Sokolov *et al. Mechanics of Advanced Materials and Modern Processes* (2018) 4:7
https://doi.org/10.1186/s40759-018-0040-x

Mechanics of Advanced Materials and Modern Processes

RESEARCH Open Access

A new hypothesis on the mechanism of nano-filled elastomers reinforcement

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Abstract

Incorporation of active fillers to rubber markedly improves the strength properties and deformation characteristics of such materials. One possible explanation of this phenomenon is suggested in this work. It is based on the fact that for large deformations the binder (high-elastic, cross-linked elastomer) in the gaps between the filler particles (carbon black) is in a state close to the uniaxial extension. The greater part of polymer molecular chains are oriented along the loading axis in this situation. Therefore it can be assumed that the material in this state has a higher strength compared to other ones at the same intensity of deformation. In this paper, a new strength criterion is proposed, and a few examples are given to illustrate its possible use. It is shown that microscopic ruptures that occur during materials deformation happen not in the space between filler particles but at some distance around from it without breaking particle "interactions" through these gaps. The verification of this approach in modeling the stretching of a sample from an unfilled elastomer showed that in this case it works in full accordance with the classical strength criteria, where the presence in the material of a small defect (microscopic incision) leads to the appearance and catastrophic growth of the macrocrack.

Keywords: Damage generation, Nanocomposite, Finite deformations, Computational modeling, Fracture criterion, Elastomer, Filler, Nanoparticles

Introduction

Elastomeric nanocomposites contains a highly elastic rubber matrix, where rigid grain nanoparticles or aggregates of nanoparticles are dispersed. Over the past years, a lot of practical experience has been gained in creating such materials for a variety of applications. Elastomers in which nanoparticles are used as filler are characterized by increased strength and ultimate deformation (strain at break). However, the reasons for such improvement of their mechanical characteristics are still the subject of discussions among materials experts. Since the beginning of the 20-th century, it has been well established that the reinforcement of rubbers with carbon black (20–30% by volume) significantly improves their operational characteristics. In particular, such materials possess enhanced rigidity; their tensile strength and ultimate strains increase by 5–15 times and 2–4 times, respectively. Intensive study of the mechanical properties of elastomeric nanocomposites in relation to the type of filler and its concentration and manufacturing technology is still in progress. An example are the works related to the study of the elastomers properties filled with carbon black, carbon nanotubes, nanodiamonds, various mineral particles (montmorillonite, palygorskite, schungite etc.) (Rodgers & Waddel, 2013; Jovanovic et al., 2013; Le et al., 2015; Lvov et al., 2016; Mokhireva et al., 2017; He et al., 2015; Huili et al., 2017; Stöckelhuber et al., 2011; Garishin et al., 2017). A part from numerous experimental investigations, there are many theoretical works devoted to structural modeling of the physical-mechanical properties of materials, which takes into account the characteristic features of the internal structure and processes at micro- and nanolevels (Garishin & Moshev, 2005; Reese, 2003; Österlöf et al., 2015; Ivaneiko et al., 2016; Raghunath et al., 2016; Plagge & Klüppel, 2017; Svistkov et al., 2016; Svistkov, 2010).

An important feature of elastomeric composites is the ability to change their mechanical properties (softening) as a result of preliminary deformation (the Mullins-Patrikeev effect) (Svistkov, 2010; Patrikeev, 1946; Mullins, 1947; Mullins & Tobin, 1965; Mullins, 1986; Diani et al., 2009). This

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feature can significantly influence the mechanical behavior of the products made of filled elastomer (Sokolov et al., 2016; Sokolov et al., 2018). To date, the Mullins effect is an object of intensive theoretical and experimental study. In the literature there is still no single settled opinion about its nature.

