ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program «8D07113 – Nanomaterials and nanotechnology in chemistry»

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Modification of petroleum bitumen with nanomaterials

The relevance of the topic. The development of road infrastructure is an important condition for economic growth and improving the quality of life of the population. One of the key materials used in road construction is petroleum bitumen. It is susceptible to aging, deformation, thermal destruction and the effects of aggressive external factors, which limits the operation of road surfaces and requires frequent repairs.

In conditions of increasing requirements for the reliability and strength of road surfaces, the task of improving the physical, mechanical and operational characteristics of bitumen is particularly relevant. One of the promising areas is the modification of bitumen using nanomaterials. Nanostructured additives, due to their high specific surface area and chemical activity, improve aging resistance, and heat resistance, water and frost resistance, and plasticity of bitumen. The addition of small amounts of nanomaterials allows for a positive effect, which makes the modification economically advantageous.

Thus, the modification of petroleum bitumen with nanomaterials is an urgent scientific and practical task, the solution of which will improve the quality and durability of road surfaces, as well as reduce the cost of their maintenance and repair.

The aim of the work is to obtain nanostructured modifiers and establish their effect as additives to bitumen to improve performance.

Research objectives. To achieve this goal, the following tasks were solved:

- obtaining nanostructured shungite samples and determining their composition and physico-chemical characteristics;
- investigation of the effect of nanostructured shungite as a modifier for BND 100/130 road bitumen and determination of physico-mechanical and rheological characteristics;
- obtaining biochar from several types of biomasses and analyzing its composition and structure;
- investigation of the effect of biochar on the rheological properties of bitumen PG 70/100;
- synthesis of graphene oxide from biochar of lemon peel and investigation of its effect on rheological characteristics of bitumen BND 100/130;
- - study of the effect of rejuvenation of bitumen PG 70/100 with oil based on polymer waste;
- investigation of the effect of carbonized rice husk on the properties of construction bitumen BN 90/10 and the production of bitumen mastic.

Research methods. Devices of modern methods of analysis were used to conduct research on the topic of the dissertation: Bruker Alpha IR spectrometer (Bruker Optics GmbH, Karlsruhe, Germany), rheometers SR5000 (Rheometrics, USA) and Smart Pave 102 rheometers (Anton Paar GmbH), Quanta 3D 200i scanning electron microscope (FEI Company, USA), Winner 2000E laser analyzer (Jinan Winner Particle Instruments Stock Co., Ltd, China), Solver Spectrum atomic force microscope (NT-MDT), STA6000 thermogravimetric analyzer (Perkin-Elmer), DSC 131 differential scanning calorimeter (Setaram Instrumentation, France), Solver Spectrum Raman spectrometer (NT-MDT).

The objects of the research are shungite from the Koksu deposit, biochars from plant waste, graphene oxide, and bitumen grades BND 100/130, PG 70/100, and BN 90/10.

The subject of the research is the processes for producing nanomaterials and modifying bitumen with them.

The main provisions submitted for defense:

