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MECHANICAL STUDIES OF RUBBER MICRO- AND NANOCOMPOSITES PROMISING FOR THE TIRE INDUSTRY. UNIAXIAL AND BIAXIAL TESTS

O.K. Garishin[1*], V.V. Shadrin[1,2], Yu.V. Kornev[3]

[1]Institute of Continuous Media Mechanics UB RAS, Academician Korolev st. 1, Perm, Russia

[2]Perm State National Research University, Bukireva st. 15, Perm, Russia

[3]Institute of Applied Mechanics RAS, Leningradsky prt. 7, Moscow, Russia

*e-mail: gar@icmm.ru

Abstract. Complex studies of the mechanical properties of composites based on rubber vulcanizates with various micro and nanofillers (which are already used or intended to be used in the tire industry) were carried out. Testing of composites for uniaxial stretching to rupture allowed us to determine the reinforcing effects of the input of fillers, as well as materials strength and deformability. Cyclic tests for biaxial loading in two mutually perpendicular directions were also carried out. As a result, the effects of softening and the occurrence of induced mechanical anisotropy in filled elastomers under the action of a biaxial load were studied. It was shown that there are no hysteresis losses in the unfilled elastomer, and there is no induced anisotropy. For a filled elastomer, the value of hysteresis and induced anisotropy depend on the type of filler, its concentration and particle size.

Keywords: rubber, mineral fillers, strength, ultimate strain, biaxial loading, viscous-elasticity, softening, induced mechanical anisotropy

1. Introduction

It is well known that carbon black (technical carbon) is the most common and studied filler of elastomeric composites based on natural and synthetic rubbers. Its use can significantly improve the mechanical characteristics of the composite (especially strength and deformability). To date, these effects have been well studied, and it can be said that this approach to the modifying rubber properties "has reached its ceiling" [1-4].

Further progress requires a continuous search for new unconventional micro and nanoscale fillers [5-8]. One promising area is the use of various clay minerals that are fairly easily dispersed down to nanoparticles and, after appropriate treatment by surfactants, have good adhesion with elastomers [9-15].

These materials are structurally inhomogeneous systems consisting of a highly elastic low modulus rubber matrix (continuous phase) into which rigid and durable filler particles (dispersed phase) are embedded randomly. Their industrial analogs can be considered for a lot of rubbers used for various purposes – automobile tires, solid rocket propellants, dampers, gaskets etc. Such composite materials are characterized by complicated mechanical behavior (finite deformations, nonlinear elasticity, viscoelasticity, etc.), which is due to various reversible and irreversible structural changes occurring during deformation [16-18]. In particular, they are often characterized by a phenomenon such as "softening" during repeated

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deformation (the Patrikeev-Mullins effect) [19-20], which causes certain problems in the operation of such rubber in tires.

At present elastomer composites with various mineral fillers are the object of intensive theoretical and experimental research [21-25].

2. The object of study

The main object of study was composite materials based on the synthetic styrene-butadiene rubber SBR-1500 with various nano- and micro fillers (which are already used or intended to be used in the tire industry). These are white soot (WS), nanoshungite (NS), microshungite (MS), diatomite sorbent (DS), and the product of rice husk pyrolysis (RHW) – rigid particles consisting of a combination of amorphous silica and graphite. A brief description of the fillers used is given below.

Shungite is a clay-like mineral consisting mainly of fullerene-like carbon (30%-mas.) and silicon dioxide SiO_2 (60%-mas.) [26-28]. It is fairly widely distributed in nature, inexpensive and characterized by high ecological safety. There is a strong bond between the carbon and silicate components. The material is characterized by good chemical resistance and electrical conductivity. Rubbers, filled with micro and nanoparticles of shungite, are characterized by increased resistance to wear. It also helps to improve their fire and heat resistance. Currently, shungite is being used in the tire industry in order to produce active and semi-active fillers of a new generation [23-24]. In our case, the composite samples contained two types of shungite filler: 1) nanoshungite particles with an average characteristic size about 60–80 nm; 2) nanoshungite particles size of 400-500 nm. The special grinding technology in a planetary ball mill was used [29,30].

White soot is particulate hydrogenated silicon dioxide ($mSiO_2 \cdot nH_2O$) [31]. 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 severe conditions. It is also recommended as an additive in frame rubber to increase the bond strength of these rubbers with cords. White soot grade BS-120 particles with an average size of 20–30 nm [21] was used in our samples.

