

Mechanochemically Activated Shungite as an Additive to Improve Bitumen Characteristics

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ABSTRACT

One of the urgent problems of improving the quality of road surfaces is to improve the properties of bitumen used as binders. For this purpose, various modifiers are used, which are mainly obtained synthetically. Modification of bitumen with natural raw materials is favorable from an economic and environmental points of view. The modification of road oil bitumen with samples of shungite from the Koksus deposit (Kazakhstan) was carried out in the work. The shungite samples were previously crushed by mechanochemical activation to improve their surface and adhesive properties. As a result of modification with shungite, an increase in the softening temperature and a decrease in the extensibility and penetration of bitumen were observed. The optimal amount of added shungite turned out to be 1 mass %. The shungite of carbonate origin on a mineral basis is more favorable as a modifier compared to samples of shale origin.

Keywords: bitumen, modification, shungite, mechanochemical activation, grinding.

INTRODUCTION

Petroleum bitumen is one of the main products of processing heavy oil residues. They are used as a road-building material due to their adhesive and hydrophobic properties. Road viscous bitumen is used as a binder between stone materials. Depending on the brand of the mixture and its quality, which determine the durability of the mixtures the bitumen content in asphalt concrete mixtures is 5.5–8.0%.

To improve the physical and mechanical characteristics of bitumen, various types of modifiers are used, among which polymer materials predominate. One of the priority directions of bitumen modification is the use of carbon materials with new structures and quality that can improve the technical characteristics of bitumen. Promising carbon-containing raw materials are shungite rocks – natural composite materials [Ongarbayev et al., 2022a].

Shungite rocks are divided in mineral basis into aluminosilicate, siliceous, carbonate and in carbon content (mass %) into low- (less than 5%), medium- (5–25%) and high-carbon (25–80%) shungites [Khromushin et al., 2014]. Shungite carbon substance is a product of a high degree of carbonization and is a solid carbon that is in various states: disordered, close to graphite, carbon black, glass carbon.

To increase the efficiency of using shungites as a component of composite materials, it is necessary to modify their surface. Increasing the dispersion of the powder is possible with the use of intensive and energy-intensive crushing technologies. Various methods have been proposed to create materials based on shungite with a micro- and nanomolecular structure. One of these methods is mechanochemical activation (MA) [Ongarbayev et al., 2022b].

In the method of obtaining nanoscale particles [Yanovsky et al., 2012], shungite with particle

sizes up to 100 microns was crushed in a planetary ball mill in a mixture with branched alcohol and grinding balls with a diameter of 0.5–5 mm at a ratio of 1.5:1:1.5 to 2.5:1:3. The temperature of the mixture did not exceed 150°C and the grinding process was carried out with at a speed of 100–700 rpm for up to 6 hours. After grinding to shungite particles of 5–50 nm in size, drying was carried out for 0.5–6 hours at 80–250°C. The disadvantage of the method is the long duration of the grinding and drying processes.

By processing shungite rocks at a temperature of 1400°C, a set of nanomaterials was obtained [Kovalevskii et al., 2018]: hollow carbon fibers, spherical or ellipsoid particles, crystalline nanofibers and nanoparticles, as well as iron and iron silicide nanoparticles encapsulated in carbon shells. A disadvantage of the method is the high processing temperature.

By low-temperature treatment of shungite with ultrasound at 25°C, graphene films with a surface length of 200 nm with a hexagonal-centered graphene structure with a lattice pitch of 0.335 nm were obtained [Novikova et al., 2022].

[Kovalchuk et al., 2018] described the properties of thin films made of shungite nanocarbon by sublimation in vacuum on glass substrates with applied coatings. Carbon nanoparticles were found on quartz glass coated with an In_2O_3 film, which have a size distribution of 50–100 nm.

A number of fullerenes have been identified in the carbonaceous substance of shungite rocks, the basis of which are hollow, multilayer fullerene-like spherical globules with a diameter of 10–30 nm containing packages of smoothly curved carbon layers covering nanopores. Such globules can contain from tens to several hundred carbon atoms and vary in shape and size.

In the method of obtaining fullerenes [Rak et al., 2004], shungite was crushed and a product with a dispersion of 2–0.005 μm was obtained. Crushed shungite was heat treated in vacuum or in an inert gas medium in the range of 100–1800°C at a temperature rate of 10–60°C/min. Condensed fullerenes were sublimated stepwise with a temperature difference between the steps of 200–4000°C.