- modification of bitumen BND 100/130 by shungite from the Koksu deposit in the amount of 1 wt. %, previously mechanochemically activated in an isopropanol medium at a grinding speed of 700 rpm with a mass ratio of 1.5:1:1.5 shungite, isopropanol and steel balls for 60 minutes, increases the temperature of bitumen transition from a viscoelastic state to a liquid by 5,7 °C, after aging by 4,8 °C due to the formation of graphene-like crystallites structures measuring 27,6 nm with 3-5 layers and the presence of graphene sheets of a "bee structure" up to 100 nm high with fragments less than 20 nm on the surface of modified bitumen;
- biochar obtained by pyrolysis of lemon peel at 550 ° C for 1,5 hours in a nitrogen atmosphere in an amount of 3 wt. % increases the transition temperature of bitumen PG 70/100 from viscoelastic to liquid state by 2,2 °C, the modulus of elasticity at 50 ° C by 1,8 kPa and shows an antioxidant effect, which is explained by the graphite plate-like structure and low hydrophobicity (28,9 °);
- modification of BND 100/130 bitumen with graphene oxide obtained by the Hammers method from biochar by pyrolysis of lemon peel at 500-600 °C, in an amount of 3 wt. % led to an increase in its strength and ductility with an increase in the effective shear stress by 25 kPa and resistance to fracture under cyclic load, fatigue life by 2 times due to the uniform height distribution in the graphene oxide surface profile in the range of 20-250 nm with a high degree of dispersibility and the predominance of the nanosheet structure;
- modification of bitumen BN 90/10 with rice husk, carbonized at a temperature of 600 °C in an argon atmosphere for 1 hour and mechanochemically activated at a speed of 1600 rpm for 60 minutes, in an amount of 1 wt. % made it possible to obtain waterproofing bitumen mastic with increased softening temperature by 10 °C, hydrophobicity with an average contact angle of 112,3 °, due to an increase in the carbon content in rice husks to 57,5% and the formation of graphene-like crystallites 36,5 nm in size with 3-5 layers.

The main results of the work:

1. Nanostructured samples of shungite rocks from the Koksu deposit with particles measuring 67,2-91,3 nm was obtained by mechanochemical activation in

an isopropanol medium at a grinding speed of 700 rpm with a mass ratio of 1.5:1:1.5 for shungite, isopropanol and steel balls for 60 minutes. Raman spectroscopic analysis of shungite samples showed the formation of graphene-like crystallites with dimensions of 27,6 nm with 3-5 layers.

2. Modification of bitumen BND 100/130 with mechanochemically activated shungite in an amount of 1 wt. % increases its transition temperature from viscoelastic to liquid state (T*) of bitumen by 5,7 °C, after aging by 4,8 °C. Atomic force microscopic (AFM) analysis showed folded graphene sheets of a "bee structure" up to 100 nm high on the surface of the modified bitumen. The addition of mechanochemically activated shungite in isopropanol forms bitumen with a uniform surface with fragments of less than 20 nm, according to AFM analysis, improves the resistance of the bitumen structure to aging.

3. Biochar obtained by pyrolysis of lemon peel at 550 °C for 1,5 hours in a nitrogen atmosphere showed an increase in the transition temperature T* by 2,2 °C, modulus of elasticity at 50 °C by 1,8 kPa when added to bitumen PG 70/100 in an amount of 3 wt. % This positive effect explained by formation of the graphite plate-like structure and low hydrophobicity.

4. Graphene oxide was synthesized from biochar obtained by pyrolysis of lemon peel by the modified Hammers method at 500-600 °C. According to AFM analysis, the surface profile has a uniform height distribution in the range of 20-250 nm, which indicates its high dispersion and the predominance of mainly nanolayer structures. Modification of bitumen BND 100/130 with graphene oxide in an amount of 3 wt. % has led to an increase in its strength and ductility, increases the effective shear stress by 25 kPa, and resistance to fracture under cyclic load, increases fatigue life by 2 times.

5. Modification of bitumen PG 70/100 with oil based on polymer waste (PFU) in an amount of 3 wt. % showed rejuvenating efficacy after aging with a decrease in the transition temperature T*, which is explained by an increase in the content of saturated compounds in asphaltenes according to IR spectroscopic analysis.

6. By carbonation of rice husks at a temperature of 600 °C in an argon atmosphere for 1 hour and mechanochemical activation at a speed of 1600 rpm for 60 minutes, samples with an increase in carbon content of 57,5%, a crystallite size of 36,5 nm and a number of layers of 3-5 were obtained. Modification of bitumen BN 90/10 with carbonized and mechanochemically activated rice husk in an amount of 1 wt. % allowed the preparation of waterproofing bitumen mastic with increased softening temperatures by 10 °C, hydrophobicity with an average contact angle of 112,3 °.

Scientific novelty of the obtained results.

