Materials Physics and Mechanics. 2022;50(3): 495-508
Research article
http://dx.doi.org/10.18149/MPM.5032022_12

Submitted: July 29, 2022
Approved: October 11, 2022
Accepted: November 10, 2022

Anisotropic mechanical properties of elastomeric nanocomposites filled by carbon black, few-layer graphene, and carbon nanotubes

O.K. Garishin[1]✉, A.L. Svistkov[1], A.P. Voznyakovskii[2], I.M. Tchypkina[2],
A.Yu. Neverovskaya[2], V.V. Shadrin[1]

[1]Institute of Continuous Media Mechanics of the Ural Branch of Russian Academy of Science, 1, Academician Korolev Street, Perm, Russia, 613013

[2]Federal unitary state enterprise "Lebedev Research Institute for Synthetic Rubber", 1, Gapsal'skaya St., St. Petersburg, Russia, 198035

✉ gar@icmm.ru

Abstract. The mechanical properties of nanocomposites based on styrene-butadiene rubber with fillers of carbon black, few-layer graphene and single-walled and multi-walled carbon nanotubes have been studied. Carbon nanotubes were subjected to preliminary purification according to a special technology developed by the authors using self-propagating high-temperature synthesis. It has been established that in elastomers filled with single-walled carbon nanotubes, the anisotropy of mechanical properties may appear, which is expressed in a significant increase of material rigidity and growth of dissipative tensile losses in the direction corresponding to the movement of vulcanized rubber compound during rolling. This effect was absent in composites filled with carbon black and few-layer graphene.

Keywords: styrene-butadiene rubber, few-layer graphene, single-walled and multi-walled carbon nanotubes, SHS purification of carbon nanotubes, cyclic loading, viscoelasticity, anisotropy of mechanical properties

Acknowledgements. *Regional Grant of RFBR and Perm Territory, project number 20-48-596013.*

Citation: Garishin OK, Svistkov AL, Voznyakovskii AP, Tchypkina IM, Neverovskaya AYu, Shadrin VV. Anisotropic mechanical properties of elastomeric nanocomposites filled by carbon black, few-layer graphene, and carbon nanotubes. *Materials Physics and Mechanics*. 2022;50(3):495-508. DOI: 10.18149/MPM.5032022_12.

1. Introduction

In recent decades, the use of nanosized fillers in elastomeric composites has become increasingly widespread in various industries, successfully competing with traditionally used materials [1,2].

Historically, one of the first, and still the most common nanofillers is carbon black (CB). The addition of CB into an elastomer significantly improves its mechanical characteristics (especially strength and deformability) [3-6]. Its particles are globules (3D filler) consisting of degraded graphite structures. These globules can form strong associations of several dozen particles ranging in size from 13 to 350 nm, and these, in turn, stick together into even larger, but much less durable agglomerates with sizes up to a micron. That is, these

Publisher: Peter the Great St. Petersburg Polytechnic University

are structures that are very complex in their morphology. Today, CB is more often used not in pure form but in conjunction with other fillers [7-12].

The effects of carbon black used in elastomeric composites are well studied, and further progress requires the search for new non-traditional types of fillers. One of the promising directions is the use of carbon in other allotropic states. These are mainly detonation nanodiamonds, graphene, and its oxides, as well as carbon nanotubes.

Detonation nanodiamonds (3D filler) are synthesized by the explosive decomposition of powerful mixed explosives with a negative oxygen balance in a non-oxidizing environment. Such explosive compositions are both a source of energy and carbon. Detonation nanodiamonds combine nanosize (4-6 nm), chemical resistance of the core, and chemical activity of the peripheral shell. These fillers are currently widely used in the production of filled elastomers [13-16].

Graphene particles are 2D plates made of one or more layers of this material. According to its structure, graphene is a two-dimensional crystal consisting of a single layer of carbon atoms assembled into a hexagonal lattice. Graphene filler, as well as its oxides [11,17], are widely used in the production of elastomeric composites, both in pure form and together with other fillers [13,16,18-20].

Carbon nanotubes (it would be more correct to call them graphene nanotubes) are 1D filler in the form of randomly oriented flexible fibers from 2D single-crystal graphene plates "rolled into a tube" [21,22]. Depending on the synthesis technology, both single-walled (SWCNT) [23-25] and multi-walled carbon nanotubes (MWCNT) can be obtained – several SWCNTs (usually 15-20) inserted one into the other) [26-31]. It is still impossible to justify which type of nanotubes will be preferable for use as fillers in elastomers. Until recently, the advantage of MWNTs was a good development of the technology of their synthesis and, accordingly, unlike SWNTs, an acceptable price for real application. However, the development in 2013 by the firm "OCSiAl" (Novosibirsk, Russia) of a high-performance technology for the synthesis of single-walled carbon nanotubes largely leveled this shortcoming.

Quite often, nanotubes are used as a second filler [11,12,32-35]. Also, [36] described the combined use of a mixture of SWCNTs and MWCNTs in silicone elastomers.

Elastomeric nanocomposites are the subject of intensive fundamental and applied research both at the structural and macro levels today. In experimental studies of the internal structure of polymer nanocomposites, both electronic (scanning – SEM, transmission – TEM) [37-39] and atomic force microscopes (AFM) [37,41] are widely used, and quite often they are used together. The inner structure geometry is studied with the help of electron microscopy, and atomic force microscopes make it possible to obtain additional information about the "local" physical and mechanical properties of the material at the microlevel (which can differ very significantly from the macroscopic ones [42]).

At the macro level, elastomeric nanocomposites exhibit complex mechanical behavior. They are able to withstand significant deformations (up to hundreds of percent) without loss of performance, and can demonstrate elastic, viscous, and plastic properties. Therefore, in experimental studies of these materials, in addition to standard monotonic tension-compression tests, special methods with complex loading trajectories are often used. As usual, they are based on the cyclic deformation of samples with a variable amplitude over deformations and periodic stops to reveal relaxation processes and creep [10,13,43-51]. Such an approach, which makes it possible to obtain complex data on the viscoelastic and elastoplastic properties of a material in one test, was used in the experiments presented in this study.