To increase the stability of the aqueous dispersion of carbon nanoparticles [Rozhkova et al., 2018], the shungite rock was crushed, filled with water at a ratio of 1:2 and settled for three days, after which it was filtered. The remaining shungite powder on the filter was dried and dispersed

in water using grinding media with a diameter of 1–3 mm at a ratio of 1:4:3 for 60 minutes. Then the mixture was filtered and the shungite powder was dried. Next, the shungite powder was dispersed in water at a ratio of 1:20 by ultrasound with a frequency of 22 kHz and a power of 1000 watts for 35 minutes and filtration. The resulting aqueous dispersion of carbon nanoparticles was centrifuged for 15 min at 10000 rpm.

The presence of a complex of hydrophilic (silicon and metal oxides, aluminosilicates) and hydrophobic (carbon in various modifications) components in the composition of shungite contributes to a better distribution of mineral particles in the structure of bitumen, which also has diphlic properties. Crystals of finely ground shungite have pronounced bipolar properties – they have a high level of adhesion and are mixed with almost all substances. Therefore, shungite was used as a filler of rubber and road-building materials.

Filling rubber with shungite led to an increase in the softening temperature of the binder by 48%, an increase in its elasticity and extensibility, especially at 0°C [Yadykina et al., 2020]. In [Vysotskaya et al., 2017], addition of 5–10% shungite into the mastic made it possible to reduce the polymer content in the composition, while simultaneously increasing the softening temperature, elasticity and adhesive strength. The addition of shungite (Karelite) into bitumen led to an increase in the viscosity, softening temperature, strength and elasticity of composites [Sorokina et al., 2018].

It was found in [Vysotskaya et al., 2015] that the total number of active centers on the surface of shungite is several times higher than in the case of limestone. The authors of [Sheverdyayev et al., 2007] also found that reducing the particle size of shungite to ultrafine particles can lead to an improvement in the properties of bitumen binders.

The effect of shungite additives in the amount of 1–15 wt. % on the properties of materials based on dielectric elastomers was compared [Olewnik-Kruszkowska et al., 2022]. Improved thermal stability of materials was established, which is due to the high content of silicon in the composition of shungite, which can form a protective layer on the polymer surface when decomposed at high temperatures.

In the method of activating water for mixing concrete mixtures [Smirnov et al., 2014], shungite in an amount of at least 1% of the water mass was placed in a vessel with water and treated

with ultrasound at a frequency of 20–100 kHz for 5–10 minutes until the concentration of fullerene released from shungite into water was 10^{-3} – $10^{-5}\%$. Then the water was passed through a filter and used as a sealing liquid. As a result, the physical and mechanical characteristics of concrete improved, whereas water and cement costs were reduced.

It is proposed to improve the physical and mechanical properties of fine-grained concrete with micro- and nanodisperse additives based on the shungite from the Zazhoginsky deposit [Pykin et al., 2011]. Ultrasonic particle dispersion for 15 minutes contributed to the production of a suspension with a particle size of 62–716 nm. As a result of the additives, the hardening of the concrete mixture accelerated, porosity decreased, density and strength increased by 1.5–2 times, water absorption decreased by half.

The influence of waste shungite rock processing on concrete indicators and features of the processes occurring in the hardening silicate system “cement – dispersed shungite particles” and contributing to an increase in the strength of concrete, as well as a reduction in the duration of its heat and water treatment were studied [Yes-temessova et al., 2020].

The morphology of shungite particles was studied, as well as the compatibility of shungite microfillers with a polycarboxylate-based superplasticizer in cement compositions [Smirnova et al., 2018]. After heating shungite rocks at 950°C and grinding, three types of shungite microparticles are formed: spherical, porous with an increased number of nanoscale pores and smooth particles.

The introduction of the mineral additive “Taurite” based on fine-grained shungite from 0.1 mm to 10 μm and the “Kratosol” naphthalene superplasticizer into concrete increased the strength of normally hardening concrete after 28 days by 2.5–30%, and heat-hardening concrete after 28 days by 0.6–25% [Lukutsova et al., 2011]. The surface of the mineral filler particles was subjected to hydration, which contributed to the production of concretes and solutions with improved physical and mechanical properties. Amorphous SiO₂ particles in the mineral filler contributed to the formation of crystals of hydroaluminates and calcium hydrosilicates.

