Mechanical properties of filled elastomers subjected to alternate loading along two orthogonal axes

Vladimir V. Shadrin, Kseniya A. Mokhireva, Anton Yu. Beljaev,
Lyudmila A. Komar
shadrin@icmm.ru

Abstract

We present the results of an experimental study of the behavior of carbon black filled rubber and rubber with carbon nanofibers. Tests were carried out using a 4-vector test stand Zwick (biaxial testing machine), a uniaxial testing machine Testometric FS100kN CT and a dynamic mechanical analyzer DMA/SDTA861^{e}. Our investigations revealed the induced anisotropy of mechanical properties in the material with grain filler — stretching along one axis does not, in any way, affect mechanical properties along the other axis. It is shown that uniaxial stretching of an elastomer with nanofibers changes the structure and mechanical properties of the material in all directions.

Cyclic tests where tensile forces acted in two mutually perpendicular directions were performed to determine the influence of the type of filler on the mechanical properties of filled vulcanizates subjected to external forces. One vulcanizate was prepared by mixing methylstyrene and divinyl rubbers (85 parts by weight of rubber SKMS-30 ARK + 15 parts by weight of rubber SKD), and the other using butadiene-styrene rubber SBR1502. Elastomers were reinforced with different fillers. Carbon black was added to rubber mixture SKMS+SKD: 60 parts by weight of carbon black П514 and 5 parts by weight of carbon black П234 per 100 parts by weight of rubber. Rubber SBR1502 was reinforced by 30 parts by weight of carbon black N220 and 5 parts by weight of carbon nanofibers (CNFs).

1 Experimental study of induced anisotropy effect in elastomers with granular filler

The behavior of vulcanizates subjected to complex biaxial loading was investigated using a 4-vector test stand Zwick (biaxial testing machine), a uniaxial testing machine Testometric FS100kN CT and a dynamic mechanical analyzer DMA/SDTA861^{e}. Preliminary tests on rubbers stretched in two mutually perpendicular directions showed only slight difference in their properties.

Cross-shaped samples were manufactured for tests with a biaxial testing machine (Fig. 1). The working zone of the sample showed in Fig. 1 is a square with a side of 3 cm. The applied load is transferred through a loading tube of length 4.5 cm. To achieve loading uniformity in the central part and, as a consequence, heterogeneity of stress and strain fields, loading tubes are cut into stripes — strands. Hence, the area of uniform stress-strain state distribution covers 73% of the working zone [1].

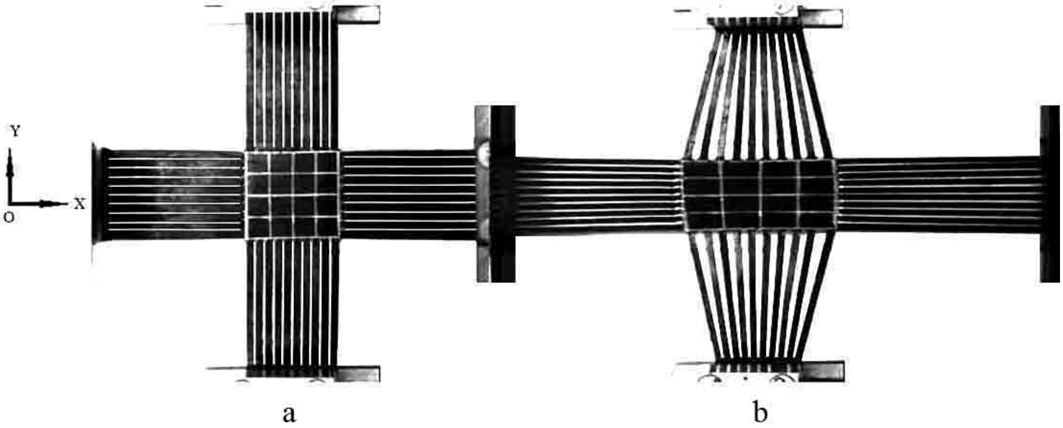


Figure 1: Shape of the cross-shaped sample subjected to cyclic loading along each axis using the biaxial test stand Zwick. The initial state of the sample (a); the sample extended along the 0X-axis (b)

