Anisotropic properties of styrene-butadiene rubber filled with single-wall nanotubes

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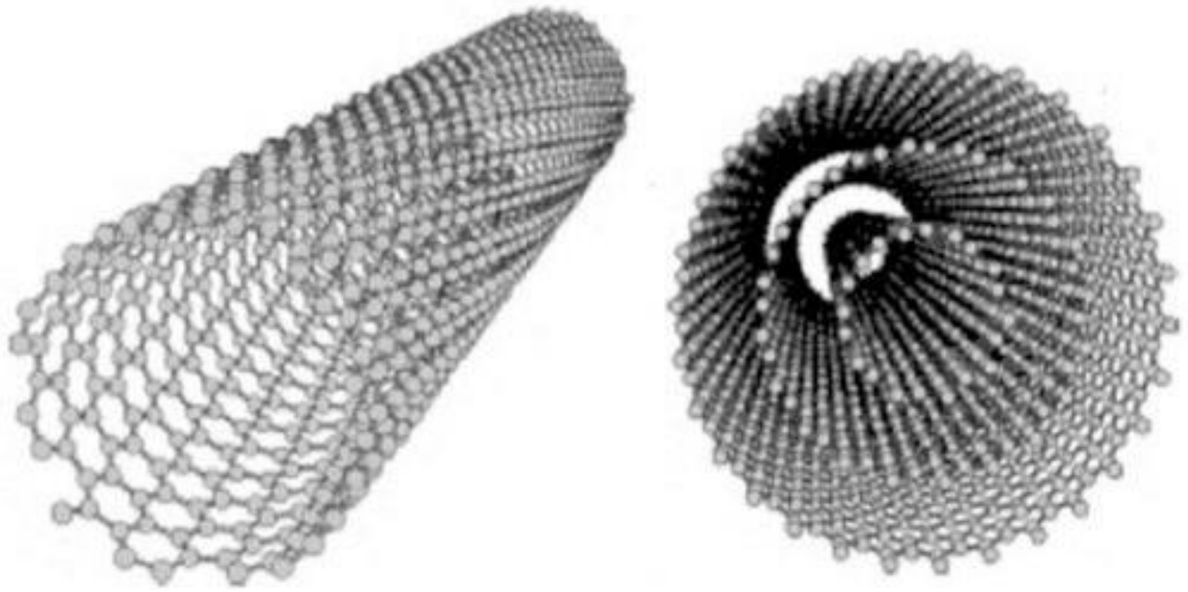
Introduction

The discovery that the addition of carbon black to rubber gum significantly changes the mechanical properties of the material gave impetus to the study of elastomeric composites. Over the years many studies have been carried out on various fillers, ranging from classic carbon black to various fillers of mineral origin. With the discovery of various nanocarbons (graphene, fullerenes, carbon nanotubes, etc.), the question about their usage as fillers for polymer composites was posed.

Special attention should be paid to the usage of nanotubes. Due to the fact that one linear particle size of such filler significantly exceeds the other two, this can significantly change the mechanical behavior of the material in comparison with granular fillers. One of the interesting properties of composites with carbon nanotubes is anisotropy. In this case, the induced anisotropy is a consequence of the milling.

A significant problem, that complicates the usage of nanotubes as filler in industry, is the complexity and high cost of manufacturing. Therefore it is of interest to study TUBALL ™ nanotubes, the production of which has already been launched on an industrial scale by OCSiAl, as filler for elastomeric materials. These are single-walled nanotubes (SWCNT) with a length of about 5 μm.

This work is devoted to the study of elastomeric nanocomposites with styrene-butadiene (SBR) matrix, where SWCNT TUBALL ™ are used as filler.