As it can be seen from the literature, the shungite rocks of Karelia (Russia) after various types of activation were used to modify

road-building and composite materials, which led to an improvement in their physical and mechanical characteristics. However, the shungite deposits of Kazakhstan have not been used for such purposes and their effect on the physical as well as mechanical properties of bitumen has not been investigated.

The Koksus deposit (Kazakhstan) of shungite rocks has been developed since 2002; it has significant estimated reserves – more than 620 million tons. The shungite rocks of the Koksus deposit have not been studied as additives to petroleum bitumen and other types of road construction materials, which is due to the peculiarities of their composition and properties, as well as the complex morphology of carbon inclusion in the silicate matrix. In this regard, the purpose of this work was to study the possibility of using the shungite from the Koksus deposit to improve the physical and mechanical properties of road oil bitumen.

MATERIALS AND METHODS

In the work, the shungite from the Koksus deposit (Almaty region) of the brand “Taurite” of shale TS and carbonate TC origin was used as a modifying additive. The initial samples of shungite had a particle size of 1 mm. “Mining Company “Koksus” LLP also produces samples of shungite grades TS-D and TC-D, which have a particle size of 20 μm.

Table 1 shows the composition and basic physico-chemical parameters of samples of shungite brand “Taurite”. The shungite of the TS and TC brands samples in appearance are grains and dust of irregular geometric shape from dark gray to black. As it can be seen from Table 1, they differ in the mass fraction of carbon and silicon oxide. In the carbonate samples, the carbon content is 12 mass %, which is twice more than in shale rocks (5.6 mass %). The mass fraction of silicon oxide in shale rocks is 76.1%, while in carbonate rocks it is less – 48.1%. The content of water-soluble substances in the samples is not more than 1.0%. The mass fraction of moisture in the carbonate samples is 1.0%, and in the shale samples – 3.5%. The pH value of the aqueous suspension is in the range of 8.2–8.8. These indicators meet the requirements of ST 60-1907-23-LLP-001-2014.

Mechanochemical activation of the samples of shungite rocks with particle sizes of 1 mm

Table 1. Qualitative indicators of the samples of shungite of the brand “Taurite”

Indicator	Normative value according to ST 60-1907-23-LLP-001-2014 carbonate / shale	Carbonate TC	Shale TS
Mass fraction of carbon, %	7-15 / 4-8	12,0	5,6
Mass fraction SiO ₂ , %	30-55 / 72-85	48,1	76,1
The content of water-soluble substances, %	no more than 1,5	0,72	0,91
Mass fraction of moisture, %	-	1,0	3,5
pH of the aqueous suspension	7-10	8,8	8,2
Size, mm	-	0-1	0-1

was carried out in a GT 300 mill with two mass ratios of shungite samples and steel balls of 1:1 and 1:1.5 with a rotation speed of 750 rpm for 20 minutes.

The particle size of the samples after mechanochemical activation was measured by the Winner 2000E laser particle size analyzer (Jinan Winner Particle Instruments Stock Co., Ltd, China). Electron microscopic images were taken on a scanning electron microscope SEM FEI Quanta 3D 200i.

The road oil bitumen of the BND 100/130 brand produced by the Pavlodar Petrochemical Factory was used in the work. Bitumen has the following physical and mechanical parameters: the penetration depth of the needle at 25°C is 129.60.1 mm, the softening temperature is 46.9°C, the extensibility at 25°C is 111.6 cm.

Bitumen modification was carried out as follows: bitumen was loaded into a metal cup equipped with a thermometer and a heated stirrer and the glass was heated to 180°C; then, the required amount of shungite was added (from 0.2 to 5 mass %) with constant stirring for 1 hour.

After modification, the basic physico-mechanical parameters of bitumen were determined, such as penetration, softening point and ductility. The penetration of modified bitumen at 25°C was determined by an APN-360MG4 penetrometer in accordance with the ST RK 1226–2003 standard [ST RK 1226-2003, 2003]. The softening point of the samples was determined by the “Ring and Ball” method on an IKSH-MG4 device in accordance with the ST RK 1227–2003 standard [ST RK 1227-2003, 2003]. The ductility of modified bitumen was measured at 25°C in accordance with the ST RK 1374–2005 standard [ST RK 1374-2005, 2005] on a DAF 14–80 device. The molded bitumen sample, kept at the test temperature, is stretched in the device at a constant speed and the maximum elongation is determined.