Diatomite sorbent is a highly porous inert material derived from the natural mineral diatomite via mechanical crushing and heat treatment. Diatomite sorbent is relatively cheap, has good adsorption ability, acid resistance, refractoriness and low thermal conductivity. It is used as a reinforcing element in the rubber industry. The average particle size of granulated DS particles is 10–20 μm.

SBR-composites were also manufactured and tested with the new mineral filler RHW (not yet used in the rubber industry). RHB is the product of the rice husk pyrolysis. It is the combination of amorphous silica and graphite (95–98%-mas SiO_2 and 2–5%-mas C). This is one of the promising fillers for elastomeric composites. It is similar in structure to the existing, widely used zeosil and white soot. Its advantage is that it is obtained from natural raw materials with parallel waste disposal and heat generation. This process is less energy intensive than existing white soot or carbon black production technologies. The average particle size of RHW was about 25–30 microns.

All samples were manufactured on the same technology using a HAAKE Rheomix laboratory mixer. The process was carried out in two stages. At the first step, pure rubber was mixed with fillers, modifiers (to improve matrix and filler adhesion) and plasticizers (to improve processing). Rotor speed was 70 rpm. Temperature from 110 to 160°C. Before mixing, the filler was placed in ethanol, which, in the matrix, makes it possible to better distribute and, facilitates the addition of lightweight particles. The mixing itself took place in an open mixer, which consists of two heated shafts, rotating to meet each other with different angular speeds. In the second step, a vulcanizing group was introduced into the mixture at

70 rpm, 110–150°C. The resulting material was cut into pieces, then pressed into a square mold, where vulcanization took place. For results comparison convenience, the mass concentration for all fillers was taken 65 phr (parts of filler per hundred parts of rubber in weight).

3. Experiment and results discussion

Studies of the mechanical behavior of rubber composites consisted of two types of tests: 1) uniaxial tension to rupture; 2) sequential cyclic deformation in two mutually perpendicular directions. In the first test, the rigidity and strength of materials were studied. The second test studied the viscoelastic properties and the effects of the emergence and development of anisotropy of mechanical properties and material softening under repeated loads.

Uniaxial testing. Testing of composites for uniaxial stretching to rupture allowed us to determine the reinforcing effects of the input of fillers, as well as materials ultimate characteristics (strength and deformability). The experiments were carried out on a Testometric FS100kN CT universal tensile testing machine. Standard dog-bone specimens with the dimensions of the working part 10×2×2 mm (standard ISO 527-25A) were used. The sample monotonously stretched to break at a rate of 25%/min. during testing (10–12 experiments on one type of material). The averaged experimental results are presented in Fig. 1.

