Testing Mechanical Features of Rubber Composites under Biaxial Loading

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Abstract. The main object of studies were composites on the base of synthetic rubber filled with various nano- and micro particles, which are already used or intended to be used in the tire industry. Mechanical behavior of such materials under biaxial cyclic loading was studied experimentally. The tests were carried out using the four-vector test rig Zwick/Roell. It allows to define complex deformation trajectories in two mutually perpendicular directions independently. The test program consisted of two or three cycles of load-unload (with stops for relaxation) in one direction and then two or three more such cycles in the perpendicular one. Experiments made it possible to study viscous-elastic properties as well as the effects of softening and the occurrence of induced anisotropy in filled elastomers under the action of a biaxial load. In the case of pure rubber, they are practically absent, so unfilled system can be considered as elastic and isotropic. A different picture is observed for filled systems. All the tested composites become viscoelastic after filler input: a hysteresis loop appeared and its area (dissipative losses) enlarged with increasing amplitude of cyclic deform. Also the dependences of induced anisotropy of mechanical properties and softening on the type of filler in the composite were investigated.

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 propellants, etc. At present they are the object of intensive research both theoretical and experimental [1, 2]. Such materials are characterized by complicated mechanical behavior (finite deformations, nonlinear elasticity and 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) [12-15], which causes certain problems in their operation.

It is well known from practice that structurally inhomogeneous materials, when used in real devices, often behave far from what was observed during standard testing of samples. Biaxial tests can significantly approach the solution of this problem by setting complex loading trajectories along different axes. This means that it is possible to test samples in a wider range of loads under conditions closer to reality.

2. The object of study
The main object of biaxial studies was the synthetic butadiene-styrene rubber SBR-1500, in which various fillers different in their mechanical and physicochemical properties were added such as: 1) microshugite (MS); 2) nanoshugite (NS); 4) white soot (WS); 4) carbon black (CB); 5) carbon nanofibers (CNF) with carbon black. Also the similar tests were carried out for the pure elastomer without filler. For the convenience of the results comparing, the mass concentration for all fillers was taken 65 phr (filler weight parts per hundred rubber weight parts).

A brief description of the fillers used is given below.
Shungite is a clay-like mineral consisting mainly of fullerene-like carbon (30%) and silicon dioxide \( \text{SiO}_2 \) (60%) [16-18]. It is fairly widely distributed in nature, inexpensive and characterized by high ecological safety. As for their structure, shungites are natural composites with a uniform distribution of highly disperse crystalline silicate particles in a carbon matrix. There is a strong bond between the carbon and silicate components. The particles of the shungite powder contain different phases with respect to polarity. Due to the bipolarity, powders of shungite rocks mix well practically with all known substances (aqueous suspensions and fluoroplastics, rubbers, resins and cements, etc.). Therefore, they are one of the most promising fillers in terms of universality. 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 two types of shungite filler: 1) microshungite particles with an average characteristic size about 500 nm; 2) nanoshungite particles size of 60-80 nm.

White soot (m\( \text{SiO}_2 \cdot n\text{H}_2\text{O} \)) is a particulate hydrated silicon dioxide. Depending on the method of obtaining the hydrate bond can vary from a strong chemical to a weak adsorption. This filler is usually added into rubber products operating in difficult conditions. White soot grade BS-120 particles with an average size of 20-30 nm [21] was used in our samples.

Carbon black (or technical carbon) is one of the most popular fillers in tire industry. Carbon black grade N220 (ASTM standard) was taken: the average particles size is about 30 nm.

Carbon nanofibers are also one of the very promising nanostructured materials, which are currently becoming widely used in various industries (including tire manufacturing). According to their structure, these ones consist of distorted cones with graphene grids (similar to layers in graphite) nested into each other. We used carbon nanofibers grade VGCF [22, 23]. They have an average length from 10 to 20 \( \mu \text{m} \) and a diameter about 150-200 nm. Their weight concentration was taken equal 5 phr. This concentration is rather significant for fibers, because, these ones (by specific shape and size) "extend their influence" to much larger distances than the granular inclusions. Carbon black (phr = 60) was also added to these samples with nanofibers.

3. Experiment and results discussion
The biaxial tests were carried out using the four-vector test rig Zwick/Roell (the only one in Russia). This test bench is capable of performing experiments with a complex trajectory of loading along two mutually perpendicular directions independently (Figure 1). The original cross-shaped samples were used (Figure 2). Their shape and dimensions were set on the basis of special theoretical studies carried out in ICMM UB RAS. A corresponding patent was obtained [24].