The article describes the technology for producing elastomeric composites with carbon black fillers, as well as single-walled and multi-walled carbon nanotubes. Its novelty lies in the method proposed by the authors for the purification of nanotubes from harmful impurities by the method of self-propagating high-temperature synthesis (SHS). Chemical reactions under the conditions of the SHS process proceed according to a specific mechanism of non-isothermal branched-chain processes, which are characterized by the combined action of two fundamentally different factors accelerating the process - avalanche multiplication of active intermediate particles and self-heating. Branched-chain ignition, in contrast to thermal one, is caused by an avalanche multiplication of active intermediate products – free atoms, radicals, and sometimes also excited particles – in their rapid reactions with the initial reagents and among themselves. Physically, SHS is a process of moving a wave of a strongly exothermic reaction through a mixture of reactants (oxidizing agent and reducing agent), in which heat release is localized in a layer and is transferred from layer to layer by heat transfer. The SHS version we use refers to the "solid-gas" systems, that is, the active component of the process is not the oxidizer itself, but the gaseous products of its thermal decomposition. This dramatically reduces the requirements for reactors, both in terms of design and thermal stability. To date, the most common method of such purification is oxidation with strong acids [52-55]. In this case, the impact of aggressive oxidizing media on SWCNTs and MWCNTs often leads to both an increase in the number of structural defects and the disintegration of the tubes themselves. It is also impossible not to take into account the inconsistency of such a technique with modern stringent environmental requirements – the formation of a significant amount of acid effluents, the disposal of which is a separate task.

The approach proposed, based on the use of self-propagating high-temperature synthesis (SHS) in the production of elastomeric nanocomposites with fillers from single-walled and multi-walled carbon nanotubes in combination with carbon black (or few-layer graphene), is largely free from these disadvantages, which makes it rather promising.

It is established that the resulting composite samples are significantly anisotropic in terms of viscoelastic properties. This effect was studied in detail in this article using specially developed by us techniques of mechanical testing.

2. Materials, equipment, and experimental technique

Materials. The main object of research was elastomeric nanocomposites containing carbon black or few-layer graphene and combinations of these fillers with single-walled and multi-walled carbon nanotubes.

A styrene-butadiene rubber SBR-1500 (Russian analog is SKMS-30ARKM-15) was chosen as a binder (matrix). It is a well-known elastomer that is commercially produced. For example, it is, widely used in car tires and various rubber shock absorbers (i.e., in rather complex and difficult operating conditions).

Industrial carbon black of the N-330 grade with a particle size of 28-36 nm and a specific surface area of 82 m^2/g was taken as 3D filler.

A few-layer graphene (FLG) was applied as the 2D filler. It was manufactured according to the original method developed by the authors from NIISK [56]. The method is based on the SHS synthesis of graphene nanostructures from hydrolytic lignin, a natural biopolymer that is a waste product of the woodworking industry. The characteristic particle size of few-layer graphene was about 100-300 nm, and the specific surface area was 499 m^2/g.

Two types of carbon nanotubes were used as a 1D filler: single-walled TUBALL (manufactured by OCSiAl) and multi-walled (manufactured at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Both manufacturers are from Novosibirsk, that is, these are domestic developments. The characteristic dimensions of SWCNT and MWCNT (according to the manufacturer data) are presented in Table 1 (d is the nanotube diameter, L – its length, S – its specific surface area).

Table 1. Characteristic dimensions of single-walled and multi-walled carbon nanotubes

Filler	*d*, nm	*L*, μm	*S*, m^2/g	Nested layers (walls) number
SWCNT	1.6±0.4	> 5	500–1000	1
MWCNT	10–12	30–40	260±15	5–15

Purification of carbon nanotubes. It should be noted that carbon nanotubes contain rather significant amounts of amorphous carbon and undesirable inorganic impurities (mainly metallic) formed during the technological process. For example, according to the information provided by OCSiAl, the mass fraction of SWCNTs in dry powder was only 75%-wt. The rest accounted for inorganic impurities (9%-wt.) and carbon of unknown structure (16%-wt.). For MWCNTs, the situation with impurities was approximately similar. Therefore, it is necessary to somehow remove these impurities for further practical application of carbon nanotubes as composite fillers.

The method developed by the authors from NIISK for the purification of carbon nanotubes using self-propagating high-temperature synthesis (SHS) is largely devoid of the disadvantages inherent in more conventional methods based on the use of strong acids. This approach involves simultaneous exposure of nanotubes to extremely high temperatures generated by the SHS process in an aggressive oxidizing environment [24]. With this treatment, amorphous carbon passes into the gas phase and is removed from the reaction zone, while metal impurities are converted into nitrate salts (water-soluble form) and washed with water.

The purification process began with the addition of crushed ammonium nitrate in a ratio of 1/1 to a sample of the initial nanotubes. NH_4NO_3 plays the role of a precursor that generates powerful oxidizing agents upon thermal degradation. Thus, under conditions of rapid heating to a temperature of (220±10)°C, ammonium nitrate decomposes into highly active atomic nitrogen, oxygen, and water. The reaction products may also contain a trace amount of NO_2 and NO.

The mixture obtained after stirring was transferred into a heat-resistant vessel and placed in a bath preheated to 220°C. The passage of the SHS process reaction was judged by the power of gas evolution. After the onset of intense gas formation, the heating was turned off, and the reaction continued in an autonomous mode. The SHS process was considered completed when the evolution of gases from the heated mixture completely stopped. Next, the resulting powder was washed with distilled water and dried in a thermostat to constant weight.

Figures 1(a) (scale size 5 μm) and 1(b) (scale size 1 μm) show images of dry SWCNT powder taken by scanning and transmission electron microscopy before (SEM) and after (TEM) SHS purification, respectively.

A visual analysis of these pictures showed that the SHS method, although it does not allow the complete destruction of SWCNT aggregates to the level of individual nanotubes, still significantly increases the dispersity of SWCNTs compared to that obtained using the "OCSiAl" technology.