RESULTS AND DISCUSSION

The samples of shungite of the TS and TC grades with an initial particle size of 1 mm were subjected to mechanochemical activation. The finely dispersed samples TS-D and TC-D were not subjected to mechanochemical activation, they had a particle size of 20 µm. After mechanochemical activation, the particle size distribution in the shungite samples was determined, which is shown in Figure 1. As it can be seen from the Figure 1, after mechanochemical activation, the volume content of particles with a smaller size increases. A sample of TS-D grade shungite with particle sizes of 20 µm showed a maximum volume content of 7.73% with a size value of 11.7 µm. After mechanochemical activation, curves 2 and 3 of the particle size distribution of the TS sample merge (Figure 1a), since the maximum value of the volume content increases to 8.6% with a mass ratio of the sample and the balls 1:1 and up to 8.58% with a ratio of 1:1.5. The increase in the mass ratio of the TC sample and the balls practically had no effect on particle sizes in this grinding mode.

In the case of the samples of shungite of carbonate origin, the effect of changes in the mass ratio of the sample and the balls on the volume content of particle sizes is observed. For the TC-D sample, the maximum volume content of 7.91% is observed for a particle size of 9.7 µm. After mechanochemical activation, with a mass ratio of the sample and the balls of 1:1, the maximum value of the volume content increases to 9.46%, with a mass ratio of 1:1.5 to 8.51%.

Table 2 shows the values of particle diameters corresponding to 10%, 50% and 90% of the cumulative distribution, as well as the average diameters of particles by volume and by surface, also surface area per unit volume. As it can be seen from Table 2, after mechanochemical activation, there is a decrease in the average particle

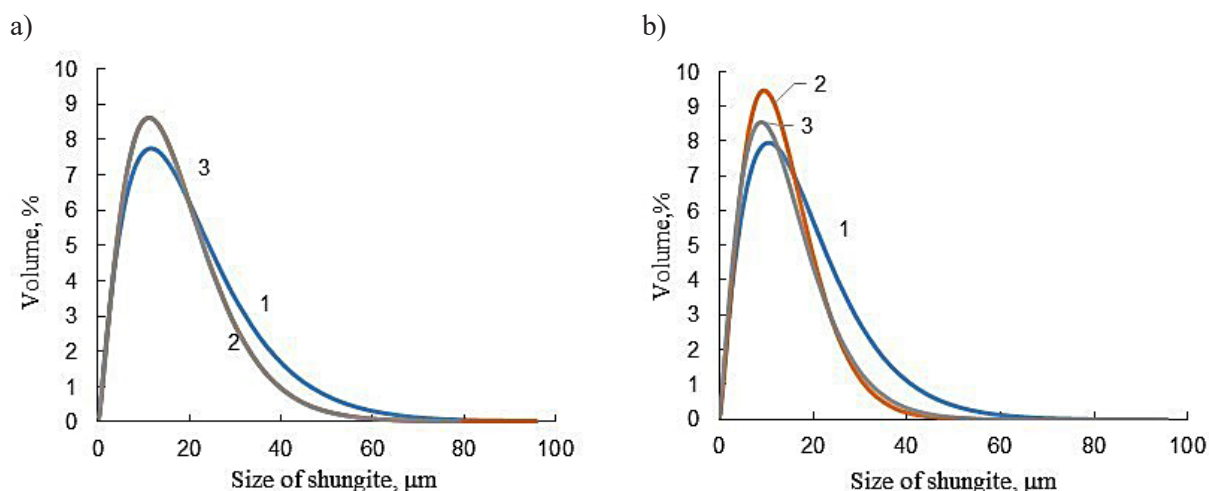


Figure 1. The dependence of the volume content of particles on the particle size: a – TS, b – TC; 1 – TS-D and TC-D; the samples after mechanochemical activation with the mass ratio of sample and balls: 2 – 1:1, 3 – 1:1.5

size to 7,773 μm compared to the initial sample size of 1 mm. The samples of shungite of carbonate origin compared to the samples of shale origin were easier to grind and showed a relatively smaller average particle diameter. At the same time, these samples have an increase in surface area per unit volume.