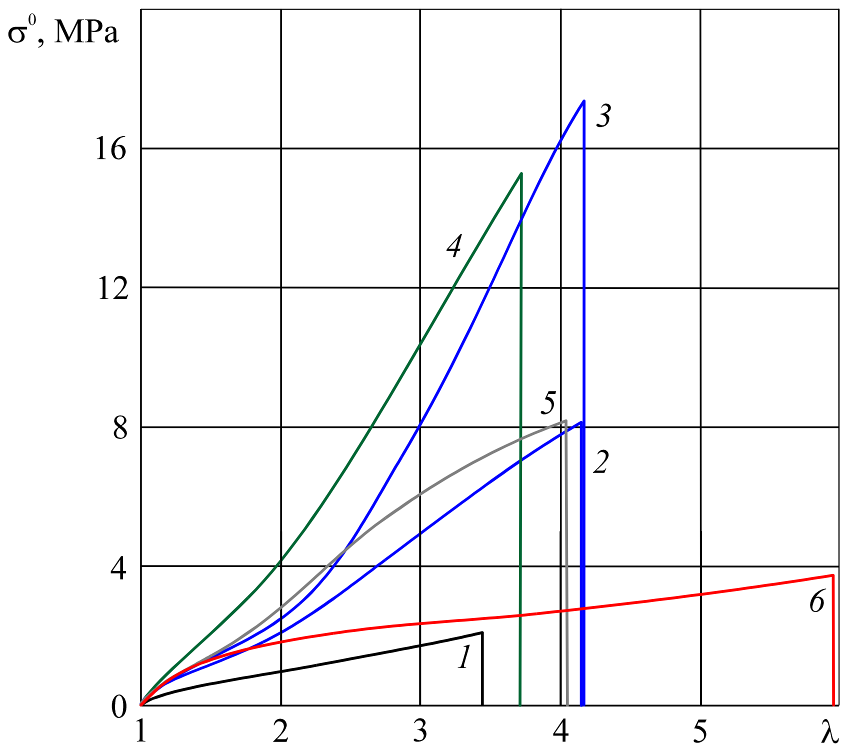


Fig. 1. Nominal stresses σ^0 versus extension ratio λ at stretching of pure rubber SBR-1500 (*1*) and composites based on it (mass concentration 65 phr): microhungite (2), nanoshungite (*3*), white soot (*4*), diatomite sorbent (*5*), RHW (*6*)

Experiments showed that all the used fillers contribute to an increase in the strength and rigidity of the composite system. The highest strength was demonstrated by samples with fillers of nanoshungite and white soot, the smallest – samples filled with RHW. The strength and deformability of composites containing particles of diatomite sorbent and microshungite turned out to be close and lay somewhere in the middle.

The use of nanoshungite (curve 3) increases the strength of the material by more than 2 times as compared to microshungite (curve 2) with almost the same maximum deformability. The difference between these fillers is only in particle size (MS – 500 nm, NS – 75 nm). Apparently, the nanoshungite particles have a much larger specific surface. This contributes to an increase in strength due to the good chemical affinity of the filler and the matrix.

RHW is a new for tire industry filler. The reinforcing effect of it was relatively small, but its input almost doubled the strain of the rubber break compared to the pure SBR-1500. Perhaps composites with this additive will improve tire durability or some other performance characteristics, but this is beyond the scope of our research.

Biaxial testing. When used in real devices, structurally inhomogeneous materials often behave far from that observed during standard testing of samples. Biaxial tests can significantly solve this problem by setting complex loading trajectories along different axes making it is possible to test samples in a wider range of loads under conditions closer to reality.

Biaxial mechanical tests were carried out at the Perm State National Research University (PGNIU) on the four-vector Zwick/Roell test rig (made in Germany). This unique device (only one in Russia) has two mutually perpendicular traverses with four grippers. Each gripper can be set to its own independent speed and displacement value (Fig. 2). Zwick/Roell is particularly well suited for the study of highly deformable elastomeric materials. The machine allows one to set complex diverse trajectories (uniaxial and biaxial loading). Main performance characteristics: the greatest force is 2500 N, the maximum stroke of each grip is 400 mm. The speed of its movement varies from 0.001 to 7500 mm/min. (15000 mm/min in total).

