Biaxial tests of elastomeric nanocomposites with various types of dispersed fillers

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Abstract

Mechanical tests under biaxial cyclic loading of elastomeric nanocomposites with various types of filler under biaxial cyclic loading were carried out. The object of research were elastomeric composites based on synthetic butadiene-styrene rubber SBR-1500 (matrix) and the following fillers: nanoshungite; silicic acid (fumed silica), carbon black, carbon nanofibers.

The biaxial tests were carried out on a four-vector test rig Zwick/Roell (the only one in Russia), which allows to define complex deformation trajectories in two mutually perpendicular directions. Original cross-shaped specimens were used. Their form and dimensions were established on the basis of special theoretical studies held in ICMM UB RAS (Perm).

The experiments carried out made it possible to study the effects of softening and the appearance of induced anisotropy in filled elastomers under the action of a biaxial load. It is established that the nature of their manifestation depends on the type of filler. It is also shown that in the case of pure rubber they are practically absent.

In samples filled with nanoshungite particles or carbon black, cyclic deformation along one axis causes a corresponding softening along the same axis, but does not affect the mechanical behavior of the material in the perpendicular direction.

When using the filler as a mixture of carbon black and carbon nanofibers cyclic deformation along one axis causes similar softening the other axis. In elastomers filled with silica particles (fumed silica), this effect is also present, but it is much weaker than in case of carbon nanofibers.

Thus, one can say, that it is possible to change the mechanical properties of the composite to the desired side, making the system more or less anisotropic, due to the variation in the filler composition.

1 Introduction

Disperse-filled elastomeric composites are systems consisting of a highly elastic low modulus rubber matrix (continuous phase) into which solid particulate filler particles (dispersed phase) are embedded. Their industrial analogs can be considered rubbers for various purposes (from automobile tires to current-conducting high-elastic gaskets), solid rocket fuels, etc. At present they are the object of intensive research both theoretical and experimental [1, 2]. Such materials have complex mechanical behavior (finite deformations, nonlinear elasticity, viscoelasticity), which is due to various reversible and irreversible structural changes occurring during deformation [3–11]. In particular, they are characterized by a phenomenon such as "softening" during repeated deformation (the Patrikeev-Mullins effect) [12, 13, 14, 15], which causes certain problems in their operation.

2 The object of study

The main object of research was the synthetic butadiene-styrene rubber SBR-1500, in which various fillers different in their mechanical and physicochemical properties were added: 1) nano-shugite; 2) technical carbon (carbon black); 3) carbon nanofibers with technical carbon; 4) silicic acid (white soot). In addition, similar tests were carried out for the pure elastomer without filler. Shungite is a clay mineral consisting mainly of fullerene-like carbon (30%) and silicon dioxide SiO_2 (60%) [16, 17, 18]. It is fairly widely distributed in nature, inexpensive and characterized by high ecological safety. Nanoparticles of the globular type are formed when shungite is dispersed. Rubbers filled with shungite nanoparticles are characterized by increased wear resistance. Currently, they are used in the tire industry [19, 20]. In our case, the composite samples contained 65 parts by weight (phr) of shungite nanoparticles with an average size of 60–80 nm. Carbon black grade N220 (ASTM standard) was taken: the average particle size was about 30 nm, the mass concentration was 60 phr. Carbon nanofibers VGCF [21, 22] were of length from 10 to 20 μm and a diameter of 150–200 nm. Their concentration was 5 phr. This concentration is rather significant for fibers, because, these particles (by their shape and size) "extend their influence" to much larger distances than granular inclusions. The filler of silicic acid BS-120 (white soot) was a particulate hydrated silicon dioxide with an average size of 20–30 nm [23]. Its concentration was also 65 phr.

3 Experiment and results discussion

The biaxial tests were carried out using the four-vector test rig Zwick/Roell (the only one in Russia), which allows to define complex deformation trajectories in two mutually perpendicular directions (Fig. 1). The original cross-shaped samples were used (Fig. 2). Their shape and dimensions were set on the basis of special theoretical studies carried out in ICMM UB RAS. These samples are optimal from the viewpoint of obtaining uniform stress fields at the working part of the specimen and minimizing the size of the non-working part [24].