It has been found that, the anisotropic properties can also be formed in filled elastomers under softening (Govindjee & Simo, 1991; Machado et al., 2012). The anisotropy features are clearly seen in the samples the second loading of which is executed at some angle to the direction of the force applied during the first loading (Machado et al., 2014). Some authors try to describe these effects using purely phenomenological models (without specifying the physical meaning of the internal variables used) (Ragni et al., 2018; Itskov et al., 2010). A model based on the features of the interaction of polymer chains with filler particles is proposed in (Dorfmann & Pancheri, 2012). In particular, it is assumed that the anisotropic softening of the material during its cyclic loading is due to the peculiarities of interaction of polymer network with filler particles, including breaking and mutual slipping of macromolecules segments.

However, despite the undoubted progress in the analysis of possible mechanisms responsible for the formation of properties of nanofilled elastomers, there are still ambiguities to be clarified. An increase in strength and the appearance of anisotropic properties after the first deformation can be attributed to the existence of micro and nanostrands in its structure. Their existence is confirmed by experimental studies (Marckmann et al., 2016; Reichert et al., 1993; Le Cam et al., 2004; Watabe et al., 2005; Beurrot et al., 2010; Marco et al., 2010). In (Matos et al., 2012), based on the results of experimental studies of the carbon-filled rubber structure (using electron microtomography) and computer simulation, it was shown that the macrodeformation of about 15% can cause significant microdeformation of the matrix of 100 and more percent in the zones between the agglomerates of carbon black particles. Investigations of the nanostructure of filled rubbers in a stretched (up to pre-rupture) state by the atomic force microscopy methods (AFM) demonstrate the formation of a fibrous texture between filler particles (Morozov et al., 2012). Tomograms of the microstructure of rubber (electron microscopy), obtained in (Akutagava et al., 2008) also show strands and strand-linked aggregates of carbon black particles.

The results of experimental studies indicate that the fraction of polymer is not extractable from uncured filled rubber compounds by a good solvent of the gum elastomer. A polymer layer remains on the surface of the filler particles remains, called “bound rubber”. The simplest and most obvious explanation for this fact is the phenomenon of adsorption of polymer chains on the surface of particles and the occurrence of a strong bond between the polymer and the particles. So, the basis of the Meissner theory and its further refinements (Meissner, 1974; Meissner, 1993; Karásek & Meissner, 1994; Karásek & Meissner, 1998) is the idea of random adsorption of portions of polymer chains on the reactive sites which are assumed to exist on the surface of filler particles. In this approach, the filler particles are considered as a polyfunctional crosslinking agent for the polymer chains. Carbon black particles are assembled into aggregates with a strong bond that is difficult to destroy. These aggregates have dimensions of 100 to 300 nm. Therefore, many authors, when constructing models of the behavior of filled elastomers, consider the state of the polymer around particle aggregates within the framework of continuum mechanics. It is reasonable to consider nanofiller not as multifunctional stitching of polymer chains, but as nanoinclusions of a composite material.

The appearance of the interfacial layer may be the result of a chemical reaction in the process of manufacturing the material (Kondyurin et al., 2018). The thicknesses of the layers near the filler particles and their properties can be specially selected to obtain a good agreement between the results of numerical calculations on relatively simple models with experimental data (Goudarzi et al., 2015). Numerical experiments allow us to find arguments in favor of the rationality of one or another hypothesis. A possible connection between the layers near the filler particles and the macroscopic properties of the material was considered in (Fukahori, 2003; Fukahori, 2005; Fukahori, 2007). An assumption was made about the existence of two layers with special properties, which the author of the hypothesis called Glassy Hard and Sticky Hard layers. The first layer is formed by a rigid material, in which molecular chain seem to be strongly adhered to the surface of the particle, whether physically or chemically. In contrast to it Sticky Hard layer is tightly entangled with the molecules extended from the Glassy Hard layer. Under large extension, themolecules in the Sticky Hard layer sandwiched between two adjacent carbon particles are stronglyextended by the separation of the carbon particles accompanied with molecular sliding and orientation. As a result the network of the strands of oriented molecules interconnected by carbon particles is formed. The hypothesis proposed explains the Mullins effect and the increase in the strength of the elastomer when the active filler is embedded into it.