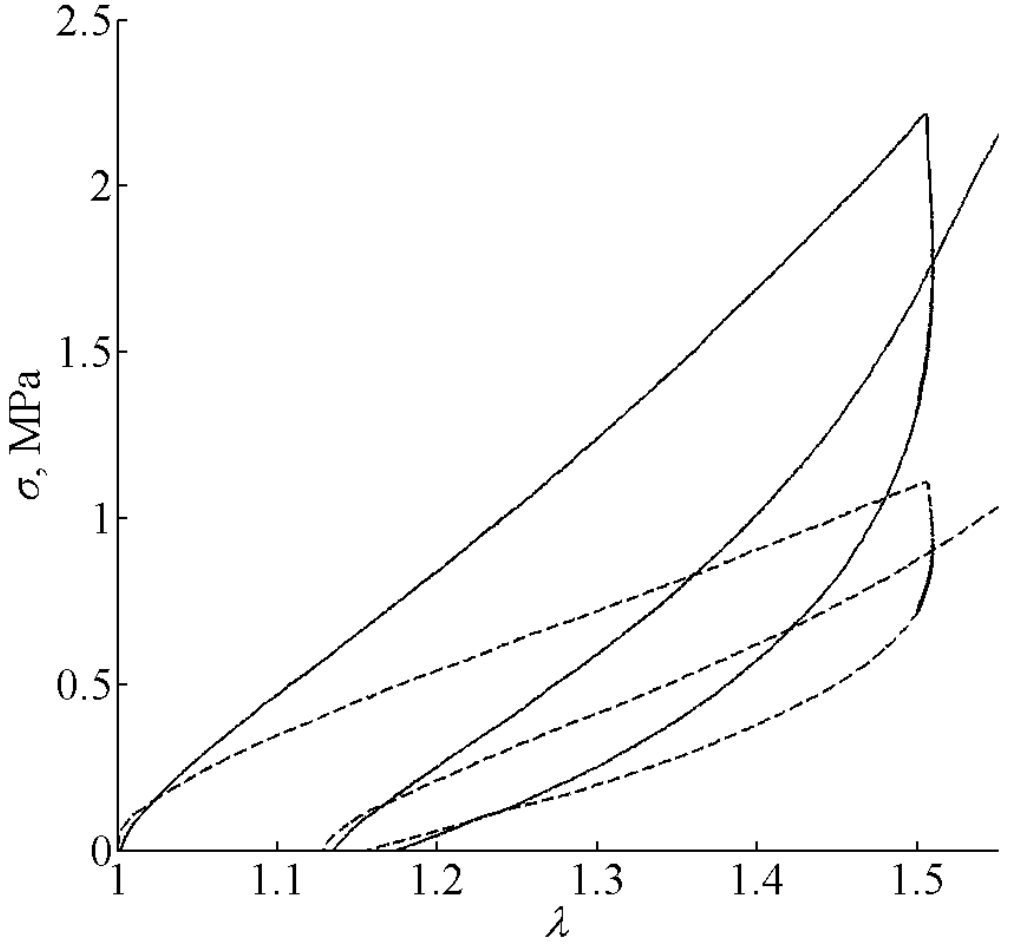


Materials and methods

The objects of research are elastomeric composites based on SBR-1705 HI-AR. Purification of TUBALL ™ nanotubes from impurities of amorphous carbon and metal-catalysts was carried out at Federal State Unitary Enterprise S.V. Lebedev Institute of synthetic rubber by the method of self-propagating high-temperature synthesis. Filler, used for comparison, was Carbon Black N-330.

The most interesting effects from the usage of nanotubes are significant increase of the rigidity of the material when a relatively small amount of nanotubes is introduced into the elastomer and the material acquires anisotropic properties. The passage of the material through the rollers, in a process of milling, affects the preferred orientation of nanotubes. As a result material anisotropy appears. In accordance with this fact samples were cut in two directions for each material. This is the direction of the last passage of the material through the rollers and the direction perpendicular to it.