It is known that in cyclic tests on filled elastomers the pronounced Mullins softening effect is observed immediately after the first loading cycle. In addition, elastomers exhibit a viscoelastic behavior that depends on the molecular and structural interfacial layers formed at the filler-matrix boundary [2]. Such a feature can be attributed, in our opinion, to the formation of strands in the case when long molecules are drawn from the polymer surface [3]. Experimental observations support this hypothesis. For example, it was shown that the softening of rubbers is mainly attributable to viscoelastic processes [4, 5]. At a 50% deformation of the sample no internal damages are accumulated in the material, and on unloading the inverse process (polymer molecules return back to their original state) takes place. At temperature of 60°C and over a 24-hour thermostatting period the sample recovers its original structure and properties completely. This process develops much more slowly than the slippage of these molecules off the surface of inclusions under stretching and is temperature dependent. At large deformations, simultaneously with the viscoelastic process, the damage accumulation process begins in rubber, and the stress-strain curve lies below the curve of the undamaged material [5].

Our tests on carbon black filled vulcanizate were performed according to the following scheme. Cross-shaped samples were stretched alternately along the two mutually perpendicular directions 0X and 0Y to elongate by a factor of two. The value of sample elongation was determined utilizing the grid lines given in white color (Fig. 1). Initially, the samples were stretched along the 0Y-axis, and the 0X-axis remained loading-free. To do this, we have developed a special program, where the load is applied along one of the axes, and the grips move along the other axis so that the load remains zero. Then the samples are aged for 7 minutes to achieve complete relaxation, unloaded to the primary position, and aged again for 7 minutes to complete the fast recovery of the material structure. Note that the structure recovery rate is temperature dependent, and therefore at room temperature the structure may not recover its original structure even in a year [5]. Such a sequence of loading-unloading along the 0Y-axis is repeated twice until the softening of the material was stabilized and the repeatability of its cyclic loading curves is achieved.

The same program has been realized along the 0X-axis. In this case, the 0Y-axis remains free of loading. Figure 2 presents the biaxial loading curves: the solid lines denote the behavior of the material in the 0Y-direction, and the dashed lines in the orthogonal 0X-direction.

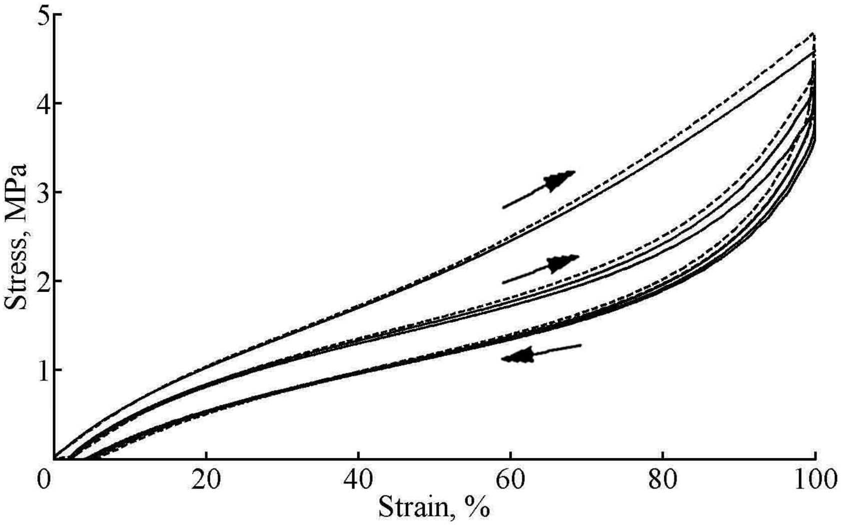


Figure 2: Loading curves for cross-shaped carbon black-filled vulcanizate samples obtained using the biaxial testing machine. Solid line — loading along the 0Y-axis, dashed line — loading along the orthogonal 0X-axis. The arrows show the direction of loading

Typically, during cyclic stretching of rubbers (beginning with the second cycle, the curves for loading along the 0Y-axis are, in fact, repeated), the sample becomes softer, and the hysteresis loss reduces. So, after the second cycle the properties of the sample in this direction are practically stabilized. The analysis of the curves for loading in the orthogonal 0X-direction indicates that the material behaves like it has never been loaded at all — no softening and changes associated with loading along the 0Y axis have been observed. A slight discrepancy between the curves for loading along the 0X- and 0Y-axes can be related to some initial anisotropy of the material caused by the production technique.