Figure 1: The four-vector test rig Zwick/Roell

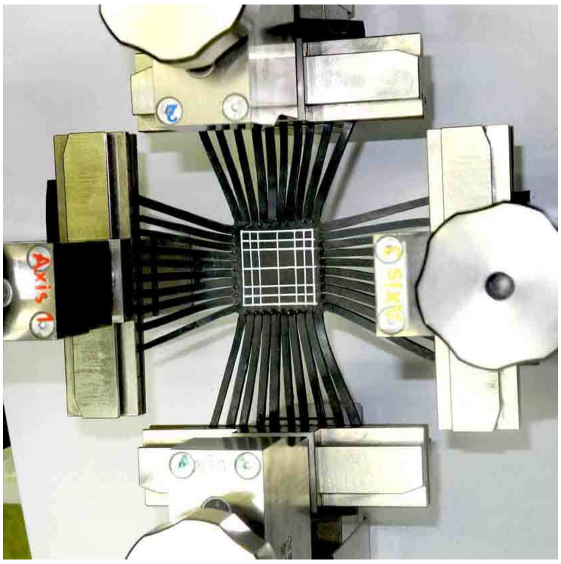


Figure 2: General view of cross-shaped specimens used in biaxial tests

Tests for pure elastomer and composites filled with nanoshungite and silicic acid were performed according to a program of 4 cycles (Program I). Each cycle consisted of the following steps: Stretching along one axis (direction X) to a given deformation, stopping for stress relaxation, compressing to the initial state and again stopping for relaxation. The rate of deformation was 25%/min, the stop for relaxation was 30 min. In the first and second cycles, the sample was stretched along the X axis to a deformation of 25% and 50%, respectively. In the third and fourth cycles, the same procedure was repeated along the Y axis.

For samples filled with carbon black, as well as carbon fibers with technical carbon, the Program II was applied (deformation rate 25%/min, stop time for relaxation 20 min.):

1) Stretching along the X axis to a deformation of 150% and stopping for relaxation.
2) Compression along the X axis to the initial state and stopping for relaxation.
Procedures 1) and 2) were repeated 3 times.
3) Stretching along the Y axis to a deformation of 150% and stopping for relaxation.
4) Compression along the Y axis to the initial state and stopping for relaxation.
Procedures 3) and 4) were also repeated 3 times.

Testing of pure rubber SBR-1500 according to Program I established (Fig. 3) that uniaxial cyclic deformation practically does not affect its properties in other directions. The hysteresis loops in the "load-unload" mode are also very weakly expressed. That is, such material can be considered as a high degree of reliability to be elastic and isotropic.

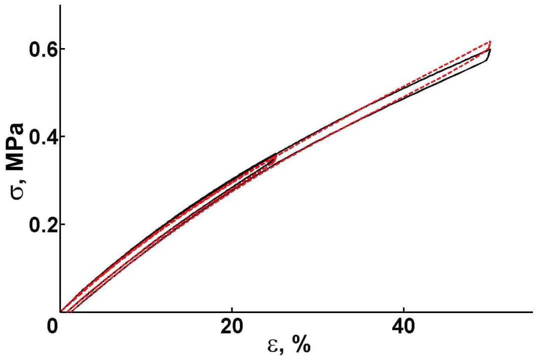


Figure 3: Biaxial tests of pure elastomer; solid lines — tensile curves along the X axis, dashed lines — along the Y axis (σ — nominal stress, ε – stretching deformation)

A different picture is observed for samples with nanoshungite (Fig. 4). The graphs show that the addition of this filler enhances the viscosity properties of the composite — hysteresis loops appear. At the same time softening of the material under repeated loading does not occur. Dependences of stresses on deformation, constructed under loading along the X and Y axes, practically coincide, i.e. the appearance of anisotropy induced by the deformation is not observed.

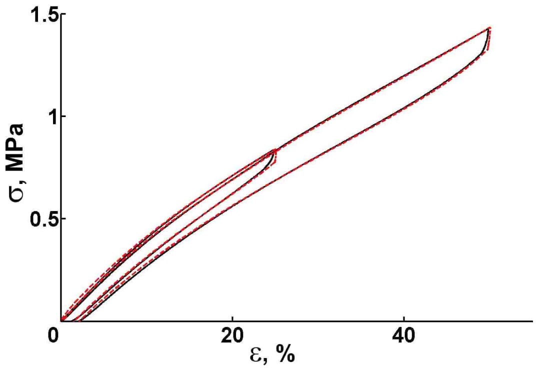


Figure 4: Biaxial testing of an elastomer filled by shungite nanoparticles; solid lines — tensile curves along the X axis, dashed lines — along the Y axis

Fig. 5 shows the results of tests of composites with white soot as a filler. In this case, the hysteresis curves turned out to be larger than in the previous experiment which indicates an increase in the viscosity properties of the composite. The stiffness decreases with repeated loading (the Patrikeev-Mullins effect) for curves corresponding to deformation along the same axis. Also, the appearance of an induced anisotropy of properties is observed for these samples. The curves $\sigma(\varepsilon)$ obtained under loading along the Y axis lie lower than those constructed for the X axis.