The fan-folding links connecting cruciform specimen with grippers (Figure 2) were used to provide the uniform stress-strain field in the working region of the sample. Such fastening provides the good uniformity of stresses not less than for 87% of the sample area.

When stretching the cruciform specimens only along one axis, care must be taken to avoid distorting influence from the grippers that are responsible for the loading in perpendicular direction. Therefore, when the specimen was uniaxially stretched, a simultaneous displacement of the perpendicular grips was carried out, so that their "lateral" mechanical effect on the sample was minimized.

![Figure 1. The four-vector test rig Zwick/Roell.](image)
The cruciform samples used in the experiments had a working zone in the form of a square with a side of 35 mm. The links connecting this zone with the grippers of the tensile machine (10 pieces per side) had the form of long thin rods of rectangular cross-section (length 45 mm, thickness $3 \times 2$ mm). They were manufactured of the same material as the whole specimen. Actually, all the measurements of displacements in the sample were made only in the central region of the working area with a size of $30 \times 30$ mm (it is highlighted by white lines in Figure 2). This additional restriction allowed to provide practically 100% guarantee of the stress-strain state uniformity [25].

Two programs were used for biaxial testing. Tests for pure elastomer and composites filled with microshungite, nanoshungite and white soot were performed according to Program I (four cycled). Each test cycle consisted of the following steps:

1) Stretching along one axis to a given deformation.
2) Stopping for stress relaxation.
3) Return to the initial state and again stopping for relaxation.

The rate of deformation was 25%/min, the stop for relaxation lasted 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 perpendicular $Y$ axis.

Program II (four cycled) was applied to the specimens with two fillers: 1) carbon black particles; 2) carbon nanofibers with carbon black particles:

1) Stretching along the $X$ axis to a deformation of 150% and stopping for relaxation.
2) Return to the initial state 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) Return to the initial state along the $Y$ axis and stopping for relaxation.

Procedures 3) and 4) were also repeated 3 times.

Deformation rate in Program II was 25%/min, stop time for relaxation was 20 min.

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

Figure 2. General view of cross-shaped specimens used in biaxial tests; (a) – initial unloaded state, (b) – the sample is deformed by 80% along each of the axes.
A different pictures were observed for composite samples with micro- and nanoshungite fillers (Figure 4 and Figure 5). The graphs show that the addition of these micro or nanoparticles enhances the viscosity properties of the composite: a hysteresis loop appeared and its area (dissipative losses) enlarged with increasing amplitude of cyclic deformation.

For nanoshungite 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. But in for the case of microshungite filler cycle curves along Y axis lie below than those along X. So, microparticles contribute to the material softening in the perpendicular direction (unlike nanoparticles) and to appearance of induced anisotropy.

It should also be noted that at the same filler concentration, nanoshungite causes greater material enhancement than microshungite.

Figure 6 shows the results of tests for composites with white soot as filler. In this case, the hysteresis curves turned out to be larger than in the previous experiment which indicates a significant 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 σ(ε) obtained under loading along the Y axis lie much lower than those constructed for the X axis.

Experiments for composites filled by carbon black and nanofibers with carbon black (Program II) are represented in Figure 7 and 8. Figure 7 depicts the dependences of nominal stresses on deformation for the composite with the carbon black filler only. These plots show that the material under cyclic loading along the first axis (X) undergoes considerable softening after the first cycle, in the second and third cycles the situation stabilizes (Figure 7a). 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 Y direction (Figure 7b). That is, the load history for X practically has no effect on the Y loading history for a given composite.
The addition of just 5 phr of carbon nanofibers to this composite significantly changes the behavior of the material. Figure 8a shows the results of the first three cyclic loads along the $X$ axis, and in Figure 8b – the three subsequent cycles along the $Y$ axis. When loaded along $X$, the plot is qualitatively the same as in the case of 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 white soot nanoparticles (phr = 65); black lines – tensile curves along the $X$ axis, gray lines – along the $Y$ axis.

Figure 7. Biaxial testing of an elastomer filled by carbon black nanoparticles: $a$ – tensile curves along the $X$ axis, $b$ – along the $Y$ axis.
4. Conclusions
Experimental studies showed that the mechanical behavior of dispersed filled elastomers (softening, induced stiffness anisotropy 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. But the addition of the filler to the elastomer leads to a significant change in its mechanical behavior. The composite begins to exhibit viscoelastic properties (a hysteresis loop is), also the induced anisotropy of mechanical features and softening of the material during cyclic loading may occur.

Thus, it makes us possible to change the mechanical properties of the composite in the desired direction by varying the composition and type of the filler, thereby making the system more or less anisotropic or viscoelastic.

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