Microshungite – perspective fillers for rubber compounds used in the tire industry

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Abstract

Strength and viscoelastic properties of nanocomposites based on butadiene-styrene rubber (SBR-1500) with dispersed mineral filler (micro-shungite) were studied experimentally. In its structure shungites represent natural composite with a uniform distribution of finely crystalline silicate particles in the carbon matrix. These minerals sufficiently disperse readily into particles globular (spherical) form, with appropriate processing. The mineral is characterized by high density, chemical resistance and electrical conductivity. Currently, shungite is being used in the tire industry to produce active and semi-active fillers of a new generation. The tests were carried out on samples with various volumetric concentrations. The average particle size of the micro-shungite filler was about 500 nm. Experiments on uniaxial tensile at break showed that micro-shungite input leads to a significant increase in the material strength. At the same time, its deformability grew, but not so much. Thus, it can be said that the good chemical affinity of the filler and matrix contributes to improving the material's ultimate characteristics. Studies of the thermo-visco-elastic properties of these materials on a 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.

1 Introduction

The use of various mineral fillers in the production of elastomeric composites with improved performance properties (in particular automobile tires) is a relatively new and very promising perspective direction of material science development. These materials are characterized by a combination of such important properties as increased thermal stability, resistance to burning, low diffusion permeability, ecological purity and relative cheapness of production [1, 2]. At its core, they represent a complex structural heterogeneous systems consisting of a low-modulus highly elastic matrix, which embedded by a much more rigid and 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 [3, 4, 5]. Currently, elastomer composites with various mineral fillers are the subject of intensive research, both experimental and theoretical [6, 7, 8, 9, 10, 11, 12].
One of the most promising areas of use of elastomers with mineral fillers are automobile tires. Rubbers with such filling are cheaper and have higher wear resistance [13, 14].

2 The object of study

The main object of research was elastomeric nanocomposites based on SBR-1500 synthetic butadiene rubber, filled with micro-shungite (granular particles with a typical average size of about 500 nm). This is a relatively new (for elastomers) type of filler. Shungite represent natural mineral composite with a uniform distribution of highly disperse silicate particles in the carbon matrix [15, 16, 17]. Depending on the 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., $A_{l2}O_3$, FeO, MgO, CaO, etc.). 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 [18, 19]. Such a structure and composition give shungite materials several unusual physical-chemical and technological properties. The particles of shungite powder, even micron-sized, contain phases different in polarity. Due to bipolarity, powders of shungite rocks mix well with most known substances (aqueous suspensions and fluoroplastics, rubbers, resins and cements, etc.). Therefore, they are one of the promising modern fillers. 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 [13, 14, 20]:
1) Improving the ability of rubber compounds to process (in comparison with carbon black and white soot).
2) Shungiton-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.

3 Experiment and results discussion

All experiments were performed on samples prepared in IAPM RAS. The volume micro-shungite concentration φ was 0% (pure rubber), 10%, 18%, and 27%. The studies consisted of two stages: 1) uniaxial stretching up to rupture rupture; 2) tests on a dynamo-mechanical analyzer (DMA). Experimental studies were carried out on the universal tensile testing machine Testometric FS100kN CT. Samples were manufactured in accordance with the standard ISO 527-25A with working part 2 on 2 by 10 mm. During the test, each sample was monotonically stretched to a break at a rate of 25 %/min. 9–12 samples were tested for each filling. The averaged results of the experiments are shown in Fig. 1.

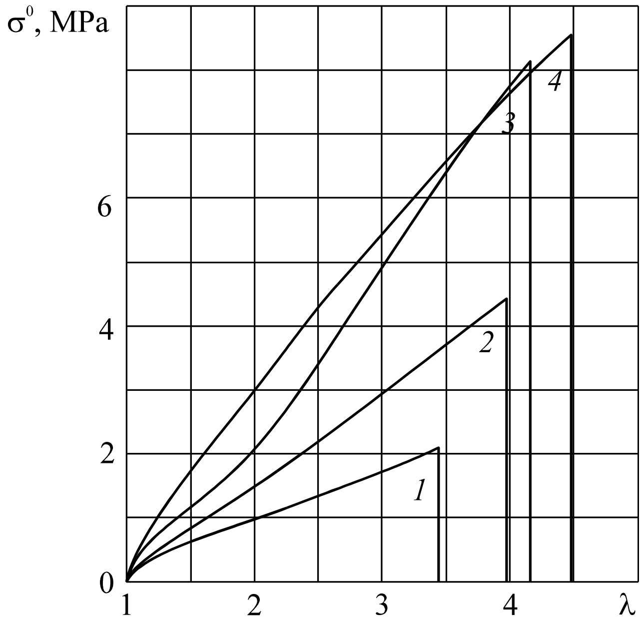

Figure 1: Nominal stresses σ^0 versus extension ratio λ at stretching of elastomers filled by micro-schungite particles; $\varphi = 0\%$ (*1*), 10% (*2*), 18% (*3*), 27% (*4*)

It was found that the addition of micro-shungite filler leads to a significant increase in the strength of the elastomer. For example: for $\varphi = 27\%$ it was more than 3 times. At the same time, its deformability grew, but not so much (from 10 to 30%). Thus, it can be said that the good chemical affinity of the filler and matrix contributes to improving the ultimate characteristics of the material. In the near future, it is planned to carry out the similar experiments with nano-shugite filler. There, we think, these effects should appear even stronger.