In contrast to the Fukachori hypothesis, Wang used another illustration of the change in the properties of an elastomeric material with distance from the surface of the filler particles (Wang, 1998). The stiffness of the binder slowly decreases with removal until it becomes equal to the stiffness of the elastomer, which it has in the absence of filler. Work related to the study of bound rubber properties near the filler is currently underway. However, many things remain unclear as to the properties of the layers near the particles and the mechanism of their formation.

In our work, a new hypothesis is considered, which makes it possible to explain one of the possible mechanisms for the formation of the strength properties of a filled elastomeric material.

Criterion predicting the generation of microdamages in the filled elastomers

A new hypothesis that the elastomeric matrix in the gaps between adjacent filler particles is capable of withstanding very high loads is analyzed through computational modeling in this work. This is possible for the following reason. In an unloaded elastomer, molecular chains have a form of “polymer coils”. When the material is stretched in one direction, polymer chains unfold and may orient along the loading axis. The elastomeric material is converted into a state in which most chains are oriented approximately identically. In the case of a semi-crystalline polymer, so-called crystallites will arise in such regions (zones of increased rigidity with densely and orderly stacked polymer chains, so that the intermolecular forces acting at a small distance reliably connect them). If the polymer is not capable of semi-crystallization (amorphous), then these similar supramolecular formations do not arise in it. But, nevertheless, there is every reason to believe that the preferential orientation of the polymer chains along one common axis contributes to the ability of the elastomer to withstand a higher load in the direction of orientation than in other loaded states.

In order to quantify the moment of appearance of damage in the elastomeric composite, taking into account this factor, an appropriate strength criterion is needed. Classical approaches, when structural microdamages should occur in the most stressed places, that is, in the gaps between closely spaced particles, in this case do not work. Therefore, we propose to use a new criterion of strength in the form of the following condition: the destruction of a given point of the material is impossible if inequality (1) is satisfied.

$$f(\lambda_1,\lambda_2,\lambda_3) = \alpha\left(\sum_{i=1}^{3}\lambda_i^{-2}-3\right) + \beta\left|\ln\frac{\lambda_1}{\lambda_2}\ \ln\frac{\lambda_2}{\lambda_3}\ \ln\frac{\lambda_3}{\lambda_1}\right| + \gamma p < 1, \qquad (1)$$

where λ_i are the extension ratios, p is the average stress (the first invariant of the Cauchy stress tensor divided by three). The strain strength criterion includes two dimensionless α, β and one dimensional γ constants, which characterize the strength properties of the material. The values of theses constants can be determined experimentally. The first term yields a non-zero contribution to criterion (1) for the material in any deformation state. The second term is equal to zero for the material under uniaxial stretching. In the case of other types of the stress-strain state, it provides only an additional positive contribution to the function *f*. Note that this contribution can be very significant if the value of the parameter β is sufficiently large. The third term takes into account the fact that when the material is compressed comprehensively, the damage appears much more difficult. It was assumed that the value of γ is equal to zero in this investigation.

Thus, the main distinctive feature of the proposed criterion is that the value of function f under uniaxial stretching is minimal in comparison with other types of the stress-strain state at the same values of the strain invariant $I = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$ and the values of average stress p.

Figure 1 presents a map to illustrate the region of an incompressible medium (the inequality $\lambda_1\lambda_2\lambda_3 = 1$ is always fulfilled) where no microdamages may occur. It is the domain of extension ratios where the condition $f(\lambda_1,\lambda_2,\lambda_3) < 1$ is fulfilled. Three solid lines correspond to uniaxial stretching along each of the principal axes. The map is plotted for the following values of constants: α = 0.25; β = 0.05; γ=0. These values were used further as a basis for