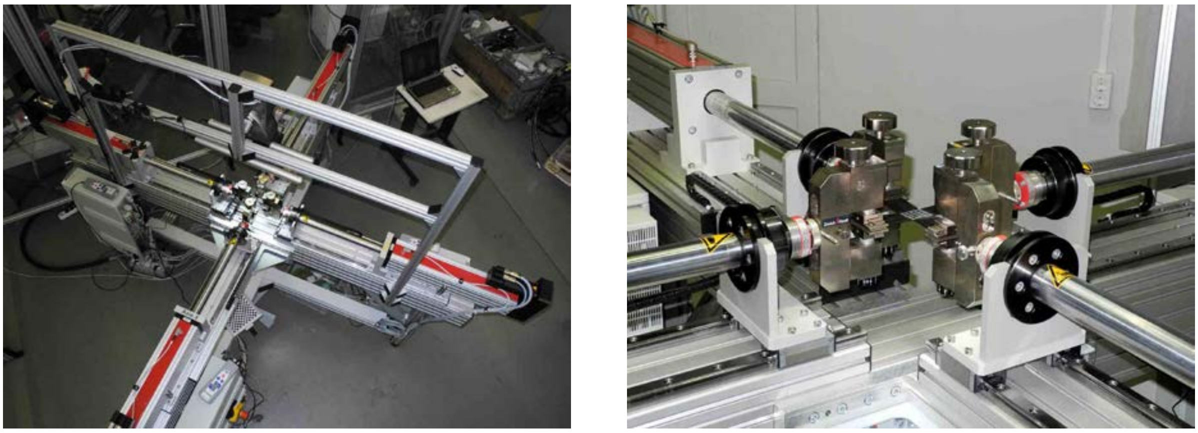
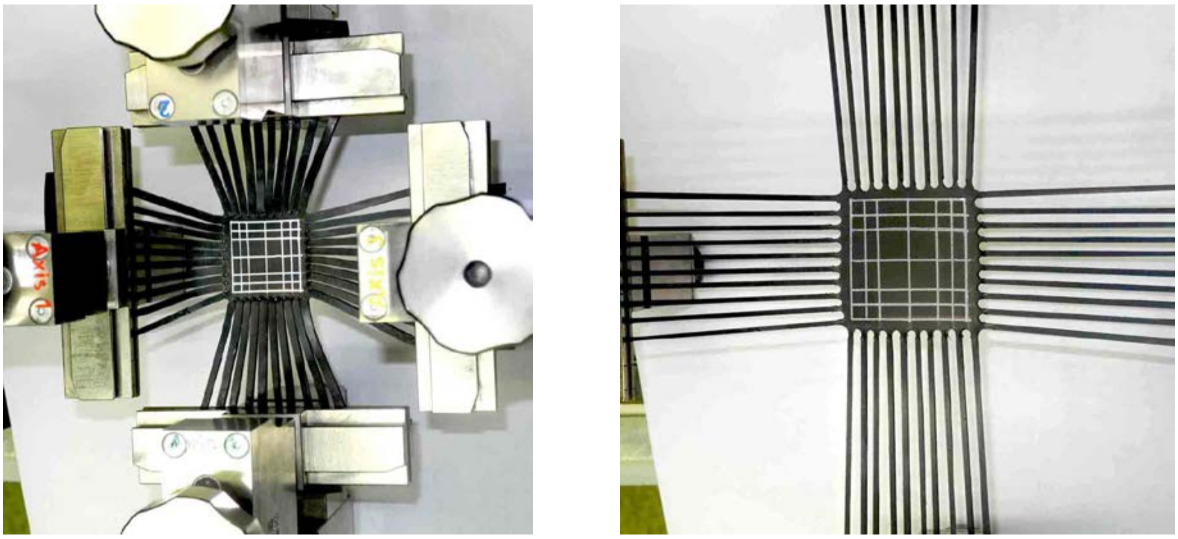


Fig. 2. The four-vector test rig Zwick/Roell

The machine is also equipped with a videoXtens video extensometer, which can be used to measure displacements in a contactless way using special marks on the sample. The influence of distorting factors of the sample, such as "creeping" from the grip, can be excluded and deformation studied directly in the working area of the sample.

The original cross-shaped samples were used (Fig. 3). Their shape and dimensions were set on the basis of special theoretical studies carried out in ICMM UB RAS [31]. A corresponding patent was obtained [32]. They are optimal for obtaining homogeneous stress-strain fields, stresses in the working part of the sample and minimizing the sizes of non-working part. The work area had the shape of a 35 mm square. The links connecting this zone with the grippers of the tensile machine (10 pieces per side) were long thin rectangular cross-section rods (length 45 mm, cross-section 3×2 mm). They were manufactured of the same material as the whole specimen and in initial (not loaded) state were arranged in a fan-like manner (Fig. 3a). All the measurements of displacements in the sample were made only in the central region of the working area with a size of 30×30 mm (it is highlighted by white lines in Figs. 3a, 3b). This additional restriction provided a practically 95% guarantee of the stress-strain state uniformity.



a *b*

Fig. 3. 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

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

The biaxial testing program consisted of four cycles. Each carried out the following operations:

1) Stretching along one axis to a given deformation;
2) Stopping for relaxation;
3) Return to the initial state;
4) Stopping for relaxation.

The rate of deformation was 25%/min, and the stop for relaxation lasted 30 min. In the first and second cycles, the sample was stretched along the *X* axis to an extension ratio equal 1.25 and 1.5, respectively. In the third and fourth cycles, the same procedure was repeated along the perpendicular *Y* axis. When changing the direction of grips movement, stops were made to relax and restore the equilibrium state in the material.

The averaged results of biaxial experiments (5 implementations per material) are presented in Figs. 4-9 (σ^0 – nominal stress, λ – extension ratio).

Tests of pure SBR-1500 rubber showed (Fig. 4) that cyclic deformation along one axis had almost no effect on its properties in other directions. Hysteresis loops in the "load-unload" mode are very weakly expressed. Such material can be considered as elastic and isotropic.

A completely different picture was observed for filled systems. In varying degrees, all of them showed viscoelastic properties: the occurrence of hysteresis on the cyclic loading curves (dissipative losses), as well as the development of relaxation processes at stops at the beginning and end of the cycle.