The thermo-visco-elastic properties of these composite materials were investigated in the second stage. The experiments were held on a dynamo-mechanical analyzer DMA/STDA861^e (METTLER TOLEDO STAR^e). This device allows to obtain 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, 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 frequency range 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 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. It was also found that in this frequency range the dynamic and viscous modules retained almost constant values. Thus, we can assume that these composites have sufficiently stable viscoelastic characteristics in this frequency range of tire rotation.

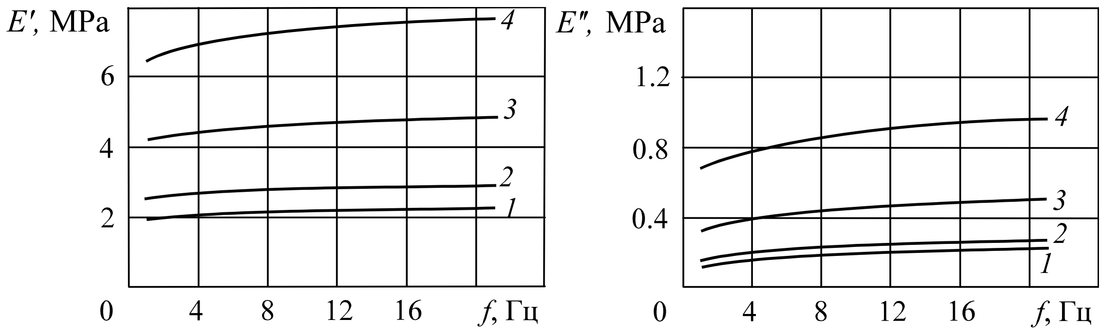

Figure 2: Frequency dependences of dynamic (E') and viscous (E'') modules for microchungite filler concentrations of $\varphi = 0\%$ (*1*), 10% (*2*), 18% (*3*), 27% (*4*)

Temperature tests:

At temperatures below −30 °C there was a sharp increase in E' and E'', while for shungite-filled rubbers the values increased by several orders of magnitude. The pure elastomer changed its properties considerably less. From the analysis of the temperature dependences of the loss tangent ($\tan\delta = E''/E'$), it is seen that when a micro-shungite is added, the characteristic peak corresponding to the glass transition temperature shifts from −45°C (pure elastomer) to −25°C (27%). 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. At higher temperatures, all samples demonstrated the stability of their mechanical properties.

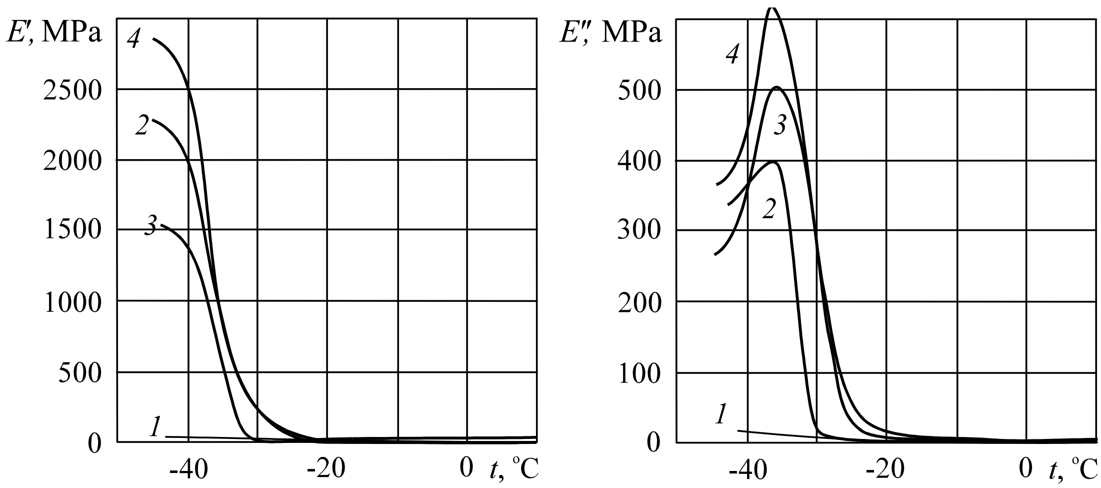

Figure 3: Temperature dependences of dynamic (E') and viscous (E'') modules for microchungite filler concentrations of $\varphi = 0\%$ (*1*), 10% (*2*), 18% (*3*), 27% (*4*)

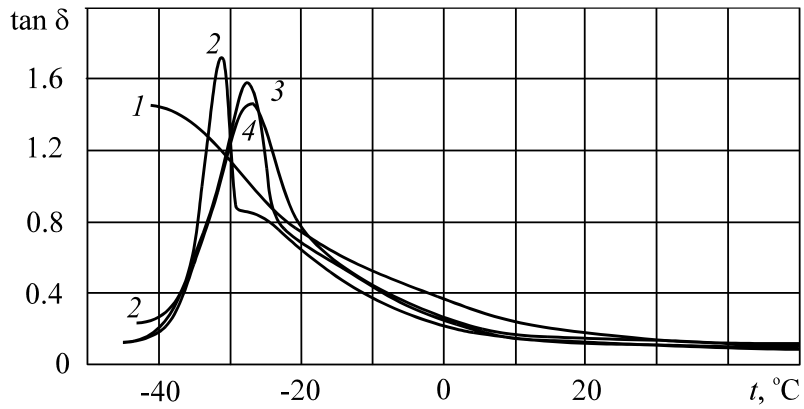

Figure 4: Temperature dependences of loss tangent ($\tan\delta = E''/E'$) for microchungite filler concentrations of $\varphi = 0\%$ (*1*), 10% (*2*), 18% (*3*), 27% (*4*)

Acknowledgements

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