We performed analogous tests with the rest of cross-shaped carbon black-filled vulcanizate samples and obtained qualitatively similar results. This evidence led to the conclusion that the loading of the sample in one direction causes the orientation rearrangement of its structure in this direction only. In the orthogonal direction the sample continues to retain its original properties until it is subjected to loading in this direction. That is, being loaded along one direction, the material is solely softened along this direction. In the case of induced anisotropy, the material is softened because of its loading in one direction, which is referred to as the Mullins effect, but its mechanical properties do not change in any way in the perpendicular direction.

2 Investigation of mechanical behavior of nanofibers-filled elastomers in two orthogonal directions

A number of experiments have been carried out to study the behavior of the polymer reinforced by 30 parts by weight of carbon black and 5 parts by weight of carbon nanofibers. Firstly, a cyclic load was applied to a sample having the form of a rectangular plate of length 50.6 mm, thickness 2.18 mm and width 28 mm using the uniaxial Testometric FS100kN CT machine. After every loading cycle the sample was returned to its initial position and then aged for 10 minutes to complete rapid recovery of the structure (Fig. 4). As one can see, softening takes place along the loading axis. The material under study possesses some initial anisotropy of mechanical properties that is associated with the production technique (Fig. 3). This circumstance should be taken into account when analyzing the data obtained during the testing along two orthogonal axes. Secondly, samples in the form of rectangular strips of thickness 4 mm and length 28 mm were cut from the plate in two mutually perpendicular directions. The samples cut in the direction of initial stretching of the plate and after its ageing were called "longitudinal", and those cut in the orthogonal direction — "transverse". Tests on these samples were performed 24 hours after they were stretched in the longitudinal direction.

Some samples were subjected to cyclic loading using the uniaxial machine (Fig. 5), and the remaining ones were tested with the dynamic mechanical analyzer DMA/SDTA861^e (Fig. 6).

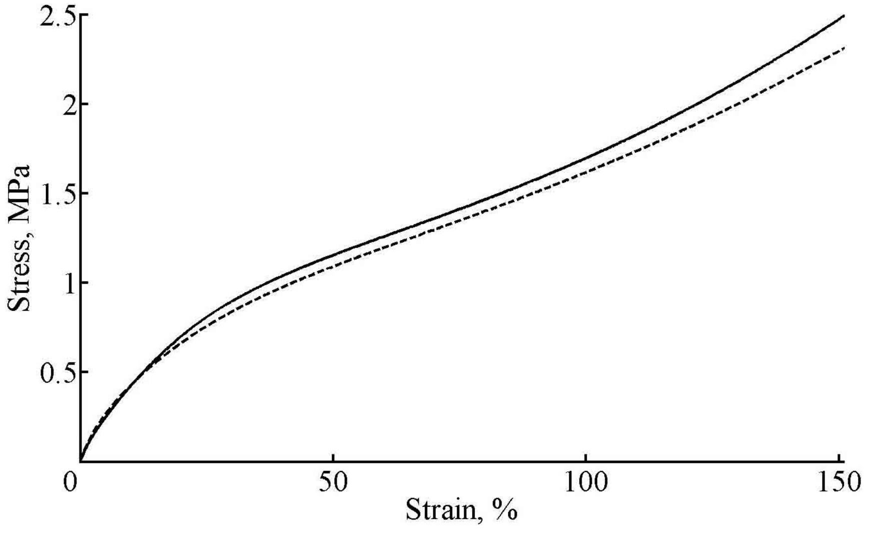


Figure 3: Initial anisotropy of the mechanical properties of the filled elastomeric material. The solid and dashed lines show stretching along two orthogonal directions

The experiments performed with the uniaxial machine indicate that the behavior of the fiber-filled rubber is different from that of the rubber with grain filler. Figure 5 shows that the preliminary ageing in the longitudinal direction causes the material to soften in all directions — longitudinal and transverse. When the initial anisotropy of the material is considered (Fig. 3), softening in the transverse direction corresponds to the same softening in the longitudinal, preliminary aged direction.