In addition, the filler input contributed to the softening of the composite with repeated cyclic deformation (the Patrikeev-Mullins effect [19]) and the appearance of induced mechanical anisotropy: the $\sigma^0(\lambda)$ curves obtained when loaded in one axis differed from similar dependences for the perpendicular direction.

The exception was the samples with nanoshungite. The stress-strains dependences constructed under loading along the *X* and *Y* axes almost coincided (Fig. 5). Although the composite became viscoelastic, it remained isotropic.

Certain anisotropy of the mechanical properties and softening of the material was observed in the rubbers filled with microshungite (Fig. 6). Dissipative losses for samples with nanoshungite and microshungite were close. Since these fillers differ only in particle size, it can be concluded that the use of smaller inclusions enhances these effects.

The test results of composites with white soot as a filler are presented in Fig. 7. In this case, the hysteresis appeared much stronger than for nanoshungite and microshungite. It indicates an increase in the viscosity properties of the composite. The area of hysteresis, as well as the effects of softening and induced anisotropy, turned out to be the greatest for these samples as compared with other materials studied.

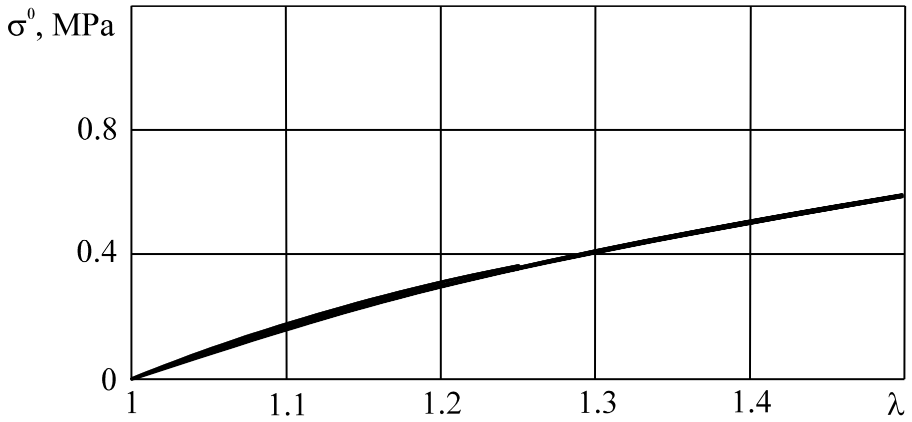


Fig. 4. Biaxial tests of pure rubber SBR-1500: black lines – loading on *X* axis, gray lines – on *Y* axis.

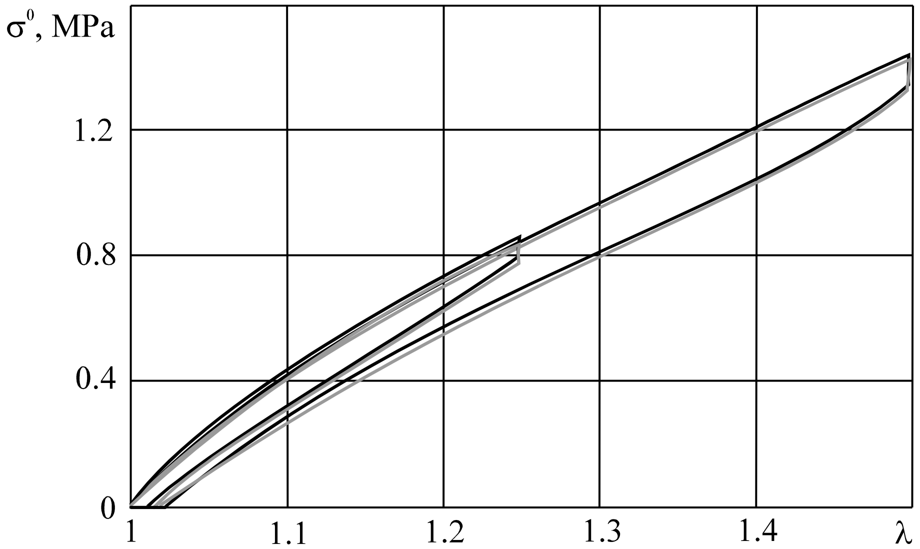


Fig. 5. Biaxial tests of SBR-1500 filled with nanoshungite (65 phr) black lines – loading on *X* axis, gray lines – on *Y* axis