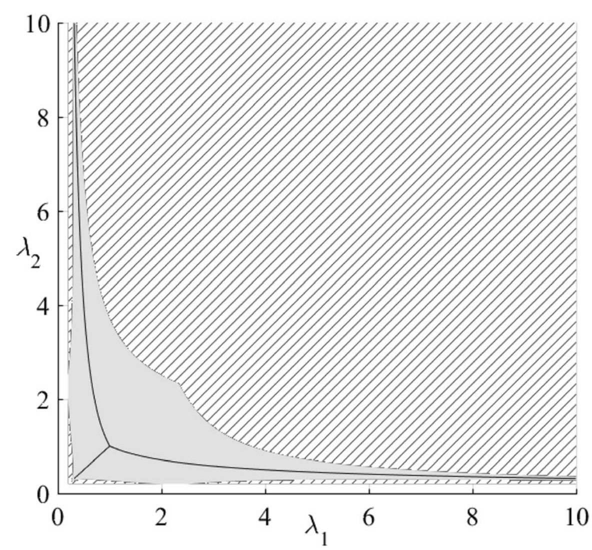

Fig. 1 A map illustrating the states where no damages (shown in grey) occur and the states where microdamages should happen (shaded areas). Solid curves correspond to uniaxial tensile loading conditions

our computational modeling. The drawing illustrates the main peculiar features of the criterion applied. As one can see, the material under uniaxial stretching can be deformed along the loading axis up to significantly high extension ratios. In other states, the onset of damage is observed at a much lower deformations.

The use of the circuit shown in Fig. 2, when the filler particles are arranged in the form of a regular rectangular lattice is The simplest and most suitable for computer experiments on modeling structural changes in an elastomeric composite.

If the filler particles are located close enough to each other, the stress-strain state of the binder in the gaps is close to the state obtained during the analysis of the pair interaction of hard inclusions in an "soft" elastic matrix (Fig. 3), when the axis passing through the centers of inclusions coincides with the direction of the medium stretching (Dohi et al., 2007; Moshev & Garishin, 2005). In this case the macroscopic extension ratios can be calculated as a relative change in the distance between particles centers. Again, we must say that we are dealing here with the uniaxial loading of the composite in the direction shown by arrows in Fig. 3. For the convenience of computational experiments, we investigate the generation of damages near the pair of inclusions loaded by forces applied to the centers of particles.

Methods

The following geometric relationships are used in the problem under study. Finite elements methods (ANSYS) have been used for modeling elastic composite materials (license ANSYS Academic Research Mechanical and CFD). Isoparametric quadrilateral elements of the 2-nd order (8 nodes in elements) were used in the calculation. Finite elements mesh was used: 12600 elements, 26,600 nodes (filler particles — 1600 elements, 3600 nodes, elastic matrix — 11,000 elements, 23,000 nodes).

Simulations are performed for the cylindrical cell, in which two rigid spheres of radius R are located. The inclusions are placed on the symmetry axis at a distance δ_0 from each other. The cylinder height H_c and its diameter D_c are assumed to be equal to $15R$. Thus provides the condition under which the effects of remote boundaries on the stress-strain state around this pair are absent.. The external boundaries of the structural cells are considered to be free of stress. The system is loaded on moving apart the spheres along the center-to-center axis to a certain distance δ. As a measure to characterize macroscopic strains, we use the parameter $\lambda = (\delta + 2R) / (\delta_0 + 2R)$.

All calculations were performed for the case when the initial gap between filler particles, δ_0, was equal to $0.4R$. The choice of this value has been made reasoning from the fact that at this distance stress gradients in the gap