- For the first time, the presence of folded graphene sheets of a "bee structure" up to 100 nm high with fragments less than 20 nm on the surface of BND 100/130 bitumen modified with mechanochemically activated shungite from the Coke deposit has been shown.;
- for the first time, graphene oxide was synthesized by the Hammers method from biochar obtained by pyrolysis of lemon peel at 500-600 ° C and its effect on the rheological characteristics of BND 100/130 bitumen was established due to the

formation of a strong and flexible mesh structure during the interaction of hydroxyl, carboxyl, epoxy groups of graphene oxide with asphaltene-resinous bitumen components, which absorbs and redistributes mechanical loads, preventing the development of cracks and increasing the strength and rigidity of bitumen;

- for the first time, waterproofing bitumen mastic with improved physical and mechanical characteristics was obtained when modifying bitumen BN 90/10 1 wt. % of carbonized and mechanochemically activated rice husks, an increase in carbon content, the distribution of graphene-like nanostructures with the formation of a nano-reinforcing mesh and the presence of residual functional groups on the surface increases the softening temperature, hydrophobicity and adhesion of bitumen.

The theoretical significance of the work lies in substantiating the positive influence of nanomaterials such as nanostructured shungite, lemon peel biochar, graphene oxide, and carbonized rice husk on the properties of bitumen through the distribution of graphene-like nanostructures. **The practical significance of the research** lies in improving the performance characteristics of bitumen materials - increasing strength, elasticity and resistance to aging, increases the service life of road surfaces and reduces the cost of repair and maintenance of roads.

Compliance with scientific development directions or government programs. The dissertation work was carried out within the framework of the Zhas Galim grant project on the topic AP25795719 "Development of technology for modifying bitumen with a solid product of pyrolysis of used tires and food waste to impart antioxidant properties".

Publications. 12 publications have been published, including 5 articles in international journals indexed in the Web of Science and Scopus databases, 3 articles in republican journals from the List of Recommended publications, and 4 reports in conference proceedings.

The doctoral student's personal contribution to the preparation of each publication:

1. Article «Modification of petroleum bitumen by mechanochemically activated shungite from the Koksu deposit» in the journal «Combustion and Plasma Chemistry»: preparation of a review and analysis of literature data, obtaining and processing results.
2. Article «Mechanochemically Activated Shungite as an Additional to Improve Bitumen Characteristics» in the «Journal of Ecological Engineering»: preparation of a review and analysis of literary sources, obtaining and processing analysis results.
3. Article "Influence of Adhesion Additives on the Grip of Bitumen to Stone Material and Water Resistance of Asphalt Concrete" in the «Eurasian Chemical-Technological Journal»: obtaining and discussing experimental data, preparing a review of literature data.
4. Article «Modification of bitumen and asphalt concrete by carbon nanomaterials» in the journal «Combustion and Plasma Chemistry»: preparation of a review and analysis of literary sources.

5. Article «Effect of Nanostructured Shungite on the Rheological Properties of Bitumen» in the journal «Infrastructures»: obtaining and discussing experimental data.

6. Articles «Modification of bitumen with char from pyrolysis of lemon peel waste» and «Modification of Bitumen with Carbonized Rice Husk» in the «Journal of Physics: Conference Series»: obtaining and discussing experimental data.

7. Article «Rheological characteristics of petroleum bitumen according to the Superpave system» in the journal «Combustion and Plasma Chemistry»: obtaining and discussing experimental data.

8. Article «Integration of Coke and CNMs with Bitumen: Synthesis, Methods, and Characterization» in the journal «Nanomaterials»: preparation of a review and analysis of literary sources.

9. Article «Valorization of Agricultural Wastes into Environmentally Sustainable Asphalt Binders» in the journal «Molecules»: obtaining and discussing experimental data.

10. Proceedings of scientific conferences and symposia: description and presentation of experimental data and analysis results.

The structure and scope of the dissertation. The dissertation consists of an introduction, 5 chapters and conclusion. The work is presented on 152 pages, contains 27 tables, 52 figures. The list of sources used includes 186 titles.