Results and discussion



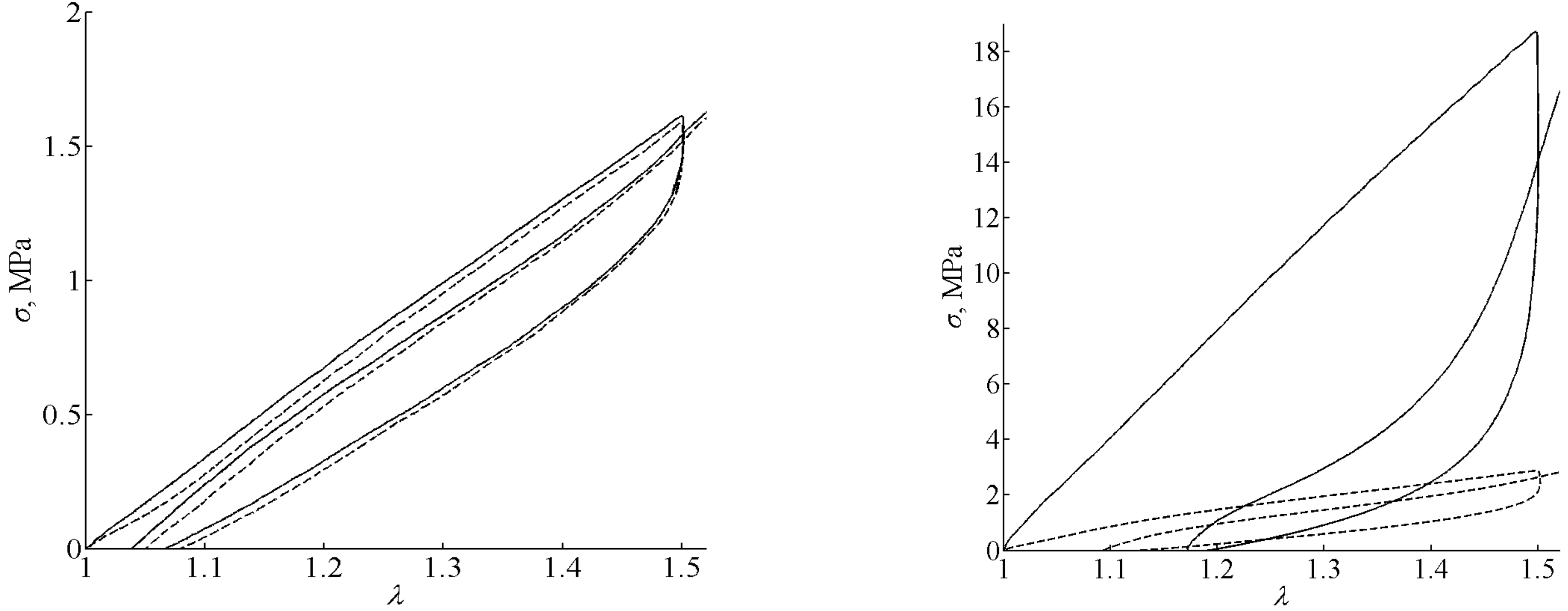
Test results of an elastomeric nanocomposite based on 7 mph SWCNT filling. The solid line the sample is cut along the direction of rolling, the dotted line – across

- Sample, cut in the rolling direction, is approximately 2 times more rigid than in the perpendicular direction.
- Residual strains after unloading are about 17-18%, which is a lot in order to use this nanocomposite as a construction material.
- The strong softening effect of the material indicates damage appearing during the first deformation.

This effect is probably connected with movements of the nanotubes relative to each other, which lead to the appearance of ruptures in the elastomeric binder.

The way to reduce the damage of the nanocomposite upon deformation?
Combination of different fillers?

