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Article

Experimental study of the influence of modified sulfur components on physical and mechanical characteristics of bitumen compositions

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Abstract. In this research work, the physical, mechanical and performance characteristics of bituminous binder 90/130 before and after its modification with sulfur in the proportions of 10%, 30% and 50% of the binder weight were analyzed. Experimental results showed the effect of sulfur content on the mechanical characteristics of bituminous binder. By elemental analysis of the spectra of modified bitumen binder samples, it was found that there were no significant chemical changes with increasing sulfur content. The formation of new chemical compounds was not revealed, which is confirmed by the absence of new characteristic peaks in the spectra. Analysis and comparison of the experimental data of softening temperature showed an insignificant influence of the liquid heating rate on the concentration of the modifying agent. However, the increase of sulfur concentration more than 10% in the modified bitumen leads to an increase in softening temperature. This is due to the formation of denser structure and increase in viscosity of bitumen with increasing amount of sulfur in the system. Thus, the presence of sulfur as a dispersed phase in polymer bitumen has a natural effect on the mechanical characteristics of sulfur asphalt concretes, leading to an increase in their mechanical properties with increasing sulfur content.
Keywords: bituminous binders, modified bitumen, sulfur, ring and ball method, softening point, penetration.

1. Introduction

Modern highways, especially those subjected to significant dynamic loads, as well as airfield runways and cargo areas, require high quality standards for their asphalt concrete pavements [1]. Petroleum bitumens, which are dispersed colloidal systems of complex chemical composition, are used as road binders. To improve the quality and durability of road surfaces, modified road binders are now widely used [2]. The modification process is aimed at improving the properties of bitumen by combining it with special components.

Nowadays, not pure bitumen, but modified with different components, the main difference of which is higher performance characteristics and qualities, is used quite actively in the field of construction [3-6].

Studies on the use of sulfur as a modifying constituent in bituminous binders have started relatively recently and are not fully understood [7]. Crystalline sulfur, produced as are product in the oil and gas industry, it's an available resource that, when in solid state, is non-toxic and has high chemical resistance in a variety of aggressive industrial environments [8].

The authors of the works revealed [9, 10] that sulfur not only serves as a mixture filler, but also acts as a stabilizer of bitumen mixture. Another work presents that the addition of sulfur content in paving materials above 30%, with the correct design and methodology of bitumen binder modification, leads to effective stabilization of these materials [9].

According to standard normative documents [11], one of the key indicators of binders are the values of softening point and brittleness temperature. The working range of a binder is defined as the difference between the brittleness temperature (usually below -17°C) and the softening point (usually above +43°C). In this range, the substance is in a visco-plastic state characterized by moderate plasticity without brittleness and the ability to retain shape without fluidity under small shear loads. Thus, materials based on such a binder have the required consumer properties, such as moderate ductility and shear stability, over the operating temperature range.

Due to the need to ensure the stability of bituminous binder properties at all stages of the technological process there is a need to improve a set of methods for assessing its quality.

This paper presents the results of research into one of the most effective directions in road construction - modification of petroleum road bitumen and obtaining sulfur asphalt concrete on their basis.

2. Methods

In this study, a consecutive series of experiments was carried out in order to identify in detail the nature of interaction between gray and oil bitumen. The object of the study was oil road bitumen 90/130 produced by Promstroybitum, LLP, corresponding to [11].

In the manufacture of sulfur-bitumen binder was used granulated crystalline sulfur according to [12] in proportions of 10%, 30% and 50% of bitumen weight. The process of modification was carried out by heating on a water bath to 100^{o}C of pure bitumen grade 90/130 and adding sulfur and with careful and continuous stirring with a propeller mixer at a speed of 100 rpm for 90 min. Multi-element analysis of a wide range of matrices of modified bitumen was carried out on a Rigaku EDXRF spectrometer (Japan), which use X-rays in the energy range 1-65 eV and photoelectric effect to determine the elemental composition.

The study of mechanical properties of modified bitumen was based on the study of mechanical properties of the base sample of bitumen 90/130 relative to the samples with the addition of sulfur.

