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MICRO AND NANOSHUNGITES – PERSPECTIVE MINERAL FILLERS FOR RUBBER COMPOSITES USED IN THE TIRES

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

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

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

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

*e-mail: gar@icmm.ru

Abstract. Physical-mechanical properties of rubber filled by mineral filler (micro and nanoparticles of shungite) were studied experimentally. To date, shungite is one of the most promising materials used in the tire industry as active reinforcing fillers. Experiments on uniaxial tensile at break showed that input of this filler leads to a significant increase in rubber strength. Investigation of thermo-viscoelastic properties of these materials using dynamo-mechanical analyzer (DMA) were also carried out. As a result, the dynamic and viscous modulus dependences on the frequency (at 20°C) and their temperature dependences (from –50 to +100°C) were constructed.

Keywords: rubber composite, shungite filler, strength, dynamo-mechanical analyzer

1. Introduction

Carbon black (technical carbon) and white soot (hydrated silicon dioxide $mSiO_2 \cdot nH_2O$) are traditionally the most common fillers (reinforcing agents) of elastomeric composites based on natural and synthetic rubbers. The incorporation of these fillers into elastomers significantly improve their mechanical characteristics, especially the strength and stress-strain behavior of the material. 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 – 3].

The further progress in this area requires a continuous search for new unconventional fillers [4 – 7]. One promising direction is the use of dispersed clay minerals (monmorillonite, halloysite, palygorskite, shungite, etc.) [8 – 16]. This allows to vary the shape of filler particles in a natural way depending on the task and according to the peculiar structure of these materials. For example, dispersion of montmorillonite produces ultra-thin plates [17, 18], palygorskite – needle-like particles [19 – 20], shungite – globules [21].

It should be noted that all the aforementioned mineral fillers are made from loose and soft sedimentary rocks (Mohs hardness from 1 to 4). At the same time, the filler particles obtained after dispersing the original mineral are much more rigid and durable than their progenitor. That is, the "low hardness" of the mineral is one of the signs of its good dispersibility.

The input of clay dispersed particles into rubber allows not only to improve its physical and mechanical characteristics, but also to give it a number of additional important operational properties: increased thermal stability, resistance to burning, low diffusion permeability, ecological purity and relative cheapness of production [22, 23].

At its core, these materials represent a complex structural heterogeneous systems consisting of a low-modulus highly elastic matrix, which embedded by a much more rigid and

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durable particles of the particulate filler. Such materials are characterized by a complex mechanical behavior (finite deformations, nonlinear elasticity, viscoelasticity), which is caused by a different nature reversible and irreversible structural changes occurring under deformation [24, 25]. Currently, elastomer composites with various mineral fillers are the subject of intensive research, both experimental and theoretical [26 – 30]. As for application, the most promising direction of using such materials is the production of automobile tires.

2. The object of study

The main object of research were elastomeric composites with a dispersed filler made of micro and nanoshungite dispersed particles. Shungite is a sedimentary mineral formed from organic bottom sediments in freshwater reservoirs (sapropel). As for their structure, shungites are natural composites with a uniform distribution of highly disperse crystalline silicate particles in a carbon matrix [21, 31]. Depending on a deposit, the composition of shungite rocks can vary within fairly wide limits. On average, these materials contain about 60-70%-wt. of silicates and 30%-wt. of shungite carbon with an admixture of other inorganic substances (< 4%-wt., Al_2O_3, FeO, MgO, CaO, etc.) [32].

Shungite carbon is a mixture of various allotropes of carbon, whose crystal lattices are joined with amorphous carbon. It is reliably established that the shungite carbon in the rock is lined up by globules connected together (that is, particles of approximately spherical shape). The diameter of the shungite globules is about 10 nm (which is unique for materials of natural origin). There is a strong bond between the carbon and silicate components. The rock is characterized by high density (1.9–2.4 g/cm^3), chemical resistance and electrical conductivity ((1-3)$\times 10^3$ S/m), hardness on mineralogical Mohs scale is 3.5–4 [33 – 36].

Such structure and composition impart a number of unusual physicochemical and technological properties to shungite material. 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.

Currently, shungite is being used in the tire industry to produce active and semi-active fillers of a new generation. In general, the experimental testing of shungite in rubber compounds revealed the following main effects [37 – 40]

1) Improving the ability of rubber compounds to process (in comparison with carbon black and white soot).

2) Shungite-filled rubber has improved dynamic properties: resistance to growth of cracks in bending with puncture, reduced heat generation under alternating bending, dynamic endurance under angular rotation.