Figure 2 shows electron microscopic images of the shungite samples after mechanochemical activation. The samples are uneven in size granules of different shapes with a rough surface formed by numerous pits, differing in diameter and depth. The main structural element of shungites are globules, which are spherical or ellipsoidal carbon formations, within which the presence of voids, interglobular voids or pores were established. The figure highlights the sizes of some particles, according to which the average particle size is calculated. The average particle size of the TS sample after mechanochemical activation with a mass ratio of samples and balls of 1:1 was 2.75 μm , with a ratio of 1:1.5 – 3.57 μm . The average particle sizes of TC samples after mechanochemical activation were 4.78 μm – with a mass

ratio of samples and balls of 1:1 and 8.78 μm – with a ratio of 1:1.5.

Next, the initial and crushed samples of shungite in an amount from 0.2 to 5 mass % were added to BND 100/130 bitumen. Figures 3-6 show the dependences of the physico-mechanical parameters of bitumen on the added amount of shungite. As it can be seen from Figure 3, the softening point of bitumen with the addition of shungite samples first increases, then decreases, i.e. passes through the maximum. The value of the softening point of bitumen increases by 3°C, with the addition of shungite TS, its maximum value of 50.2°C was shown by bitumen with the addition of 0.2% of the shungite sample after mechanochemical activation. An increase in the softening point shows a favorable effect of shungite additives on the quality of bitumen, since it characterizes the temperature of the transition of bitumen from a solid to a liquid state.

In comparison with shale shungite, carbonate shungite has a more favorable effect on the increase in the softening point, in this case its value increases by 4–4.5°C. When adding samples of shungite TC, the maximum softening point of 51.5°C was

Table 2. Results of particle size measurement of the shungite samples after mechanochemical activation

Brand of shungite	Mass ratio of sample and balls	d_{10} , μm	d_{50} , μm	d_{90} , μm	d_{av} by vol., μm	d_{av} by surface, μm	S/V, cm^2/cm^3
TS-D	-	1,420	7,583	22,705	10,196	2,882	20820,590
TS	1:1	1,660	7,541	20,073	9,487	3,259	18407,970
TS	1:1,5	1,646	7,505	20,030	9,454	3,237	18538,400
TC-D	-	1,383	7,063	20,375	9,322	2,806	21385,640
TC	1:1	1,683	6,709	16,434	8,075	3,258	18418,950
TC	1:1,5	1,341	6,146	16,521	7,773	2,700	22275,790