Figure 2 shows micrographs of dry MWCNT powder after cleaning by the SHS method, taken using a transmission electron microscope with different resolutions. The frame size in Fig. 2(a) is 500 nm, in Fig. 2(b) – 100 nm, and in Fig. 2(c) – 10 nm. It can be seen from them that the multi-walled carbon nanotubes after cleaning are quite well dispersed over the volume of the powder.

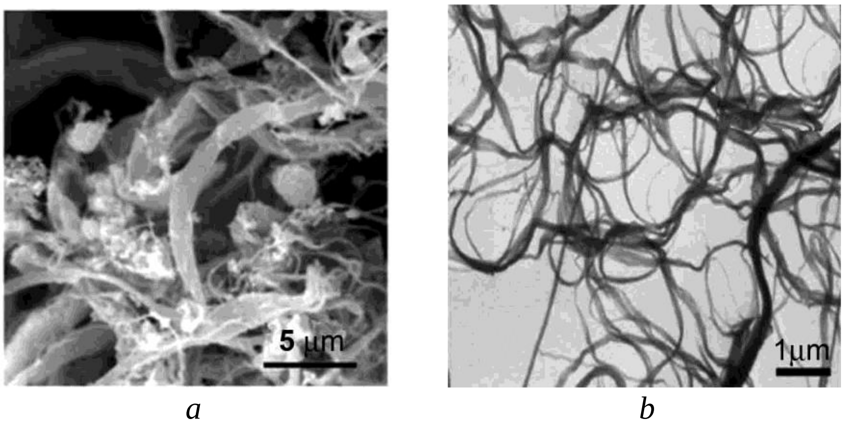

Fig. 1. Electron micrographs of the initial dry SWCNT powder (SEM) (*a*) and purified by the SHS method (TEM) (*b*)

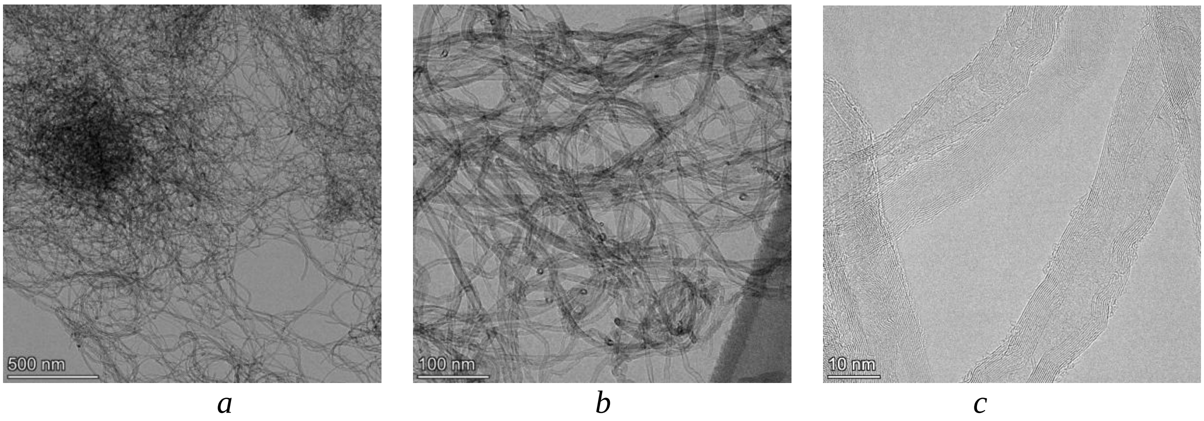

Fig. 2. Micrographs of purified MWCNT powder taken with a transmission electron microscope. Frame size: *a* – 500 nm, *b* – 100 nm, *c* – 10 nm

These microphotographs were taken on a Supra55VP scanning microscope (Carl Zeiss Group, Germany) and a Tesla BS-500 transmission electron microscope (Tesla, Czech Republic).

Composites manufacturing. A standard rubber formulation based on styrene-butadiene rubber was used to obtain composite materials. The composition of the standard rubber compound included (phr – parts per hundred of rubber): rubber (100 phr), zinc oxide (3 phr), N-tert-butyl-2-benzothiazolylsulfenamide (1 phr), sulfur (1.75 phr), stearic acid (1 phr) and carbon black grade N-330 (50 phr). Rubber compounds containing nanocarbons were produced on rubber processing rollers. The mass fraction of CB decreased by the corresponding value with the addition of MWCNTs or SWCNTs. The addition of nanotubes was carried out first of all before all technological additives for the purpose of more efficient interaction of nanocarbon with the polymer matrix. The vulcanization process was carried out at 145°C for 35 minutes in a vulcanizing press.

The production of rubber mixtures was carried out on laboratory rollers LB 320160/160; Mooney viscosity was determined on the MV-2000 viscometer manufactured by Alfa Technology.

Equipment and technique of mechanical experiments. A Zwick/Roell (Germany) four-vector biaxial test bench was used for mechanical testing. It also includes a video extensometer that can non-contactly measure displacements between any selected points on the sample surface. The experimental samples had a blade shape, corresponding to the international standard ISO 527-2 5A. The dimensions of the working part were 20×4×2 mm.

The same program of cyclic tests with increasing amplitude over deformations was used for all samples. It consisted of five cycles, on each of which the following actions were carried out:

1) stretching at a constant rate of 25%/min. up to the value of deformation ε_n (n=1÷5) specified for the given n-th cycle;

2) stop for 10 minutes (to relieve stress);

3) unloading at a constant rate of 25%/min. until the applied load is completely removed;

4) again stop for 10 minutes (check for residual deformations).

The deformation amplitude increased by 10% at each subsequent cycle, respectively, and the cycle maximum extension ratio of sample λ_n ($\lambda_n=1+\varepsilon_n$) was 1.10, 1.20, 1.30, 1.40, and 1.50.