3) Filling rubber with shungite significantly increases their thermal and fire resistance.

The main goal of this work was to study experimentally the strength properties of shungite-filled rubbers depending on the size of the filler particles and their concentration, as well as their thermo-viscoelastic behavior using the dynamo-mechanical analyzer (DMA).

Experimental studies were carried out on samples of synthetic butadiene-styrene rubber SBR-1500, filled with dispersed shungite particles, shredded to micro and nano-state in the planetary ball mill. The average characteristic size of the microshungite particles was about 500 nm, nanoshungite – 60-80 nm. The volume concentration (φ) of microfiller was equal to 10% (phr = 25), 18% (phr = 65) and (phr = 105), for the nanofiller φ = 18% (phr = 65). All particles were pretreated with a surfactant (3-Mercaptopropyltriethoxysilane) to improve the interfacial adhesion between the filler and the matrix (and improving the overall strength of the composite). The elastomeric compositions were prepared in the standard laboratory mixer

HAAKE Rheomix. All samples were manufactured at the Institute of Applied Mechanics RAS (by Yu.V. Kornev).

3. Experiment and results discussion

Experimental studies of shungite-filled elastomers consisted of two stages: 1) uniaxial stretching prior to rupture; 2) tests on the dynamo-mechanical analyzer (DMA).

Experiments on uniaxial stretching were carried out using the universal tensile testing machine Testometric FS100kN CT. Samples were manufactured in accordance with the standard ISO 527-25A with working part 10×2×2 mm. During the test, each sample was monotonically stretched to a break at a deformation rate of 25%/min. 9-12 samples were tested for each particle size and filler concentration. The averaged results of the experiments are shown in Fig. 1.

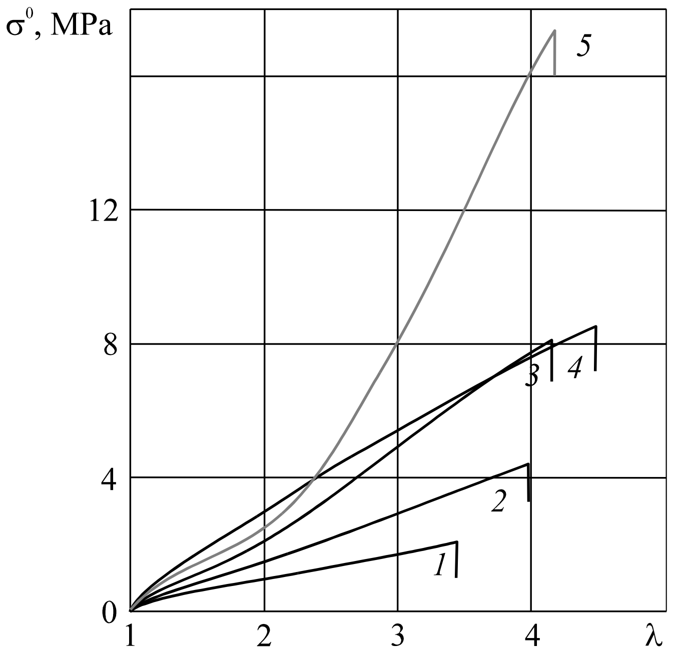

Fig. 1. Nominal stresses σ^0 versus extension ratio λ at stretching of elastomers filled with micro- and nanoshungite particles. Microshungite filler (black lines): φ=0% (*1*), 10% (*2*), 18% (*3*), 27% (*4*); nanoshungite filler (gray line) – φ=18% (*5*)

It was found that the addition of micro-shungite filler to the rubber leads to increase in the composite strength. At the same time, its deformability grew too, but not so much (by about 10-30%).

A more interesting picture is observed for nanoshungite filler. Comparison of dependencies *3* and *5* in Fig. 1 shows, that at the same volume concentration of 18%, the use of the nanoshungite filler increases the strength of material more than 2 times compared with the microshungite and 8.5 times with respect to the pure elastomer (see curve *1* in Fig. 1). The limiting deformations of micro- and nanoshungite rubbers turned out to be quite close. From the structural point of view, the main difference between micro and nano shungite is that the particles of the latter have approximately 4 times the specific surface area. That is, it can be argued that an increase in the specific surface area of the filler improves stiffness and the strength characteristics of the material (provided good adhesion (chemical affinity) between the matrix and the dispersed phase). These results are consistent with known literature data on testing of filled elastomers with other clay fillers [29].