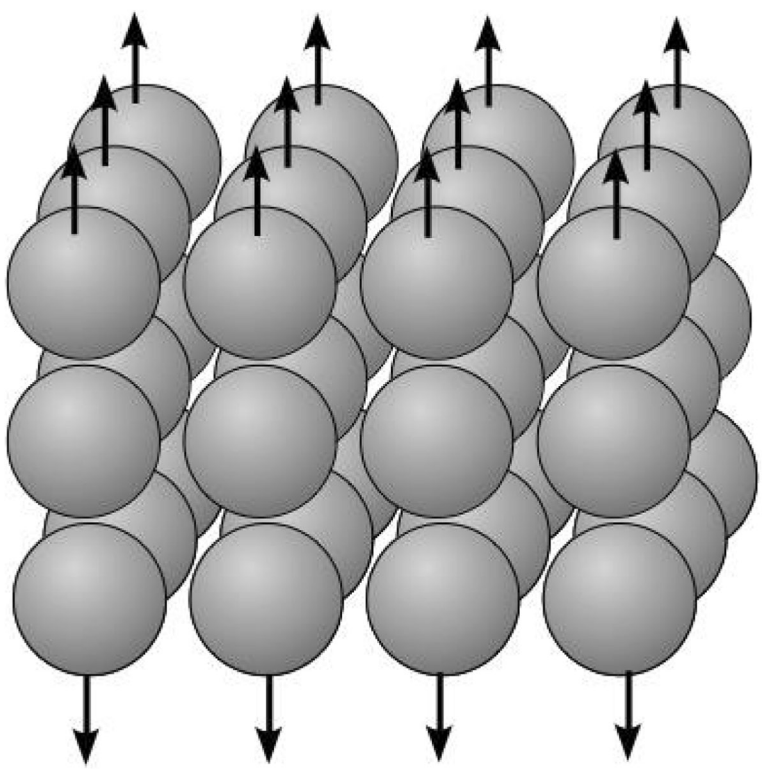

Fig. 2 The simplest calculation scheme for modeling the structure of an elastomeric composite. The centers of spherical inclusions are located in the nodes of a regular rectangular lattice. Arrows show the direction of uniaxial loading of the material

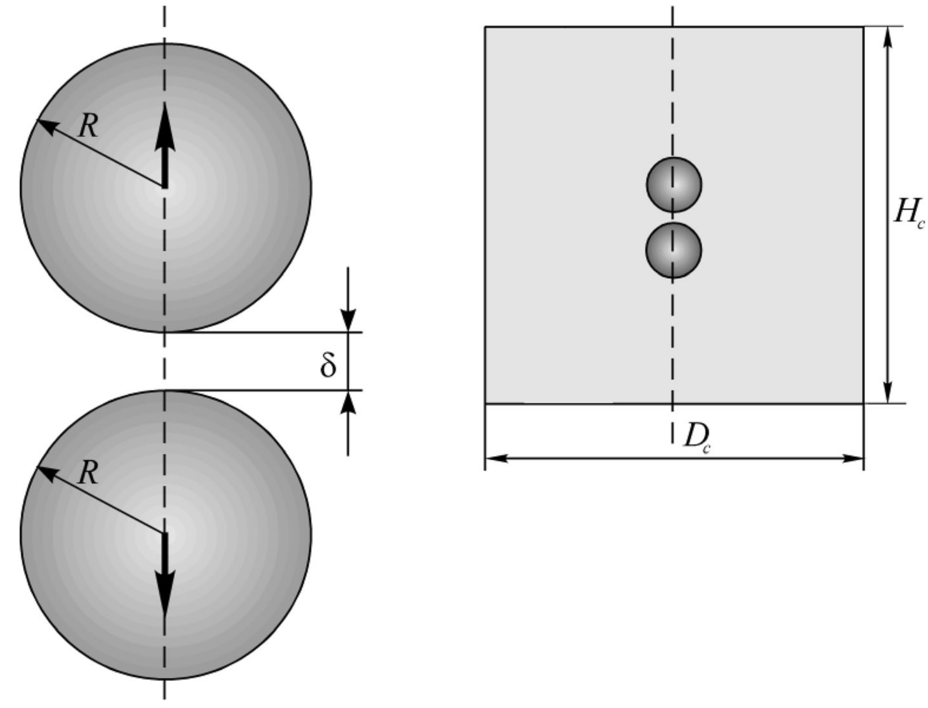

Fig. 3 Calculation scheme of the problem of two rigid spherical inclusions in a nonlinear elastic matrix

are still not so high as to pose technical difficulties during the solution of the problem, and at the same time the "mutual influence" of particles is sufficient enough for our purposes (microstrand generation modeling) (Garishin & Moshev, 2002; Garishin, 2012).