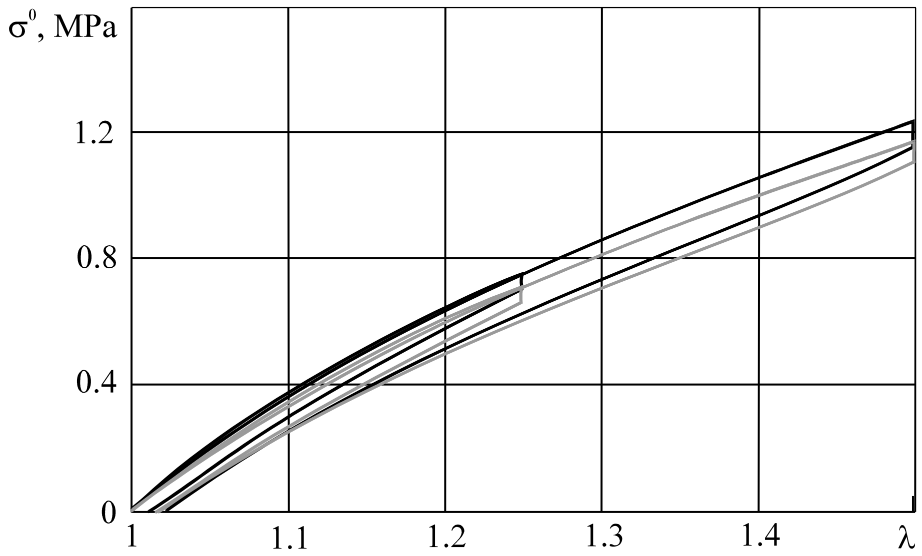


Fig. 6. Biaxial tests of SBR-1500 filled with microshungite (65 phr)
black lines – loading on *X* axis, gray lines – on *Y* axis

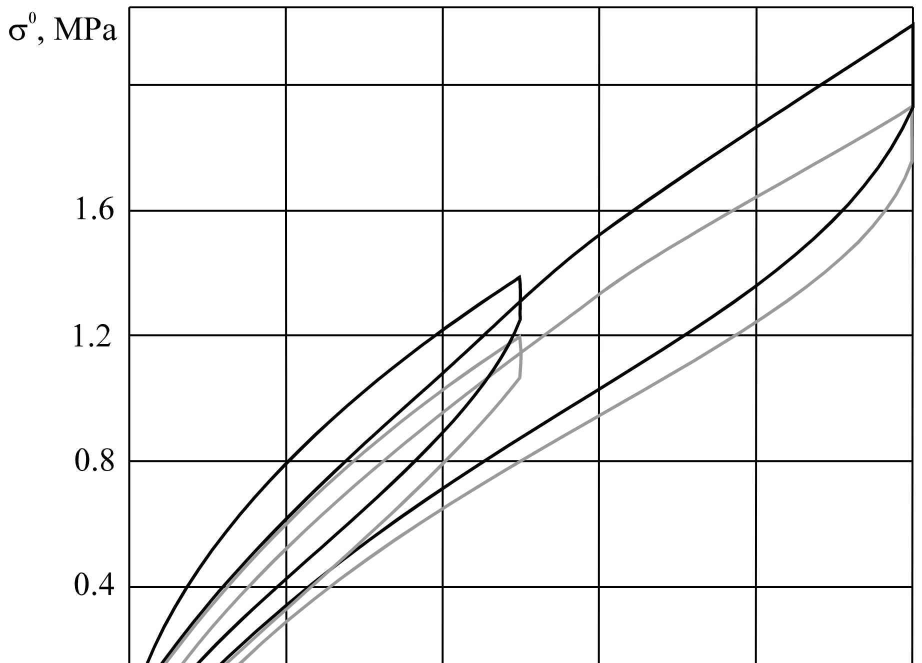


Fig. 7. Biaxial tests of SBR-1500 filled with white soot (65 phr)
black lines – loading on *X* axis, gray lines – on *Y* axis

The addition of diatomite sorbent (Fig. 8) also contributed to the material softening and growth of induced anisotropy. It was not as much as in the case of white soot, but more than microshungite. The hysteresis areas were approximately at the level of composites with nanoshungite and microshungite.