The thermo-viscous-elastic properties of these composite materials were investigated in the second stage. The experiments were held on a dynamo-mechanical analyzer DMA/STDA861e (METTLER TOLEDO STAR^e). This device allows obtaining information about the change in the viscoelastic characteristics of the material under the action of a dynamic cyclical load (linear viscoelasticity model) for given temperature values from –150 to +500°C. Rectangular samples were used for the tests: base (working part) 10 mm, width 3 mm and thickness 2 mm. One-point loading scheme was applied: cyclic uniaxial stretching–compression of a pre-stretched sample with dynamic load applied according to a harmonic law.

The range of assigned frequencies *f* varied from 1 to 20 Hz, which corresponds to the rolling speed of a standard automotive wheel (landing diameter 15 inches) in the range from 6 to 136 km/h, respectively. The amplitude of specimen deformations ε_0 was set at 3% in all cases.

As a result, the dependences of the dynamic (*E'*) and viscous (*E''*) modules on the loading frequency f were plotted. Their temperature dependences (–50 to +100°C) at a constant frequency of 13 Hz (which corresponds to approximately 90 km/h) were built too. The corresponding graphs are shown in Figures 2-4. The analysis of results obtained by DMA showed the following.

Frequency tests. The addition of micro-shungite filler to rubber promoted an increase in both *E'* and *E''*, and with concentration growth this effect intensified. The replacement of microparticles with a nanofiller (at the same concentration) also contributed to an increase in the values of these characteristics (curves 3 and 5 in Fig. 2). It was also found that in this frequency range the dynamic and viscous modules retained almost constant values (increasing slightly with φ rising). Thus, we can assume that the studied rubber composites have sufficiently stable viscoelastic characteristics in this frequency range of tire rotation.

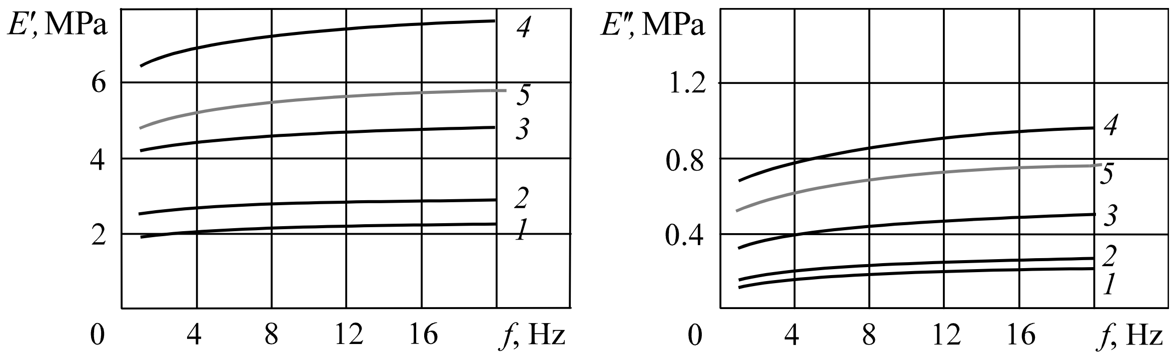

Fig. 2. Frequency dependences of dynamic (*E'*) and viscous (*E''*) modules for rubbers filled with micro and nanoshungite particles. Microshungite filler (black lines): φ=0% (*1*), 10% (*2*), 18% (*3*), 27% (*4*); nanoshungite filler (gray line) – φ=18% (*5*)

Temperature tests. The conducted studies showed that all samples demonstrated the stability of their mechanical characteristics at temperatures in the range of about –25°C and above, that is, they are quite suitable for operation in temperate climates.

A sharp increase in both the dynamic and viscous modules (by several orders of magnitude) occurred in the rubbers filled with micro and nanoshungite if the temperature dropped below –30°C. The values of *E'* and *E''* also increased with the filler concentration growth, but, interestingly, the effect of "cold amplification" on nanoparticles was somewhat weaker than for microshungite for the same concentration (curves *3* and *5* in Fig. 3). The pure elastomer was much more stable: E' at t= –50°C increased approximately 15 times, and E' – in 70.

The analysis of the temperature dependences of the loss tangent ($\tan\delta = E''/E'$) (Fig. 4) showed that when both in case of micro and nanoshungite fillers added, the characteristic peaks corresponding to the glass transition temperature shifts toward increasing it: from –45°C (pure elastomer) to –25°C (volume concentration 27%).

