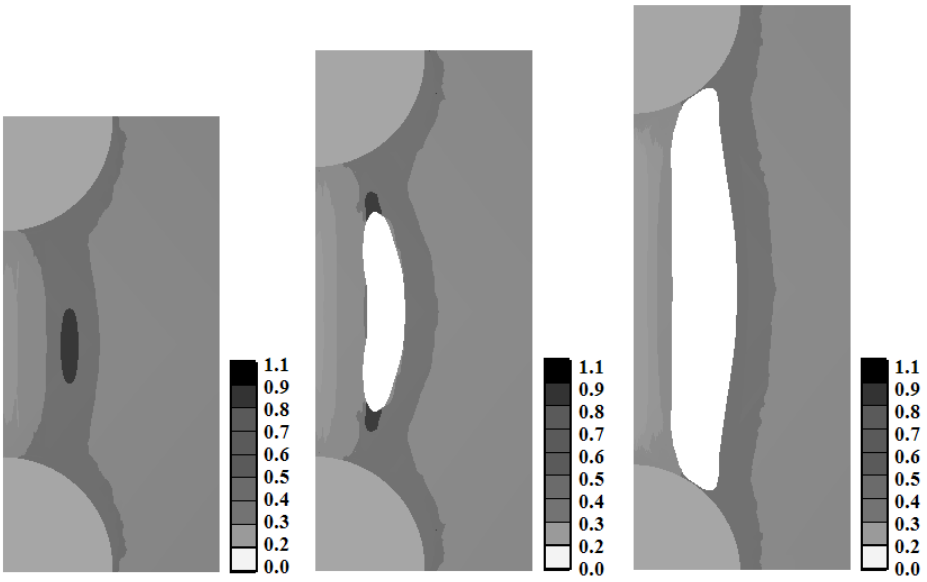
The main load during the deformation of elastomeric composites with a rigid granular filler occurs in the matrix interlayers between the inclusions (gaps). The rest of the elastomer is loaded much weaker. Accordingly, structural damage occurs, as a rule, near the gaps between the particles [10] these are the most dangerous zones. The appearance of strands in the composite structure occurs precisely there. Therefore, in modeling the development of internal damage in a composite, its structure was represented as a cell of incompressible nonlinear elastic matrix and two rigid spherical inclusions of radius R located at a distance δ from each other along the vertical. The mechanical properties of the matrix were described by neo-Hookean potential (2)

$$w = C(tr\boldsymbol{V}^2 - 3), \tag{2}$$

where C is the elastic constant, which according to its physical sense is equal 1/6 from initial Young's modulus E (for the incompressible medium). E was taken equal to 10 MPa in the calculations. The values of model constants were taken as follows: α=0.5; β=0.5; A=1. The choice was made for reasons of clarity of demonstration of process of the strand formation.

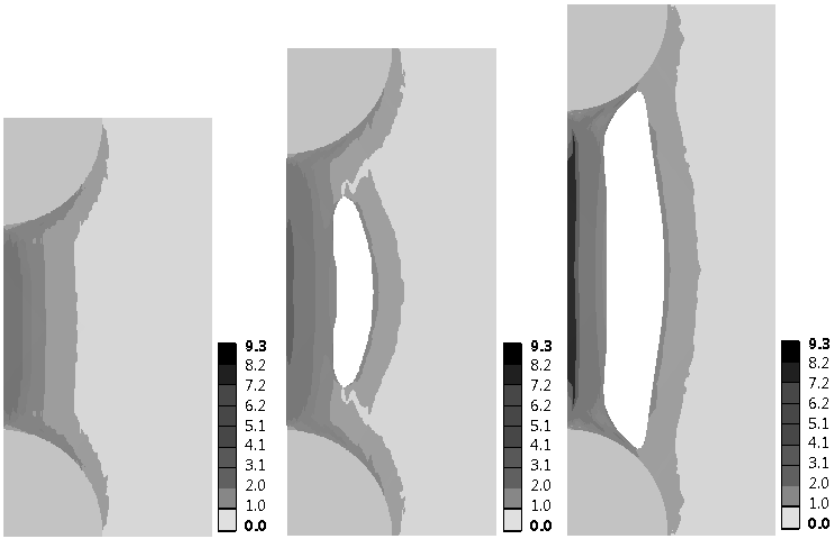
The initial gap between the inclusions was 40% of their radius. Inclusions were moving apart step-by-step apart vertically. The problem was solved by the finite element method. At each step, the stress-strain state in the cell was calculated and the fracture zones of the material were determined using deformation strength criterion. At the following loading steps, these areas were replaced by pores (i.e., the corresponding elements were excluded from the finite element mesh).

In Fig. 3 shows distribution maps of deformation strength parameter f at cell elongation (ratio of current and initial distances between centers of spheres) 160%, 200% and 250%. Fig. 4 depicts maps of deformation intensity λ_e at the same elongations.



a *b* *c*

Figure 3: Distribution maps f, elongation: *a* - 160%; *b* - 200%; *c* - 250%



a *b* *c*

Figure 4: Distribution maps λ_e, elongation: *a* - 160%; *b* - 200%; *c* - 250%

The pores in the matrix began to appear at the elongation of 160%; at 250% of the the nanostrand was fully formed; complete destruction of the cell (strand breakage) occurred at approximately 500%.
The results of computer simulation showed that in case of a new strength criterion using matrix breaks occurred not in the gap between the inclusions, but on some removal from it. Thus, the formation of a weakened zone in the form of a "hollow ring" occurred around the gap between the particles, that is quite be interpreted as a possible appearance of the elastic strand between the particles.
As a result, we can say that the formation of strands in an elastomeric composite is possible in the event that an anisotropic change of matrix strength properties will occur during deformation. And this is quite possible due to the reorientation of polymer molecular chains.

Acknowledgements

This work is executed at a financial support of RFBR Grants: 16-08-00756 and 16-08-00914.

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