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ON CHANGES IN THE PERFORMANCE CHARACTERISTICS OF SBS-POLYMERS IN BITUMEN BINDERS UNDER SHORT-TERM INTENSIVE UV IRRADIATION

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Abstract. *Nowadays, more stringent quality requirements are imposed on road construction materials. One of the ever-present but less obvious natural influences accelerating pavement erosion is UV radiation. Despite the shallow penetration depth of this type of radiation, its energy is sufficient to initiate irreversible physical and chemical processes. Taking into account the constant exposure of the pavement to sunlight during highway operation in conjunction with the natural wear of the top layer of the pavement, the resulting damage becomes significant. The study examines the dynamics of changes in the strength characteristics of functional polymers dispersed in bituminous binder during paving. The interval of change in properties is traced and qualitative analysis of several grades of commercially available SBS polymers is carried out. The qualitative change of functional characteristics leading to the subsequent degradation of the pavement is made already after an interval of ten hours after paving the mixture. The highest UV resistance and tendency to restructuring and cross-linking is demonstrated by KRATON D1192 among the tested grades.*

Keywords: Discoloration Meter, UV irradiation, SBS polymers, IR-spectroscopy, bitumen binder

Introduction

Modern trends in the development of road construction in Russia, together with unpredictably changing climatic conditions and increasing load on transportation routes imply the use of materials whose structural properties are able to meet the increased requirements for the quality of modern road surfaces [1, 2].

When considering the essence of the problem, it is impossible not to take into account the different behavior of materials used in different structural layers of pavements. Distribution of temperature, solar radiation, shear stresses, dissipation and accumulation of residual deformations, moisture retention - all these factors are perceived differently by each structural component of the pavement, which makes the need to change the qualitative composition of applied road binders urgent [3, 4].

Despite the small penetration depth, ultraviolet radiation has a significant impact on the change of performance properties of bituminous-containing materials. Three main segments of the UV spectrum are distinguished: UV-A, UV-B and UV-C with wavelengths of 315-400 nm, 280-315 nm and 100-280 nm, respectively. As sunlight passes through the Earth's atmosphere, all of the C-type rays and 90 % of the B-type rays are absorbed by water vapor and atmospheric gases. UV-A is much less affected by atmospheric factors, making the radiation reaching the planet's surface about 95 % UV-A and 5 % UV-B. Exposure to these two radiation ranges is the cause of surface degradation of bituminous binders [5, 6].

Prolonged aging provokes curing of asphalt concrete surface layers, resulting in active cracking and further pavement degradation [7, 8, 9].

It is simply not possible to avoid the effects of the sun on the pavement due to the long length and obvious operational purpose of highways, which makes unpredictable damage along the entire length inevitable. These features motivate to modify the formulation so as to minimize photodegradation as much as possible [10, 11].

Objects and methods of research

The purpose of the study is to determine the effect of isolated UV radiation on the change of performance characteristics of SBS polymers which are included in the composition of polymer-bitumen binders. Finding the precise moment of change of properties will allow to determine the sufficient irradiation dose for initiation of primary processes of destruction and cross-linking of macromolecular structures. Understanding the boundaries of the property change interval is important for optimizing the composition of the mixture capable of leveling the loss of coating integrity from irradiation in the long term [12, 13].

As research objects, this paper considers samples of commercially available TPE used as components of polymer-bitumen binders used in pavements [10, 11].

A GOTECH GT-7035-EUAB light aging chamber was used to simulate the effects of a specific part of the solar radiation spectrum. During operation, the temperature of road pavement under the influence of sunlight can increase, so the value of 50oC was chosen as a constant temperature value for all conducted stages of irradiation. This value allows to reduce to a minimum level oxidative processes during thermo-oxidation in the process of activation of chemical reactions of bituminous binder components. The GOTECH GT-7035-EUAB chamber is equipped with a sunlight lamp with a power of 300 W and two lamps generating UV radiation with a wavelength of 280-315 nm. The inner surfaces of the chamber are mirror-like, which allows to achieve reliable conditions of absorption of the generated radiation by the samples [14].

Technical characteristics of the studied SBS are shown in (Fig. 1).

Properties	СБС	KRATON		
	P 30-01	D-1192	D-0243	D-0246
Kinematic viscosity of 5.23% solution in toluene at 25°C, cSt/Pa*s	26±4	-	-	-
Volatile matter,%	□0,8	□0,3	□0,4	□0,3
Styrene content,%	30±1,5	30	32	26
Diblock content,%	15±2,0	<10	75	55
Vinyl content, %	8-12	48	35	28
Melt flow, 190°C, 5 kgf, g/10min	<1	<1	20	<4
Tensile strength, MPa	□2,0	4,8	1,0	2,9
300% Modulus	□550	1000	820	880
Hardness, Shore A	82±5	70	64	68

Figure 1 – Comparison of technical properties of researched SBS samples

Testing of polymer materials characteristics before and after irradiation was carried out in accordance with interstate standards.