To determine the thermal sensitivity and resistance of the sample of bitumen 90/130 to deformation, studies of its softening temperature (T_S) were carried out on the automatic equipment B072 "Automatic apparatus ring and ball" of the company "Matest" (Italy). Two chromium-plated rings of step form were filled with 6 g of base bitumen without modifier each. For the purpose of additional fixation two centering rings and two steel balls Ø9.5 mm. each were placed on top of them. The finished samples were mounted in a special brass frame for immersion in a beaker made of pyrexerglass, i.e. the medium. Freshly distilled cooled distilled water of 600 ml volume was used as a thermoregulating medium. The process of water heating not exceeding 80^{o}C was carried out using an integrated glass-ceramic heating surface providing a heating rate of 5°C/min. in accordance with the requirements of [11]. Uniform heating was provided by the built-in magnetic stirrer with electronic speed controller, capable of providing rotation in the range from 0 to 160 rpm. The temperature sensor connected to the B072 apparatus was inserted in the center of the brass frame, providing accurate recording of the temperature change of the medium. Two integrated laser sensors were used to record the ball drop moment used to determine the softening temperature. These were placed on either side of a beaker containing distilled water. The difference in T_S between the base and modified bitumen is not more than 1°C, which is within the normalized measurement error.

Studies of specific viscosity of modified bitumen were carried out on penetrometer B056-02 KIT of "Matest" (Italy). Penetration was subjected to modified bitumen with a mass of 1500 g., preheated in a steam bath to 100^{o}C. Penetrometer equipped with digital micrometric adjustment was automatically fixed at zero position at the boundary of the needle and modified bitumen touching. Special 50 g and 100 g weights were mounted on the penetrometer to ensure vertical penetration of the standard needle. A magnetic controller with an electronic digital programmable timer, automatically releasing the plunger head with the specified mass, ensured free fall of the needle during the 5-second test. Depth, penetration time and sample temperature were recorded automatically.

3. Results and Discussion

In order to control the process of bituminous binder modification and to determine the chemical composition of bitumen 90/130 after modification with sulfur in the proportions of 10%, 30% and 50% of the initial sample weight, elemental analysis was carried out on a Rigaku EDXRF spectrometer in the energy range from 4 to 23 eV (Figure 1).

Graph 1 shows the spectra of elemental analysis of bitumen 90/130 before and after modification with sulfur 10%, 30% and 50%. In the obtained spectra intense characteristic peaks of bitumen 90/130 binder at 17 eV and 18 eV corresponding to stretching vibrations of C-H noodles in CH_2 elements are noticeable. These peaks indicate the presence of a high concentration of arene in bitumen binder [13].

The first observed peak around 4.5 eV corresponds to deformation vibrations of CH_2 elements in alkane pairs. Three consecutive peaks with energies of 4.6 eV, 5.0 eV and 5.2 eV indicate out-of-plane vibrations of CH and also indicate the presence of arene compounds. These results are in agreement with previous studies [13], confirming the structural features and composition of the bituminous binder.

Further analysis of the spectra demonstrates an insignificant change in intensity at energies of 6.3 eV, 6.6 eV and 9.7 eV. The absence of significant peaks in these regions indicates that the modification of bituminous binder 90/130 does not lead to significant changes in its chemical composition. In other words, new chemical compounds formed due to the interaction of sulfur and oil bitumen were not detected. Similar results were obtained earlier in other studies [14], which confirms the continuity of this phenomenon. The intense peaks found around 8.5 eV and 9 eV correspond to the strain vibrations $\delta(CH_3)$ and $\delta(CH_2)$, respectively. These maxima are characteristic of saturated hydrocarbons, paraffins, and oils.