The results of biaxial tests for composites with RHW-filler (Fig. 9) were closest to the systems containing particles of diatomite sorbent. Although the RHW composite has dissipative losses, the Mullins effect and induced anisotropy manifested more strongly.

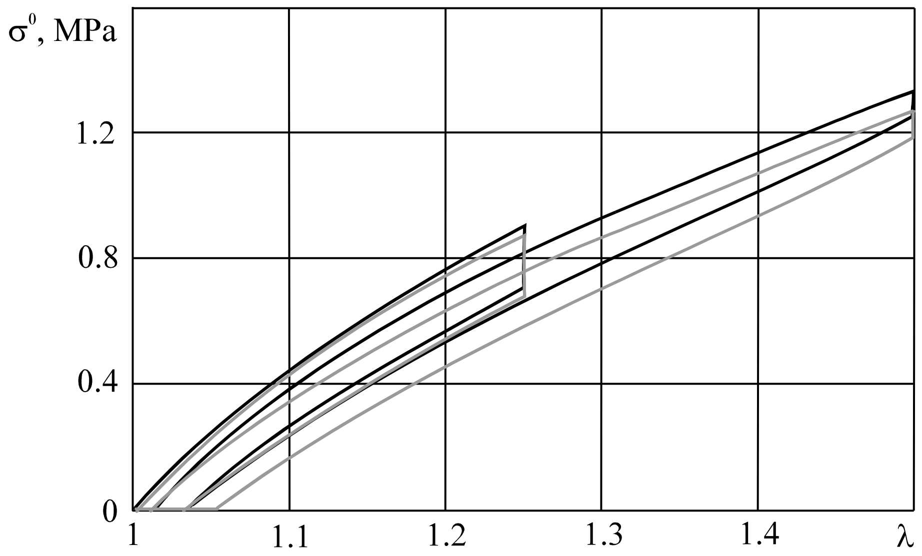


Fig. 8. Biaxial tests of SBR-1500 filled with diatomite sorbent (65 phr) black lines – loading on *X* axis, gray lines – on *Y* axis

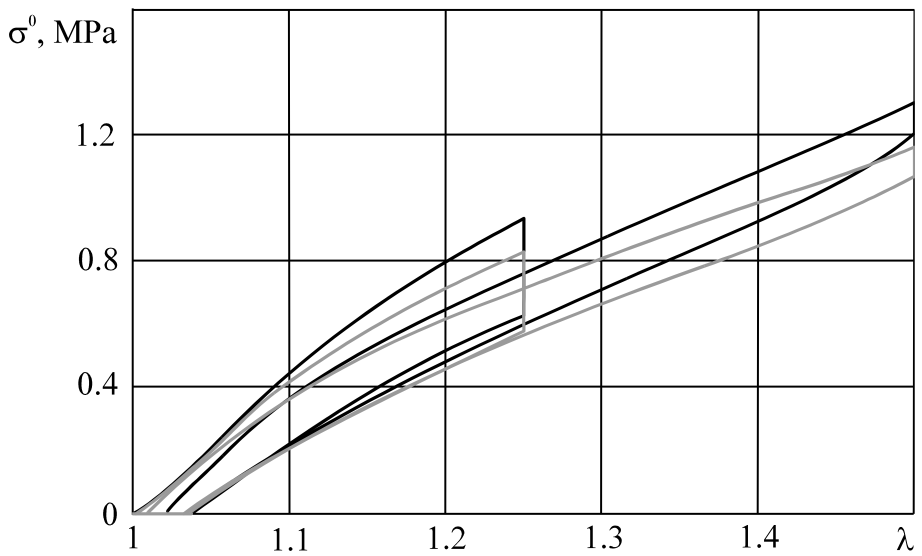


Fig. 9. Biaxial tests of SBR-1500 filled with RHB particles (65 phr) black lines – loading on *X* axis, gray lines – on *Y* axis

4. Conclusions

Experimental studies for rubber and five different fillers showed that the mechanical behavior of rubber (in pure state elastic and isotropic) can change significantly after the introduction of dispersed particles. These changes depend both on the type of filler and on the type of loading – uniaxial or biaxial.

Uniaxial tests evaluated the effects of different types of filler on the strength and rigidity of material. Biaxial tests showed that viscoelasticity developed in the filled systems. Processes occurred that contribute to material softening and the appearance of induced anisotropy of mechanical properties. The research made it possible to estimate the effect of the type of the filler on the development and depth of these processes for the "working" range of deformations usual for car tires.

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