Polymer granules, as well as samples of dumbbell-cut and cylinder-cut samples were sequentially irradiated for intervals of 5 hours with a set of tests. The granules were placed in pallets made of writing paper and loaded onto a grid located in the center of the test chamber along with sets of cut specimens. In the case of the “cylinder” type specimens, the hardness and elastic rebound measurements are made on the side facing the lamp.

The hardness and elasticity of SBS polymers increases with increasing irradiation time. KRATON D0246 shows the smallest increase in elasticity among the considered grades, whereas KRATON D0243, which had the highest elasticity values at the beginning of the test, increased it with prolonged irradiation.

The hardness growth is less intensive. The most significant increase in hardness for the first 15 hours of exposure can be seen in the brand KRATON D0246, which amounted to about 9.6%, while analogs show an increase in the index only by 2-3 %. The values of the remaining three grades increase more slowly, remaining at approximately the same level.

With increasing exposure time, the ultimate strength of KRATON D1192 increases, while KRATON D0243 and D0246 overcome the peak strength value between 5 and 10 hours. Similar properties are also noticeable when analyzing the dependence of 300 % modulus. The modulus continues to increase for KRATON D1192, while for the remaining two the tensile modulus steadily decreases after overcoming the 10 hours mark.

An increase in the maximum elongation value with increasing irradiation time is also demonstrated by KRATON D1192, in contrast to KRATON D0243, which had an increased value that progressively decreased, and KRATON D0246, which showed a peak in elongation value between 5 and 10 hours.

To study in detail the changes in the internal structure of polymeric materials during irradiation, IR spectra of KRATON D-0243, KRATON D-0246 and KRATON D-1192 were obtained on an infrared spectrometer “Spectrometer ALPHA II” by BRUKER (Fig. 2).

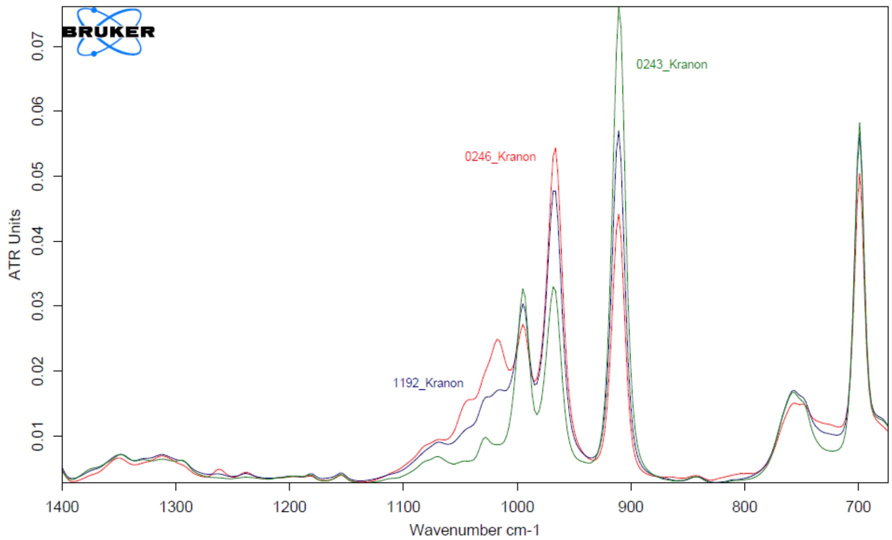

Figure 2 – IR spectra of the three grades of SBS polymers (KRATON D0243, KRATON D0246 and KRATON D1192) used in the study

UV-irradiation aging is monitored by examining changes in the obtained spectra, in particular affecting three characteristic bands: hydroxyl functions (around 3600-3200 cm^{-1}), CH stretching vibrations (around 2950-2800 cm^{-1}) and carbonyl functions (centered around 1700 cm^{-1}). The increase of both C=O and hydroxyl bands provides oxidation monitoring, while the decrease of CH stretching bands allows monitoring of chain immobilization and/or cross-linking, also according to the literature. In addition, changes in the C = C double bonds of butadiene (centered around 965 cm^{-1}) allow monitoring the deterioration of the SBS copolymer as a result of modification of the butadiene copolymer, usually by reducing the double bond content [15].

The highest number of multiple C=C bonds comprising the macromolecular chain is observed in KRATON D0246 grade, which can be explained by the high content of diblock structures. The performance of the KRATON D1192 grade is slightly lower despite the lower diblock content than KRATON D0246. We also note the fluctuations of the peaks in the bands 730-665 cm^{-1} and 980-960 cm^{-1}. This shape of the curves is determined by the difference in the content of cis- and trans-conformations of butadiene blocks of the mentioned brands. Differences in the location of multiple bonds relative to the shielding phenyl groups will suggest a different behavior of the macromolecule under irradiation, suggesting a greater tendency of KRATON D1192 to chain cross-linking when exposed to UV radiation.

Conclusion

Even during the short time interval under investigation it is already possible to trace qualitative changes in the composition of polymeric materials, which leads to significant changes in the test readings already in the first ten hours of use. It is reasonable to assume that the occurrence of degradation and macromolecular restructuring reactions will lead to a gradual increase in residual stresses in the pavement thickness and, together with subsequent curing, will increase the surface failure of asphalt concrete in service.

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