3. Experiment and results discussion

Before carrying out mechanical tests of rubbers based on composite samples, the rheometric parameters of their unvulcanized mixtures were studied. SWCNTs (only purified), MWNTs (purified and unpurified), and carbon black were used for filling. The choice of only purified SWCNTs for experiments is associated with a large number of variable valence metals in their composition, which negatively affects the thermomechanical stability of rubbers. The analysis of publications available to date has shown that such studies of the rheological properties of unvulcanized composite mixtures containing purified or unpurified carbon nanotubes have not yet been carried out by anyone.

Figure 3 shows the dependences of the torque moment [57] on the vulcanization time, obtained on a non-rotor rheometer.

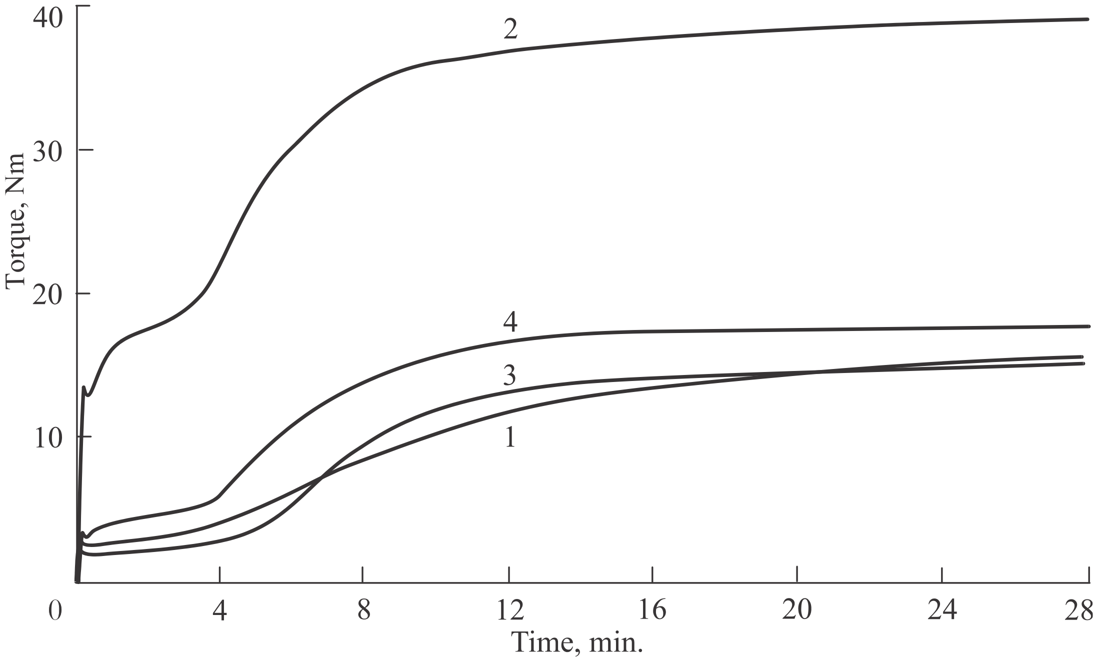

Fig. 3. Kinetics of isothermal vulcanization of rubber mixtures filled with SWCNT, MWCNT, and CB: 1 – 50 phr CB; 2 – 43 phr CB + 7 phr purified SWNTs; 3 – 43 phr CB + 7 phr original MWCNTs; 4 – 43 phr CB + 7 phr purified MWCNTs

It has been found that purification of all types of nanotubes shortens the induction period of vulcanization. It can be assumed that the process of purification and activation of nanotubes affects the efficiency of interaction between the nanotube surface and the binder. So, if the input of unpurified MWCNTs (curve 3 in Fig. 3) has practically no effect on the vulcanization process in comparison with SBR-1500 filled with only CB (curve 1), then the use of purified MWCNTs gives a fairly noticeable increase in torque, i.e., the mixture viscosity growth. A particularly strong effect of increasing the viscosity of the rubber mixture was observed for purified SWNTs (curve 2). In this case, the torque increased by more than 2.5 times. It can be assumed that such a strong effect is associated with the activation of SWCNTs, namely, with the removal of decorating unstructured impurities from their surface.

A significant increase in the viscosity of the rubber mixture containing purified SWCNTs (curve 2 in Fig. 3) indicates a significant rearrangement of its internal structure under the action of a shear flow initiated in a non-rotor rheometer. As a result, long and flexible SWNTs are reoriented in the corresponding direction, which is confirmed by the viscosity indices of these composites (Table 2).

Table 2. Viscosity values (Mooney viscosity) of composite mixtures

	50 phr CB	43 phr CB + 7 phr purified SWNT	43 phr CB + 7 phr original MWCNT	43 phr CB + 7 phr purified MWCNT
Mooney viscosity	61.4	219.0	78.1	87.2

However, such processes should be accompanied by the appearance of anisotropy of mechanical properties (along and across the shear). Similar phenomena can also occur in the manufacture of elastomeric composites after processing on a roller. That is, there is a technological possibility of creating composite materials with a given anisotropy of mechanical properties. To test this hypothesis, the following experimental studies were carried out.

In accordance with the technology described in the previous section, composite materials for mechanical testing were obtained in the form of rectangular plates with a thickness of about 2 mm. The sides of the plates were oriented along and across the direction of their rolling during manufacture. Accordingly, the blade samples for each of the studied materials were cut in two mutually perpendicular directions parallel to the sides of the original plate, that is, so that the expected anisotropy of mechanical properties would manifest itself to the maximum.

Since the main goal of the work was to study precisely the anisotropic properties of elastomeric nanocomposites depending on the type of filler, and not its limiting characteristics, the maximum stretching deformation of samples was limited to 50%. That is, the loading range most typical for the operation of these materials was considered.

The test results are depicted in Figs. 4-7. The ordinate shows the nominal stress σ (the force related to the initial cross-sectional area of the sample working part), and the abscissa shows the extension ratio λ (the ratio of the length of the deformed sample to the original length). The dashed lines correspond to samples cut along the rolling direction (further, for convenience, we will call them "longitudinal"), and the solid lines correspond to samples cut across the rolling ("transverse").