Results and discussion



a b

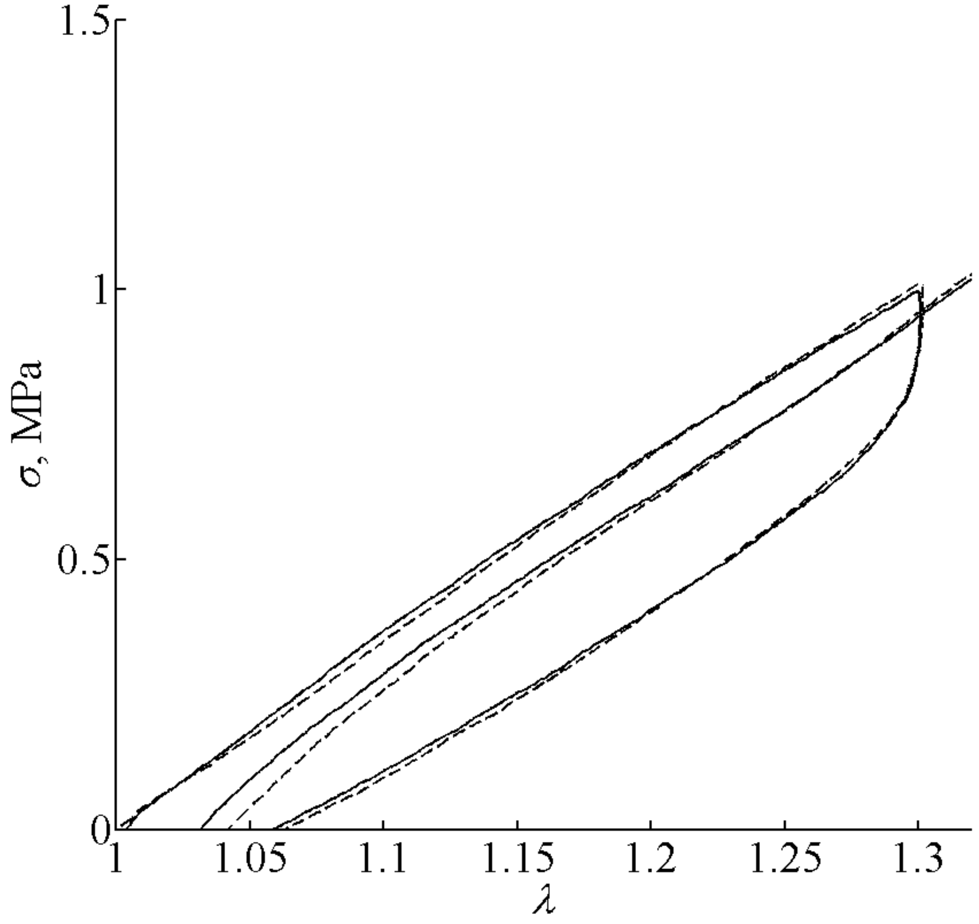
Test results of an elastomeric nanocomposite based on BSK with fillings: a - 50 mph of carbon black; b - 7 mph of SWCNT and 43 mph of carbon black at the maximum elongation ratio $\lambda = 1.5$. The solid line corresponds to the sample cut along the rolling direction, the dotted line – across