The adhesion strength of the contact between the dispersed phase and the continuum is assumed to be much greater the matrix strength (no debonding), i.e. for the "matrix-inclusion" boundaries the condition for complete adhesion is specified. The rigidity of filler particles in reinforced elastomeric composites is, as rule, markedly higher compared to the matrix. Therefore, the elastic modulus of spherical inclusions E_p was given to be equal to $10^4 E_m$ (E_m – initial Young's modulus of the matrix). That is, the inclusions considered in the numerical calculation are practically undeformable and undamageable. So damages could appear only in the elastomer. The matrix is assumed to be an incompressible nonlinear-elastic medium, the mechanical properties of which are set were using the neo-Hookean potential w:

$$w = \frac{E_m}{6}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right). \qquad (2)$$

Results and discussion

The solutions of the above-described boundary-value problem using of various conventional strength criteria (destruction upon exceeding the limiting values of such invariants of the stress-strain state as stress or strain intensities, principal stresses or strains, hydrostatic stresses) showed that in all these cases the rupture of the binder should occur in the gaps between the inclusions. That is, no any strands or similar formations can appear there in principle. A different picture is observed when using the new criterion (1). Calculations showed that the initial damages of the matrix do not occur in the gap, but at some distance from it. In this case, the further growth of the resulting damage caused by the increasing external load also does not affect the central gap region, but occurs in the surrounding space. Computer modeling of this process was carried out as follows. The boundary nonlinear elastic problem was solved in an axisymmetric formulation using the finite element method. In the process of incremental loading of the cylindrical cell, each finite element was checked for the fulfillment of condition (1) and if the condition $f(\lambda_1,\lambda_2,\lambda_3) > 1$ was satisfied, its modulus decreased to a value close to zero.

The isolines of parameter f values corresponding to the following moments of the formation of the nanostrand in the material are shown in Fig. 4: At $\lambda = 2$, the material is extended, but there are still no microdamages (Fig. 4*a*). At $\lambda = 2.17$, primary damages occur in the matrix (Fig. 4*b*). At $\lambda = 2.34$ the process of fracture region formation occurs in a direction parallel to the line

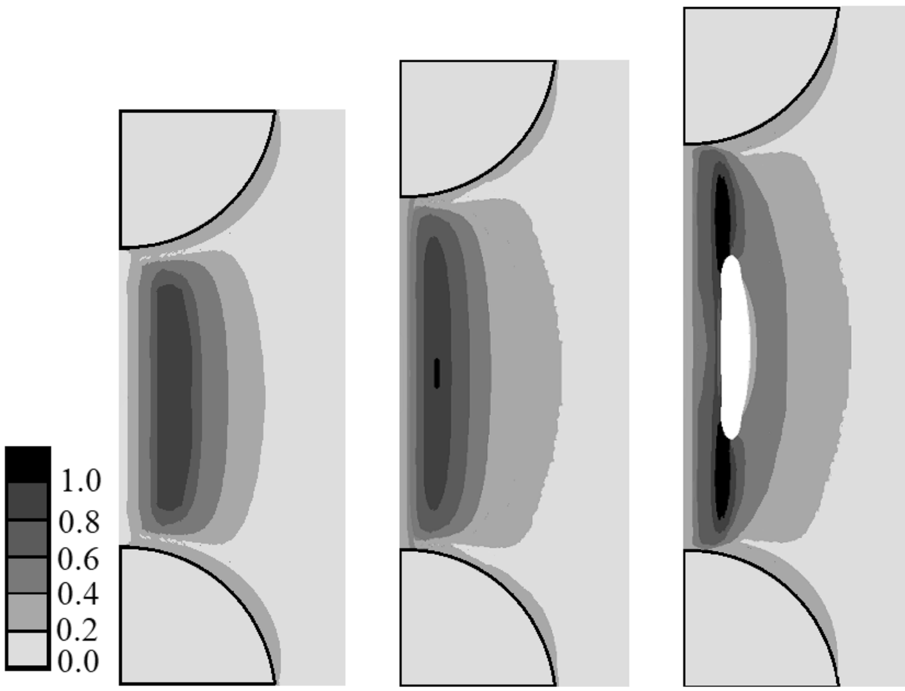

Fig. 4 Fields of distribution of parameter *f* the values in the gap between the particles: ***a*** – λ = 2.00 (matrix without damage); ***b*** – λ = 2.17 (occurrence of primary damage); ***c*** – λ = 2.34 (development of damage)

connecting the centers of inclusions (Fig. 4*c*). If we continue modeling the loading process, then a uniaxially stretched "strand" which connects the surfaces of neighbor filler particles is formed. Around it is the area of the destroyed binder.