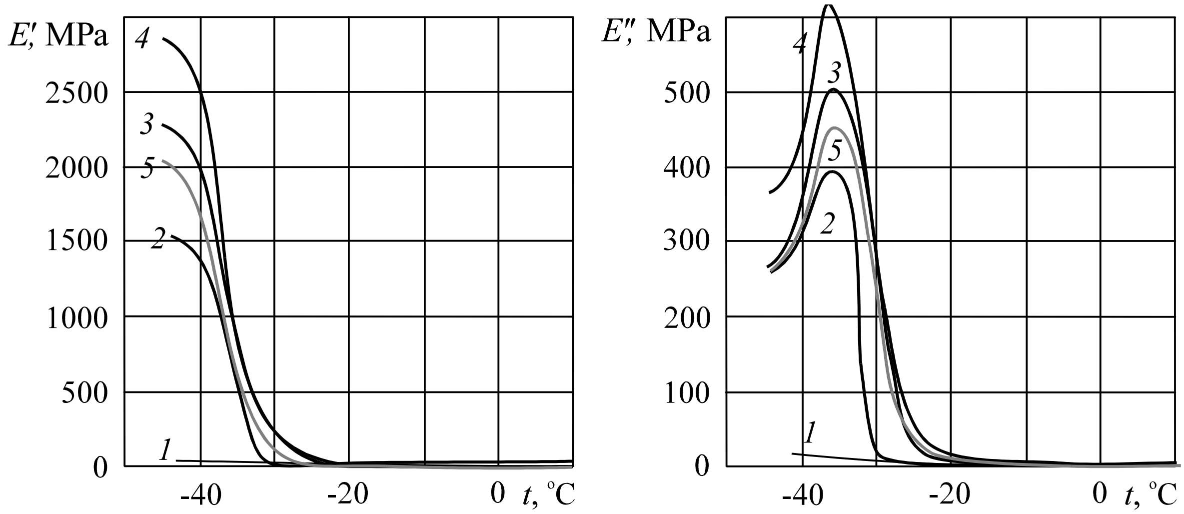

Fig. 3. Temperature dependences of dynamic (E') and viscous (E'') modules for rubbers filled with micro and nanoshungite particles. Microshungite filler (black lines): φ=0% (*1*), 10% (*2*), 18% (*3*), 27% (*4*); nanoshungite filler (gray line) – φ=18% (*5*)

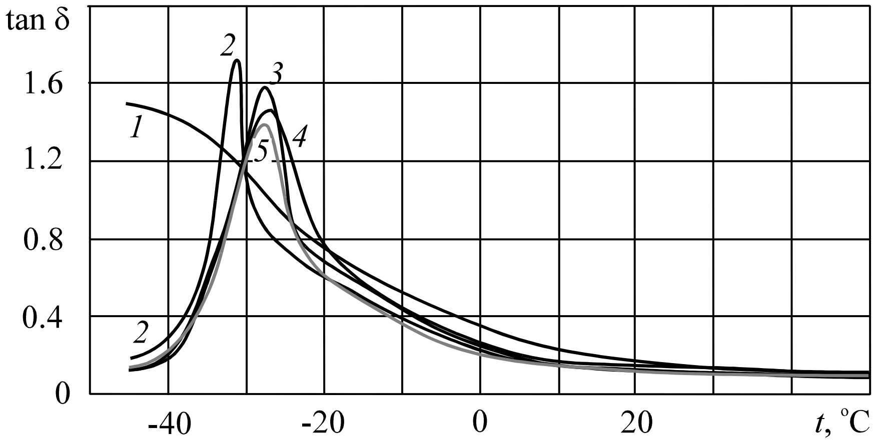

Fig. 4. Temperature dependences of loss tangent for rubbers filled with micro and nanoshungite. Microshungite filler (black lines): φ=0% (*1*), 10% (*2*), 18% (*3*), 27% (*4*); nanoshungite filler (gray line) – φ=18% (*5*)

Consequently, the use of tires with only such fillers in such low temperatures is quite problematic – some special additives are needed in the tire compound in this case.

4. Conclusions

The addition of dispersed mineral filler from micro and nanoshungite to tire rubber improves their strength and deformability, moreover in the case of nanoparticles this effect is enhanced. Studies of these rubber composites on dynamo-mechanical analyzer showed that they have stable viscoelastic properties at temperatures above -25 ° C, that is, they are quite suitable for operation in temperate climates.

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