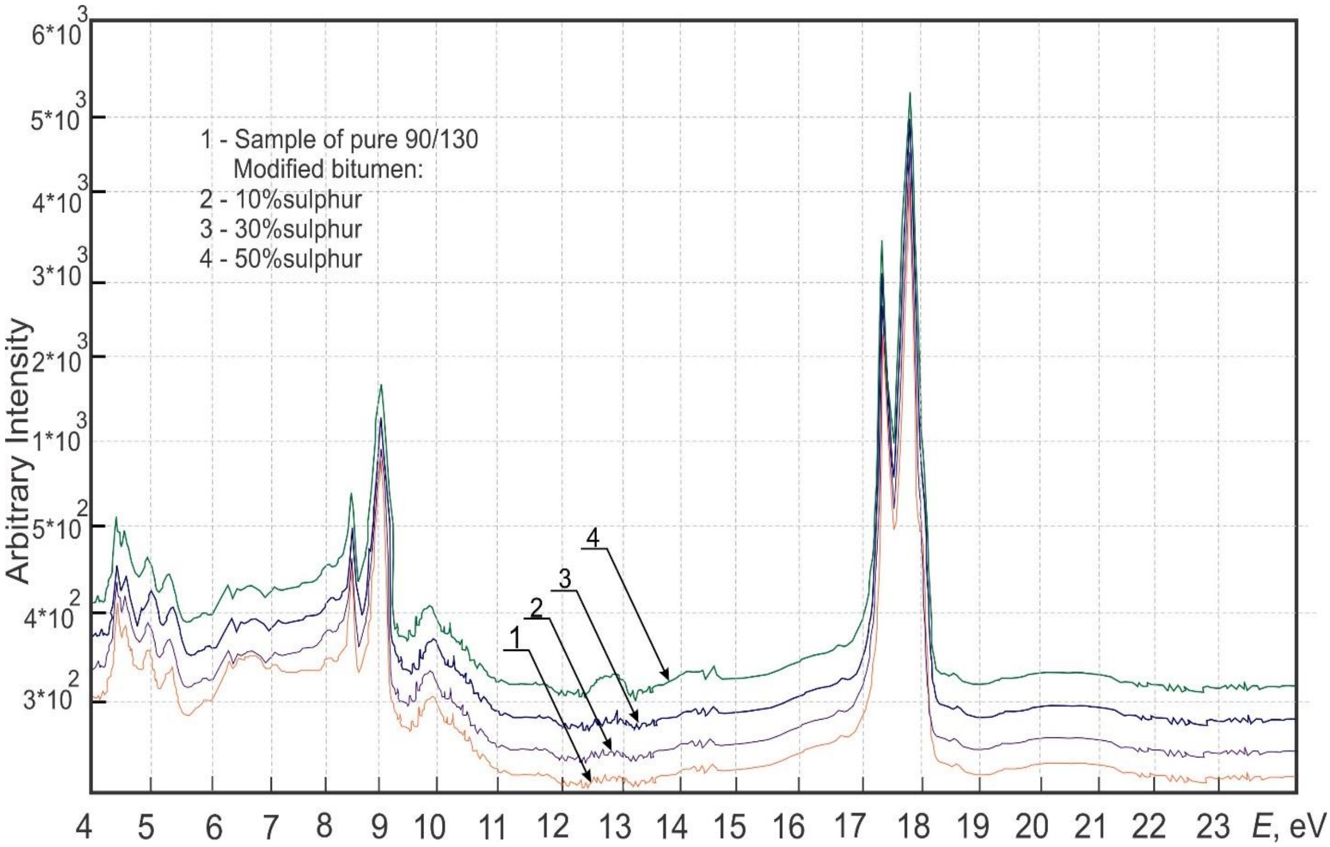

Figure 1 – Elemental analysis of a wide range of modified bitumen: 1 – Pure 90/130; 2 – modified bitumen with 10% sulphur; 3 – modified bitumen with 30% sulphur; 4 – modified bitumen with 50% sulphur

The maximum at 9.9 eV corresponds to stretching vibrations of C=C noodles; this feature is observed both in the spectra of the original sample bitumen 90/130 and in the spectra of sulfur-modified bitumen. The structural complexity of this band indicates the extensive presence of arene elements in the bitumen composition, including asphaltenes and other components [15].

When analyzing the spectra, it was also found that both the sample of the original bitumen 90/130 and the sample of modified bitumen with the addition of 10% sulfur contain bound water. This is confirmed by the presence of bands with peaks at 19 eV and 20 eV, which shows to stretching vibrations of the oxygen-hydrogen bond in hydroxyl groups involved in the formation of intermolecular hydrogen bonds. However, for samples with 30% and 50% sulfur content, these peaks are less intense, indicating less water. This suggests a potential improvement in performance properties, such as frost resistance, for bituminous binders with 30% and 50% sulfur content.