Results and discussion

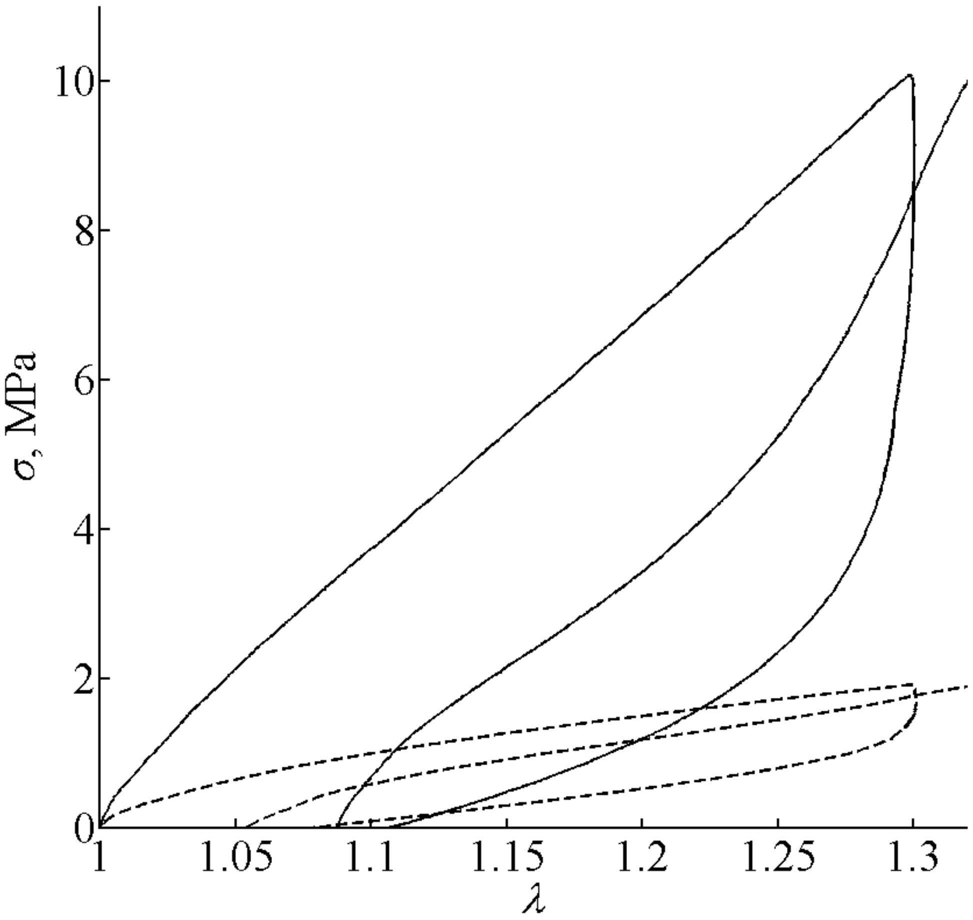
Replacing part of the carbon black with SWCNT leads to significant material properties changing. Figure 2b shows the experimental results for a material containing 43 mph of carbon black and 7 mph of SWCNT. The material has become anisotropic and its rigidity (especially in the direction of the preferred orientation of nanotubes) has increased. The effect of significant softening and growth of permanent deformations still occurs in the material with SWCNT. Residual strains after unloading of SBR filled with carbon black are about 10% while in the material with the addition of SWCNT they are about 30% in the direction of rolling and 15% in the perpendicular direction. Value of λ at break for the composite with carbon black is about 6.2. For the composite with the addition of SWCNT the λ value at break is about 4.5 in the rolling direction and 2.5 in the transverse direction respectively.

<u>Taking into account that composite operate under conditions with lower deformations in real constructions, it made sense to see how the test results would change with a decrease of the maximum elongation ratio in the considered deformation cycle.</u>

Results and discussion



a



b

Test results of an elastomeric nanocomposite based on BSK with fillings: a - 50 mph of carbon black; b - 7 mph of SWCNT and 43 mph of carbon black at the maximum elongation ratio $\lambda = 1.3$. The solid line corresponds to the sample cut along the rolling direction, the dotted line – across

Conclusion

Studies of the mechanical behavior of elastomeric composites based on SBR-1705 HI-AR with the addition of TUBALL ™ nanotubes have shown that even a small filling of SWCNT leads to a noticeable change in the mechanical characteristics of the material. Anisotropic properties, determined by the direction of the last passage of the material between the rollers, are formed during the milling process. This can be valuable in the manufacture of products with the desired anisotropy of individual parts of the construction.

The addition of TUBALL ™ SWCNT to the SBR leads to a pronounced manifestation of the effect of material softening during the first deformation (Mullins effect) and an increase in residual strains. However, in the case when material is operated in the area of deformations not exceeding 30%, the effect of accumulation of residual strains can be acceptable for many applications.

Thank you for attention!