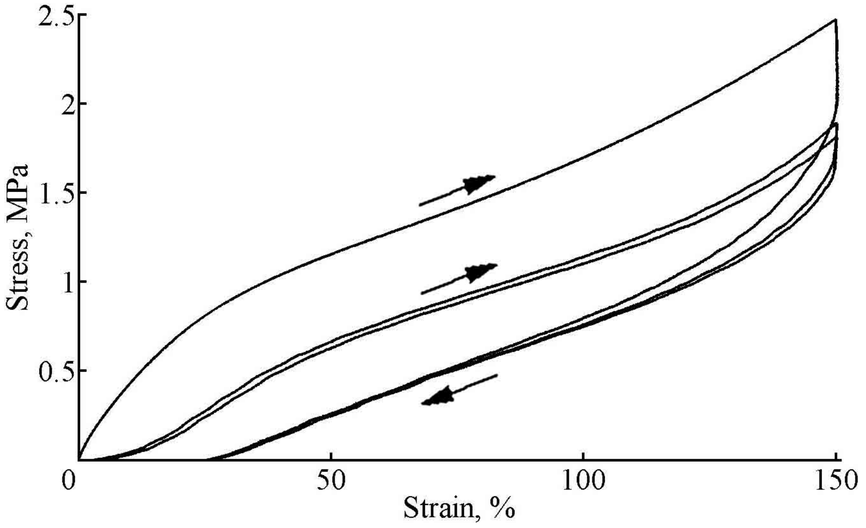


Figure 4: Curves for three cycles of loading of the rectangular plate tested on the uniaxial Testometric FS100kN CT machine. The arrows show the direction of loading

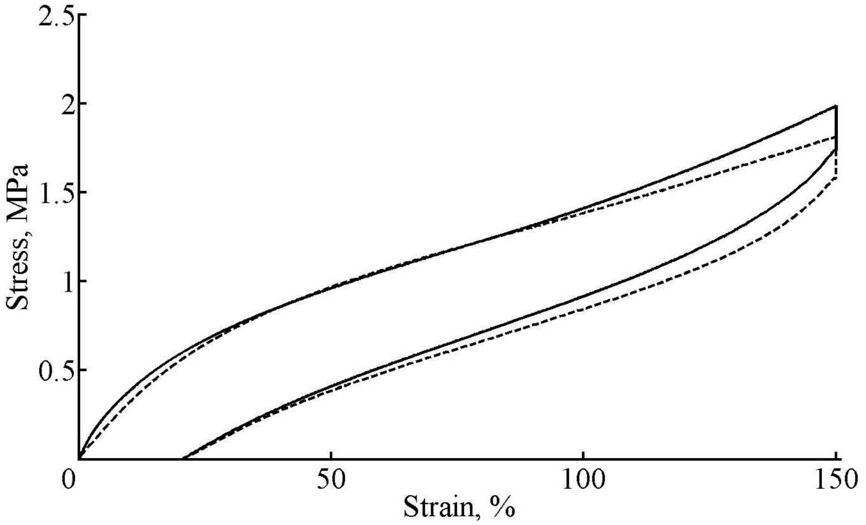
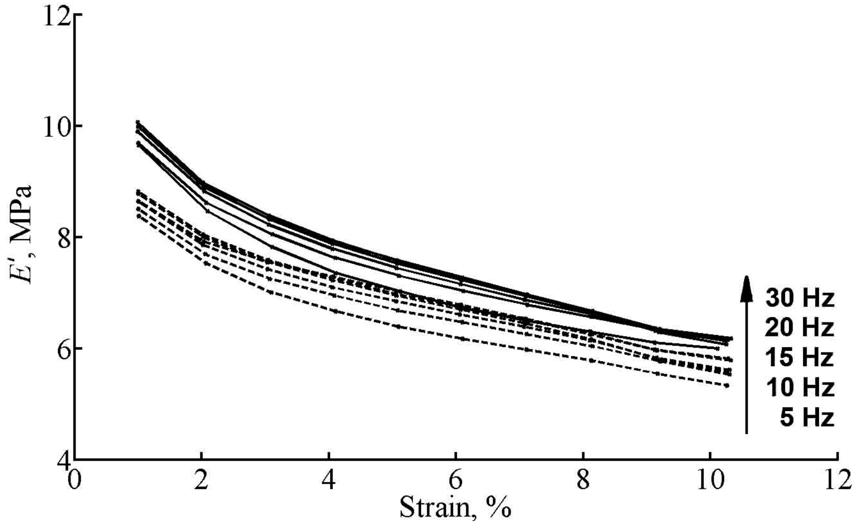


Figure 5: Cyclic testing of longitudinal and transverse samples using the uniaxial Testometric FS100kN CT testing machine. The solid lines show the behavior of longitudinal samples, and the dashed lines the behavior of transverse samples

A comparison of the curves of loading of the longitudinal and transverse samples (solid and dashed lines in Fig. 5) gives evidence that structural changes in the nanofiber filled elastomer under uniaxial deformation take place in all directions. Hence, the suggestion can be made that filler fibers subjected to stretching take a turn, and the long elastomeric molecules slide not only along the axis of elongation, but in the orthogonal direction as well.