The results of the study of physical and mechanical properties of the modified binder indicate the effect of changing the concentration of sulfur on all analyzed characteristics of the binder. At the same time, the analysis of concentration dependences confirms the linear relationship between the sulfur concentration and the relative change in these properties.

Figure 2 shows the temperature dependence of the heating rate of the medium, demonstrating that increasing sulfur concentration leads to an increase in the Ts at all heating rates. The Ts is indicated as the average value of temperatures at a fixed rate at which two disks soften sufficiently for each ball wrapped with binder to fall a distance of 25 mm. The analysis of the results shows that varying the heating rate within 0.5 °C causes an error in the Ts measurement between 1.0 and 1.5 °C.

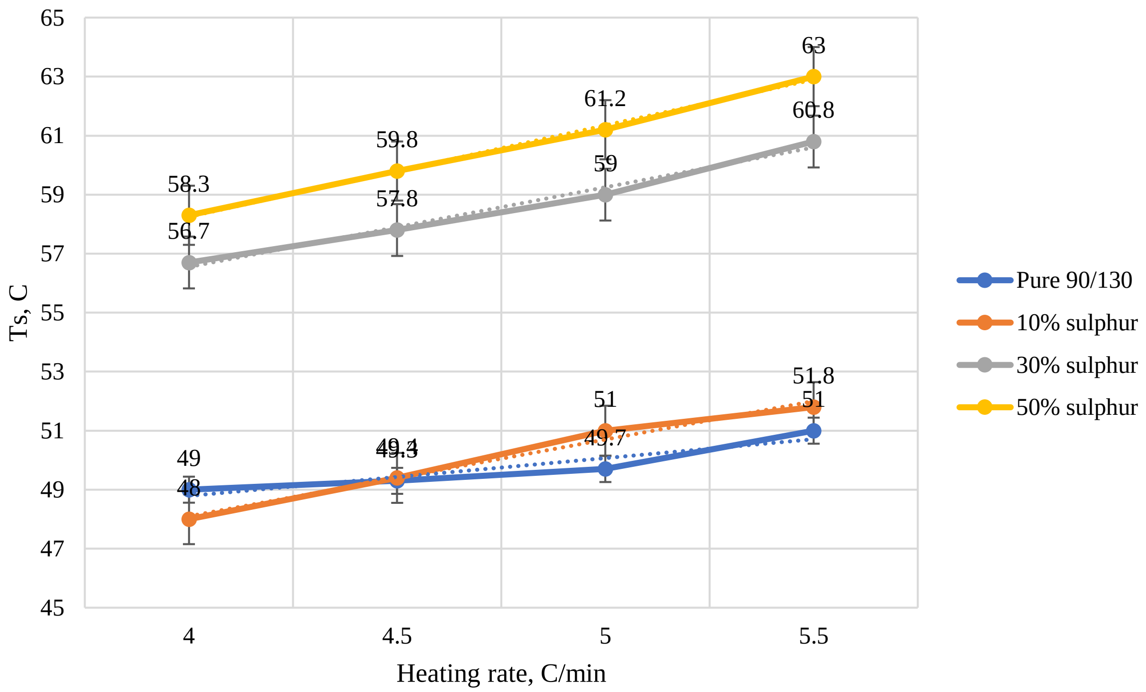

Figure 2 – Effect of medium heating rate on softening point of bitumen 90/130 before and after modification

From the graph 2 shows that the initial sample of bituminous binders grade 90/130 did not show a significant effect on the range of operating temperatures. However, at a concentration of sulfur not exceeding 10%, there is a decrease in softening temperature by 10%. This effect can be explained by the insufficient amount of sulfur formed and its low molecular weight, which does not contribute to the formation of a spatial mesh of the polymer, improving the working temperature range. When increasing the concentration of sulfur as a filler, the amount of formed mixture increases significantly, which leads to a marked increase in the viscosity of the system and, consequently, an increase in the softening temperature. It is worth noting that when introducing crystalline sulfur into bitumen 90/130 in the amount of 10%, 30% and 50% of the mass of the binder, the physical and chemical parameters meet the requirements of RK 218-145-2019.