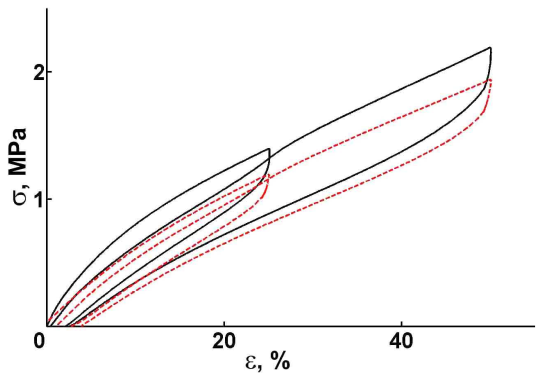


Figure 5: Biaxial testing of an elastomer filled by white soot nanoparticles; solid lines — tensile curves along the X axis, dashed lines — along the Y axis

Experiments for composites filled by carbon black and nanofibers with carbon black (program II) are represented in Fig. 6 and Fig. 7. Fig. 6 presents the dependences of σ on ε for the composite with the carbon black filler only. These plots show that the material as a result of cyclic loading along the first axis (X) undergoes considerable softening after the first cycle, in the second and third cycles the situation stabilizes. The hysteresis loop on the first cycle is also much larger than in the second and third ones. Most interestingly, almost exactly the same curves were obtained for subsequent loading in the perpendicular direction (Y-axis), that is, for a given composite, the load history for X has no effect on the Y loading history.

The addition of just 5 phr of carbon nanofibers to this composite significantly changes the behavior of the material. Fig. 7a shows the results of the first three cyclic loads along the X axis, and in Fig. 7b — the three subsequent cycles along the Y axis. When loaded along X, the plot is qualitatively the same as in the case of a only carbon black filler: the first cycle is characterized by the largest area of hysteresis and the greatest softening of the material. The curves corresponding to the second and third cycles lie nearby. In the subsequent deforming along Y, the material behaves quite differently. The previous deformation in the perpendicular direction led to the fact that all three cycles in Y coincide with the second and third cycles in X, that is, the uniaxial "training" of this composite causes its isotropic softening.

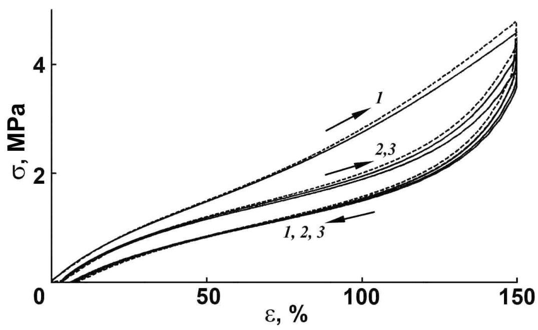
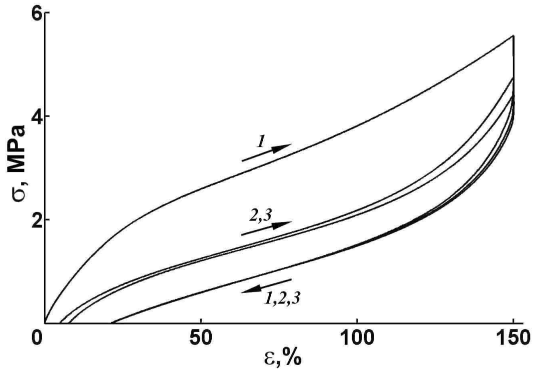


Figure 6: Biaxial testing of an elastomer filled by carbon black nanoparticles; solid lines — tensile curves along the X axis, dashed lines — along the Y axis



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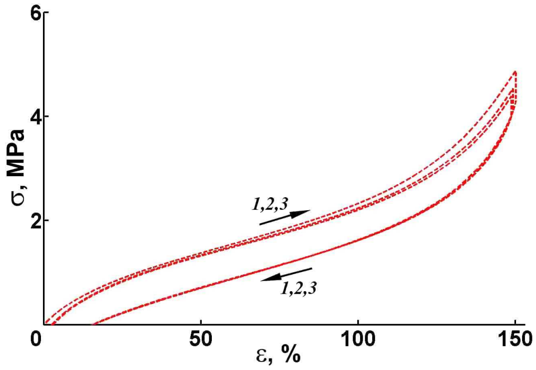

b

Figure 7: Biaxial testing of an elastomer filled by nanofibers and carbon black; (a) — deformation along the X axis, (b) — deformation along the Y axis. 1, 2 и 3 — cycle numbers

4 Summary

Experimental studies showed that the mechanical behavior of dispersed filled elastomers (induced anisotropy of the module and viscoelastic properties) at biaxial tests depends on what materials are used as filler. Pure rubber remains practically elastic and isotropic material, regardless of the type of applied load. For samples with shungite or technical carbon as filler, cyclic deformation along one axis causes a corresponding softening along the same axis, but does not affect the mechanical behavior of the material in the perpendicular direction. In the case of filler made of carbon black with nanofibers, cyclic deformation along one axis causes similar softening along another axis (isotropic softening). This effect can also be observed for the filler of silicic acid particles, but it is much weaker than for carbon nanofibers.

Acknowledgements

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