Figure 4 shows the results of cyclic tests for SBR-1500 filled only with carbon black (50 phr). The deformation curves under loading along and across the rolling direction practically coincided, that is, this material can be considered isotropic.

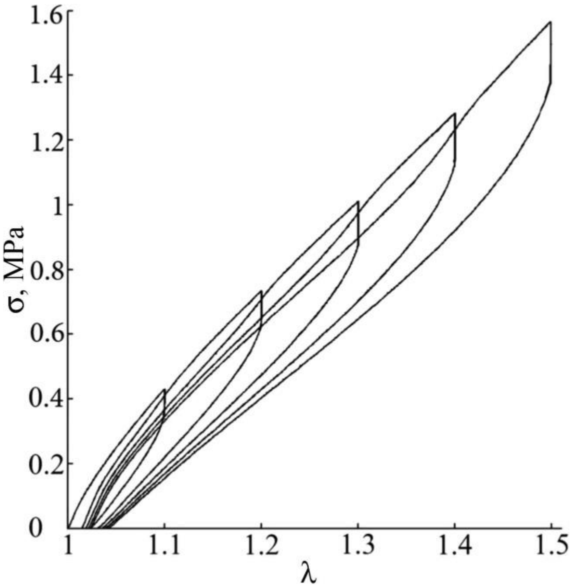

Fig. 4. Cyclic tests of SBR-1500 (100 phr), filled with 50 phr CB

Figure 5 depicts similar dependencies for SBR-1500, filled with 43 phr CB and 7 phr purified MWCNT.

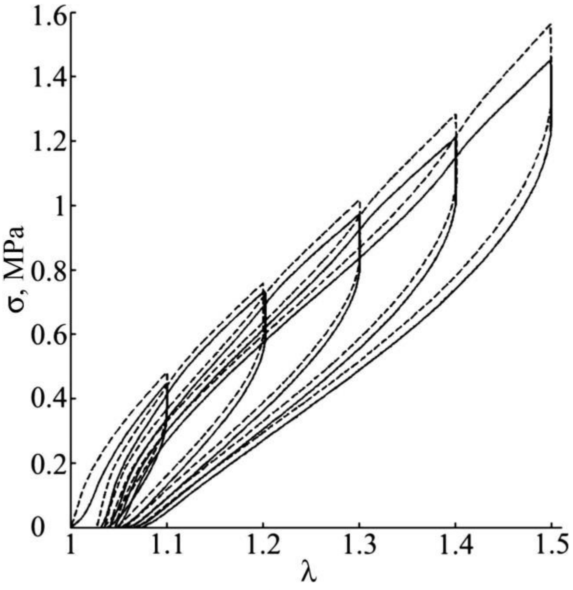

Fig. 5. Cyclic tests of SBR-1500 (100 phr), filled with 43 phr CB + 7 phr purified MWCNT

The graphs show that this material has a slight anisotropy of mechanical properties. The hysteresis areas (that is, dissipative losses) are about the same, but the sample cut along the rolling direction turned out to be slightly stiffer.

We also tested samples of a composite based on SBR-1500, in which not carbon black, but nanoparticles of few-layer graphene were used as the first filler. The second filler was purified multilayer carbon nanotubes. The obtained deformation dependencies are shown in Fig. 6. As a result of this replacement, the mechanical rigidity of the material has almost halved, and the residual deformations have approximately doubled. Dissipative losses (viscous properties) remained virtually unchanged. Thus, the introduction of graphene nanoparticles into the elastomer instead of CB and MWCNTs leads to a significant softening of the material, but the anisotropy of mechanical properties remains at the same level (i.e., insignificant).

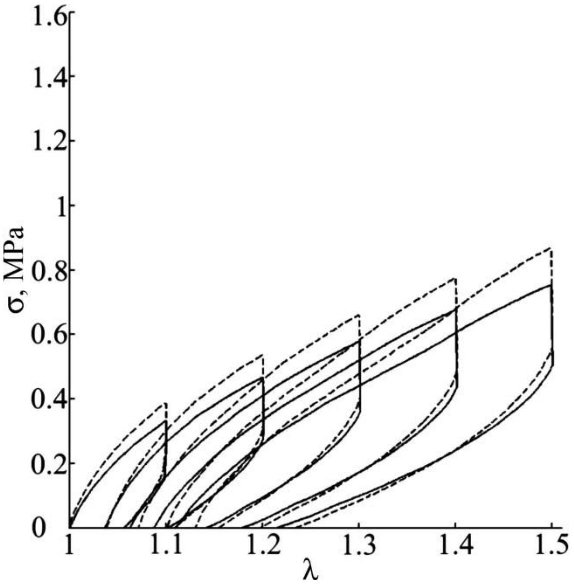

Fig. 6. Cyclic tests of SBR-1500 (100 phr), filled with 43 phr FLG + 7 phr purified MWCNTs

In our opinion, of greatest interest are the results obtained on samples filled with carbon black and purified single-walled carbon nanotubes (Fig. 7).

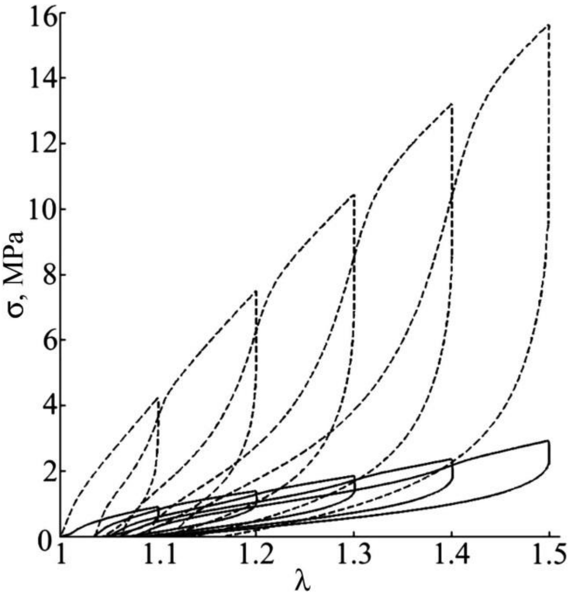

Fig. 7. Cyclic tests of SBR-1500 (100 phr), filled with 43 phr CB + 7 phr purified SWCNT