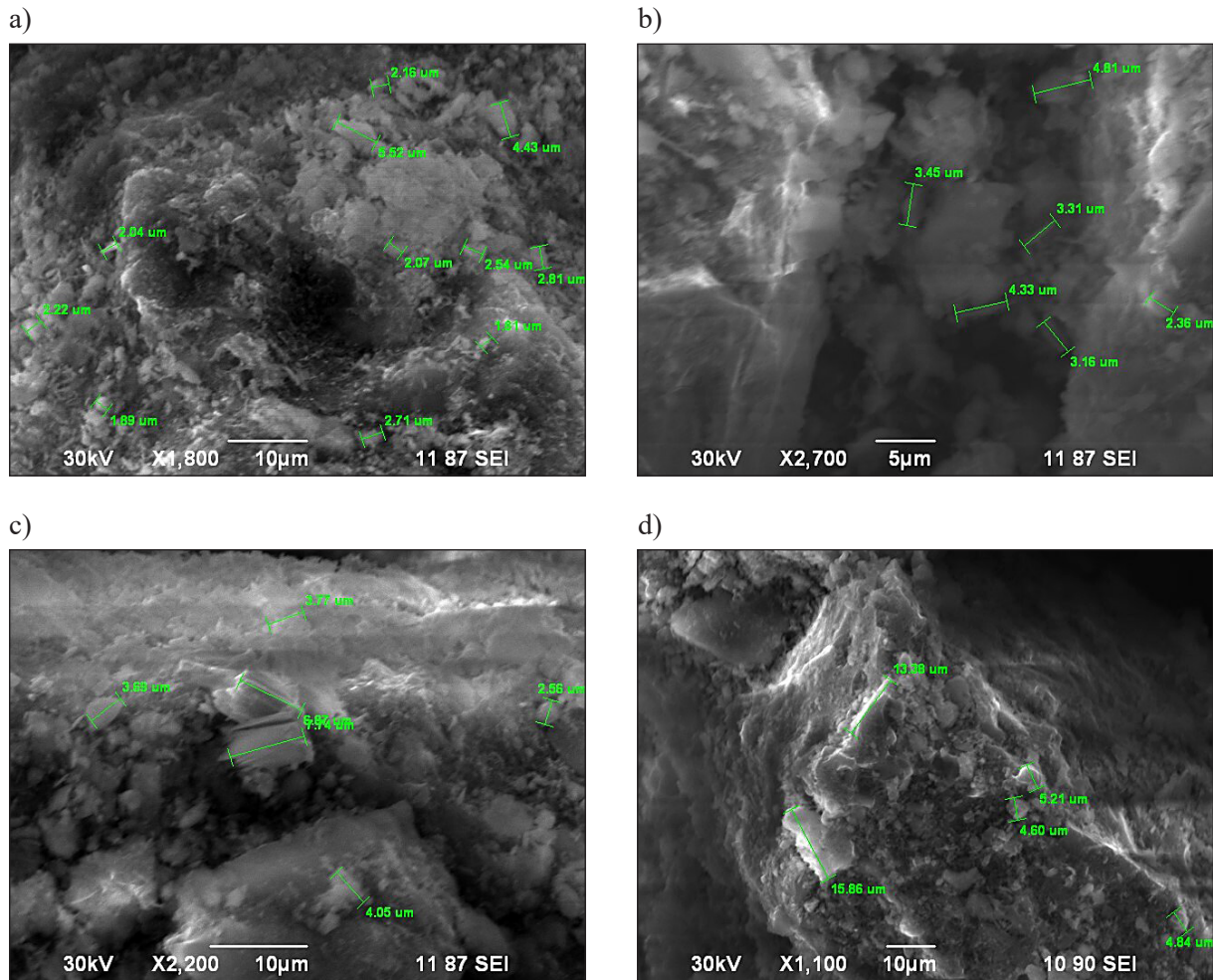


Figure 2. Electron microscopic images of the shungite samples after mechanochemical activation at the mass ratio of sample and balls: a – TS, 1:1, b – TS, 1:1.5; c – TC, 1:1, d – TC, 1:1.5

shown by the bitumen with the addition of 0.2 and 1% of shungite after mechanochemical activation. This is explained by the fact that the carbonate origin of shungite is similar in mineralogical composition to the compositions of mineral powders (limestone, shell rock), which further favors the improvement of the performance characteristics of asphalt concrete mixtures with their addition.

The ductility of bitumen characterizes its plastic properties or elasticity. As expected, the addition of shungite reduces this value of bitumen, since the addition of a carbon-containing modifier reduces the plasticity of bitumen. As it can be seen from Figure 4, the ductility of bitumen first decreases sharply, then decreases gradually or becomes constant. The ductility of bitumen is reduced from 111 cm to 51–52 cm with the addition of up to 5 mass % shungite of both origins. The smallest decrease in the extensibility of bitumen is observed when modifying shungite grades TS-D and TC-D with particle sizes of 20 µm.

The hardness of bitumen is characterized by penetration. As it can be seen from Figure 5, the addition of a modifier leads to a decrease in bitumen penetration. In the case of the addition of the shungite of the TS brand before and after mechanochemical activation, the penetration value decreases from 130 to 90–0.1 mm. The addition of the shungite of carbonate origin led to a decrease in bitumen penetration from 130 to 100–0.1 mm. For road bitumen grades, a significant decrease in penetration is undesirable, depending on the bitumen grades, its value should be within certain regulatory value. In this regard, the addition of carbonate grade shungite in comparison with the shale grade is considered acceptable.

After mechanochemical activation, superfine shungite, due to a change in the structure and amorphization of the components, will have a high porosity compared to known tire fillers and asphalt concrete modifiers. In shungite particles, a significant amount of bitumen resins will be accumulated in surface micropores, and some of the