One of the important parameters of physical and mechanical properties of binders is the measure of resistance under gravity. Studies on the effect of temperature on the penetration depth at 25°C of binders can be considered optimal, because such data allow us to evaluate the behavior of the material under conditions of comfortable temperature, which can be significant in the design and use of materials in different climatic zones [16].

To evaluate the dynamic viscosity of modified bitumen, we conducted studies aimed at revealing the dependence of penetration depth on temperature when adding weights weighing 50 g and 100 g, the data of which are shown in Figures 2 - 3.

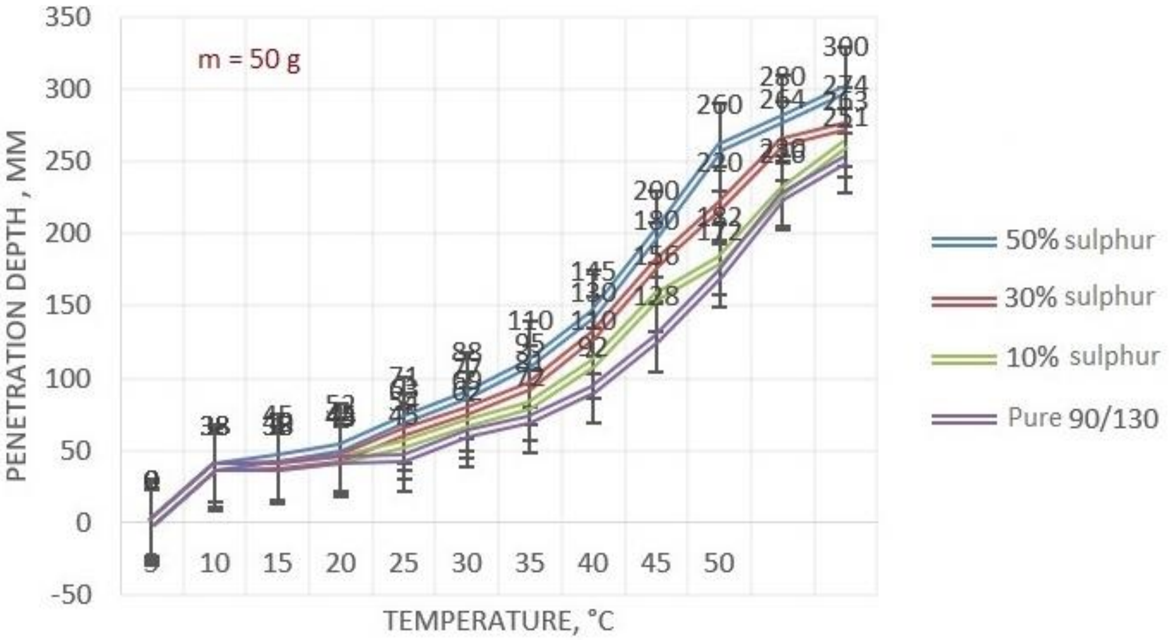

Figure 3 – Dependence of penetration depth on temperature of bitumen 90/130 before and after modification with additional mass of 50 g

Figure 3 shows the results of the analysis, which indicate that the changes in the properties of sulfur-bitumen binder associated with an increase in sulfur content. Note that to a large extent such changes are due to the presence of an additional dispersed phase due to physically free sulfur, which significantly affects the viscosity of the materials. Diagram 3 shows that at a standard temperature of 25°C and a mass of 50 g. the depth of penetration of the needle in the original sample of bitumen grade 90/130 is less than in the modified samples with the addition of sulfur. It is observed that the penetration depth increases with increasing sulfur concentration (10%, 30% and 50% of bitumen mass). This indicates an increase in the plasticity and softening of the material with increasing penetration, indicating a decrease in its brittleness. The experimental data in Figure 3 indicates that the effect of sulfur, which has a melting point of 120°C, becomes more prominent as the operating or testing temperature increases, which is consistent with the pattern of increasing its effect on material properties.