The graphs show that the maximum cycle stress amplitudes for the "longitudinal" samples are about 5 or more times higher than for the "transverse" ones, while the differences in the unloading curves for both turned out to be much smaller. Thus, in the first case, there was simply a huge increase in dissipative losses (4-5 times) and, accordingly, an improvement in damping properties. The areas of cyclic hysteresis loops for transverse samples were approximate of the same order as for other composites studied in this work (see Figs. 4-6). As regards residual deformations, for “longitudinal” samples filled with CB+SWCNT, they turned out to be 1.5-2 times greater than for composites filled with CB or CB+MWCNT. For "transverse" samples with CB+SWCNTs, these values turned out to be approximate of the same order as for elastomers containing CB and CB+MWCNTs.

The master Table 3 presents the values of the initial modules E_x and E_y, as well as the maximum values of conditional stresses σ_x and σ_y (at λ=1.5). Index "*x*" corresponds to specimens cut along the rolling direction, and index "*y*" – to the transverse direction.

Table 3. Mechanical characteristics of composite samples (test results)

Filler	E_x, MPa	E_y, MPa	σ_x, MPa	σ_y, MPa
50 phr CB (fig. 4)	7.14	7.13	1.56	1.56
43 phr CB + 7 phr purified MWCNT (fig. 5)	9.70	7.01	1.57	1.46
43 phr FLG + 7 phr purified MWCNT (fig. 6)	5.42	4.34	0.85	0.75
43 phr CB + 7 phr purified SWCNT (fig. 7)	74.67	16.17	15.65	2.94

According to the authors, such a difference in the mechanical properties of composites is due to the length of single-walled nanotubes, which is much longer than that of multi-walled ones. In the case of SWCNTs, a spatial framework can be formed in the composite from interconnected (both physically and chemically) very long fibers even at low filler concentrations. In the process of mechanical processing of a vulcanizing rubber compound (rolling), this carcass is reoriented in a certain direction and, accordingly, the material eventually becomes anisotropic. The same phenomena can also be observed when filling an elastomer with multilayer nanotubes, but due to the fact that they are much shorter, the effect should be much less pronounced.

4. Conclusion

As a result of the studies, it was found that in elastomers filled and purified with single-walled carbon nanotubes, the appearance of a significant anisotropy of mechanical properties associated with the peculiarities of sample preparation is possible. It is expressed in multiple increases in the rigidity of the material and an increase in dissipative losses during its deformation in the direction corresponding to the movement of the vulcanized mixture during rolling (whereas this effect is much less pronounced in the perpendicular direction). The initial modulus for composites filled with CB+SWCNT was about 7.7 times greater than for composites containing CB+MWCNT, and the maximum stresses (at λ=1.5) were 10 times greater. For composites with CB+SWCNT, the anisotropy in modulus (E_x/E_y) was 4.6, and in maximum stresses (σ_x/σ_y) it reached 5.3.

According to the authors, this is due to the fact that the length of SWCNTs is much larger compared to MWCNTs, and even more so with the characteristic sizes of soot and graphene particles.

This effect can be very important and useful in terms of various applications. For example, with the help of several fairly easy-to-implement technological operations, it is possible to significantly improve the damping properties of a rubber shock absorber made of rubber filled with SWCNTs.

References

1. Caldona EB, De Leon ACC, Pajarito BB, Advincula RC. A review on rubber-enhanced polymeric materials. *Polymer Reviews.* 2016;57(2): 311-338.

2. Roy K, Debnath SC, Potiyaraj P. A critical review on the utilization of various reinforcement modifiers in filled rubber composites. *Journal of Elastomers & Plastics.* 2019;52(2): 167-193.

3. Kraus G. Reinforcement of elastomers by carbon black. *Rubber Chemistry and Technology*. 1978;51(1): 297-321.
4. Kim J-H, Jeong H-Y. A study on the material properties and fatigue life of natural rubber with different carbon blacks. *International Journal of Fatigue.* 2005;27: 263-272.
5. Koga T, Takenaka M, Aizawa K, Nakamura M, Hashimoto T. Structure factors of dispersible units of carbon black filler in rubbers. *Langmuir.* 2005;21: 11409-11413.
6. Jovanovich V, Smarzija-Jovanovich S, Budinski-Simendich J, Markovich G, Marinović-Cincovich M. Composites based on carbon black reinforced NBR/EPDM rubber blends. *Composites Part B: Engineering.* 2013;45(1): 333-340.
7. Ulfah IM, Fidyaningsih M, Rahayu S, Fitriani DA, Saputra DA, Winarto DA, Wisojodharmo LA. Influence of carbon black and silica filler on the rheological and mechanical properties of natural rubber compound. Procedia Chemistry. 2015;16: 258-264.
8. Bokobza L, Rahmani M, Belin C, Brunell J-L, El Bouni N-E. Blends of carbon blacks and multiwall carbon nanotubes as reinforcing fillers for hydrocarbon rubbers. *Journal of Polymer Science: Part B: Polymer Physics.* 2008;46: 1939-1951.
9. Gao J, He Y, Gong X, Xu J. The role of carbon nanotubes in promoting the properties of carbon black-filled natural rubber/butadiene rubber composites. *Results in Physics.* 2017;7: 4352-4358.
10. Garishin OK, Shadrin VV, Svistkov AL, Sokolov AK, Stockelhuber WK. Visco-elastic-plastic properties of natural rubber filled with carbon black and layered clay nanoparticles Experiment and simulation. *Polymer Testing.* 2017;63: 133-140.
11. Zhang H, Wei YT, Kang ZR, Zhao GZ, Liu YQ. Influence of graphene oxide and multiwalled carbon nanotubes on the dynamic mechanical properties and heat buildup of natural rubber/carbon black composites. *Journal of Elastomers and Plastics.* 2017;50(5): 403-418.
12. Negri RBP, da Silva AHMFT, de Sousa AMF, da Silva ALN, da Rocha EBD. Improved mechanical and rheological behavior of nitrile rubber reinforced with multi-walled carbon nanotubes and carbon black dual-filler system. *Materials Today Communications*. 2021;26: 101884(1-10).
13. Mokhireva KA, Svistkov AL, Solod'ko VN, Komar LA, Stöckelhuber KW. Experimental analysis of the effect of carbon nanoparticles with different geometry on the appearance of anisotropy of mechanical properties in elastomeric composites. *Polymer Testing.* 2017;59: 46-54.
14. Karami P, Khasraghi S, Hashemi M, Rabiei S, Shojaei A. Polymer/nanodiamond composites – a comprehensive review from synthesis and fabrication to properties and applications. *Advances in Colloid and Interface Science.* 2019;269: 122-151.
15. Liu C, Zang J, Yan S, Yuan Y, Xu H, Yang G, Wang Y. Synthesis of novel nanocomposites reinforced with 3D graphene/highly-dispersible nanodiamonds nano-hybrids. *Ceramics International.* 2019;45(10): 13158-13163.
16. Bisht A, Samant SS, Jaiswal S, Dasgupta K, Lahiri D. Quantifying nanodiamonds assisted exfoliation of graphene and its effect on toughening behavior of composite structure. *Composites Part A: Applied Science and Manufacturing.* 2020;132: 105840-105853.
17. Maya MG, Abraham J, Arif PM, Moni G, Jacob George JJ, George SC, Thomas S. A comprehensive study on the impact of RGO/MWCNT hybrid filler reinforced polychloroprene rubber multifunctional nanocomposites. *Polymer Testing*. 2020;87: 106525(1-13).
18. Mittal G, Dhand V, Rhee KY, Park S-J, Lee WR. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. *Journal of Industrial and Engineering Chemistry*. 2015;21: 11-25.