Application of the strength criterion (1) for uniaxial stretching of a homogeneous in mechanical properties elastomeric sample with a small defect in the form of an elliptical cut on the lateral side, gave a completely different picture of damage development.

This boundary value problem was also solved by the finite element method, but already for the case of a plane deformed state. The model sample was in the form of a square with side H (Fig. 5). There was a microdefect on the lateral side. It has the form of a small notch shaped like an elongated half-ellipse The distance between the edges of the notch h_1 is $0.05H$, and its length $h_2 = 0.075H$. The sample is stretched vertically due to the displacement of the upper and lower faces, and the side surfaces are free.

The mechanical properties of the matrix material and the constants of the strength criterion α, β and γ were set to the same as for a cylindrical cell with two inclusions. The calculation scheme for modeling the appearance and growth of damage was also taken without changes, that is, when the condition $f > 1$ was satisfied, the modulus of this finite element was changed to values close to zero.

The isolines of the strength parameter f distribution for an unfilled elastomer sample stretched 2.5 times are shown in Fig. 6. The map given in this figure corresponds to the instant of fracture initiation near the defect. Computer simulation has revealed that in this case, the destruction of a single finite element leads to a redistribution of its share of the load to "neighbors", that is, to their additional overload. The computational experiment has revealed that once the elastic modulus of the binder is specified for the elements where fracture should occur, the neighboring elements become immediately overloaded. Accordingly, the risk of their own