In order to determine the viscosity more accurately, we conducted an experiment at 100 g and the results are shown in Figure 4. The analysis of the obtained data shows that when increasing the temperature of sulfur-bitumen binder and increasing the additional load there is a slight increase in the depth of penetration of the needle into the bitumen. Consequently, we can conclude that the additional external load practically does not affect the increase in viscosity of bitumen 90/130 before and after modification with sulfur. It is worth noting that with increasing temperature in the range from 30ºC - 50 ºC penetration depth increases sharply, which indicates increased plasticity properties of pure and modified bitumen 90/130.

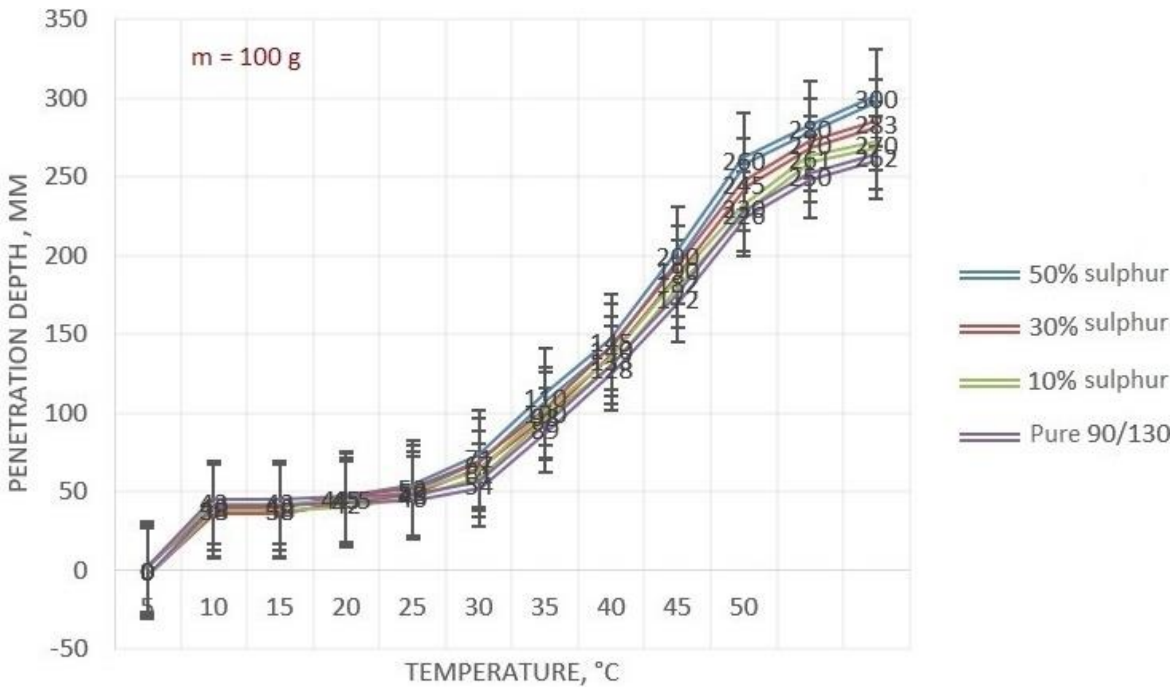

Figure 4 – Dependence of penetration depth on temperature of bitumen 90/130 before and after modification with additional mass of 100 g

4. Conclusions

In this work were investigated physical-mechanical and performance indicators of bituminous binder 90/130 before and after modification with sulfur in proportions of 10%, 30% and 50% of the binder weight. At elemental analysis of spectra of sulfur-modified bitumen binder samples no noticeable chemical changes were revealed. Increasing the mass fraction of sulfur from 10% to 50% in the binder bitumen 90/130 did not lead to the formation of new chemical compounds, which is confirmed by new characteristic peaks. Note that the positions of the main maxima of the recorded spectra did not differ significantly.

Analysis and experimental comparison of softening temperature allowed to reveal insignificant influence of liquid heating rate from the concentration of modifying component. Increase of sulfur concentration more than 10% in the modified bitumen leads to an increase in softening temperature. This is explained by an increase in the amount of sulfur in the system, which causes the formation of a denser structure and an increase in the viscosity of bitumen.

It is revealed that the presence of sulfur as a dispersed phase in bitumen has a regular effect on the mechanical characteristics of sulfur asphalt concretes: there is an increase in mechanical properties with increasing sulfur content.

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