19. Li Y, Wang S, Wang Q, Xing M. A comparison study on mechanical properties of polymer composites reinforced by carbon nanotubes and graphene sheet. *Composites: Part B.* 2018;133: 35-41.
20. Mensah B, Gupta KC, Kim H, Wang W, Jeong K-U, Nah C. Graphene-reinforced elastomeric nanocomposites: A review. *Polymer Testing.* 2018;68: 160-184.
21. Lu Y, Liu J, Hou G, Ma J, Wang W, Wei F, Zhang L. From nano to giant? Designing carbon nanotubes for rubber reinforcement and their applications for high performance tires. *Composites Science and Technology.* 2016;137: 94-101.
22. Mitrofanov VV, Slepchenkov MM, Zhang G, Glukhova OE. Hybrid carbon nanotube-graphene monolayer films: Regularities of structure, electronic and optical properties. *Carbon.* 2017;115: 803-810.
23. Krestinin AV, Dremov NN, Knerel'man EI, Blinova LN, Zhigalina VG, Kiselev NA. Characterization of SWCNT products manufactured in Russia and the prospects for their industrial application. *Nanotechnologies in Russia.* 2015;10(7-8): 537-548.
24. Voznyakovskii AP, Neverovskaya AY, Melenevskaya EY, Chubarova EV, Kutin AA, Sukhanova TE. Peculiarities of single-walled carbon nanotubes distribution in polystyrene matrix. *Nanotechnologies: Science and Production.* 2018; N4: 64-72. (In Russian)
25. Gumede JI, Carson J, Hlangothi SP, Bolo LL. Effect of single-walled carbon nanotubes on the cure and mechanical properties of reclaimed rubber/natural rubber blends. *Materials Today Communications.* 2020;23: 100852.
26. Jia Z, Wang Z, Liang J, Wei B, Wu D. Production of short multi-walled carbon nanotubes. *Carbon.* 1999;37: 903-906.
27. Fakhru'l-Razi A, Atieh MA, Girun N, Chuah TG, El-Sadig M, Biak DRA. Effect of multi-wall carbon nanotubes on the mechanical properties of natural rubber. *Composite Structures.* 2006;75: 496-500.
28. Elango N, Srinivasa Gupta NS, Jiun YL, Golshahr A. The effect of high loaded multiwall carbon nanotubes in natural rubber and their nonlinear material constants. *Journal of Nanomaterials.* 2017;2017: 6193961.
29. Kong L, Li F, Wang F, Miao Y, Huang X, Zhu H, Lu Y. High-performing multi-walled carbon nanotubes/silica nanocomposites for elastomer application. *Composites Science and Technology.* 2018;162(7): 23-32.
30. Zhan Y, Yan N, Fei G, Xia H, Meng Y. Crack growth resistance of natural rubber reinforced with carbon nanotubes. *J. Appl. Polym. Sci.* 2020;137: 48447(1-9).
31. Sementsov Yu, Yang W, Ivanenko K, Makhno S, Kartel M. Modification of rubber compositions by carbon nanotubes. *Applied Nanoscience.* 2022;12: 621–628.
32. Li P, Duan HY, Liu YF, Chi WD, Huang QG. Multi-walled carbon nanotubes as secondary fibre fillers for property improvement of short carbon fibre-reinforced silicone rubber. *Bull. Mater. Sci.* 2019;42: 177(1-8).
33. Krainoi A, Kummerlöwe C, Nakaramontri Y, Wisunthorn S, Vennemann N, Pichaiyut S, Kiatkamjornwong S, Nakason C. Novel natural rubber composites based on silver nanoparticles and carbon nanotubes hybrid filler. *Polymer Composites.* 2020;41: 443-458.
34. Xu Z, Jerrams S, Guo H, Zhou Y, Jiang L, Gao Y, Zhang L, Li LL, Wen S. Influence of graphene oxide and carbon nanotubes on the fatigue properties of silica/styrene-butadiene rubber composites under uniaxial and multiaxial cyclic loading. *International Journal of Fatigue.* 2020;131: 105388.
35. Kitisavetjit W, Nakaramontri Y, Pichaiyut S, Wisunthorn S, Nakason C, Kiatkamjornwong S. Influences of carbon nanotubes and graphite hybrid filler on properties of natural rubber nanocomposites. *Polymer Testing.* 2021;93: 106981.