Tests with the dynamic mechanical analyzer DMA/SDTA861^e were performed at oscillation frequency of 5, 10, 15, 20 and 30 Hz. This can be seen graphically in Fig. 6, where solid lines indicate the behavior of longitudinal samples, and dashed lines the behavior of transverse samples.



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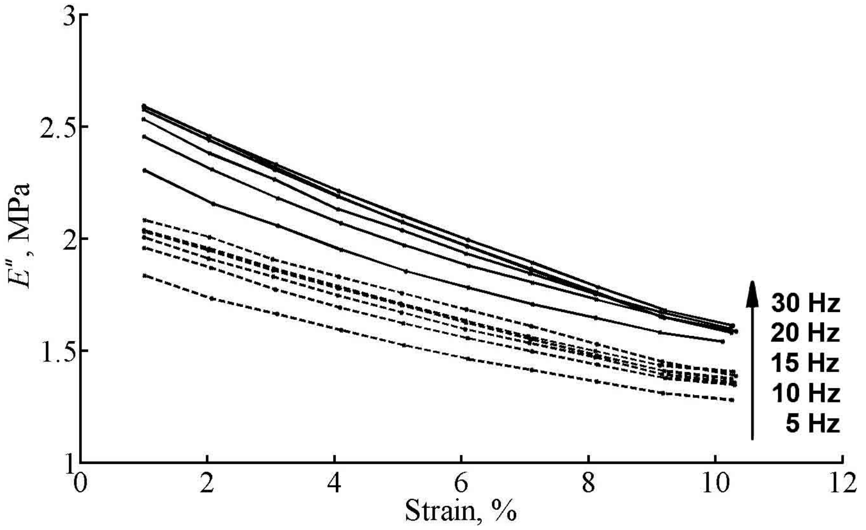

b

Figure 6: Dynamic characteristics of longitudinal and transverse samples obtained in tests with the dynamic mechanical analyzer DMA/SDTA861^e at oscillation frequencies of 5, 10, 15, 20 and 30 Hz; storage modulus E' (a), loss modulus E'' (b). The solid lines show the behavior of longitudinal samples, and the dashed lines — the behavior of transverse samples

During the uniaxial stretching tests it has been found that under small deformations (deformations measured by the DMA/SDTA861^e did not exceed 10%) the fiber filled elastomer exhibits strong softening. The storage modulus E' in the transverse direction turns out to be lower than that in the longitudinal direction (Fig. 6a). The softening of the material in the transverse direction appears to be stronger than in the longitudinal direction, and therefore the loss modulus E'' of the transverse sample is less than that of the longitudinal sample (Fig. 6b). Such a strong softening in the transverse direction can be attributed to the initial orientation of carbon fibers in the elastomeric material, i.e. to the initial anisotropy of the material observed at the stage of its production (Fig. 3). Examination of the properties of elastomers filled with carbon fibers should be extended to elucidate the physical mechanisms underlying structural rearrangements driven by stretching.

Conclusions

We have found that stretching of the elastomer with grain filler in one direction causes the induced anisotropy to appear in the material. The material softens along the extension axis, yet this softening does not, in any way, influence the structural rearrangement along the orthogonal elongation axis and change the mechanical properties of the material along the transverse axis.

When the elastomer with carbon nanofibers is loaded along one of its axis, the structural rearrangement and changes in mechanical properties occur in all directions. Additional studies need to be performed in order to investigate further the behavior of such materials.

Acknowledgements

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Vladimir V. Shadrin, Institute of Continuous Media Mechanics UB RAS, Perm, Russia, Perm State National Research University, Perm, Russia

Kseniya A. Mokhireva, Institute of Continuous Media Mechanics UB RAS, Perm, Russia

Anton Yu. Beljaev, Institute of Continuous Media Mechanics UB RAS, Perm, Russia, Perm State National Research University, Perm, Russia

Lyudmila A. Komar, Institute of Continuous Media Mechanics UB RAS, Perm, Russia