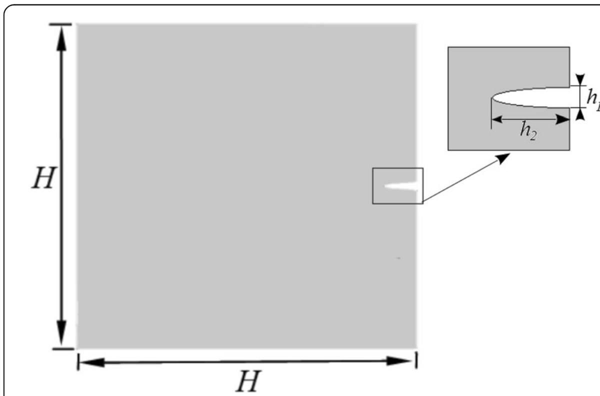

Fig. 5 Geometry of a homogeneous elastomeric sample with a lateral defect

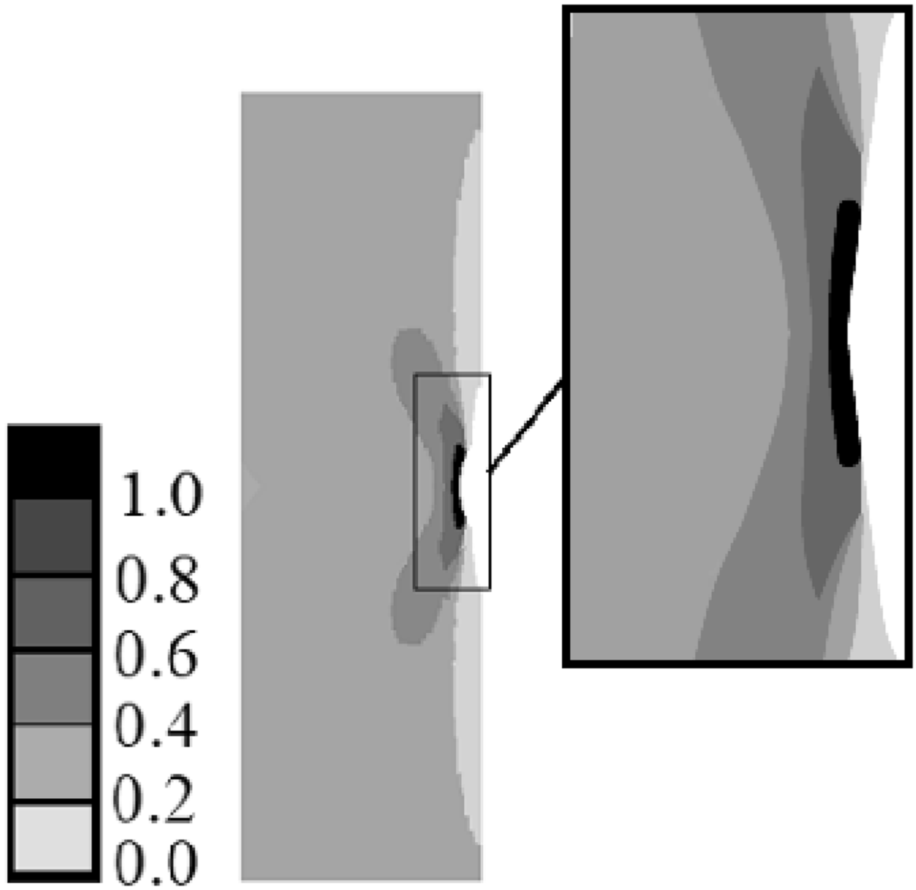

Fig. 6 A map of the strength parameter *f* values distribution in model unfilled elastomer specimen with lateral notch which is uniaxially stretched in 2.5 times

destruction increases. A system with "positive feedback" is obtained, when the presence of a microdefect leads to an avalanche-like increase in damage and, ultimately, to macroscopic rupture of the whole sample. Such a behavior of the unfilled elastomer completely agrees with the known experiments (i.e. the proposed criterion is quite operational even in this case).

The mechanism of damage development in elastomeric nanocomposites is of another character. Filler particles promote the appearance and formation of nanostrands in the matrix, which prevent the "germination" of the macroscopic crack. This circumstance can serve as one of the most plausible explanations of the well-known experimental fact that the strength and ultimate deformation of elastomeric composites can be substantially higher than that of a pure matrix.

Conclusions

It is the well known experimental fact that the input of active nanoparticles into an elastomer leads to a significant increase in tensile stresses and elongations of the material at the moment of sample rupture. To explain this fact, there are several hypotheses. Many researchers associate an increase in the strength of the material with either specific processes occurring near the filler particles or with the features of the movement of the macro-fracture in the filled elastomeric material. We drew attention to the fact that the increase in the strength of elastomers can be even in the case when the filler particles have micron dimensions (not only nanosize). In this case, this phenomenon cannot be explained with the help of hypotheses about the important role of the layers with special properties near the filler particles and specific processes in the polymer network near the surface of the filler particles.

The second fact, which we take into account, is forming of strong microfibers at the top of the macrorcrack that were observed in experiments with elastomers. These fibers connect the filler particles in the material and, apparently, inhibit the germination of the macro-fracture. To explain the features of the destruction of filled elastomers, we proposed to use a new strength criterion for an elastomeric material. According to this criterion, areas of a material whose state is close to a state of uniaxial tension have significantly greater strength compared to other states of a material with the same strain intensity. The examples given in the article show that it can be used to explain the formation of intact regions of the elastomeric binder in the gaps between the filler particles. These areas are able to change the process of the macro-fracture development in polymer sample.

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

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

Availability of data and materials
The data and materials supporting this review are available online as per the cited journal publications and conference proceedings.

Authors' contributions
All the authors contributed to preparation of the paper. All authors read and approved the final manuscript.

Consent for publication
Author agrees to publication.

Competing interests
The authors declare that they have no competing interests.

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Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Received: 30 June 2018 Accepted: 6 December 2018
Published online: 17 December 2018

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