36. Kumar V, Lee DJ. Rubber nanocomposites reinforced with single-wall and multiwall carbon nanotubes for industrial applications. *Rubber Chemistry and Technology.* 2020;93(1): 157-171.
37. Shadrinov NV, Nartakhova SI. Structure and properties of nitrile-butadiene rubber filled with carbon and basalt fibers. *Inorganic Materials: Applied Research.* 2017;8(1): 140-144.
38. Qian M, Sui J, Wang X, Zhu Y. Mechanical properties of silicon carbon black filled natural rubber elastomer. *Chemical Research in Chinese Universities.* 2019;35: 139-145.
39. Li X, Yang Q, Ye Y, Zhang L, Hong S, Ning N, Tian M. Quantifying 3D-nanosized dispersion of SiO2 in elastomer nanocomposites by 3D-scanning transmission electron microscope (STEM). *Composites Part A.* 2020;131: 105778.
40. Gabriel D, Karbach A, Drechsler D, Gutmann J, Graf K, Kheirandish S. Bound rubber morphology and loss tangent properties of carbon-black-filled rubber compounds. *Colloid and Polymer Sci.* 2016;294: 501-511.
41. Cole DP, Henry TC, Gardea F, Haynes RA. Interphase mechanical behavior of carbon fiber reinforced polymer exposed to cyclic loading. *Composites Science and Technology*. 2017;151: 202-210.
42. Butt H, Capella B, Kappl M. Force measurements with the atomic force microscope: Technique, interpretation and applications. *Surface Science Reports*. 2005;59: 1-152.
43. Ayoub G, Zairi F, Nait-Abdelaziz M, Gloaguen JM. Modelling large deformation behavior under loading–unloading of semicrystalline polymers: application to a high density polyethylene. *Int. J. Plasticity.* 2010;6: 329-347.
44. Drozdov AD, Klitkou R, Christiansen JC. Cyclic viscoplasticity of semicrystalline polymers with finite deformations. *Mechanics of Materials.* 2013;56: 53-64.
45. Svistkov AL, Shadrin VV. *Method for uniaxial cyclic testing of the material*. RU 2549841 (Patent), 2015.
46. Marckmann G, Chagnon G, Le Saux M, Charrier P. Experimental investigation and theoretical modelling of induced anisotropy during stress-softening of rubber. *Int. J. Solids Struct*. 2016;97-98: 1-43.
47. Plagge J, Klüppel M. A physically based model of stress softening and hysteresis of filled rubber including rate- and temperature dependency. *International Journal of Plasticity*. 2017;89: 173-196.
48. Ragni L, Tubaldi E, Dall'Asta A, Ahmadi H, Muhr A. Biaxial shear behaviour of HDNR with Mullins effect and deformation-induced anisotropy. *Eng. Struct.* 2018;154: 78-92.
49. Garishin OK, Shadrin VV, Kornev YuV Mechanical studies of rubber micro- and nanocomposites promising for the tire industry. Uniaxial and biaxial tests. *Materials Physics and Mechanics.* 2019;42(4): 445-454.
50. Plagge J, Ricker A, Kröger NH, Wriggers P, Klüppel M. Efficient modeling of filled rubber assuming stress-induced microscopic restructurization. *International Journal of Engineering Science.* 2020;151: 103291.
51. Garishin OK, Shadrin VV. Study of mechanical behavior of elastomeric nanocomposites under large cyclic shear deformations. *Bulletin of Perm University. Physics*. 2021;(3): 63-72. (In Russian)
52. Rinzler AG, Liu J, Dai H, Nilolaev P, Huffman CB, Rodriguez-Macias FJ, Boul PJ, Lu AH, Heymann D, Colbert DT, Lee RS, Fischer JE, Rao AM, Eklund PC, Smalley RE. Large scale purification of single-wall carbon nanotubes: process, product, and characterization. *Appl. Phys. A.* 1998; 67: 29-37.
53. Dillon AC, Gennet T, Jones KM, Alleman JL, Parilla PA, Heben MJ. A simple and complete purification of single-walled carbon nanotube materials. *J. Adv. Mater*. 1999;11: 1354-1358.

54. Holzinger M, Hirsch A, Bernier P, Duesberg GS, Burghard M. A new purification method for single-wall carbon nanotubes (SWNTs). *Appl. Phys. A.* 2000;70: 599-602.
55. Zhao B, Hu H, Niyogi S, Itkis ME, Hamon MA, Bhowmik P, Meier MS, Haddon RC. Chromatographic purification and properties of soluble single-walled carbon nanotubes. *J. Am. Chem. Soc.* 2001;123: 11673-11677.
56. Voznyakovskii AP, Neverovskaya AY, Otvalko JA, Gorelova EV, Zabelina AN, Lebedev SV. Facile synthesis of 2D carbon structures as a filler for polymer composites. *Nanosystems: Physics, Chemistry, Mathematics.* 2018;9(1): 125-128.
57. GR 54552-2011. *Rubbers and rubber compounds. Determination of viscosity, stress relaxation, and scorch characteristics using a Mooney viscometer*. Moscow: Standartinform; 2018.

THE AUTHORS

Garishin O.K.
e-mail: gar@icmm.ru
ORCID: 0000-0001-7384-7366

Svistkov A.L.
e-mail: svistkov@icmm.ru
ORCID: 0000-0002-4754-5214

Voznyakovskii A.P.
e-mail: voznap@mail.ru
ORCID: 0000-0002-5979-3661

Tchypkina I.M.
e-mail: vniisk@bk.ru

Neverovskaya A.Yu.
e-mail: anna-neverovskaya@yandex.ru
ORCID: 0000-0001-7813-666X

Shadrin V.V.
e-mail: shadrin@icmm.ru