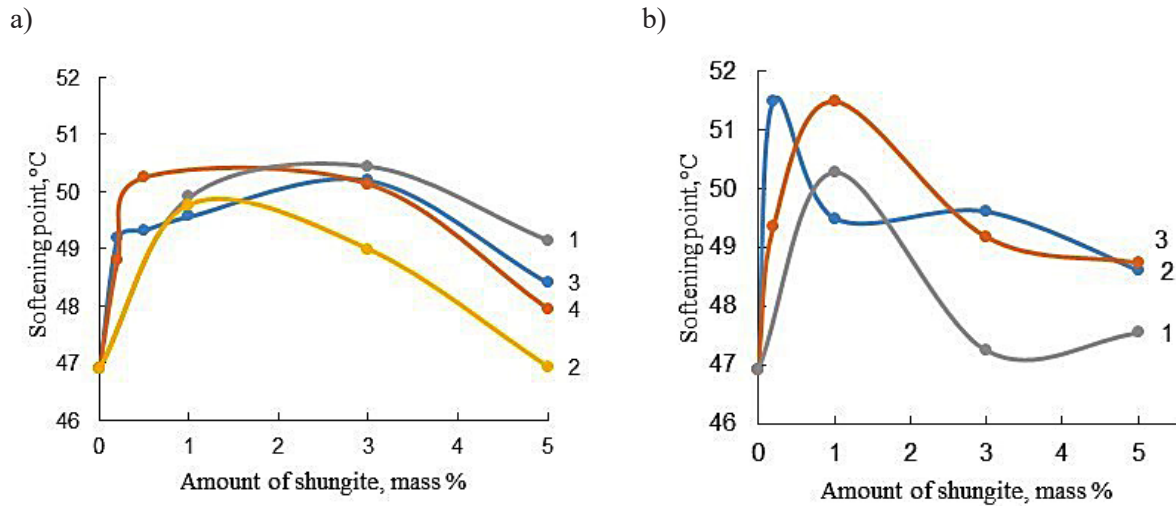


Figure 3. Dependence of the softening temperature of bitumen on the amount of shungite:
 (a) – TS: 1 – 1 mm; 2 – TS-D, 20 μm ; after MA at the mass ratio of the sample and balls: 3 – 1:1; 4 – 1:1.5;
 (b) – TC: 1 – 1 mm; after MA at the mass ratio of the sample and balls: 2 – 1:1; 3 – 1:1.5.

oils will penetrate into the material due to selective diffusion. Therefore, when using porous finely dispersed shungite, structured bitumen films on the surface of the particles will have a stronger adhesion compared to powder from dense rocks [Chernousov, 2011].

The nature of the surface of fine particles of shungite is of great importance in the formation of the structure of tires and asphalt concrete, since the chips, defects and microcracks that form during mechanochemical activation contribute to greater internal friction and better interaction of bitumen with the modifier. Due to the diphility

of shungite and the presence of active centers on its surface, when it is introduced into bitumen, an elastic mesh is formed due to the resulting bitumen-shungite bonds.

CONCLUSIONS

Thus, the grinding of the shungite of the Koksuy deposit was carried out by using the method of mechanochemical activation to micro-sizes. The shungite samples obtained after grinding had particle sizes up to 7.7 μm after measurements

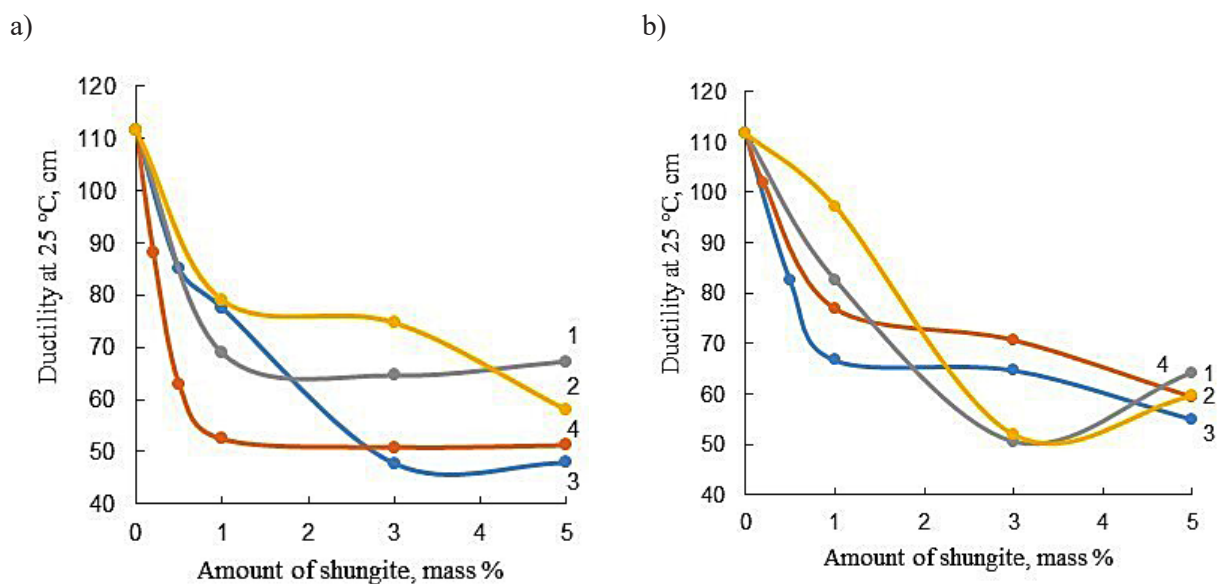


Figure 4. Dependence of the ductility of bitumen on the amount of shungite:
 (a) – TS: 1 – 1 mm; 2 – TS-D, 20 μm ; after MA at the mass ratio of the sample and balls: 3 – 1:1; 4 – 1:1.5;
 (b) – TC: 1 – 1 mm; 2 – TC-D, 20 μm ; after MA at the mass ratio of the sample and balls: 3 – 1:1; 4 – 1:1.5

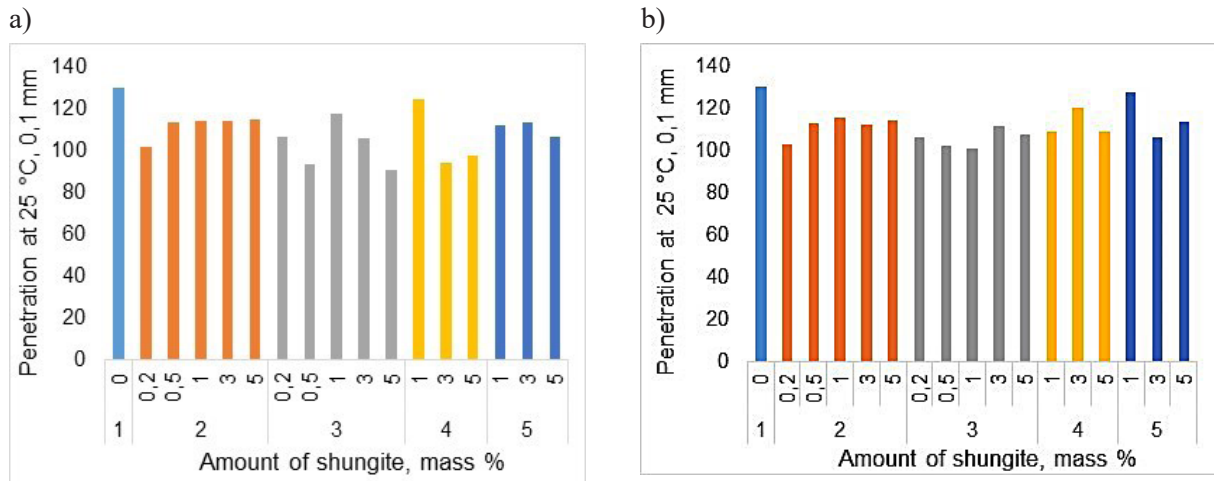


Figure 5. Dependence of bitumen penetration on the amount of shungite: 1 – initial bitumen;

- (a) – TS: 2 – 1 mm; 3 – TS-D, 20 μm ; after MA at the mass ratio of the sample and balls: 4 – 1:1; 5 – 1:1.5;
 (b) – TC: 2 – 1 mm; 3 – TC-D, 20 μm ; after MA at the mass ratio of the sample and balls: 4 – 1:1; 5 – 1:1.5

with a laser analyzer, up to 2.75 μm according to electron microscopic images. The addition of initial and crushed shungite samples to BND 100/130 bitumen led to an increase in the softening temperature, a decrease in extensibility and a decrease in bitumen penetration. The samples of shungite of carbonate origin of the TC brand showed a more favorable effect on the characteristics of bitumen, which is explained by the proximity of their mineral base to the composition of mineral components of asphalt concrete mixtures. After mechanochemical activation, defects appear in the samples that promote active absorption and interaction with bitumen components. The optimal amount of added shungite was 1 mass %, at which the maximum value of the softening temperature and a slight decrease in the extensibility and penetration of modified bitumen were observed.

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